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Studies on Plasmonically-powered Processes for Electronic Excitation

(プラズモニク電子励起プロセスに関する研究)

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Chapter 1.

General introduction

1.1 Light energy utilization

Efficient harvest of light energy is one of the environment-friendly ways to meet the increasing energy demands of human being in a low-carbon society. Conversion of light energy to chemical energy can be realized via photoelectrochemical processes, making the energy transport and storage convenient. Recent attempts to improve the efficiency of photoelectrochemical processes have focused on the optimization of light-matter interaction. However, the light-matter interaction, e.g. the absorption spectrum and quantum efficiency, for a given photosensitive material, are limited by the intrinsic electronic structure of the material.

Localized surface plasmon from metal nanostructures provides an unprecedented way to control light-matter interaction.¹⁻⁵ Typical features of localized surface plasmon include the enhanced absorption and scattering cross-sections, enhanced optical near-field intensity, large field gradient, specific patterns of near-field distribution, nanoscale localized photons, excitation of energetic carriers, and heat generation. Especially, plasmonic metal nanoparticles make it possible to control the nanoscale energies (light, energetic carriers, or heat) from far-field light (incident angle, polarization, power) and other macroscopic means.

1.2 Localized surface plasmon resonance (LSPR)

1.2.1 Surface plasmon and LSPR

Surface plasmon is a wave of charge density that propagates along the surface of a conductor.^{6,7} For a metal under illumination, the collective oscillation of free electrons (i.e. free electron plasma) interacts with the incident oscillating electrical field of light at a certain frequency, forming a hybrid quantum quasiparticle, surface plasmon-polariton

(mixed photon-plasmon mode).⁷ Due to the retardation effects, the ‘pure’ charge density waves (plasmons) cannot exist by themselves without being forced by a transverse electromagnetic wave (photons). For simplicity, the mixed mode, the surface plasmon-polariton is usually called surface plasmon. This convention is used in the rest of this thesis.

Due to the coupling between the light and the oscillation of free electrons, the surface plasmons are tightly confined to the metal surface and can be guided along the surface plane in a similar manner to that of fiber optics. Figure 1.1a shows a surface plasmon propagating at the interface between a metal and a dielectric material. The surface plasmon shows both characters of an electromagnetic wave and a charge density wave. Its magnetic component is in the transverse direction, parallel to the interface, and its electric component is normal to the interface illustrated with the oscillation of surface charge density. The electric field is enhanced near the interface and decays exponentially into both sides of the interface (Figure 1.1b). The decay length (or penetration depth) of the evanescent wave into the metal is determined by the skin depth; while that into the dielectric side could reach the order of light wavelength, when the dielectric is air or glass. The decay lengths indicate the confinement of surface plasmon in the direction normal to the interface. Thus, the electric field of surface plasmon is called near-field. During its propagation along the interface, the surface plasmon gradually loses energy due to the dissipation in metal. The propagation length is therefore determined by the metal’s dielectric function at the oscillation frequency of surface plasmon. The precondition for the coupling between light and the metal’s plasma mode is the match of both energy (frequency) and momentum (wavevector). As is shown in Figure 1.1c, at the same frequency, ω , the wavevector of surface plasmon is larger than that of a free space photon. This mismatch in the momentum could be overcome via several techniques, for example, using prism coupling to enhance the momentum of incident light; making use of the diffraction (scattering) of light by the topological defect or periodic structures (grating) to allow the light to be momentum matched; or using nanoparticles to create localized surface plasmon. The last one is what used in this thesis.

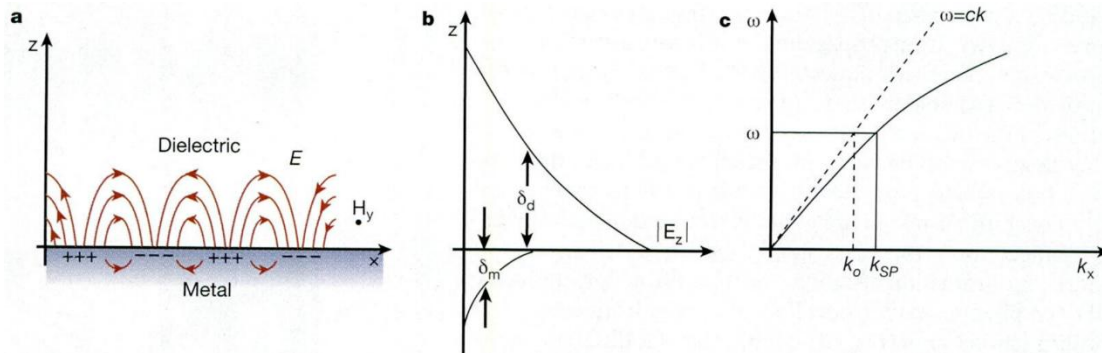


Figure 1.1 (a) Schematic illumination of surface plasmons at the interface between a metal and a dielectric material. (b) Intensity of the field component perpendicular to the surface as a function of the distance away from the interface. (c) Dispersion curves of (solid) a surface plasmon and (dash) a free space photon. E , the electric field; H_y , the magnetic component of light is in the y direction; δ_d and δ_m , the decay lengths of surface plasmon in the dielectric and metal, respectively. k_{sp} and k_0 , wave vectors of a surface plasmon and a free space photon at the same frequency, ω .⁶

Figure 1.2a schematically illustrates the localized surface plasmon oscillation of sub-wavelength metal nanoparticles. The oscillating electromagnetic field of incident light drives the free electrons of nanoparticles to oscillate collectively at the same frequency with the incident light. The curved surface and the confined volume of the nanoparticle exert an effective restoring force on the driven electrons. This restoring force determines the natural oscillating frequency of these free electrons. When the frequency of the incident light and the frequency of the natural oscillating the electric cloud match, a resonance arises. This resonance is called the localized surface plasmon resonance (LSPR). On resonance, the light absorption is greatly enhanced. In other words, the absorption cross-section becomes larger than the real physical size of the nanoparticle, as is shown in Figure 1.2b. The oscillating charges form an oscillating electrical dipole that modifies the electric field distribution in the vicinity of metal nanoparticles. On resonance, this near field electric field is distorted and amplified significantly. The feature of the near-field is described by the plasmon mode, which is determined by the incident light (polarization, wavelength, incident direction), the nanoparticle (relative permittivity, shape, size, charge density) and

the dielectric property of the surrounding medium. The optical properties of nanoparticles are usually characterized with the extinction, scattering and absorption cross-sections. For small nanoparticles (diameter $\ll$ light wavelength), the variation of the phase of the external electric field across the nanoparticle can be ignored, so an incident plane wave can be regarded as an oscillating with time but constant with space field around the metal nanoparticle ('quasistatic' approximation). The oscillating charge can be treated as a classical electric dipole. For large nanoparticles, the retardation of electric field within the metal must be accounted. For spherical or spheroidal particles, analytic solution of optical cross-sections can be calculated according to Mie theory or Gans theory.^{8,9} For more sophisticated geometries, numerical simulations, such as finite difference time domain (FDTD), discrete dipole approximation (DDA) and finite element method (FEM), are needed.¹⁰

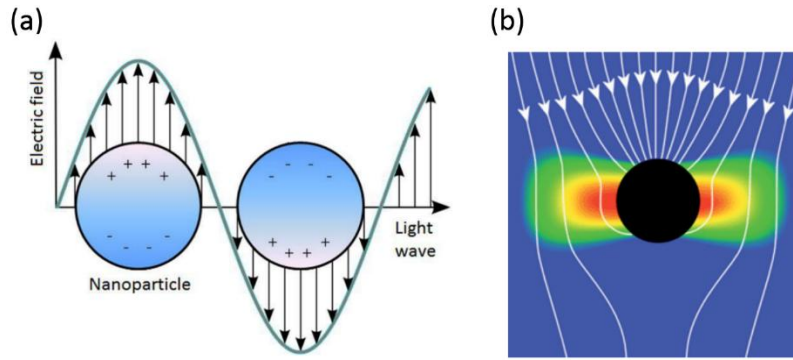


Figure 1.2 Schematic illustrations of (a) a localized surface plasmon oscillation for a sphere nanoparticle¹¹ and (b) the absorption of a plane electromagnetic wave by a nanoparticle¹².

There are differences and connections between the surface plasmon and the localized surface plasmon. Surface plasmon is confined at the surface. In other words, it is non-radiative in the normal direction of the interface but it propagates along the interface. In contrast, localized surface plasmon is confined within the metal particles, non-propagating in all three directions. Surface plasmon has a continuous dispersion relation between its frequency and wavevector, as is shown in Figure 1.1c. For a surface plasmon

is to be excited, both appropriate frequency and wavevector of incident light are required. In contrast, localized surface plasmons have discrete frequencies. The requirement for their excitation is just appropriate frequency; wavevector is not required. In other words, instead of propagating waves described by a wavevector, localized surface plasmons form standing waves defined by the geometry of the particle.¹³ In spite of such distinct features, surface plasmon and localized surface plasmon can convert to each other under appropriate conditions (e.g. similar frequencies, presence of surface defects), which is useful in photonic circuit.^{6,14}

1.2.2 Optical properties of plasmonic nanoparticles

LSPR can be characterized via near-field measurement, far-field spectroscopy and simulation. The features of LSPR, especially the resonance wavelength and the near-field distribution are affected by several factors, such as the chemical composition, shape, size, charge density (potential applied) of nanoparticles, the dielectric property of the surrounding medium, and the illumination (polarization, incident angle, power, duration). Some typical results are summarized below. These knowledges provide various ways to modify the optical properties of nanoparticles.

The plasmon resonance wavelength is affected by the size and shape of nanoparticles. As is shown in Figure 1.3, for a similar size, the LSPR wavelength of triangular nanoparticles with sharp corners are relatively longer. As the nanoparticles become rounded, the resonance peak blue-shifts. For the same shape of nanoparticles, the resonance wavelength increases with the particle size.

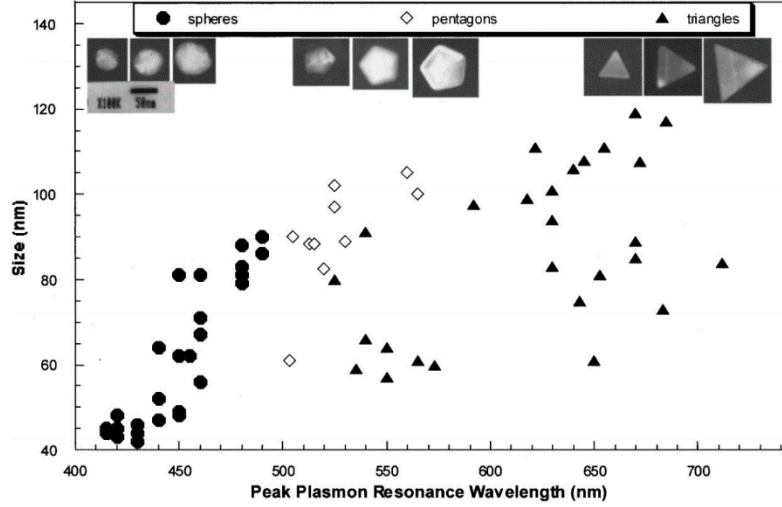


Figure 1.3 Size and shape dependence of plasmon resonance wavelength.¹⁵

The effect of particle size on the LSPR wavelength results from two different mechanisms depending on the particle size range.¹⁶ For nanoparticles smaller than 10 nm (quasi-static regime), the effects of phase retardation and multiple modes can be neglected. The relative permittivity of metal nanoparticles changes with the particle size because of quantum confinements, which dominates the size effect of the optical property. For larger nanoparticles, the effect of quantum confinement on dielectric coefficient becomes negligible; while the optical property is affected electrostatically by the phase retardation with the nanoparticle.

The extinction of nanoparticles is the sum of scattering and absorption.¹⁷ Both of the scattering and absorption depend on the particle size and the illumination wavelength. Figures 1.4 (a-c) shows the calculated spectra according to Mie theory.¹⁸ For small size nanoparticles, the absorption and extinction bands are coincident. As the particle size increases, the contribution from scattering increases; and the absorption, scattering and extinction bands shift away from each other. Thus, it is worth noticing that estimating the absorption efficiency of a nanostructure according to the experimental measured extinction spectrum, is not always reliable. Figure 1.4d shows that for a given illumination wavelength, the maximum absorption and scattering cross-sections increase with the particle size. For a spherical particle of diameter, d , much smaller than the illumination

wavelength, the absorption and scattering cross-sections are proportional to as d^3 and d^6 , respectively. As the particle size increases, these simple scaling laws become invalid, due to the phase retardation effect.¹⁹

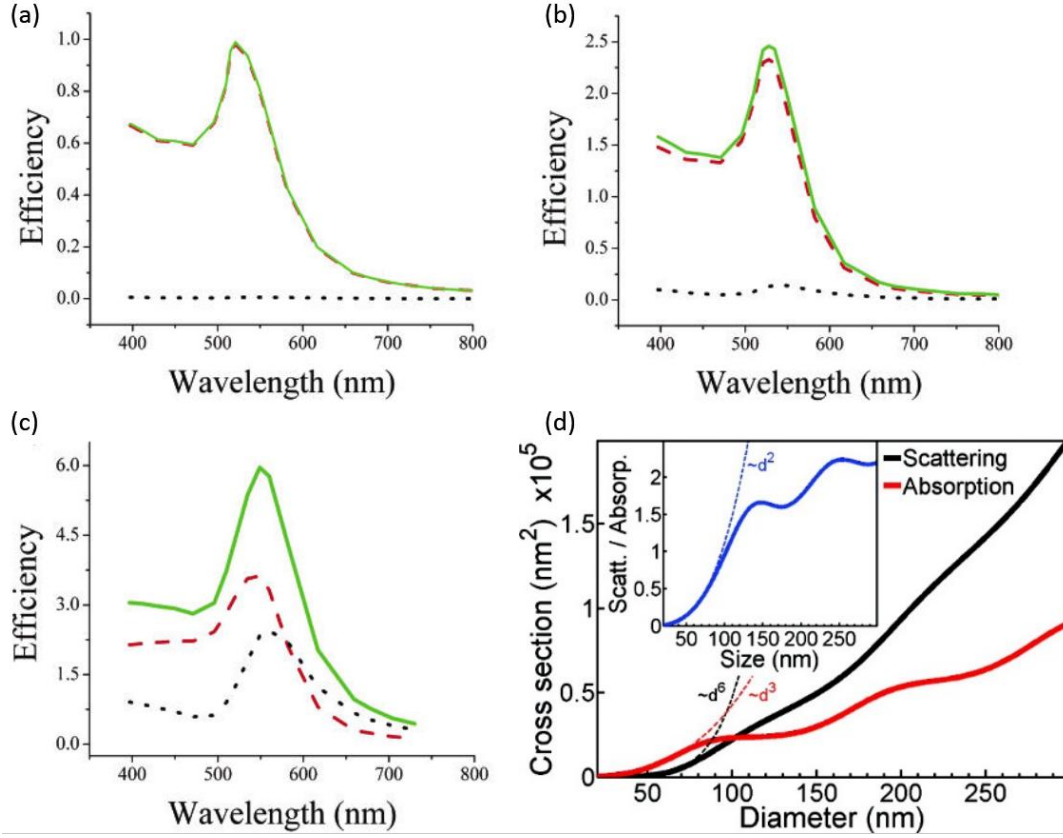


Figure 1.4 (a, b, c) Spectra of the efficiency of absorption (red dashed), scattering (black dotted), and extinction (green solid) for gold nanospheres with diameters of (a) 20 nm, (b) 40 nm, (c) 80 nm calculated according to Mie theory.¹⁸ (d) Scattering (black) and absorption (red) cross-sections as functions of particle size with 532 nm illumination and a medium index of refraction of 1.25. The inset shows the ratio of scattering and absorption cross sections as a function of particle size. The dashed lines show how simplified power dependences. d is the diameter of a spherical particle.¹⁹

Nanorod structure is an ideal model to investigate the physics of LSPR. Under linearly polarized illumination, two different plasmon modes can be excited, as is shown

in Figure 1.5. The longitudinal (transverse) mode is excited when the polarization direction of light is along (parallel to) the long axis of the rod. In the extinction or absorption spectra, the band of the longitudinal mode locates at a longer wavelength than that of transverse mode, as is shown in Figure 1.6. And the peak of longitudinal mode is more intensive, indicating a stronger resonance.

The absorption spectra of nanorods are dependent on the relative dielectric constant of the medium and the aspect ratio of rod, as is shown in Figure 1.6.²⁰ As the dielectric constant of the medium increases, both of the two modes red-shifts roughly linearly. As the aspect ratio increases, the longitudinal peak red-shifts, whereas transverse peak blue-shifts. These were calculated for ensembles of randomly oriented, ellipsoidal nanoparticles in isotropic dielectric medium according to Gans theory^{20,21} and similar tendencies were also observed for well-ordered nanorods supported on glass substrate^{22,23}.

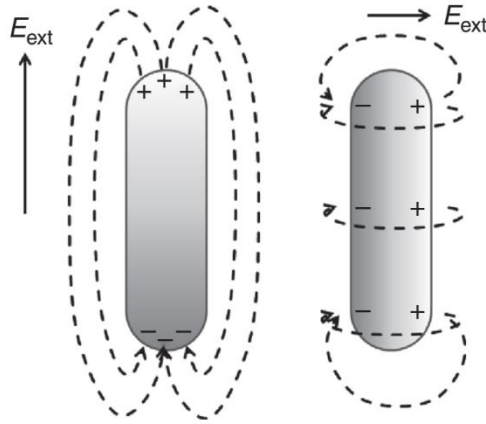


Figure 1.5 (left) The longitudinal and (right) the transverse plasmon modes of a nanorod¹³.

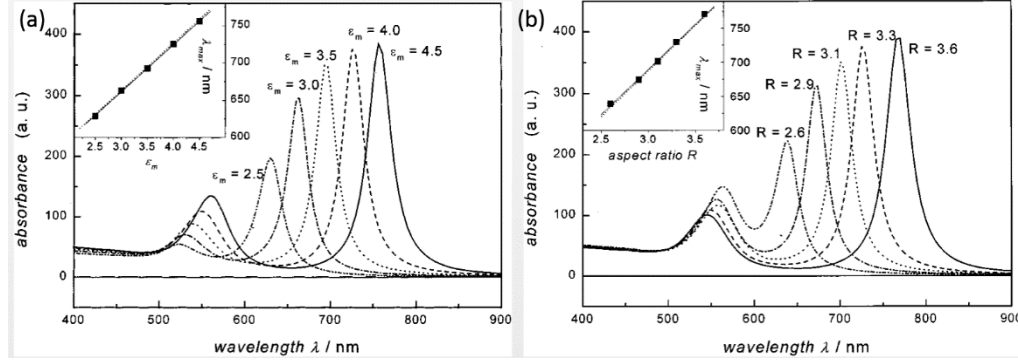


Figure 1.6 Calculated absorption spectra of elongated ellipsoids with varying (a) medium dielectric constant ϵ_m and (b) aspect ratios R according to Gans theory.²⁰ The insets show the linear fits of the peak absorbance wavelength as a function of ϵ_m and R .

The red shifts of LSPR peaks in response to the increase of the dielectric constant (or refractive index) of the surrounding medium is called the permittivity (or refractive index) sensitivity.^{24,25} This sensitivity is affected by the size, shape, and composition of metal nanostructures. For a given composition and shape, the more red-shifted a LSPR peak is, the higher its sensitivity is. Compared with spherical metal nanoparticles, those structures with sharp tips (e.g. nanobipyramids, nanotriangles and nanostars) are more sensitive to the change of permittivity of surrounding medium.²⁴ Coupled plasmons show higher refractive index sensitivity than individual plasmon modes.

The distance between nanoparticles affects the LSPR frequency and intensity. As the nanoparticles approach each other, they interact via near-field coupling and the LSPR mode evolves from the dipole mode of single nanoparticle to the gap mode between nanoparticles. As is shown in Figure 1.7a, the LSPR peak red-shifts and is enhanced as the interparticle spacing decreases. The near-field enhancement of the gap mode is usually larger than that of dipole mode of single nanoparticle, since the space confinement is larger in the gap than that at the edge of single particle. The absolute value of the red-shift of the LSPR wavelength depends on the size and shape of nanoparticles. However, a universal scaling behavior has been found which is independent of the size, shape and material of nanoparticles or the surrounding dielectric medium^{16,26,27}:

$$\frac{\Delta\lambda}{\lambda} = A \times e^{\left(\frac{-s/D}{\tau}\right)} \quad (1.1)$$

where the λ is the LSPR wavelength of single nanoparticle, $\Delta\lambda$ is the shift of LSPR wavelength due to near-field coupling, s is the edge-edge interparticle separation, D is the diameter of nanoparticle, τ is the decay length of the field away from the particle surface, and A is the pre-exponential factor. Figure 1.7b shows this universal dependence of LSPR wavelength on the interparticle spacing. The shift of LSPR wavelength is scaled by the LSPR wavelength of single nanoparticle; and the gap distance is scaled by the size of individual nanoparticle. As the gap increases, the fractional shift of LSPR wavelength decays exponentially. Equation 1.1 demonstrates that the distance dependence of plasmon coupling is a ruler quantitatively estimating the inter-particle distance.

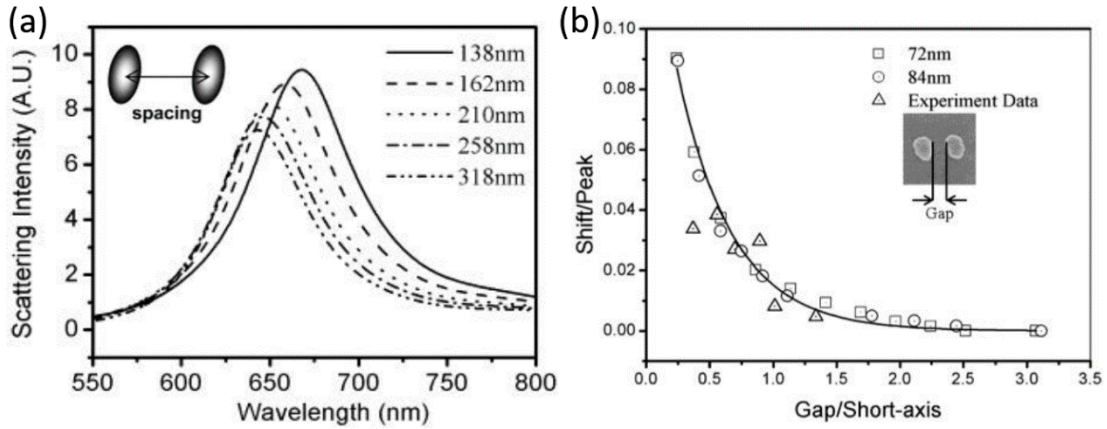


Figure 1.7 (a) Simulated scattering spectra of pairs of elliptical Au nanoparticles with center-center particle spacing from 138 nm to 318 nm. (b) Shift of LSPR wavelength as a function of the gap between two particles. Squares and circles are simulation results, and triangles are experiment data. The vertical axis is the peak shift with respect to the LSPR wavelength of an individual nanoparticle. The horizontal axis is the edge-edge spacing with respect to the size of the nanoparticle.¹⁶

1.2.3 Higher order of plasmon modes and spatial mapping of near-field distribution

When the length of nanorod is comparable or greater than the illumination wavelength λ , higher-order oscillation modes are excited. Figure 1.8a shows the charge oscillation corresponding to the first-order, second-order, and third-order longitudinal plasmon modes. The mode index number, m , counts the times the charge density changes sign along the rod. When the incident beam is perpendicular to the long axis of rod, only odd-orders of longitudinal modes are allowed; while the even-order modes are optically forbidden because the symmetrically distributed electrical polarizations are canceled out in integration along the long axis. Figure 1.8b shows the spatial distribution of electric near-field corresponding to the first three odd-order modes, where the lobes indicate the sites of local maxima of electric field intensity and charge density. The first-, third-, and fifth-order resonances have two, four, and six lobes, respectively. Figure 1.8c shows that for a given mode, the resonance wavelength increase linearly with the rod length. Note that the slope is different for different modes.

Characterization of the near-field distribution requires a nanoscale spatial resolution. Various methods have been applied, such as electron energy loss spectroscopy (EELS)²⁸, photoemission electron microscopy (PEEM)²⁹, cathodoluminescence spectroscopy (CLS)³⁰, and near-field optical microscopy (SNOM)³¹. These methods typically rely on complex setups and may have side effects. For example, the tip of SNOM may additionally alter the intrinsic response of the nanostructure under study. Alternatively, plasmon-induced chemical reactions not only have high spatial resolution but also provide the information on hot-carrier dynamics. In this case, chemical reactions selectively occur at the hot spots of the plasmonic structures. The near-field can be mapped via scanning electron-microscopy (SEM) or atomic force microscopy (AFM). The dynamics of chemical reactions can be monitored via in-situ Raman spectroscopy. Figures 1.8 (d, e) show the spatial mapping of near-field via plasmon-induced site-selective deposition of Ag nanoparticles³² and polymerization of photoresist³³.

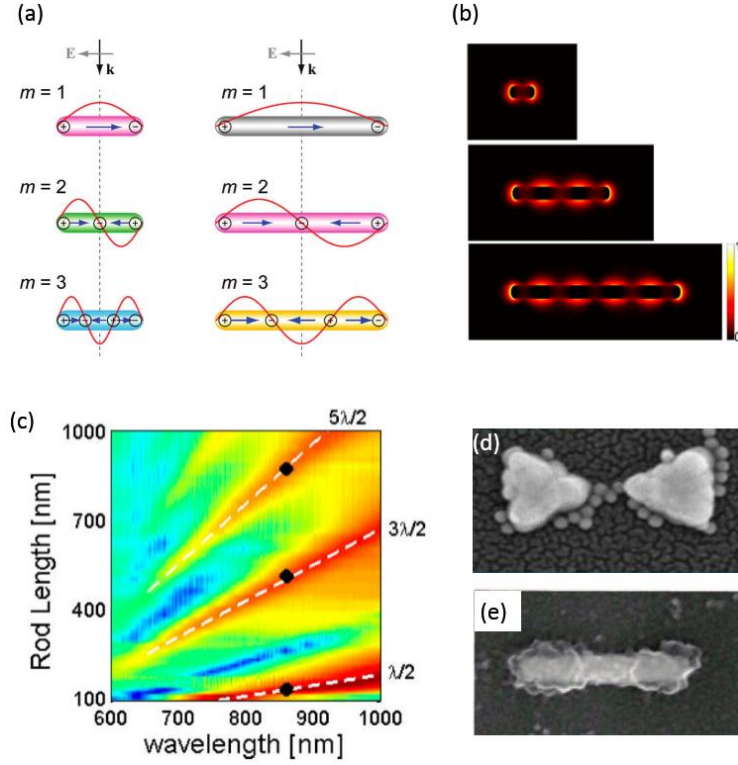


Figure 1.8 Schematic illustration of (a) the charge oscillation³⁴ and (b) the near-field distribution of longitudinal plasmon modes. (c) Linear relationship between the rod length and the resonance wavelength.³⁵ Mapping of near-field via (d) reduction of Ag nanoparticles³² and (e) photo-polymerization of photoresist³³.

1.3 Hot carrier generation and injection

1.3.1 Decay of plasmon resonance

Figure 1.9 shows the photoexcitation and the following relaxation processes.⁵ Localized surface plasmon is excited by the absorption of incident photons. On resonance, the light absorption is enhanced significantly. It is characterized by an enhanced effective absorption cross-section, which is larger than the real physical dimensions of the nanoparticle. This is demonstrated with the redirect of the light flow (Poynting vector) towards and into the nanoparticle in the figure. After being photo-excited, the metal nanoparticle sets off a cascade of complex processes. First, the plasmon resonance decays

via the Landau damping. During the Landau damping, a plasmon quantum is transferred into a pair of hot electron and hole within the first $1 \sim 100$ fs. Within metal, the plasmon-induced electric field could induce an electronic transition from occupied to unoccupied states. A possible population of the electronic states within the metal is illustrated in Figure 1.9b. In the first 1–100 fs following Landau damping, the distribution of hot carriers are athermal and highly non-thermal. The electron–hole pair could decay either through re-emitting a photon or through carrier multiplication caused by electron–electron interactions. In the following 100 fs to 1 ps, the hot carriers relax via electron–electron scattering processes, redistributing their energy among all of the electrons within the metal. This leads to a Fermi-Dirac-like distribution of electrons with an elevated effective electron temperature. Lower effective electron temperature corresponds to a reduced velocity, enables the electron-phonon scattering. Thus, the heat is transferred from electron to the lattice and finally transferred to the surrounding medium.

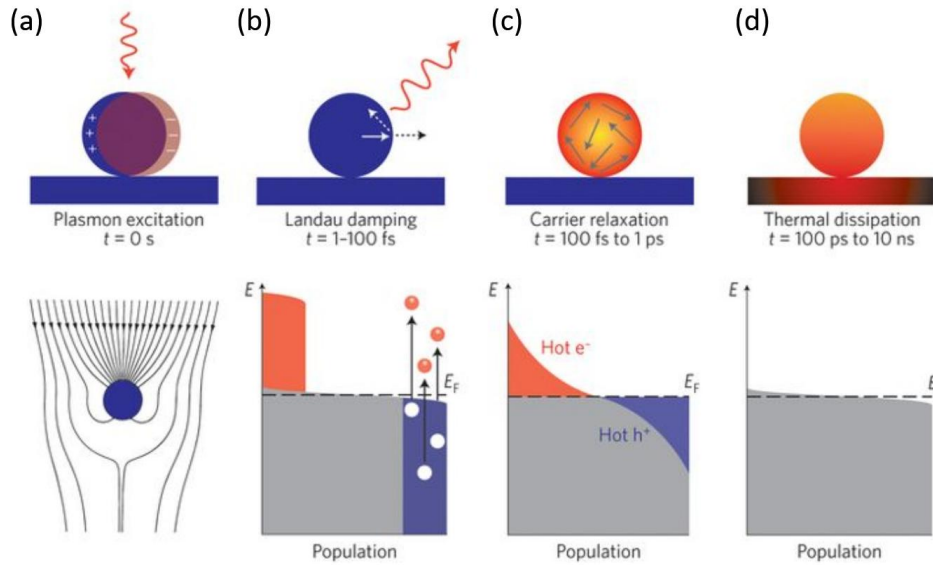


Figure 1.9 (Upper) Schematics of plasmon excitation and the subsequent relaxation processes, and (lower) the corresponding characteristic timescales.⁵

One can see that, the light energy can be used in different ways. On one hand, the energetic electrons and holes created by photoexcited electronic transition can be used to

induce redox reactions. On the other hand, the heat released from the metal nanoparticles is benefit in some situations, such as the photothermal cancer therapy and photothermal imaging. In the latter cases, metal nanoparticles could act as an ideal nanosource of heat, which enables the control of temperature within nanoscale space by far-field optical.

From the chemical reaction point of view, on one hand, the thermalization is a competing pathway reducing the number of hot carriers used in the redox reactions; on the other hand, the plasmon-induced thermal effects may also improve the chemical reaction rate via accelerating the diffusion of reactant or changing in the equilibrium potential of the redox pair³⁶. Thus, during the investigation of the mechanism of plasmon-induced chemical reactions, it is critical to decouple the impacts from hot-carrier injection and thermal effect. Control of the relative contribution of the two plasmon decay pathways is important for utilization of plasmon in photoelectrochemistry.

1.3.2 Hot carrier generation and injection

Plasmon-induced hot carrier transfer from metal nanoparticles is a potential new paradigm for photoelectrochemistry. The hot carrier injection efficiency is the key. Several typical examples on the hot electron injection are summarized in this sub-section.

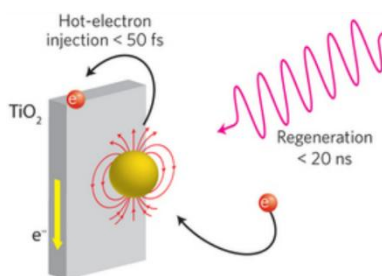


Figure 1.10 Timescale of hot-electron injection and charge regeneration at the interface between metal nanoparticles and TiO_2 substrate.^{37,38}

The time scale of hot-electron generation and injection at the metal-semiconductor interface can be investigated via the ultrafast visible-pump/infrared-probe femtosecond transient absorption spectroscopy.^{37,38,39,40} It has been found that the hot-electron generation and injection at the interface between Au nanoparticles and TiO_2 substrate was

completed within 50 fs (Figure 1.10). The thermalization of hot electrons with a non-Fermi distribution in Au nanoparticles occur through electron-electron (<100 fs), electron-phonon (1~10 ps) and phonon–phonon (~100 ps) interactions. Thus, the electron injection occurs before or during the thermalization. Charge separation before carrier recombination is a key factor for increasing the reaction efficiency.

In order to reduce the loss of hot electrons via the ultrafast electron-electron scattering within the metal nanoparticle, a novel plasmon-induced direct interfacial charge-transition (PICTT) was proposed.⁴¹ As is shown in Figure 1.11, it enables the decay of a plasmon by directly exciting an electron from Au nanoparticle to the cadmium selenide nanorods. This program is distinct from the normal decay process of localized surface plasmon, as is shown in Figure 1.9, where the decay process starts via a Landau damping within the metal nanoparticles. The PICTT program combine the hot generation and injection into one single step. This is realized due to the strong coupling between the CdSe nanorod and the Au nanotip.

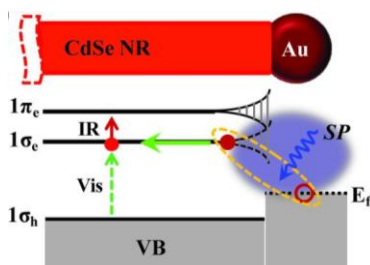


Figure 1.11 Plasmon-induce direct interfacial charge-transition.⁴¹

Similarly, the direct charge-transfer between metal nanoparticles and molecules is also proposed.^{37, 42} The direct charge-transfer could improve the selectivity of chemical reactions, as is shown in Figure 1.12. In the indirect charge-transfer mechanism, plasmon relaxation results in an electron distribution that is characterized by a high concentration of low-energy charge carriers. Those at or above the energy level of the lowest unoccupied adsorbate orbitals can transfer into those orbitals, thereby forming an excited adsorbate and potentially inducing chemical transformation. In the direct mechanism, decay of a resonant

plasmon causes direct excitation of an electron to an unoccupied adsorbate state, without the formation of an excited electron distribution in the metal.

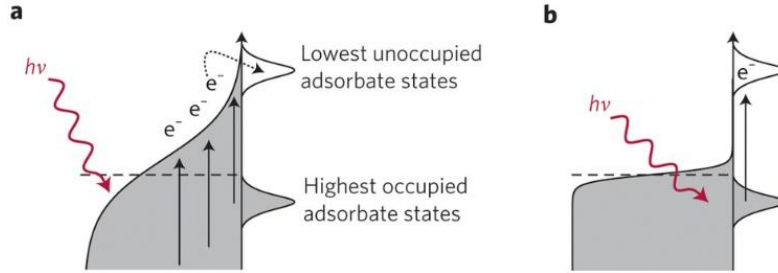


Figure 1.12 (a) Indirect and (b) direct charge-transfer mechanism.^{37, 42}

The multiple exciton generation (MEG) is the ability of quantum dots (QDs) to generate more than one electron–hole pairs by absorbing a single photon.^{43–45} When a QD is situated close to a plasmonic metal nanoparticle, the photoexcitation process could be tuned due to the interaction between the excitons of the QD and the LSPR of the metal nanoparticle.⁴⁶ Combining the MEG of semiconductor QDs and the LSPR of metal nanoparticles has shown an improved photovoltaic performance.⁴⁷ In a system consists of PbS QDs and plasmon-active Au nanoparticles embedded in a titanium dioxide thin film (Figure 1.13), the effective electron injection is demonstrated by the wavelength-dependent onset potential and the output power density.

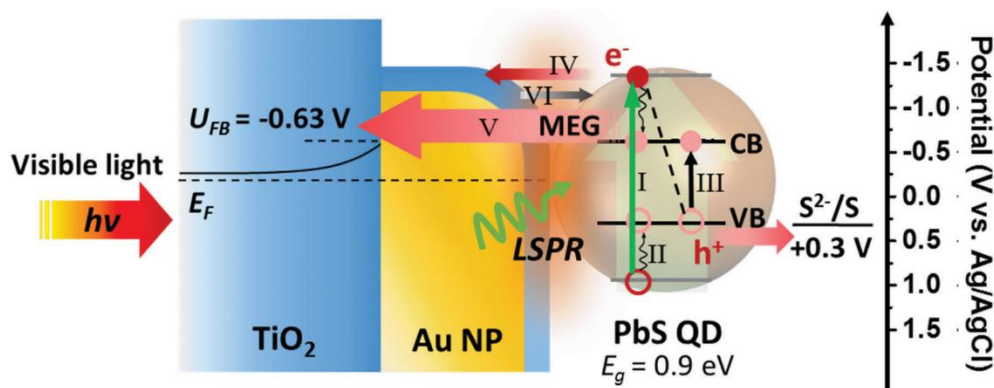


Figure 1.13 Schematic illustration of the energy diagram of multiple exciton generation (MEG) in PbS quantum dots excited by LSPR and size-dependent PbS quantum dots.⁴⁷

1.4 Electrochemical potentials of hot carriers

Besides the hot carrier generation and injection processes, the electrochemical potentials of the hot carriers are also important for photoelectrochemical reactions, since they determine whether the reactions occur or not.

A typical configuration for measurement of the electrochemical potential of hot electrons or holes consists of a metal-semiconductor Schottky contact and a molecular probe with a well-known redox potential. The photoexcited electron-hole pairs are separated at the Schottky contact by the built-in field.⁴⁸ The band-bending⁴⁹ and built-in field can be tuned with a three-electrode system and a potentiostat. For example in Figure 1.14, when the Fermi level is tuned to +0.5 V, the excited electron from Au nanoparticles can be injected into the conduction band of TiO₂, and the excited hole could be used to oxidize pyrrole. In contrast, when the potentials are too low, for example, -0.9 V, the recombination of hot electrons and holes becomes significant, which suppresses the oxidation of pyrrole. Thus, via scanning the potential, the onset potential of oxidation of pyrrole can be detected. Given the flat-band potential of TiO₂, the energy of incident photon, the electrochemical potential of the hot holes could be estimated. The calculated oxidation potential of holes corresponds well to the redox potential of pyrrole.

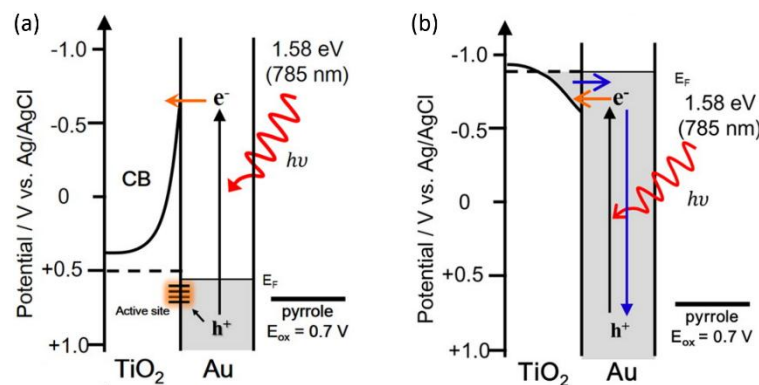


Figure 1.14 Mechanism of LSPR-induced oxidation polymerization of polypyrrole. (a) At +0.5 V, the excited hot electrons transfer into the conduction band of TiO₂ and the hot hole oxidizes the pyrrole. (b) At -0.9 V, the electron-hole pair could not be separated and the pyrrole could not capture the holes.⁵⁰

The similar configuration is also used to investigate the plasmon-assisted water oxidation.^{51,52} The stoichiometric evolution of oxygen via water oxidation was realized with a Au nanorod-loaded TiO₂ photoelectrode even under near-infrared illumination. The utilization of low energy photon is ascribed to the LSPR. As is shown in Figure 1.15, the interband electronic transition of Au requires a high excitation energy, since the density of states of *d* band reduces near the Fermi level. Under long-wavelength illumination, such as from 700 nm to 1300 nm, the interband transition is rather. However, the LSPR-induced spatially and temporally confined photons can assist the multi-electron transfer process. Except for the extension of optical response wavelength, the localized plasmon excitation also reduces the activation energy.⁵¹ This work shows the importance of the electrochemical potential of hot holes in chemical reactions.

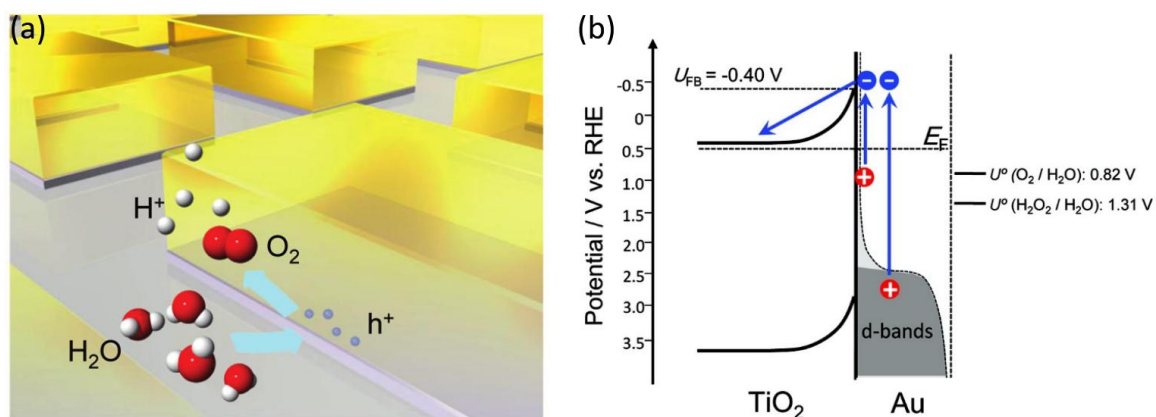


Figure 1.15 (a) Schematic illustration (b) energy diagram of plasmon-assisted water oxidation. U_{FB} is the flat band potential of TiO_2 . U^0 indicates the potentials corresponding to the four-electron and two-electron water oxidation.⁵²

1.5 Modification of photoexcitation selection rule

Usually, the electronic transitions between electronic states follow the standard selection rules under long wavelength approximation. That is, the electric field is assumed to be uniform within the size of molecule. However, due to the spatial confinement, the LSPR-induced near-field has a significantly high field gradient. This makes the long wavelength approximation and the standard selection rule invalid. The unconventional electronic transition has been experimentally observed in the SERS of single-walled carbon nanotube lying in the gap of Au nanodimer (Figure 1.16). The theoretical calculation via the extended discrete dipole approximation (EDDA) method proves that the resonant transition of the E_{41}^S and E_{14}^S ($\Delta n = \pm 2$) dark excitons become bright in the 1-nm-wide gap of Au nanodimer. These dipole-forbidden transitions explain the observed new E_2 -mode peak in the SERS spectrum under perpendicular illumination.⁵³ Achieving an optical response beyond the conventional selection rule is expected to alter the energy distribution of hot electrons and holes in materials.

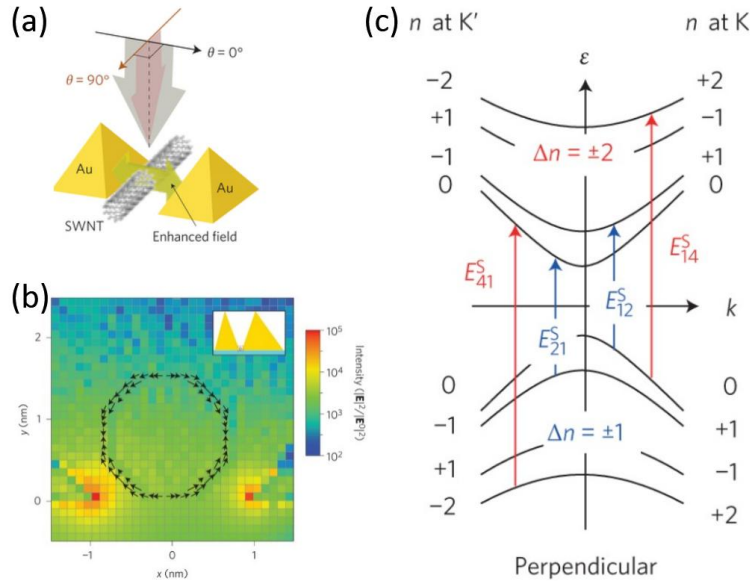


Figure 1.16 (a) illustration of a single-walled carbon nanotube placed in the nanogap of Au dimer under polarized illumination. (b) Cross-section view of the near-field distribution calculated with discrete dipole approximation (EDDA) method. (c) The allowed transitions ($\Delta n = \pm 1$) and the forbidden transitions ($\Delta n = \pm 2$).⁵³

1.6 Objective and outline of this thesis

This thesis aims to explore the plasmon modification on the photoexcitation process. Chapter 1 gives the general introduction on the localized surface plasmon, hot-carrier generation, and plasmon-induced photoexcitation. Chapter 2 shows the multiple plasmon modes of Au nanorods observed via the *in-situ* SERS measurement. Chapters 3 and 4 discuss the plasmon thermal effects on the stability of metal nanoparticles and target materials. Chapter 5 gives the main discussion of this thesis. The plasmon-modified electronic transition is observed in the SERS of graphene. Chapter 6 gives the general conclusion.

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Chapter 2.

Photoelectrochemical polymerization of polypyrrole on well-defined plasmonic structures

2.1 Introduction

The combination of the plasmon-active metal nano-structures on the wide band gap semiconductor electrode leads to the chemical reactions under the visible light region which cannot excite the electron in the semiconductor. In this system, the hot-carrier separation is realized due to the Schottky barrier at the metal-semiconductor interface.¹ Recently, molecules with a given redox potential in the vicinity of metal-semiconductor junction investigate the mechanism of the plasmon-induced photoelectrochemical reaction process.²⁻⁴ Here, the molecules play the role as an indicator of the electrochemical potential of hot carriers. With the aim of the arbitrary control of the plasmon-induced plasmonic structures, it is quite necessary to investigate not only the multi-color response ability but also the absolute potential of excited reaction species. For them, the usage of the three-electrode electrochemical system seems to be useful because it can control the arbitrary Fermi level of the electrode.

One example is plasmon-induced oxidative polymerization of polypyrrole.⁴ The onset potential of polymerization is obtained via the *in-situ* electrochemical surface enhanced Raman scattering (SERS) measurements. The electrochemical potential of plasmon-induced hot holes is estimated from the onset potential of polymerization, the flat-band potential of semiconductor electrode, and the energy of incident photon. At the initial stage of the polymer growing process, the pyrrole monomers accept hot holes directly from the Au. It is quite important fact that the polymer deposit sites correspond to the spatially distribution of the near-field distribution. The reaction continuously proceeds after the hot spots on Au surface are completely covered with the polymer layer because of the hole-conductive character for deposited polypyrrole.⁵⁻⁸ As a result, the evaluation of the enough volume of polymer via SEM and AFM measurements could lead to the visualization of the reaction active site for the plasmon-induced chemical reactions.

In this chapter, I deeply investigated the plasmon induced charge transfer process induced on the well-defined Au rod structures on titanium dioxide (TiO₂). Nanorods show very interesting two kinds of plasmon modes, the longitudinal mode and transverse mode, under different polarization illuminations.⁹ The near field properties of longitudinal mode shows a strong dependence on the aspect ratio of the rod. It is known that the dipole mode shows the highest near-field enhancement. On the other hand, the multipolar modes show relatively weaker near-field enhancement but shows the unique distribution of the near-field depending on the aspect ratio.^{10,11} In this chapter, well-defined Au nanorods are prepared on TiO₂ substrate via electron-beam lithography and investigate the plasmonic reactions induced by the plasmon-induced charge transfer process.

2.2 Experimental

2.2.1 Cleaning and recycling of TiO₂ substrate

First, as a normal cleaning recipe, acetone and Milli-Q water were used to remove the most organic contamination, in an ultrasonic bath for 10 min, in sequence.

After deposition of polypyrrole, the TiO₂ substrate was cleaned and recycled. The deposited polypyrrole was removed with piranha solution (H₂SO₄ : H₂O₂ $\approx$ 4:1 vol.). The Au nanoparticles or nanorods were dissolved with aqua regia (HCl : HNO₃ $\approx$ 3:1 vol.). Each cleaning was carried out at room temperature for 5 ~ 10 min.

To refresh the surface, the TiO₂ single crystal was etched with 20% HF aqueous solution at room temperature for 10 min, rinsed with Milli-Q water and dried with nitrogen flow. In order to improve the hydrophilicity, TiO₂ was illuminated with ultra-visible light. Finally, the cleaned TiO₂ substrate was annealed at 600 °C in air (Figure 2.1) to make an atomically smooth surface.

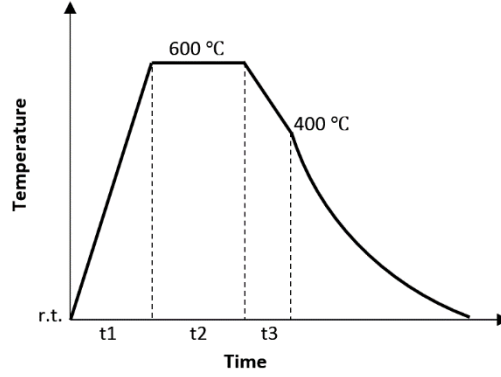


Figure 2.1 Recipe for annealing TiO₂ single crystal in air. The three periods are t₁ = 2 h 15 min, t₂ = 2 h 30 min and t₃ = 1 h 45 min.

2.2.2 Preparation and characterization of random Au nanoparticles on TiO₂ substrate.

10 nm thick gold film was deposited on the (110) surface of TiO₂ single crystal (rutile, 0.05 w.% niobium doped, 10.0 × 10.0 × 1.0 mm³, Furuuchi Chemical, Japan) via electron-beam deposition method, then was annealed in air with the program in Figure 2.2a. The temperature was increased from room temperature (r.t.) to 100 °C within 30 min and maintained for 60 min, then increased to 500 °C within 90 min and maintained for 30 min, finally decreased gradually to the room temperature.

The optical and structural property of random Au nanoparticles were characterized with extinction spectroscopy and scanning electronic microcopy (SEM). The extinction here is defined as:

$$\text{Extinction} = -\log_{10}(P/P_0) \quad (2.1)$$

where P and P_0 are the power (mW) of transmitted light measured with and without the sample before the detector. The white-light source was an iodine lamp (MC-2530 UV/VIS light source, Otsuka Electronics Co., Ltd., Japan). The detector was a spectral multi-channel photodetector (MPD-311C, Otsuka Electronics Co., Ltd., Japan) with a spectral resolution of 1 nm. Since the doped TiO₂ substrate is opaque, the extinction spectra of Au were measured with Au deposited on glass substrates. As is shown in Figure 2.2b, after annealing, the extinction changes significantly. The deposited 10 nm thick Au film transforms to random nanoparticles which show a broad extinction peak centered around

700 nm. SEM image (Figure 2.2c) shows the random Au nanoparticles are round or elongated round disks and the major has a size of 50 ~ 500 nm.

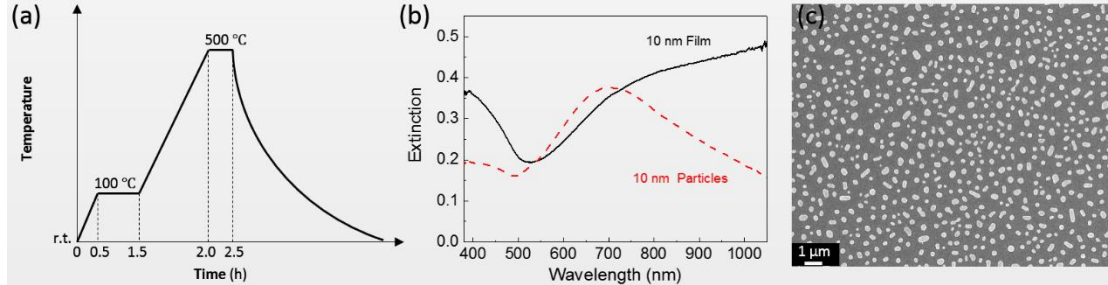


Figure 2.2 (a) Annealing program in air for preparation of random Au nanoparticles. (b) Extinction spectra of (solid line) 10 nm thick gold film deposited on glass and (dash line) random Au nanoparticles on glass obtained via the annealing program in (a). (c) SEM image of random Au nanoparticles on TiO₂ substrate.

2.2.3 Preparation of Au nanorods on TiO₂ substrate

Au nanorods were fabricated on TiO₂ substrate via electron-beam lithography and lift-off method, as is shown in Figure 2.3a. First, a drop of positive photoresist (ZEP: ZEP-A = 2:1, Zeon Co., Japan) was spin-coated (MS-A150, Mikasa Co., Japan) on TiO₂ substrate at room temperature. The spinning program was 300 rpm (round per minute) for 3 sec followed by 4000 rpm for 60 sec. The coated TiO₂ substrate was dried at 150 °C in air for 3 min. Second, the coated substrate was transferred into the electron beam lithography system (ELS-F125, Elionix inc., Japan). Conditions for e-beam drawing were: accelerating voltage = 125 kV, beam current = 50 pA, area dose = 250 μC/cm²; dose time for the nanorods and the guiders (large area squares) were 2 μsec/dot and 1.26 μsec/dot, respectively. Third, the substrate was immersed in the developing solvents (Zeon Co., Japan) in turn: ZED-N50 for 60 sec and ZMD-B for 10 sec, at room temperature. Fourth, 60 nm Au was sputtered onto the patterned substrate with a helicon plasma sputtering system (MPS-4000C1/HC1, Ulvac, Inc., Japan). Finally, the remained photoresist was left-off ultrasonically with three beakers of ZDMAC (Zeon Co., Japan) for 45 sec + 30 sec +

30 sec, in turn, and cleaned further with acetone and methanol ultrasonically for 20 sec + 20 sec.

As is shown in Figure 2.3b, the width and height of nanorods were fixed at 50 nm and 60 nm, respectively. The length varies from 60 nm to 600 nm. The edge-to-edge inter-particle distance was 500 nm, which is far enough to prevent the near-field coupling between adjacent nanorods.

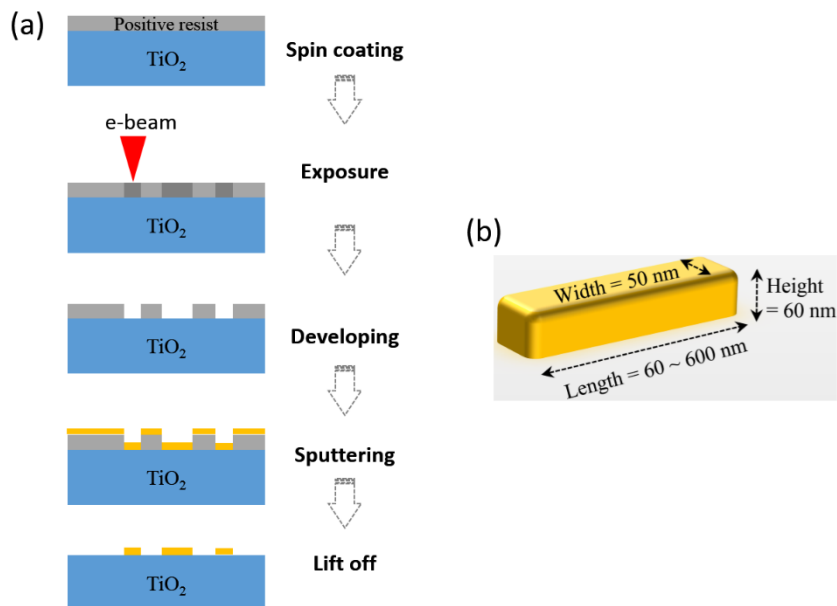


Figure 2.3 (a) Scheme of fabrication of Au nanorods on TiO₂ single crystal via electron-beam lithography and lift-off method. (b) The designed three dimensions of Au nanorod.

2.2.4 Photoelectrochemical deposition of polypyrrole and *in-situ* SERS measurement

As is shown in Figure 2.4, the photoelectrochemical deposition of polypyrrole and the *in-situ* SERS measurement were performed with a three-electrode electrochemical cell and a confocal Raman microscope. The light source was a 785 nm continuous-wave laser (XTRA II, TOPTICA Photonics AG). A water-immersion objective lens (40 $\times$, N.A. = 0.80, W.D. = 3.3 mm, Olympus) was immersed in a Teflon cell. To prevent possible contamination, the lens was covered with a 25 μ m thick transparent fluorinated ethylene propylene film (Flon industry, Japan) and a drop of Milli-Q water was enclosed between the lens and the plastic film to avoid gas bubbles. The electrode potential was controlled

via a three-electrode system with a potentiostat (HAB-151, Hokuto Denko Co., Japan). A piece of platinum plate and a home-made Ag/Ag^+ (0.1 M tetrabutylammonium perchlorate and 0.01 M AgNO_3 dissolved in anhydrous acetonitrile) electrode were the counter and reference electrodes, respectively. The working electrode, Au/TiO_2 , was connected to the potentiostat via a piece of stainless steel plate. In-Ga alloy was pasted between the semiconducting TiO_2 and stainless steel plate, in order to sustain an Ohmic contact. Current was monitored with a storage oscilloscope (GL900-4, Graphtec Co., Japan).

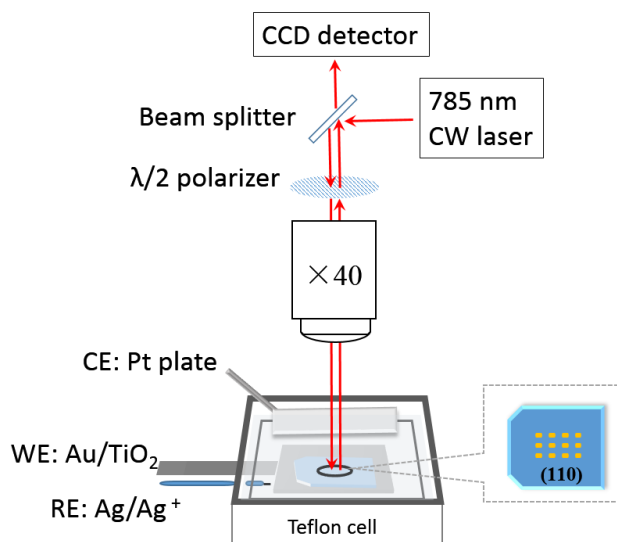


Figure 2.4 Schematic illustration of the *in-situ* SERS measurement system.

2.3 Results and discussion

2.3.1 Polymerization of pyrrole in aqueous and acetonitrile solution

Before using the well-defined structures, I have investigated the electrolyte solution effect on the reaction process using both water and acetonitrile. Figure 2.5 shows the polymer growth process in aqueous solution with increasing laser illumination time. One can see that in the initial stage (within 11 sec), the deposition sites show polarization dependence. That is pyrrole prefer to deposit at the both sides of Au nanoparticles along the polarization direction. These sites are the ‘hot spots’ of the interface between Au and TiO_2 . After a long time of deposition, the entire Au nanoparticle was covered by the polymer. The subsequent growth of polypyrrole confirms that the hot holes generated at

Au nanoparticles could transfer through the polymer layer to the polymer-solution interface. The growth of polypyrrole could be monitored via the *in-situ* SERS spectra. As is shown in Figure 2.6a, the Raman bands of polypyrrole increase with time passage. The band at about 935 cm^{-1} corresponds to the C-H vibration of polypyrrole. This band is distinct to the Raman bands of pyrrole monomer¹² so it could be used as an indicator of polypyrrole. The band intensity at about 935 cm^{-1} increases quickly at the initial stage and gradually saturated as shown in Figure 2.6b. This means that, with time passage, the hot spots are gradually covered by the polymer which leads to the lower enhancement of SERS intensity.

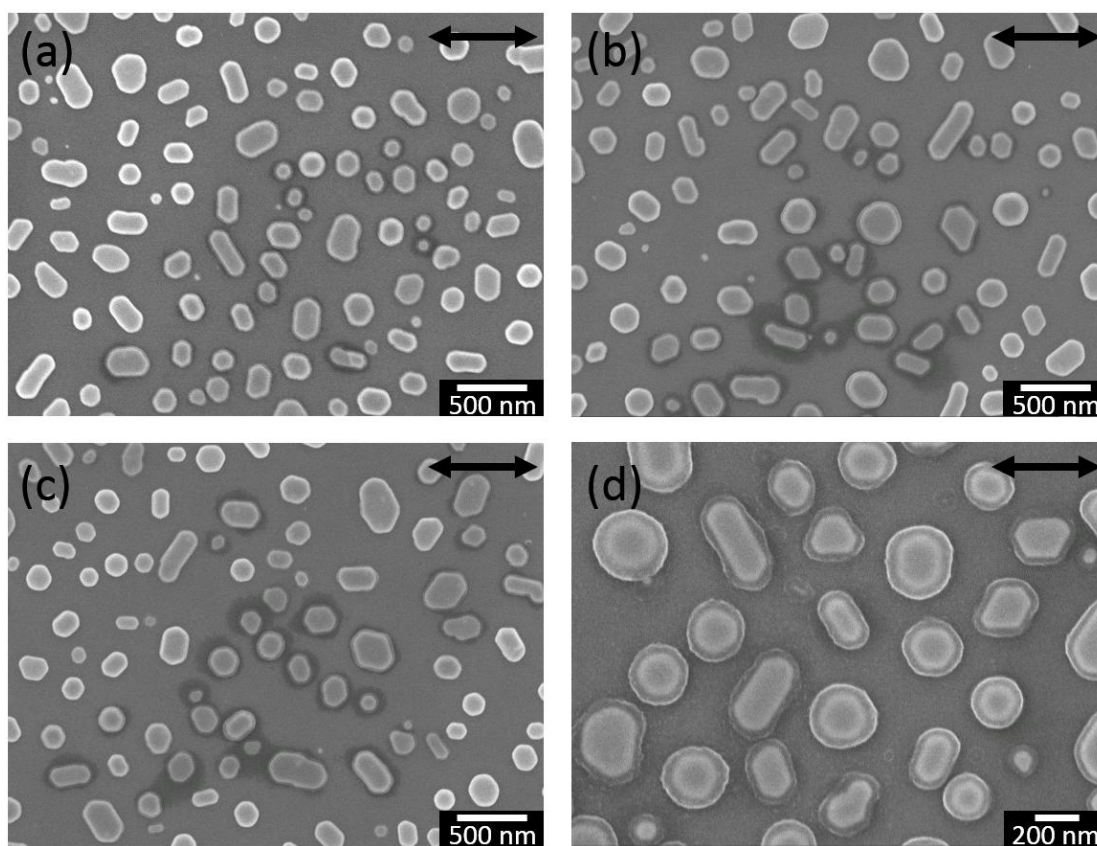


Figure 2.5 SEM images of polypyrrole deposited for (a) 2, (b) 6, (c) 11, and (d) 110sec, respectively. The illumination was 0.1mW, 785nm continuous-wave laser. The electrolyte solution was 10 mM pyrrole and 0.5 M Na_2SO_4 in water. The electrode potential was +0.5 V vs. Ag/AgCl sat.

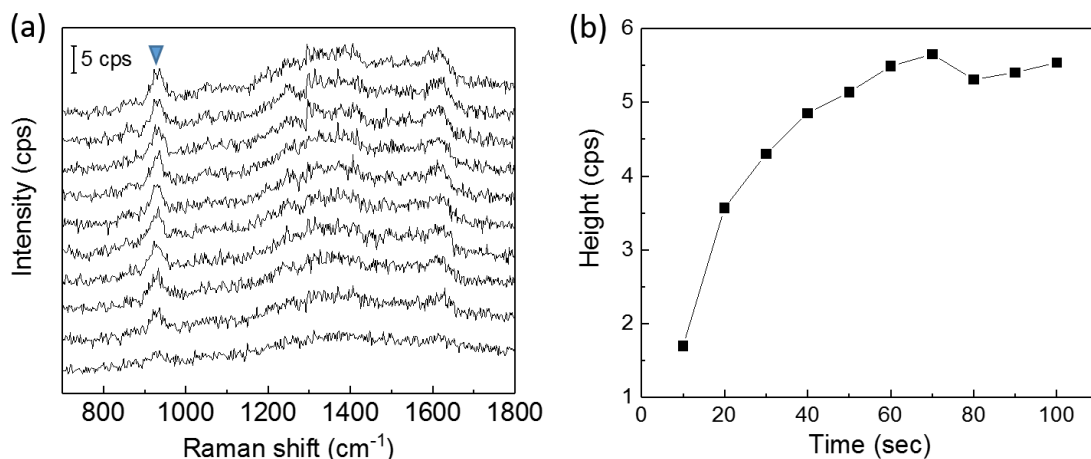


Figure 2.6 (a) *In-situ* SERS spectra obtained during the photoelectrochemical deposition of polypyrrole on Au nanoparticles supported on TiO₂ substrate. The experimental conditions are 0.1 mW 785 nm continuous-wave laser at +0.5 V vs. Ag/AgCl sat. in aqueous solution containing 0.01 M pyrrole and 0.5 M Na₂SO₄. The spectra were obtained successively every 10 sec from bottom to top. (b) Time-varying intensity of the Raman band at 935 cm⁻¹ indicated with downward triangle in (a).

On the contrary, Figure 2.7 shows the SEM images of deposition process of polypyrrole in the acetonitrile solution. Figure 2.8a shows *in-situ* SERS spectra during the growth of polypyrrole in acetonitrile. In contrast to the growth in aqueous solution (Figure 2.6), the Raman band of polypyrrole decreases with increasing laser illumination time. One significant feature is that within the first second, the surface of Au nanoparticle is almost covered by the polymer. That means that the polymer growth process is much faster than that in the aqueous system. This would be because that the polymerization of the pyrrole is the competitive reaction with the water oxidation reaction in the aqueous solution, which leads the decrease of the reaction efficiency. From the facts, I can say that the more efficient reaction system has successfully found through the present experiments.

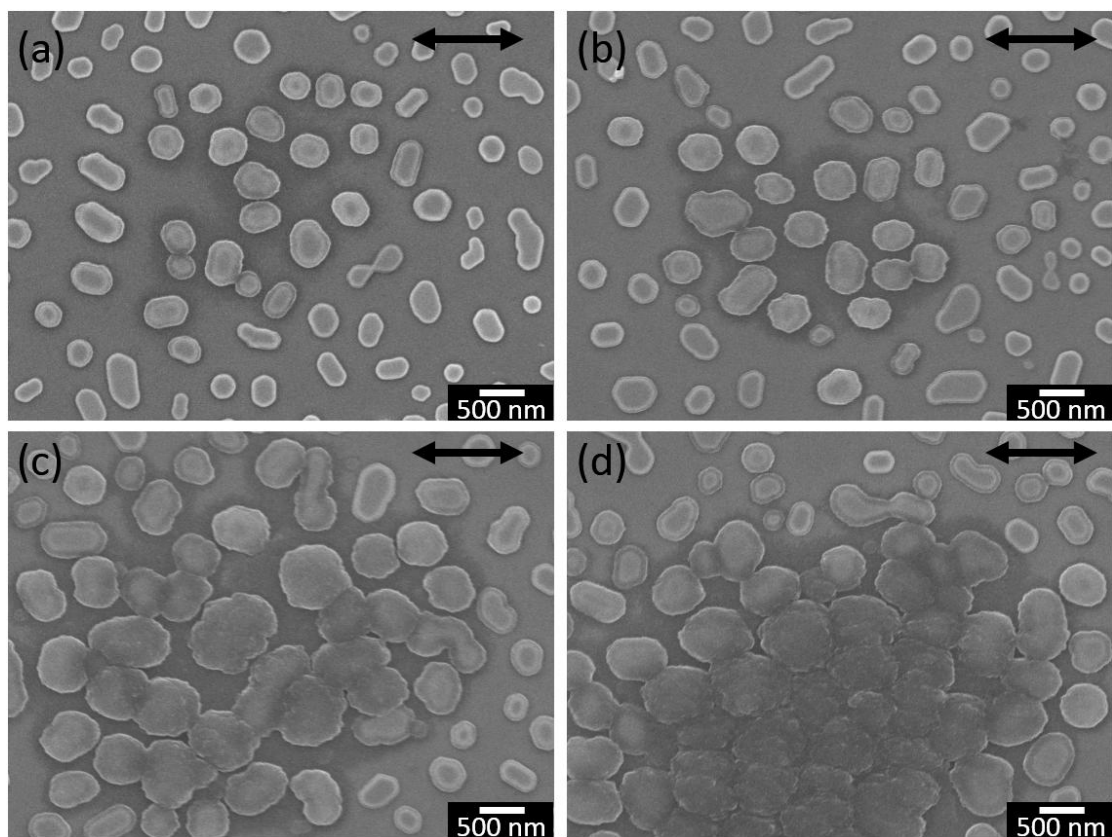


Figure 2.7 SEM images of polypyrrole deposited for (a) 1, (b) 10, (c) 50, and (d) 100sec, respectively. The illumination was 0.1 mW, 785 nm continuous-wave laser. The electrolyte solution was 0.01 M pyrrole and 0.1 M NaClO₄ in acetonitrile. The electrode potential was +0.3 V vs. home-made Ag/Ag⁺ (0.01 M AgNO₃).

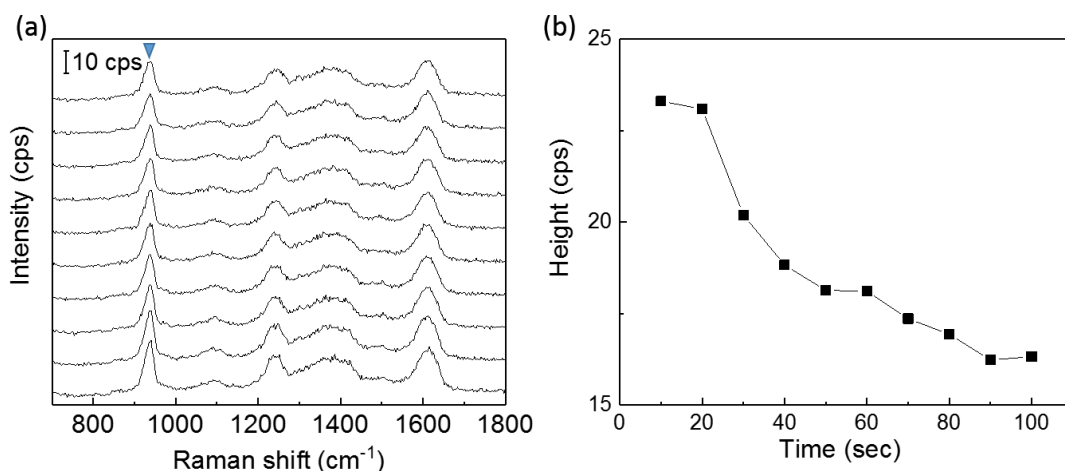


Figure 2.8 (a) *In-situ* SERS spectra obtained during the photoelectrochemical deposition of polypyrrole on Au nanoparticles supported on TiO₂ substrate. The experimental conditions are 0.1 mW 785 nm continuous-wave laser at +0.3 V vs. home-made Ag/Ag⁺ (0.01 M AgNO₃) in acetonitrile containing 0.01 M pyrrole and 0.1 M NaClO₄. The spectra were obtained successively every 10 sec from bottom to top. (b) The change in the intensity of the Raman band at 935 cm⁻¹ indicated with downward triangle in (a) as the function of the laser illuminated time. The corresponding SEM image is shown in Figure 2.7d.

2.3.3 Polymerization on Au nanorods.

For deep understanding, I have fabricated various Au rod structures with the rod lengths ranging from 10 to 1000 nm on TiO₂ single crystal. For the discussion about the reaction efficiency depending on the rod length, *in-situ* Raman measurements have been performed simultaneously. Raman intensities at 932 cm⁻¹ obtained from each structure were plotted as the function of the rod length. Obviously, the specific rod length (90 and 330 nm) shows the relatively strong Raman intensity compared to other cases. It has been recognized that the perpendicular incidence onto the rod structures excites only modes with odd index. Therefore, it can be determined that the lengths of 90 and 330 nm correspond to $n = 1$, and 3, respectively. Moreover, considering the deposition of the poly pyrrole on the length of 550 nm, this length should be assigned to $n = 5$. The relative weaker Raman intensity and small deposition amounts for the case of $n = 5$ would be resulted in the fact that the multipolar plasmon with higher index value weakly interacts with the incident light, leading to the weak resonance. From the previous paper, it can be possible to describe the

rod length (L) as the function of the n value and the plasmon resonance wavelength (λ_p). The relationship is described as following:

$$L(n)(nm) = \lambda_p n (nm) + a (nm)$$

where a is the constant value which depends on the shape of each end. Based on the equation and $\lambda_p = 785$ nm, present each value of a for $n = 1, 3$, and 5 can be estimated to be -695 , -2025 , and -3375 , respectively. Eventually, the relation between the order of the longitudinal plasmon mode, excitation wavelength and the rod length is estimated successfully using the current method. As one of the advantage of higher order plasmon mode induced charge transfer process, the localization of hot spots for chemical reactions, as is shown in Figures 2.9 (a-c), could be remotely controlled. In addition, such relation could provide useful information on the design of plasmonic antennas for broad wavelength response. It is known that the nano-rod structures with high aspect ratio could realize the multi-color excitation at different sites. So, the current founding would provide the possibility for the multi-color light harvesting for the exotic plasmon powered process.

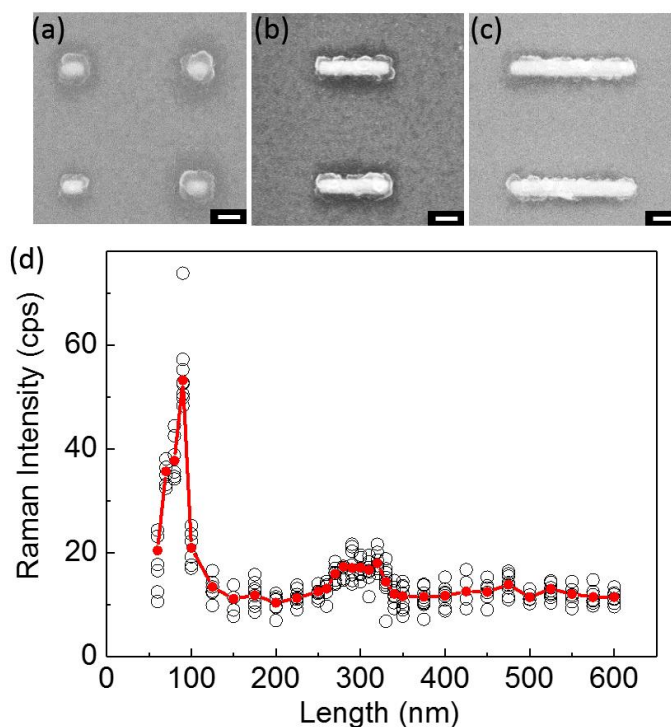


Figure 2.9 (a-c) SEM images of polypyrrole deposited on the nanorods with a length of (a) 90, (b) 330 and (c) 550 nm sec. The scale bars are 100 nm. (d) SERS intensity of ν_{C-H} at 938 cm^{-1} as a function of rod-length. Deposition conditions: 0.1 mW 785 nm continuous-

wave laser. The electrolyte solution was 1 mM pyrrole and 0.1 M NaClO₄ in acetonitrile. The electrode potential was +0.3 V vs. home-made Ag/Ag⁺ (0.01 M AgNO₃). The black circles represent the band intensity under illumination for 1 sec. For each nanorod, 10 spectra were obtained successively, in total, within 10 sec. The red solid dots show the average intensity of the 10 spectra.

Based on the above facts, I used the rod structures having the length of 60, 70, 80, and 90 nm which are almost same as the $n = 1$. Raman intensities obtained with different lengths of nanorods are significantly different as shown in Figure 2.10. Among them, the 90 nm long Au nanorod gives the strongest Raman bands of polypyrrole. Figure 2.11 shows the intensities of Raman band at 938 cm⁻¹ as a function of illumination time for different lengths of nanorods. One can see the different behavior depending on the rod length. For 60 nm rod, the band intensity increases and saturated after 6 second. It is easy to find that this is similar tendency as that in Figure 2.6b. In contrast, for 90 nm rod, the Raman band intensity decreases with time, like Figure 2.8b. This means that polypyrrole grows faster on 90 nm rod than on 60 nm rod. For other rods, the Raman intensity seems linear relationship during the illumination. From this fact, it is clear that the good resonance condition can accelerate the reaction compared to the weak resonance process.

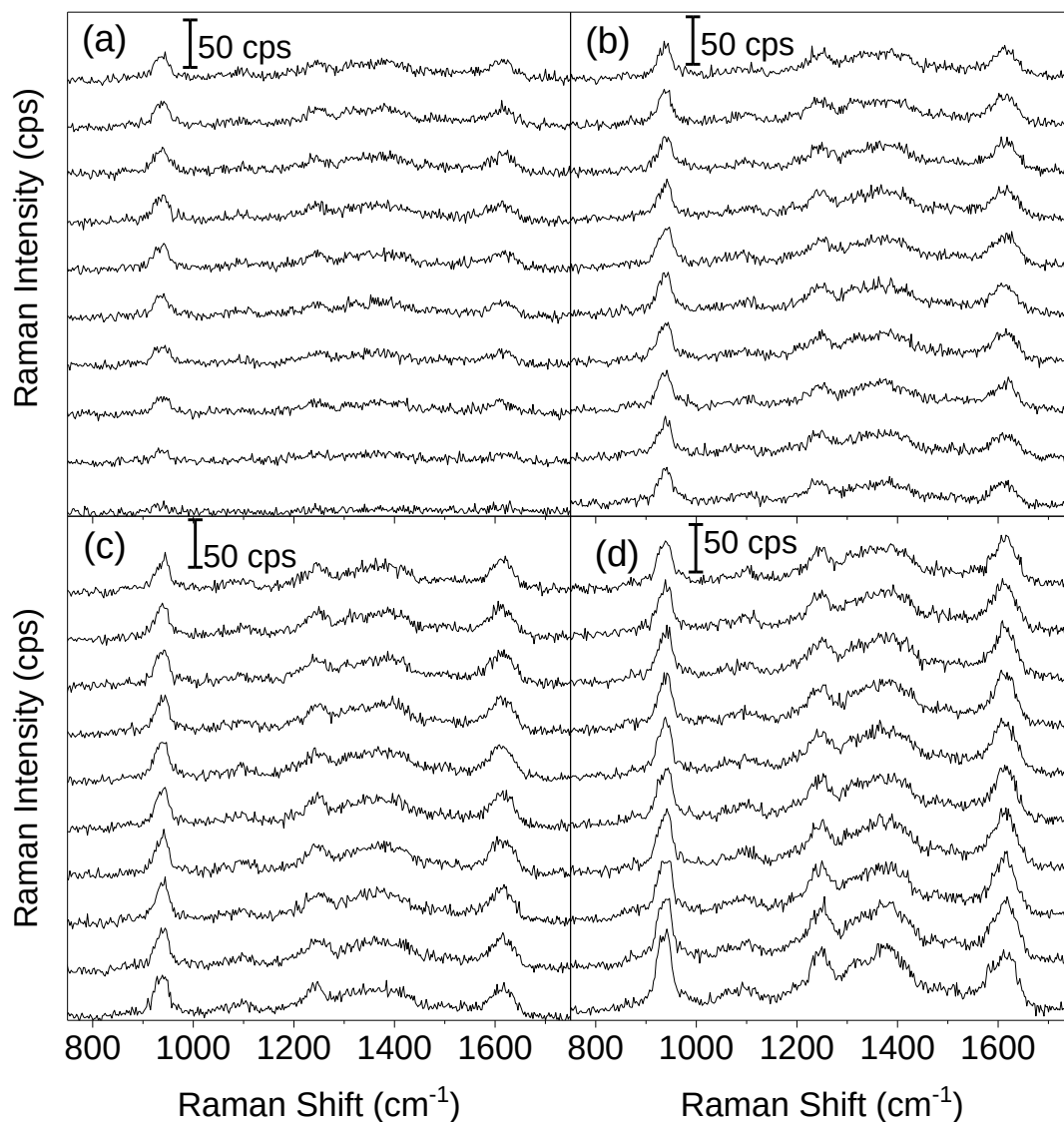


Figure 2.10 *In-situ* SERS spectra obtained during the deposition of polypyrrole on Au nanorods with a length of (a) 60, (b) 70, (c) 80, and (d) 90 nm. The experimental conditions are 0.1 mW 785 nm continuous-wave laser at +0.3 V vs. home-made Ag/Ag⁺ (0.01 M AgNO₃) in acetonitrile containing 0.001 M pyrrole and 0.1 M NaClO₄. The spectra were obtained successively every 1 sec from bottom to top in each panel.

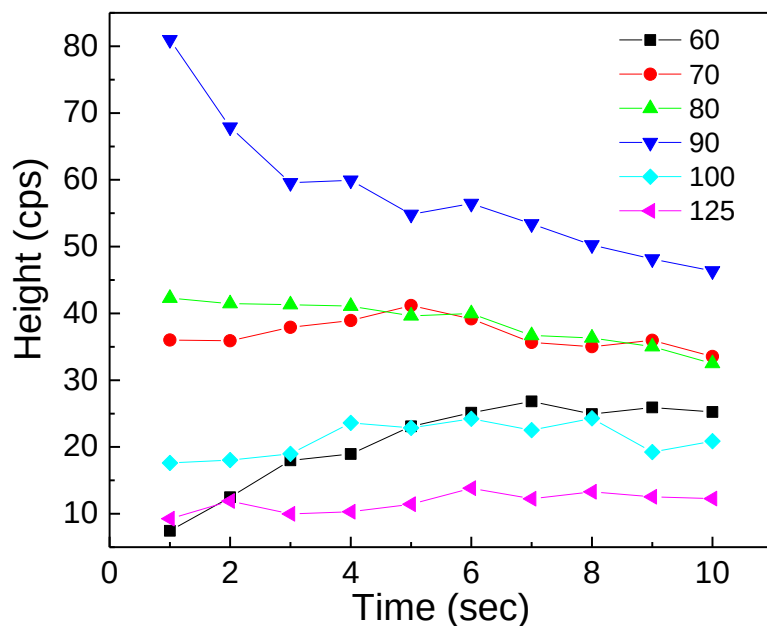


Figure 2.11 Time-varying intensity (band height) of the Raman band at 938 cm^{-1} of polypyrrole deposited on Au nanorods of different rod-length. The legends indicate the rod-length in nanometers.

2.4 Conclusion

In conclusion, polypyrrole was deposited on random Au nanoparticles and well-defined nanorods under illumination of 785 nm continuous-wave laser at controlled electrochemical potential. The spatially selective deposition of polypyrrole was confirmed under linear polarized illumination. The different stages of the polymerization process are well monitored from the time-varying Raman intensity at 935 cm^{-1} which corresponds to the C-H vibration mode of polypyrrole. The rod-length dependence of the Raman intensity shows local maxima corresponding to the different orders of longitudinal plasmon modes. The relation between the order of the longitudinal plasmon mode, excitation wavelength, and the rod length is estimated successfully using the current method. In addition, the time-series change in Raman intensity is found to be dependent on the aspect ratio of nanorods. For nanorods with a strong plasmon resonance, the Raman intensity reaches maximum even within the first second, then decreases due to the decrease of light absorption and near-field enhancement. For nanorods forming a weak resonance, the Raman intensity

gradually decreases. Taking into account the multi-color response property of the nano-rod structures, these findings would lead not only the possibility to carry out chemical reactions on a specific Au nanorod with a variety of photon energies and at the specific locations of the nanorod but also the plasmonic powered multi-color excitation process.

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Chapter 3.

Deformation of Au nanorod: plasmon thermal effect

3.1 Introduction

LSPR could decay in radiative or non-radiative ways. The latter is especially important in photochemistry and photoelectrochemistry,¹⁻³ in which the plasmon energy was transferred to electron-hole pairs, the so-called ‘hot carriers’, via intraband or interband transitions. As is previously reported⁴ and discussed in Chapter 2, using the Au nanoparticle supported on TiO₂ and a specific molecular probe, pyrrole, the active sites could be visualized in nanoscale resolution and the efficiency of plasmon-induced chemical reactions can be analyzed quantitatively. Another result of the non-radiative decay of plasmon is heat.⁵ Plasmon thermal effect affects the stability of metal nanoparticles⁶⁻¹¹ and the efficiency of (electro)chemical reactions^{12,13}. The thermalization, the process for an excited system to reach thermal equilibrium, is affected by the intrinsic properties of the material, as well as the light source.⁵ On one hand, the dielectric constant, shape and size of metal nanoparticles determine the absorption and scattering cross-sections.^{14,15} A larger absorption cross-section means more light energy is captured by the metal nanoparticle. The specific heat capacity and thermal conductivity of the metal and the surrounding medium determine the heat-transfer rate from the metal to the medium, i.e. how fast the metal cools down. On the other hand, the polarization of light affects the absorption and near-field distribution. Under continuous-wave illumination, the light absorption and thermalization overlap in time; while an ultrafast pulsed laser will separate these two processes.^{5,16} Compared with a continuous-wave laser that delivers energy in a steady way, a pulsed laser casts a large amount of energy with an ultrashort time and triggers additional effects, such as bubble formation and reshape of nanoparticles.^{5,17,18}

Chapter 2 shows the deposition of polypyrrole on Au random islands and nanorods under illumination of linearly polarized continuous-wave laser. The deposition prefers to occur at Au nanostructures with specific shape and aspect ratio. The deposition sites are the two ends of the nanostructures and along the polarization direction of incident laser.

The selectivity on nanoparticle's shape (or aspect ratio) and on spatial sites shows that the polymerization was controlled by the hot carrier generation due to LSPR.

In this chapter, the well-defined Au nanorods and pulsed laser are used. The geometric transformation of Au from rod to sphere are observed. This indicates the thermal effects of illumination. Plasmon thermal effects are discussed. It is found that the thermal effect is dominated by the plasmonic near-field.

3.2 Experimental

3.2.1 Fabrication of Au nanorods

Experimental details refer to chapter 2. Briefly, arrays of Au nanorods were fabricated on single crystalline TiO₂ (110) substrate via electron-beam lithography and lift-off method. The height and width of nanorods were fixed as 60 nm and 50 nm. The rod length (L) varies from 50 nm to 200 nm. The edge-to-edge distance between adjacent nanorods was 500 nm. Au nanorods with the rod-length were fabricated within a block of $8\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. That is, each block contains $182 \sim 252$ nanorods, depending on the respective particle size.

3.2.2 Photoelectrochemical deposition of polypyrrole

The optical path is shown in Figure 3.1. A beam of 355 nm laser produced from a Nd:YAG pulsed laser (Continuum Surelite II) was converted into two beams, 'signal' (410 ~ 710 nm) and 'idler' (710 ~ 2200 nm), via an optical parametric oscillator (OPO) (Continuum Surelite). After adjusting, the idler output a beam of 785 nm pulsed laser (pulse width = 3 ~ 5 nanoseconds; frequency = 10 Hz). A long-pass filter (cut on 700 nm) was used to filter out the unwanted remainder 645 nm light. The final output wavelength was checked with a compact spectrometer (Thorlabs CCS200/M; Range = 200 ~1000 nm). Power was measured by a thermal power meter (Gentec Laser Power & Energy Meter). The final laser spot size was measured roughly with a laser alignment burn paper. The laser spot was larger than the cell window, therefore, only part of the energy of the laser beam was utilized.

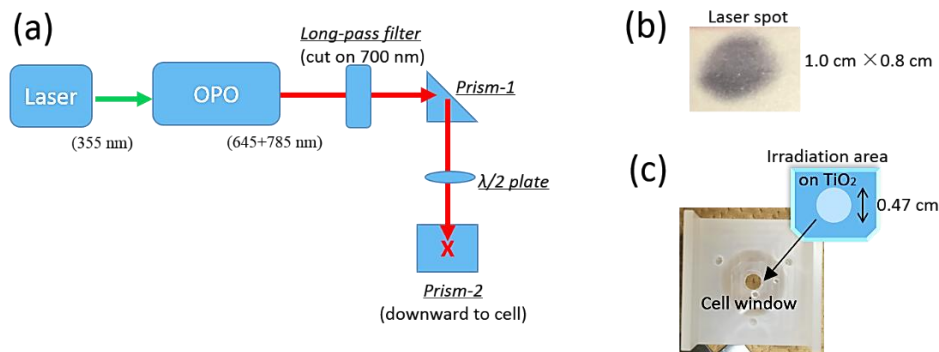


Figure 3.1 (a) Optical path of pulsed laser system. (b) Photo of laser spot (1.0 cm $\times$ 0.8 cm) that finally reaches the electrochemical cell. (c) The illumination area on TiO₂ substrate is determined by the size of cell window (diameter = 0.47 cm).

The electrolyte solution was 0.1 M NaClO₄ acetonitrile solution containing 1 M of pyrrole. The electrode potential was fixed at +0.3 V vs. a home-made Ag/Ag⁺ (0.01 M AgNO₃ and 0.1 M tetrabutylammonium perchlorate in acetonitrile) electrode. A piece of Pt plate was used as the counter electrode.

The illumination conditions were 785 nm nanosecond pulsed laser with a duration of 4 nanoseconds and a repetition rate of 10 Hz. The time-averaged power was measured with a thermal power meter. The polarization direction of laser was tuned along the long axis of the nanorod. The illumination time was 3 min.

3.2.3 Finite-difference time-domain (FDTD) calculations

The near-field distribution in the vicinity of Au nanorods was calculated via the finite difference time-domain (FDTD) analysis using commercially available software (EEM-FDM, IMS Lab Inc.). Au nano-rod structures are supported on a 25 nm thick TiO₂ substrate. The width and height for Au nano-rod structure were 50 and 60 nm, respectively. The incident light wavelength was set to 785 nm and the polarization direction of the incident light was parallel to the long axis of the nanorod to excite the longitudinal plasmon modes.

3.3 Results and discussion

3.3.1 Deposition of polypyrrole on random Au nanoparticles

Figure 3.2 shows the deposition of polypyrrole around random Au nanoparticles under the illumination of the polarized pulsed laser ($I_{\text{ex}} = 18 \text{ mJ cm}^{-2}$). Polarization direction is indicated with the double-headed arrows. Apparently, the deposition of polypyrrole has been successfully observed. The deposition position sites agree with the distribution of the generated electromagnetic field defined by the polarization of the incident light.

One interesting feature is that the morphology of polypyrrole is different from that under CW illumination. This may be ascribed to that pyrrole has enough time for diffusion during the dark period between the laser pulses, compared with the continuous illumination.

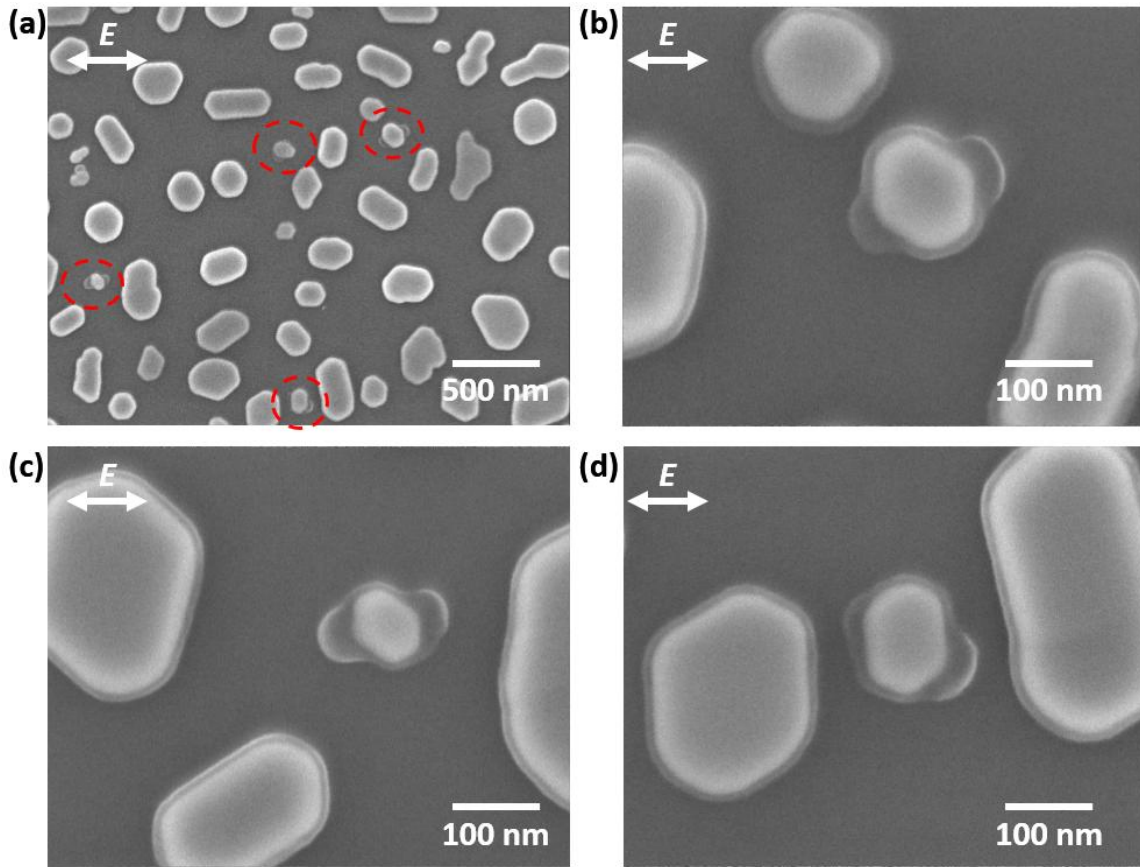


Figure 3.2 SEM images of localized deposition of polypyrrole around random Au nanoparticles. Deposition conditions: 785 nm pulsed laser, 85~88 mW; 0.5 M pyrrole in

acetonitrile solution; 3 min; +0.3 V vs. Ag/Ag⁺. Figures (b), (c), and (d) are the magnified images of the broken red circles in (a). The double-headed arrow indicates the polarization direction of laser.

3.2.3 Position-shift and reshaping of Au nanorods

Figure 3.3 shows the SEM images of Au nanorods on TiO₂ substrate before and after being illuminated by 27 mJ cm⁻² pulsed laser for 3 min. It was found that arrays of nanorods with a rod-length shorter than 130 nm were distorted to different extent. And, although pyrrole was present in the electrolyte solution and a positive enough potential was applied, no deposition of polypyrrole could be found in the vicinity of the nanorods. Comparing the position of Au nanorods before and after light illumination, one could judge that these nanorods were peeled-off then moved to a new position. During the fabrication, no adhesion layer, such as Ti or Cr, had been pre-deposited between the Au layer and the TiO₂ substrate. Thus, the adhesion between Au and TiO₂ is expected to be relatively weak. Usually, for a certain interface, the strength of adhesion depends on the contact area between deposited metal and the substrate. The smaller the size of the metal nanostructure is, the easier it was lost, during the electron-beam lithography. What's interesting is, the peeled-off phenomenon is shown to be dependent on the aspect ratio. That is, the most distorted array is not the smallest ones ($L=50$ in Figure 3.3)

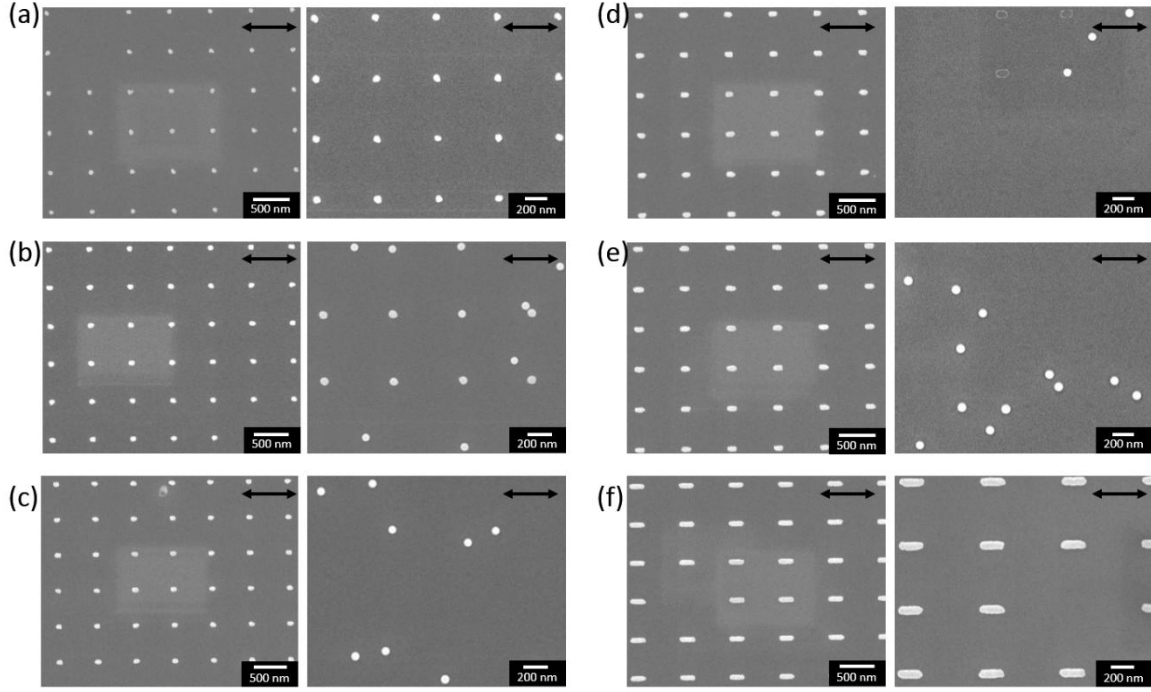


Figure 3.3 SEM images showing the position shift of Au nanorods before and after $270 \pm 10 \text{ mW/cm}^2$ 785 nm pulsed laser illumination for 3 min. The left and right images are corresponding to the images obtained before and after laser illumination, respectively. The designed rod length are (a) 50, (b) 70, (c) 80, (d) 100, (e) 120 and (f) 200 nm, respectively. The double-headed arrow indicates the polarization direction of laser.

To make clear this phenomenon, I made a statistics on the percent of Au nanorods whose were peeled off and removed. Several blocks of nanorods with a rod-length of 50 nm ~ 160 nm were analyzed, as is shown in Figure 3.4. For the smallest nanorods, L50, all of them bare the pulsed laser illumination and retains at the initial positions. As the rod length increases from 40 to 100 nm, the percent of the peeled-off Au nanorods gradually increased. When the rod is longer than 130 nm, no peeled-off was observed. This rod-length dependence could be correlated with the dipolar plasmon mode which is revealed by the Raman intensity as a function of rod length in section 2.3.3 (Figure 2.9d). Similar dimensions (100 nm long, 60 nm thick and 50 nm wide) of Au nanorods fabricated on glass substrate show a resonance wavelength at around 800 nm.^{19,20} For further conformation, the near-field distribution in the vicinity of Au nanorods supported on the TiO₂ substrate immersed in water under illumination of 785 nm plane wave was simulated via the finite-

difference time-domain (FDTD) calculation (Figure 3.5). As the rod length increases from 40 nm to 160 nm, the near-field intensity increases first, then decreases. The maximum intensity appears at 100 nm rod. This is in coincidence with the curve of peeled-off percent in Figure 3.4, where the block of 100 nm rods was the most distorted one. This means that the strong near-field due to LSPR significantly affects the peeled-off phenomenon. According to the FDTD result, the 140 nm and 160 nm rods also show strong near-field intensity. However, for large nanorods, the adhesion also increases, which makes them difficult to be peeled off.

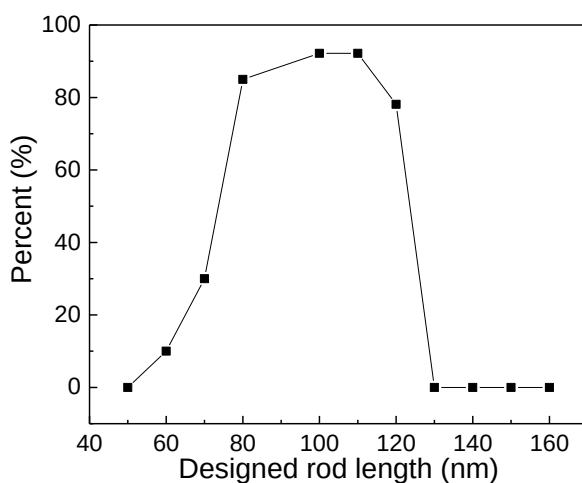


Figure 3.4 The percent of Au nanorods peeled off after illumination of 785 nm 270 ± 10 mW/cm² pulsed laser as a function of the rod length.

The difference between the FDTD simulation and the actual experiment should be noted. The theoretical estimated spatially distributions of the near field under the infrared light onto the various Au nano-rod are shown in Figure 3.5. First, the pulsed laser used in the experiment could deliver higher density of energy into the Au nanorods within the short pulse duration, compared with the continuous-wave light. This character was not accounted in the simulation. Second, the pyrrole in the electrolyte solution acts as the acceptor of hot holes, which helps the decay of LSPR and the cooling of Au nanorods. Besides, the actual dimensions of the Au nanorods prepared by electron-beam lithography are slightly

different from the designed values. SEM images show that the error of fabrication reaches 5 ~10 nm.

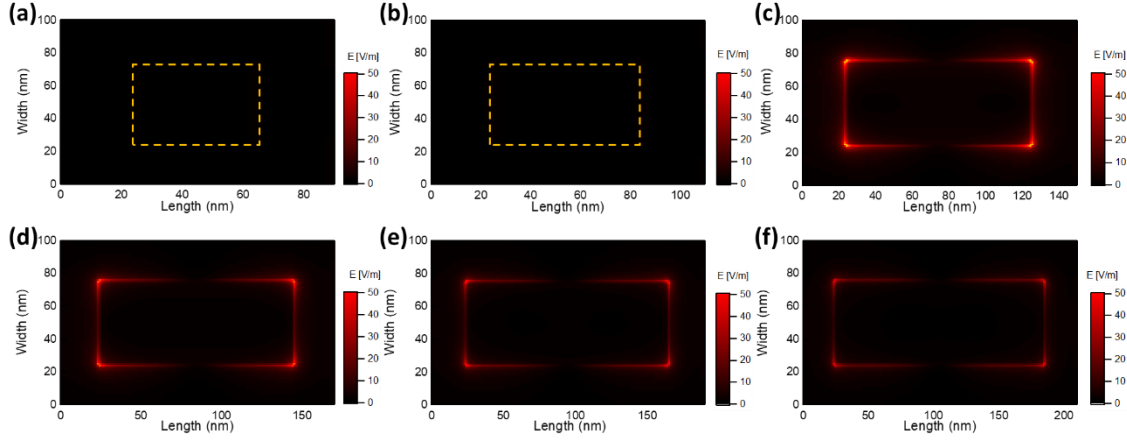


Figure 3.5 The distributions of near-field intensity on Au nanorods supported on the TiO_2 substrate immersed in water. The incident light wavelength is 785 nm. The color bars indicate the field intensity. The rod length for each structure is set to (a) 40, (b) 60, (c) 100, (d) 120, (e) 140, and (f) 160 nm, respectively. The rod width and the height were set to 50 and 60 nm, respectively. The broken lines shown in (a) and (b) indicate the boundary of the Au nanorods.

Another feature after illumination of the pulsed laser is the geometric transformation of the Au nanorods. As is shown in Figure 3.6, the rods with different initial length-to-width ratios are deformed to sphere. For a quantitative characterization, the aspect ratios before and after illumination are plotted as functions of rod length (Figure 3.7). Since the width is fixed at 50 nm, as the rod length increases from 50 nm to 160 nm, the aspect ratio is expected to increase linearly from 1.0 to 3.2. Unfortunately, due to the fabrication error, the actual aspect ratio could not strictly falls on a line. The fabrication error is obvious especially for the short rods, L50, L60 and L70. After illumination, the rods longer than 130 nm retain their shape; while those shorter than 130 nm became round and their aspect ratios approach 1.0. For rods L50, L60 and L70, it is better to evaluate the reshaping directly from the SEM images. As is shown in Figure 3.6, the change of L70 is more obvious than that of L50 and L60. Thus, the significant geometric transformation

actually occurs for rods with a length of $70 \sim 120$ nm, in coincidence with the tendency shown in Figure 3.4.

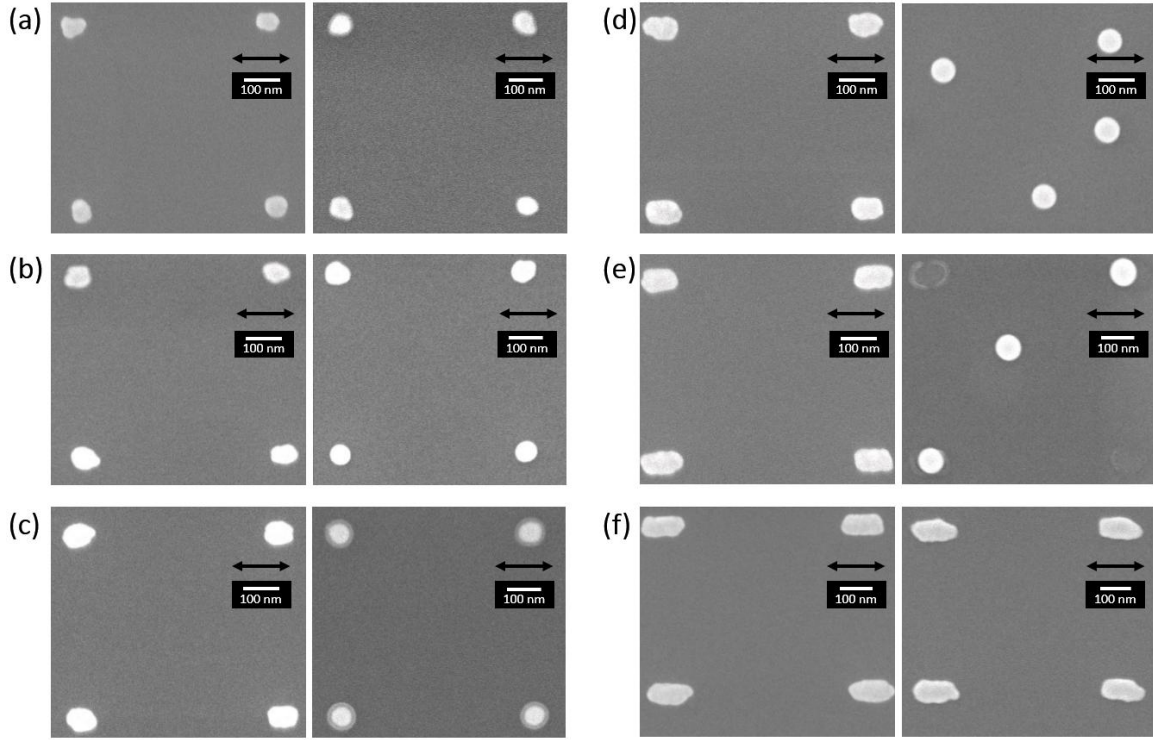


Figure 3.6 SEM images showing the reshaping of Au nanorods before and after illumination of 270 ± 10 mW/cm² 785 nm pulsed laser. The left and right images are corresponding to the images obtained before and after laser illumination, respectively. The designed rod length for each structure are (a) 50, (b) 60, (c) 70, (d) 80, (e) 100 and (f) 130 nm, respectively. The double-headed arrow indicates the polarization direction of laser.

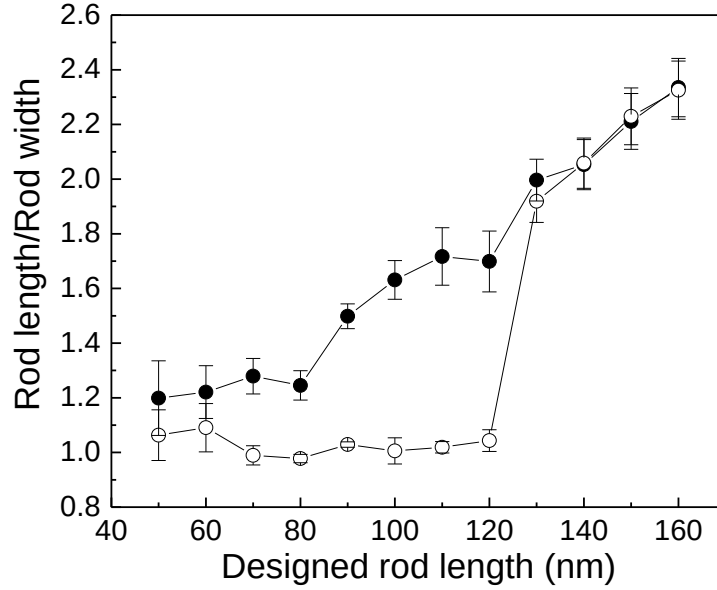


Figure 3.7 The change of aspect ratio (rod length divided by rod width) of Au nanorods after 785 nm 270 ± 10 mW/cm² OPO pulsed laser illumination as a function of the rod length. The error bars show the standard deviation of the measured aspect ratio of rods.

Combining the geometric transformation (Figure 3.6), the position shift (Figure 3.3) and the rod-length dependence (Figures 3.4 and 3.7), one can know that Au nanorods with different rod lengths were deformed to different extents. A slight deformation corresponds to the reshaping of the nanorods; while in a severe deformation, the Au nanorods were peeled-off and moved to a new position. The deformation could be ascribed to the thermal effect. The whole process could be described like that the Au nanorods were first melted, then peeled off and moved to a new position before cooling down. On one hand, if the thermal effect is only caused by the pulsed laser, the Au nanorods with large aspect ratios would be reshaped more easily. However, Figure 3.6 shows that the nanorods with large aspect ratios, for example L130, retain their initial sharp polygonal edges; while those with smaller aspect ratios became round. On the other hand, the rod-length dependence of peeled-off nanorods in Figure 3.4 appears as a peak centered around 100 nm. This 100 nm rod shows significantly enhanced near-field under 785 nm illumination due to LSPR. Thus, the change of Au nanorods is proved to be dominated by the plasmonic near-field. The nanorods under LSPR are selectively deformed due to the enhanced light absorption. This

is further confirmed by the dependence of the change of Au nanorods on the laser power density. Table 3.1 lists the change of nanorods under different illumination power densities. Under weak illumination, only L70, L80 and L90 were deformed. As the power density increases, more rods were changed, but the rod length of the deformed rods centered at about 90 nm, which should correspond to the strongest LSPR.

Table 3.1 The rod length of the deformed rods under different illumination power densities.

Laser power density (mW/cm ²)	rod length (nm) of deformed rods
170 $\pm$ 10	70 ~ 90
270 $\pm$ 10	70 ~ 120
470 $\pm$ 10	50 ~ 140

Under LSPR, the light energy is efficiently absorbed by the free electrons in Au nanorods. The generated hot carriers (hot electrons or hot holes) could be used to induce chemical reactions, such as the polymerization of pyrrole; or they would decay via delivering energy to the lattice. The latter, thermalization process, as a competing pathway, may significantly affect the efficiency of hot carrier-induced reactions. And, when pulsed laser is used, the heat could accumulate in the vicinity of the Au nanorods within a short time. The rapidly accumulated heat may gasify the surrounding solution and prevent pyrrole from diffusing to the active sites at Au nanorods. Therefore, in order to improve the efficiency of plasmon-induced chemical reactions, thermal effects should be considered. The stability of Au nanorods could be improved by increasing the volume (thickness) and the contact area with the substrate. The thermal effect could be weakened by increasing the distance between particles, using lower pulse repetition rate and lower power density. Purification of pyrrole could improve the efficiency for capturing the hot holes.

3.4 Conclusion

In conclusion, deformation of Au nanorods under illumination of pulsed laser was investigated. A slight deformation appeared as the reshaping of rods to sphere and the

severe deformed nanorods were peeled off the substrate. The deformation extent is found to be correlated with the near-field intensity in the vicinity of Au nanorods. The plasmonic thermal effect dominates the deformation of Au nanorods, rather than pure thermal effect of laser pulses. Plasmonic thermal effect as well as the pulsed laser thermal effect may affect the hot carrier-induced electrochemical reactions. This investigation provides useful information for improving the efficiency of plasmon-induced chemical reactions and optimizing the utilization of plasmon-induced heat.

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Chapter 4.

Power dependence of SERS of graphene: plasmon thermal effect and oxidation of graphene

4.1 Introduction

As is described in Chapter 3, non-radiative decay of LSPR releases large amount of heat, which could deform the Au nanoparticles and elevate the local temperature of surrounding medium. Temperature increase lead to a red-shift of Raman G band¹ and the radial breathing mode² of single-walled carbon nanotube. This demonstrates that the Raman spectroscopy of carbon nanotube could act as a nanoscopic thermometer. However, the accumulated heat within the nanoscale space would also harm the chemical stability of the target material, even for the chemically inert carbon materials. The heat generated by the LSPR of Au nanodimers could lead to the local oxidation of single-walled carbon nanotube, especially in oxygen-rich environment.³

In this chapter, the laser power effects on SERS of graphene in air were studied. It is found that the proportions between the band intensities and laser power varies significantly. The D band, which is induced by LSPR or defects, increases slower than proportionally at low laser power, but faster than proportionally at higher laser power. The low-power region is attributed to the change of metal structure morphology while the high-power region to the oxidation of graphene. Both are result of the LSPR. The findings emphasize that the Raman measurement is not always invasive. More attention on the chemical stability of target materials should be paid especially in the presence of LSPR.

4.2 Experimental

4.2.1 Synthesis and transfer of graphene.

As is shown in Figure 4.1, the graphene was synthesized on copper foil (0.025 mm thick) via chemical vapor deposition (CVD) method at 1025 °C in a mixed flow of Ar (1000 sccm), H₂ (20 sccm) and CH₄ (0.36 sccm). Then, it was transferred onto indium tin oxide covered glass

(ITO glass) using poly(methyl methacrylate). After being transferred, the graphene sheet ($\sim 1.5 \text{ cm}^2$) was characterized with Raman microspectroscopy (Nanofinder 30, Tokyo Instruments Inc., Japan) under excitation of 514 nm laser. Figure 4.2 shows the typical Raman spectra of the transferred graphene. The intensity of D band indicates the density of structural defects within the laser spot. The intensity ratio between 2D band and G band tells the number of graphene layers.⁴ For single-layer graphene, this ratio should be larger than two under excitation of 514 nm laser. In the experiment, the transferred graphene on ITO glass (Gr/ITO) was checked over a hundred random sites. Only the Gr/ITO samples with large area of monolayer and defect-free graphene were used for fabrication of Au/Gr/ITO.

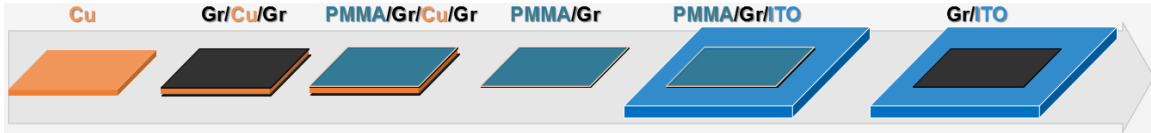


Figure 4.1 Scheme of synthesis of graphene (Gr) and its transferring onto indium tin oxide covered glass (Gr/ITO) with poly(methyl methacrylate) (PMMA).

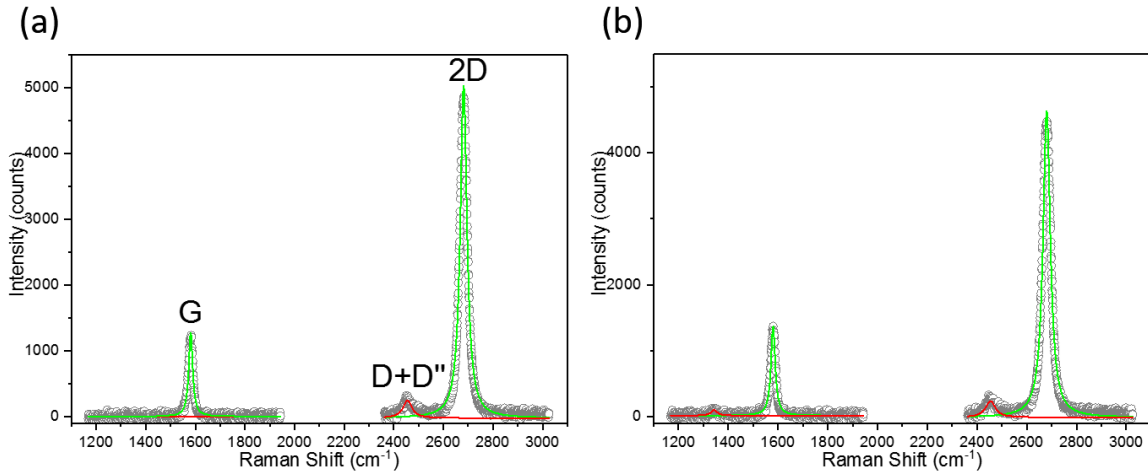


Figure 4.2 Typical Raman spectra of (a) defect-free and (b) defective single-layer graphene synthesized via CVD method and transferred onto indium tin oxide glass substrate measured in air. The excitation laser was 514 nm, 4.0 mW. The acquisition time was 60 sec. Grey circles and lines are the experimental data and Lorentzian fits, respectively.

4.2.2 Fabrication of Au nanodimers on graphene.

Au nanodimers consisting of pairs of tail-to-head triangles which were fabricated on Gr/ITO via angle-resolved nanosphere lithography. The preparation mainly consists of two parts: first, a close-packed Langmuir–Blodgett monolayer of polystyrene beads (PS beads) as mask, was fabricated on Gr/ITO; then, Au was deposited onto the mask/Gr/ITO from two different directions, as is shown in Figure 4.3. In details, 400 μL as-received aqueous suspension of PS beads (0.22 μm mean diameter, polysciences, Inc.) was concentrated in a centrifuge, then 300 μL of the supernatant liquid was removed and 150 μL ethanol was added. The PS beads were re-dispersed in the water-ethanol mixture by sonication. To form a monolayer of PS beads, about 20 μL re-dispersed PS beads suspension was dropped onto and spread over the surface of Milli-Q water in a petri dish. For steady spreading of PS beads at the air-water interface, the PS beads suspension was dropped onto the convex point of a watch glass which was immersed slightly below the water surface. As the PS beads spreads, the water surface reflected a golden color, which indicated 200 nm thick monolayer. Then, the Gr/ITO, which was immersed in the water before dropping PS beads suspension, was lift out of water with a lifter made from a stainless steel wire. Since graphene is hydrophobic, the water and PS beads above it would be easily repelled off at the moment when the Gr/ITO went out of the water. As a result, the PS beads resided on the Gr/ITO were loosely packed and the resultant Au nanostructure became lines of connected triangles. There is a tip to solve this problem: paste hydrophobic tapes around graphene region on the Gr/ITO substrate. The monolayer of PS beads could be trapped within the hydrophobic barriers and remained on the Gr/ITO. The Gr/ITO covered with monolayer of PS beads was dried gradually in air, then was used for Au deposition.

As shown in Figure 4.3b, with close-packed PS beads as the mask, gold was deposited onto the Gr/ITO from two different directions, $+10^\circ$ and -10° relative to the normal of the substrate. Most of the Au is deposited on the mask and the rest is deposited in the triangular interspaces of the PS nanospheres. Deposition from two directions make pairs of triangles. At each direction, totally 27 nm thick gold was deposit in three steps ($9\text{ nm} \times 3$). For symmetry of the dimers, after each deposition of 9 nm, the direction was altered. Finally, the mask and the gold on it were removed by sonication in Milli-Q water. The gold deposit on the graphene was left due to a stronger adhesion.

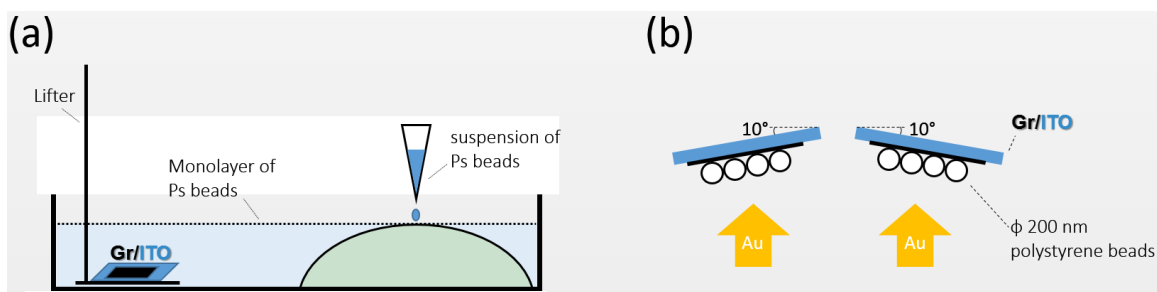


Figure 4.3 Schematic illustration of (a) fabrication of a close-packed monolayer of PS beads on Gr/ITO and (b) sputtering Au on Gr/ITO from two directions.

4.2.3 Characterization of Au/Gr/ITO

The as-prepared Au/Gr/ITO was characterized with SEM and extinction spectroscopy in air (Figure 4.4). The SEM image shows that the Au nanodimers consist of pairs of triangles and all of the long axes of dimers are aligned in the same direction. To show the presence of graphene, the view of SEM is chosen at the edge of graphene. Figure 4.4a shows that graphene is darker than the ITO in the SEM. The extinction spectra shows the anisotropic property of Au/Gr/ITO. When the polarization of incident light is parallel the long axis of dimers, the extinction shows a peak around 830 nm. This longitudinal mode of dimers originates from the coupling between plasmons of individual triangles, resulting in a significantly enhanced near-field in the gap.^{5,6} The 785 nm laser is close to the LSPR peak therefore was used as the excitation source for SERS.

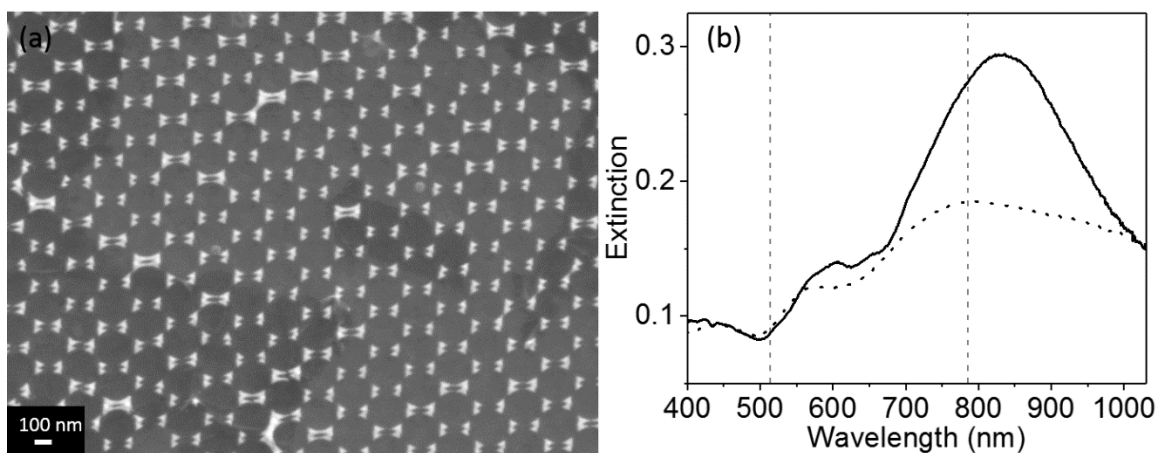


Figure 4.4 (a) SEM image and (b) polarization-dependent extinction spectra of Au/Gr/ITO. The thick and thin curves correspond to the polarization parallel and perpendicular to the axis of Au nanodimers, respectively. The dash vertical lines indicate 514 nm and 785 nm, two excitation wavelengths.

4.2.4 SERS measurements

SERS of Au/Gr/ITO was carried out with a Raman microspectroscope (Nanofinder 30, Tokyo Instruments Inc., Japan) under excitation of 785 nm continuous wave laser. The laser power started from 0.36 mW and gradually increased until 1.86 mW. For each power, the integration time was 60 sec.

4.3 Results and discussion

Figure 4.5a shows the SERS spectra of Au/Gr/ITO. Besides the G and 2D bands, which are universal for graphitic carbon, D band is also observed. Since the as-prepared graphene had been confirmed to be defect-free, the D band can be attributed to a) structural defects caused by laser illumination and/or b) the LSPR-induced breakdown of Raman selection rule. At the lowest power, the intensities of G and D bands are almost comparable, but at the highest power, the D band is significantly stronger than the G band. After the measurement at 1.85 mW, the power of laser was reset to 0.36 W. The SERS spectra at 0.36 mW measured before and after high-power measurement are shown in Figure 4.5b. Obviously, the intensity of G band does not

change significantly, but the intensity of D band is almost doubled. Moreover, the G band slightly blue-shifts. This blue-shift can be attributed to the emergence of D' band. Therefore, it is believed that graphene is oxidized during the measurement.

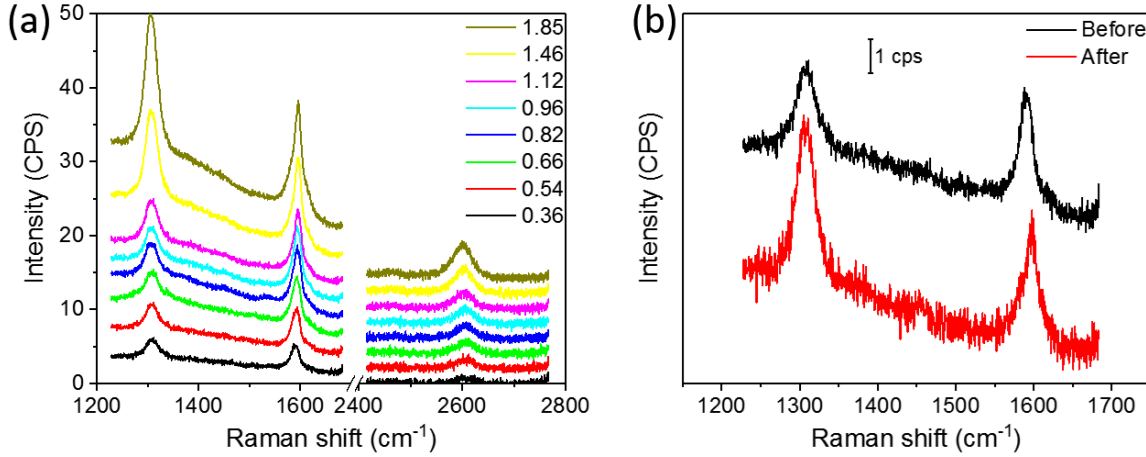


Figure 4.5 (a) SERS spectra of Au/Gr/ITO under increasing powers from (bottom) 0.36 mW to (top) 1.85 mW, in air. (b) SERS spectra of Au/Gr/ITO at 0.36 mW laser (top) before and (bottom) after illumination by at higher power of laser.

To figure out the magnitude of laser power, with which graphene oxidization starts, the heights of D and 2D bands (H_D and H_{2D}) are plotted as functions of laser power (P). They are shown in Figure 4.6a. The 2D band is selected instead of G band because G band intensity is interference by additional signal such as D' band. The height of 2D band is basically proportional to the laser power ($H_D \propto P$). However, the D band height increases slower than proportionally when laser power is less than 1 mW ($H_D \propto P^{0.72}$). Above 1.0 mW, there is a boost of D intensity with laser power ($H_D \propto P^{2.24}$). After all the measurements, the laser power was tuned back to 0.36 mW. By this, the 2D height becomes 1/3 higher compared to the initial height, while the D band height is doubled. The ratios between the areas of D and 2D bands (A_D/A_{2D}) are also plotted in Figure 4.6b. There is a significant decrease of A_D/A_{2D} from 2.3 to 1.6 below 1.0 mW, but it then increases significantly to 3.1 when laser power reaches 1.85 mW. After the laser power is reduced back to 0.36 mW, A_D/A_{2D} was kept at 3.1. These results suggest that Au/Gr/ITO experiences different changes under different laser power.

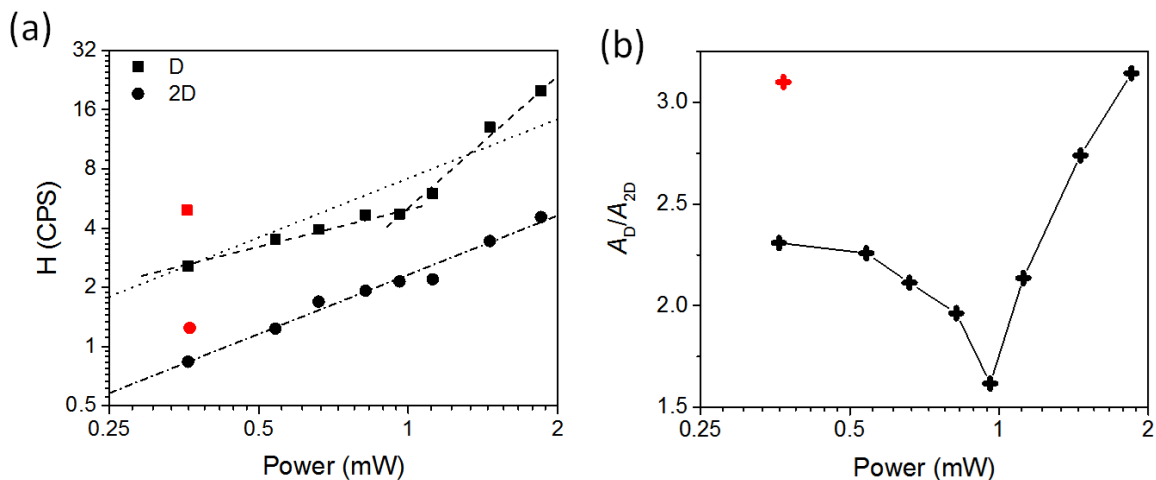


Figure 4.6 (a) D band and 2D band heights (H) at different laser powers. The dash lines represent the tendency of data points. The dot lines represent the proportional relations. b) The ratios between the areas of D and 2D bands. Red data points are after measurement at higher laser power.

Below 1.0 mW, the change of SERS spectra could be ascribed to the restructuring of Au. The D band in the SERS of defect-free graphene has been proved to be the result of breakdown of Raman selection rule.⁵ Basically, when photons are confined within a nanometer scale space, they gain wavevectors which are comparable to the reciprocal lattice vectors. Thus, the excitation from K point Dirac cone to K' point Dirac cone is enabled. This excitation is equivalent to a vertical excitation plus a defect scattering. That's why the D band is observed in SERS. The intensity of D band depends on the degree of localization i.e. the morphology of metal nanostructure. With laser illumination, the elevated temperature could mobilize the Au atoms at the very sharp tips of triangles. Thus, the sharp tips are rounded to reduce the surface energy. When the laser power increases, the temperature becomes higher, so that the A_D/A_{2D} decreases faster. On the other hand, when the temperature is high enough, the oxidation of graphene starts in air. Even though the temperature may not be high enough for graphene oxidation under normal condition, localized surface plasmon has the potential to induce oxidation owing to the formation of active oxygen. The photo-excited graphene is also more reactive. That is why D band increases significantly at high laser power.

4.4 Conclusion

In conclusion, the SERS of graphene was measured using Au nanodimer as LSPR activator. It was found that the D band intensity is not proportional to laser power. At low power, the restructuring of Au dimer reduces the plasmon-induced D band intensity. At high power, the oxidation of graphene significantly increases D band intensity. This research is very important demonstration to distinguish SERS signal of D bands from distinct origins, leading to the creation of novel technique to characterize the number of the defect in graphene.

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Chapter 5.

“G-band splitting” in SERS of graphene: non-vertical electronic excitation by plasmon

5.1 Introduction

The unique electronic dispersion of graphene makes it an ideal test bed for investigation of photoexcitation process.¹⁻⁵ Single-layer graphene is a zero-gap semiconductor. Its valence band and conduction band touch each other at the high-symmetry **K** and **K'** points of the Brillouin. The electrons near the two inequivalent valleys behave as massless Dirac Fermions, characterized by a linear Dirac dispersion, $E(k) = \hbar v_F k$, where v_F is the Fermi velocity, k the wave⁶. The two-dimension energy dispersion relation is isotropic, forming the Dirac cone.³ Such linear electronic dispersion around the Dirac point endues graphene unique optical properties, such as the frequency-independent absorption⁷ and strong Raman scattering⁴ in the visible to near-infrared range. Within this range, the optical response of a pristine graphene is dominated by resonance interband transitions. Due to the resonant character, Raman scattering is very strong, even in an atomic layer of graphene. This enables Raman spectroscopy a powerful tool to observe any tiny change in the electronic transition and electron-phonon interaction.^{8-10, 6, 11, 12} For example, Raman G band is highly dependent on the electronic population of the band structure of graphene. When the Fermi level of graphene moves away from the Dirac point, either n-type doped or p-type doped, the G band shifts to higher energies (larger wavenumbers in Raman spectra) and the G band width decreases. These features of G band is due to the change of phonon dispersion under charge doping. In turn, G band behavior reflects the photoexcitation process.

LSPR adds new features to the Raman of graphene.^{13-15, 16, 17} For instance, a significantly enhanced D band is observed in the surface enhanced Raman spectroscopy (SERS) of a defect-free graphene, as is described in Chapter 4 and previous reports^{13, 14, 18}. Recently, ‘G-band splitting’ was observed after depositing several-nanometer Au or Ag on graphene, where the G band at *ca.* 1600 cm⁻¹ became broad and could be decomposed into two or three subbands.¹⁹⁻²² Various explanations have been proposed, such as the wrinkles,²² the

strain,²¹ and the removal of the degeneracy between the in-plane transverse optical (iTO) and in-plane longitudinal optical (iLO) modes at the Γ point¹⁹. However, in these experiments, the metal nanoparticles with random structures have broad absorption spectra and weak near-fields, which results in an unclear ‘splitting’ and has limited a deep study on the interesting light-matter interaction underlying this phenomenon.

In this chapter, SERS of the Au nanodimers-decorated defect-free monolayer graphene was investigated with high spectral resolution of Raman spectroscopy. Three Raman bands around 1600 cm^{-1} were clearly resolved if the laser frequency is in resonance with the localized surface plasmon of Au nanodimer; but only a single G band was observed otherwise. Therefore, the origin of multiple bands must be a direct result of LSPR. Furthermore, the behavior of the bands under controlled electrochemical potentials was investigated. According to their distinct behaviors, these bands are assigning to the G band, D' band and D7 band. A model of plasmon-assisted Raman scattering process was proposed. With LSPR, the wavevectors of photons can be extended to be comparable with the reciprocal lattice vectors. Thus, excitons in graphene can have non-zero momenta, which enables non-vertical electronic transitions and various electron-phonon scattering pathways. Furthermore, Raman spectra of graphene at high doping levels were investigated. The quantum interference effects of intrinsic graphene disappear in SERS, as a result of additional non-vertical transition channels.

5.2 Experimental

Au/Gr/ITO and Gr/ITO samples were prepared with the same method as that introduced in Chapter 4. The Gr/ITO was confirmed to be monolayer and defect-free via Raman spectroscopy under excitation of 514 nm laser.

Electrochemical Raman spectra of Au/Gr/ITO and Gr/ITO samples were carried out with a Raman microspectroscope (Nanofinder 30, Tokyo Instruments Inc., Japan) under excitation of continuous-wave laser, as is shown in Figure 5.1. A 100 $\times$ objective with a numerical aperture = 0.80 and a working distance = 4.5 mm (TU Plan ELWD, Nikon co., Japan) was used. The groove density of the grating was 1200 grooves/mm. According to the full width at half maximum (FWHM) of Rayleigh scattering (Figure 5.1b), the spectral

resolution was 1.41 cm^{-1} . The power and illumination times are 15.4 mW, 60 sec for Gr/ITO and 1.0 mW, 10 sec for Au/Gr/ITO, respectively. The electrode potential of was controlled via a three-electrode system in which the counter and reference electrodes were a Pt plate and home-made Ag/AgCl (*sat. KCl a.q.*) electrode, respectively. For section 5.3.2 and 5.3.3, the electrolyte solution was a pH = 2 buffer solution consisting of 0.075 M NaH_2PO_4 and 0.1 M H_3PO_4 . In order to observe the behaviors of Raman bands of graphene under high doping levels (section 5.3.4), saturated NaClO_4 aqueous solution (at room temperature) was used as the electrolyte solution.

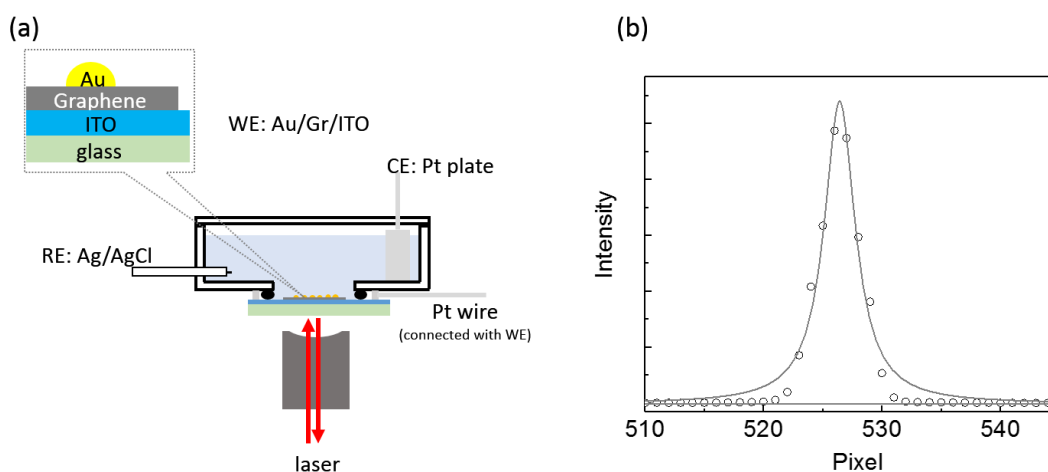


Figure 5.1 (a) Setup for the electrochemical Raman spectroscopy. WE, working electrode; RE, reference electrode; CE, counter electrode. (b) Spectrum (circles) and the Lorentzian fit (lines) of Rayleigh scattering with grating of 1200 grooves/mm. The FWHM is 3.17 pixel, corresponding to 1.41 cm^{-1} .

5.3 Results and discussion

5.3.1 ‘G-band splitting’ in SERS of Au/Gr/ITO

Raman spectra of as-prepared Gr/ITO and Au/Gr/ITO are shown in Figure 5.2a. The spectrum of pristine graphene shows a G band at $\sim 1585 \text{ cm}^{-1}$ and a 2D band at $\sim 2590 \text{ cm}^{-1}$, both of which have symmetric Lorentzian shapes. In contrast, Au/Gr/ITO shows additional bands. The band at $\sim 1305 \text{ cm}^{-1}$ under 785 nm excitation, and $\sim 1346 \text{ cm}^{-1}$ under 514 nm excitation are in accordance with the D band from structurally defective graphene.

However, our graphene has been confirmed to be defect-free. Moreover, the D band is pretty weak under 514 nm illumination (out of resonance with LSPR) but strong under 785 nm illumination (in resonance with LSPR). Thus, it should be ascribed to the influence from LSPR^{13,14}. In Raman spectroscopy of graphene, the D band requires that the electrons and holes are in neighboring Dirac cones (i.e. the difference between their wavevectors is close to that of K point), which is achieved by the elastic scattering of excited electrons by defects²³. However, in SERS of graphene, the wavevector separation is achieved by plasmon-induced electronic excitation.^{13,14}

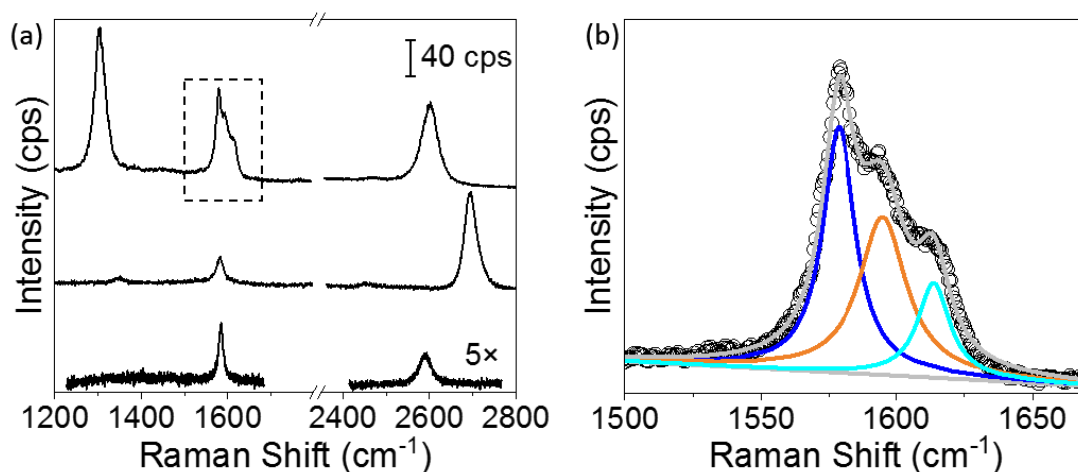


Figure 5.2 (a) Raman spectra of Gr/ITO under illumination of (bottom) 16 mW, 785 nm laser and those of Au/Gr/ITO under illumination of (middle) 1 mW, 514 nm laser and (top) 1 mW, 785 nm laser. (b) The close-up of the Raman spectrum of Au/Gr/ITO circled in the dashed box in panel a. The open circles are raw data. The blue, orange and cyan lines are Lorentzian fits. The grey lines are the baseline and envelope.

More interestingly, totally 3 subbands are found around 1600 cm^{-1} on Au/Gr/ITO under 785 nm laser excitation. The close-up of this part of spectrum is shown in Figure 5.2b. The raw data can be fitted by three Lorentzian functions. Similar “G-band splitting” was previously reported after deposition of metals on graphene^{19–22}, and other cases, for example, the graphene supported by Au nanodimers¹⁵, strained graphene²⁴ and bilayer

graphene^{25,26}. Previously, the split of G band was ascribed to several different reasons: 1) the lifting of the degeneracy of the in-plane transverse optical (iTO) and in-plane longitudinal optical (iLO) modes at the Γ point caused by some unclear kind of metal-graphene interaction²¹; 2) a uniaxial strain in graphene^{21,15,24}; 3) the localized metallic edge states of zigzag-edged graphene²⁸; 4) the optical phonon mixing in double-layer graphene^{25,26}. None of these reasons could explain the dependence of G-splitting on excitation energy. For the same Au/Gr/ITO sample, the G-splitting was never observed under 514 nm excitation. Thus, the appearance of multiple bands should be ascribed to the excitation of LSPR of Au nanoparticles.

Note that, the G-splitting in SERS of graphene supported by Au nanodimers¹⁵ should be distinguished from my result. In the former case, the resultant first two subbands both red-shift with respect to the intrinsic G band of graphene, which could be ascribed to the strain arose in graphene.¹⁵ In contrast, in my case, the first two subbands locate below and above the energy of intrinsic G band of Gr/ITO. Figure 5.3 shows the distribution of G and 2D bands measured at different positions on the same sample. For Gr/ITO under excitation of 514 nm or 785 nm laser, the 2D band position shifts linearly with G band, which is affected by the residual strain and local doping of graphene. For Au/Gr/ITO under 785 nm excitation, the first two of three subbands around 1600 cm^{-1} are plotted. Both of the first two sub-bands shift linearly with 2D band with a similar slope as that of Gr/ITO. This means that the strain distribution in graphene layer is not changed during Au deposition. It also confirms that the ‘G-splitting’ in my result is not due to mechanical strain.

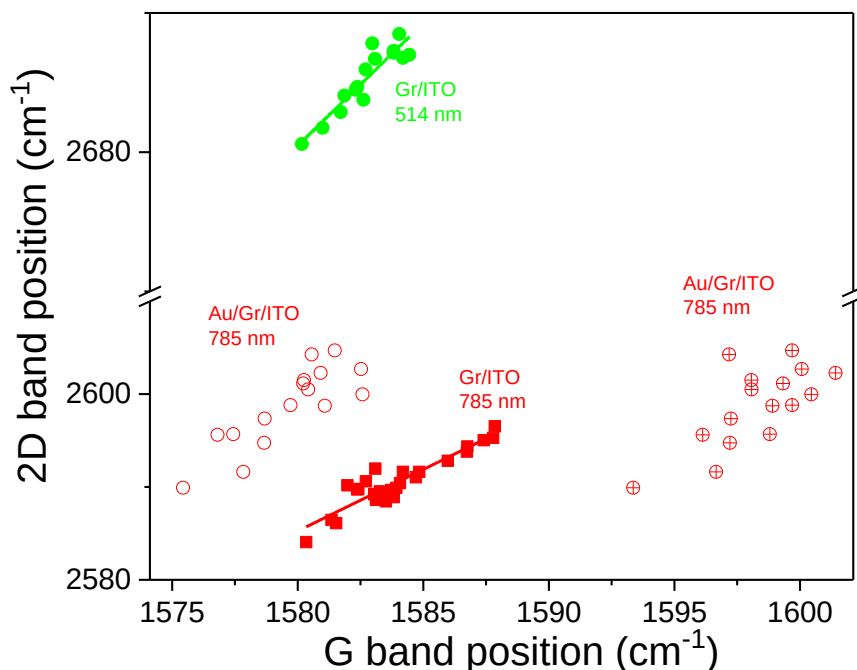


Figure 5.3 Relative position of G band and 2D band of Gr/ITO and Au/Gr/ITO under excitation of 514 nm or 785 nm laser. For Au/Gr/ITO, since the G band is split, the first two subbands are plotted instead.

Au nanodimer has anisotropic geometry and shows different plasmon modes under different polarization directions. Figure 5.4 shows the polarization dependence of SERS of Au/Gr/ITO. ‘G-band splitting’ is present at all of the polarization directions and the positions of the three subbands around 1600 cm^{-1} are not shifted by different plasmon mode (Figure 5.4b). This means that the gap (longitudinal) plasmon mode is not the necessary preconditions for ‘G-band splitting’. Actually, ‘G-band splitting’ was also observed when single nano-triangles were used. The change of polarization direction only alters the enhancement of near-field and causes different Raman band intensities (Figure 5.4c). Among all the bands, the D band intensity is most sensitive to the polarization.

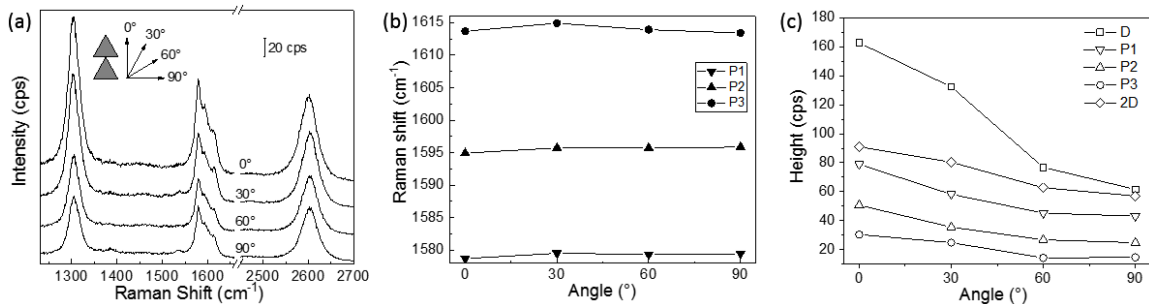


Figure 5.4 (a) Polarization-dependent Raman spectra of Au/Gr/ITO under illumination of 785 nm laser measured in air. From top to bottom, the laser polarization direction alters from 0 ° to 90 ° with respect to the long axis of Au nanodimers. The power of laser and the acquisition time were 1 mW and 20 sec, respectively. (b) Raman shift of the three subbands around 1600 cm⁻¹ as a function of polarization direction. (c) Variation of the band intensities with polarization direction.

5.3.2 Electrochemical SERS of Au/Gr/ITO

To make clear the origin of the multiple bands around 1600 cm⁻¹, electrochemical Raman spectroscopy was carried out. The potential-dependent Raman spectra and the Lorentzian fitting results are shown in Figures 5.5 and 5.6 respectively. For Gr/ITO, the G band has the lowest Raman shift when the graphene is charge-neutral, and shifts to higher frequencies when the graphene is electron- (negative potentials) or hole-doped (positive potentials). This is consistent with previous results.^{8,9,11} In contrast, the 3 sub-bands around 1600 cm⁻¹ of Au/Gr/ITO behave distinctly. The bands around 1615 cm⁻¹ can be assigned to D' band according to its Raman shift. The band around 1595 cm⁻¹ is about the frequency of G band; and its position evolves similarly to the G band (upward triangles in Figure 5.6), i.e. it red-shifts as doping level decreases. Hence, it should be the G band of graphene. The band at about 1580 cm⁻¹ behaves differently from the G band (downward triangles in Figure 5.6). According to the phonon dispersion of graphene, this band energy could correspond to an iTO phonon mode, which involves an intravalley scattering process and was previously nominated D7 band.²⁹ The visualization of these multiple bands in SERS and their distinct behaviors are explained below.

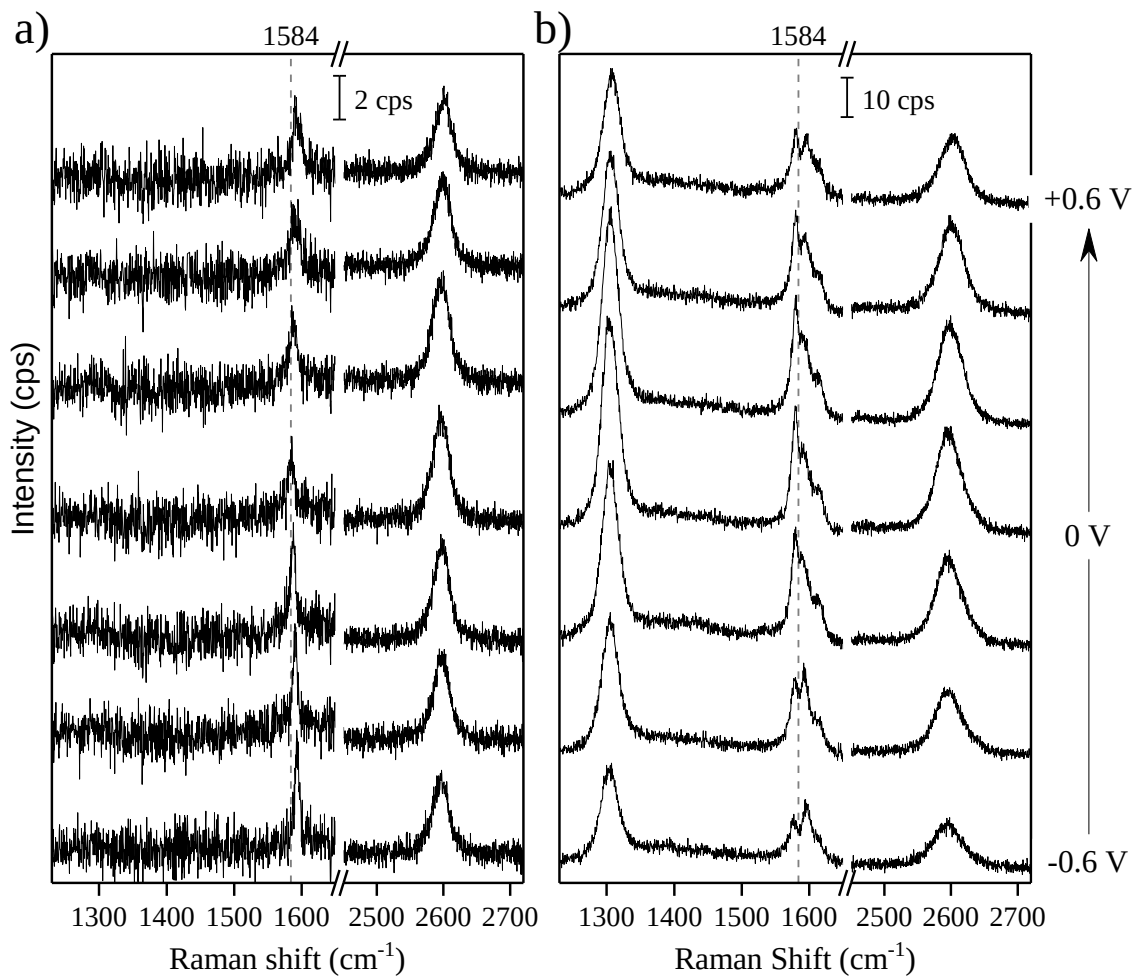


Figure 5.5 Raman spectra of (a) Gr/ITO and (b) Au/Gr/ITO excited by 785 nm laser under controlled electrochemical potentials vs. Ag/AgCl *sat.* from -0.6 V (bottom) to $+0.6$ V (top) with an interval of 0.2 V. The power and illumination time were (a) 15.4 mW, 60 sec and (b) 1.0 mW, 10 sec, respectively. The vertical broken lines are a reference for band position.

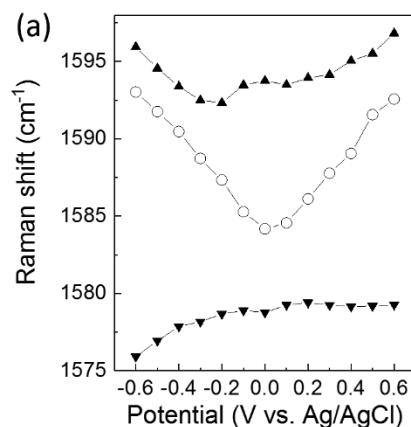


Figure 5.6 Potential-dependent Raman band position of (open circles) Gr/ITO and (solid triangles) the Au/Gr/ITO under 785 nm laser excitation. The upward and downward solid triangles represent the first two subbands around 1600 cm^{-1} , respectively.

5.3.3 Plasmon-mediated Raman scattering

In principle, all Raman scattering processes consist of three steps: excitation of electrons by photons, inelastic scattering of electrons by phonons and emission of photons by the recombination of electrons and holes. In normal Raman spectroscopy, the wavevector of the incident far-field photons are negligible compared to those of the reciprocal lattice vectors of graphene. Thus, the wavevectors of phonons involved in Raman scattering must be zero. That's why a single G band, corresponding to the phonon at the center of the Brillouin zone, is observed. If the graphene is defective, the excited electrons can be elastically scattered by the defect to states on the other side of the Dirac cone, which is then inelastically scattered by iLO phonons to the original wavevector. These phonons of nonzero wavevector observed in defective graphene are D' band.^{4,23} D7 band has a similar intraband Raman process as D' band, with an iTO phonon involved, instead. However, the iTO mode is Raman inactive because this oscillation results in symmetric polarizability. Thus, D7 band is usually not observed. Figure 5.7a illustrates the resonant Raman scattering processes of G band and plasmon-induced D7 and D' bands. In SERS, the photons are spatially confined within nanoscale due to LSPR. According to the uncertainty principle, the distribution of momenta of photons are broadened by the spatial confinement. Thus, electron excitation with change of wavevectors is enabled, such as

those in D7 and D' processes in Figure 5.7a. The excited electrons can be scattered back by iLO phonons to the original wavevector and recombine with the holes. That explains the observation of D' band in SERS of defect-free graphene. As for D7 band, the strong field gradient destroys the translational symmetry of system, making the iTO detectable by Raman spectroscopy. Note that, by adopting the non-zero wavevector excitations, all the D' and D7 processes can be resonance processes, which results in much stronger band intensities. That is why the D7 and D' bands appear so strong in SERS.

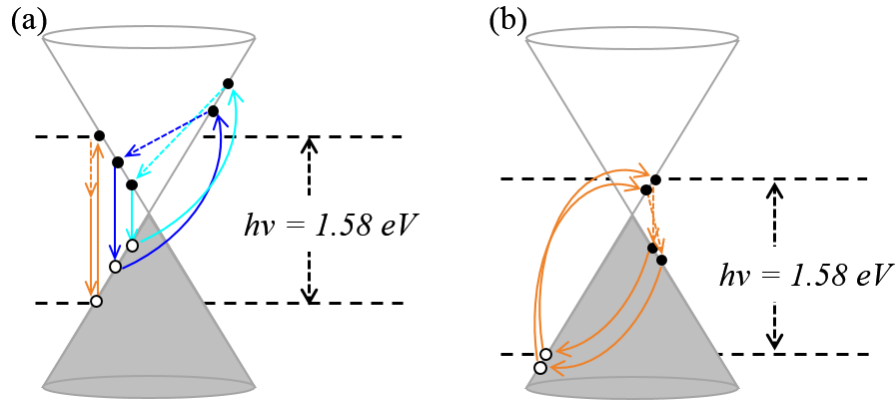


Figure 5.7 Schematic illustration of Raman scattering processes of (a) G band (orange), D7 band (blue) and D' band (cyan). (b) Plasmon-mediated G bands. The solid straight arrows represent the far-field excitation and emission. The curved arrows represent the plasmon-mediated excitation and emission. The dashed straight arrows represent the change of electron energies and momenta during inelastic scattering with phonons.

The distinct behaviors of G, D7 and D' bands under electrochemical potentials can be understood from the phonon dispersion of graphene (Figure 5.8). The G band corresponds to the doubly degenerate iTO and iLO phonons at the Γ point. Theoretical calculation shows that Kohn anomaly (softening of phonon due to electron-phonon interaction) takes place on the highest optical phonon mode at the Γ point of undoped graphene.³⁰ Experiments and calculations have shown that charge carriers remove the Kohn anomaly, resulting in an increase of G phonon frequency.^{6,31–34} However, the phonons corresponding to D7 and D' bands are away from the Γ point. They are not

affected by the Kohn anomaly so their energies are not sensitive to electrochemical potential change.

LSPR confines not only the incident photons, but also the scattered photons. Thus, the recombining electrons and holes do not need to have the same wavevector. A variety of Raman processes are enabled by it. Figure 5.7b shows plasmon-mediated G band processes, in which both excitation and emission are coupled with the localized surface plasmon. In this case, not only the phonon at Γ point but also those with non-zero wavevectors near the Γ point are detectable by Raman spectroscopy. Contribution of the wide range of wavevector of phonons results that the observed “G” band is only weakly affected by the Kohn anomaly. In other words, the Kohn anomaly is partially removed even if charge density is zero. This explains why the potential-dependent G band position of Au/Gr has a ‘flat’ bottom, distinct from that of the pristine graphene (Figure 5.6a).

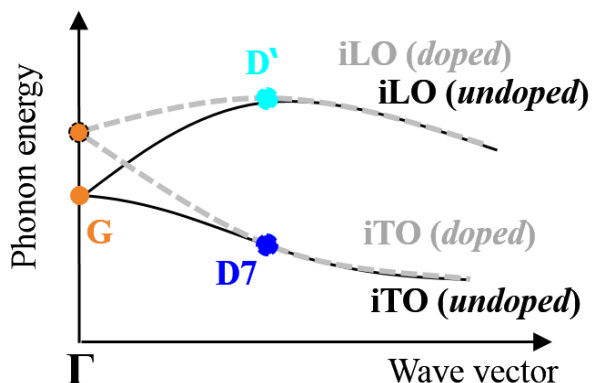


Figure 5.8 Schematic illustration of change of the phonon dispersion of graphene due to charge doping.

5.3.4 Raman and SERS of graphene under high doping levels

In order to observe the behaviors of Raman bands of graphene under high doping levels, saturated NaClO_4 aqueous solution (at room temperature) was used as the electrolyte solution. Figure 5.9 shows the cyclic voltammetry of Au/Gr/ITO and Gr/ITO in saturated NaClO_4 aqueous solution. The Gr/ITO is inert in a wide potential window from -1.0 V to $+1.5$ V vs. Ag/AgCl sat., as reported previously³⁵. However, the presence of Au nanodimers narrows it.

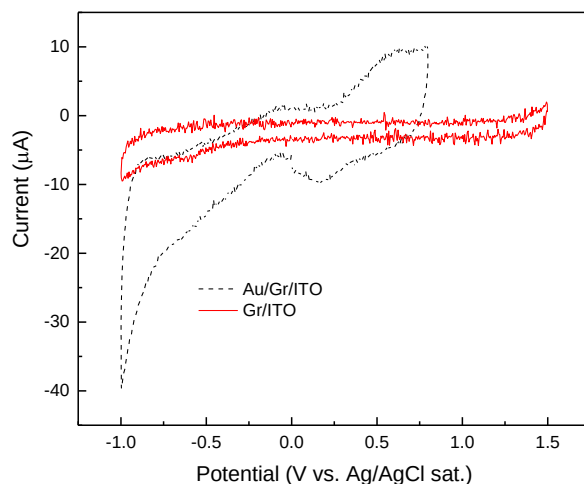


Figure 5.9 Cyclic voltammetry of (broken) Au/Gr/ITO and (solid) Gr/ITO in saturated NaClO_4 aqueous solution. The potential scanning rate was 50 mV/sec. The electrode surface was about 1.8 cm^2 .

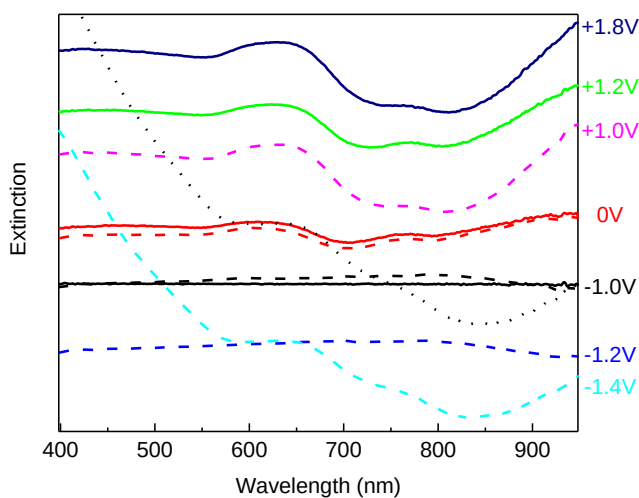


Figure 5.10 Differential extinction spectra of Au/Gr in saturated NaClO_4 aqueous solution. The reference spectrum was measured at -1.0 V vs. Ag/AgCl sat. . The potential scan sequence was (solid) $-1.0 \text{ V} \rightarrow 0 \text{ V} \rightarrow +1.2 \text{ V} \rightarrow +1.8 \text{ V}$, then to (broken) $+1.0 \text{ V} \rightarrow 0 \text{ V} \rightarrow -1.0 \text{ V} \rightarrow -1.2 \text{ V} \rightarrow -1.4 \text{ V}$, finally back to (dot) -1.0 V .

The stability of Au nanodimers and ITO layer under potential scanning was characterized with differential extinction spectra (Figure 5.10). The reference spectrum

was measured at -1.0 V vs. Ag/AgCl sat. The potential was first scanned (solid lines) from -1.0 V to $+1.8$ V, then back (broken lines) to -1.4 V, finally again to -1.0 V (dot lines). Within -1.0 V to $+1.8$ V, the extinction changes reversibly with potential. The change mainly locates at 600 nm $\sim$ 800 nm, which is caused by the shift of LSPR peak. When potential reaches -1.4 V, distinct change appears, especially at short wavelength < 600 nm, which indicates the reduction of ITO layer³⁶. The reduction of ITO layer irreversibly changes the optical property of the substrate. According to the cyclic voltammetry and the differential extinction spectra, the negative limit of electrode potential should be -1.0 V $\sim$ -1.2 V, for the stability of Au nanodimers and ITO layer. The Au and ITO could bare positive potentials up to about $+1.8$ V. However, the graphene would be oxidized under illumination of laser, which would be seen from the Raman measurement.

Figure 5.11 shows the Raman spectra and Lorentzian fitting analysis of Gr/ITO under varying potentials. The significant change is the band intensity (band height or frequency-integrated area) of G and 2D bands. The Dirac point of graphene is about -0.1 V, according to the minimum of G band energy. 2D band intensity reaches maximum at Dirac point and decreases when the doping level of graphene increases, either in *n*-doped or *p*-doped regime. This is a result of blocking of Raman scattering pathways due to charge doping. Briefly, 2D band Raman scattering is a second-order process, in which two phonons with wavevector close to the K point in the Brillouin zone are simultaneously excited. According to the quantum interference theory³⁷, there are different possible pathways for the 2D band, not only the double-resonance one³⁸, but also non-resonance ones. All the different pathways interfere constructively. Thus, as the Fermi level leaves away from the Dirac point, the intersection of valence band and conduction band, the valence band becomes empty in *p*-doping regime; or the conduction band becomes filled in *n*-doping regime. Due to Pauli exclusion principle, the allowed electronic transition paths become less. The blocking of electronic transition makes the 2D band intensity decrease.

G band intensity increases suddenly at high doping level, where 2D band becomes not detectable. According to the quantum interference theory³⁷, the Raman pathways of G band could be on resonance, close to resonance or off resonance. All of these different G band pathways interference destructively, in contrast to 2D band. As the doping level

increases, the blocking of electronic transition suppresses the destructive interference gradually. At a specific doping level, where the destructive interference is eliminated totally, G band intensity reaches the maximum. The critical doping level is

$$2|E_F| = E_L - \frac{\hbar\omega_G}{2}$$

where the E_F is the Fermi energy (eV), E_L the laser energy, and $\hbar\omega_G$ the energy of G phonon. For 785 nm (1.58 eV) laser, G band reaches the maximum as the Fermi energy reaches 0.74 eV. Using saturated NaClO₄ aqueous solution, the Fermi energy of graphene is tuned up to 0.74 eV at about +0.9 V vs. Ag/AgCl sat. For 514 nm (2.41 eV) laser, the critical Fermi energy for G band maximum is 1.65 eV, which is far beyond the potential range in the experiment (Figure 5.12).

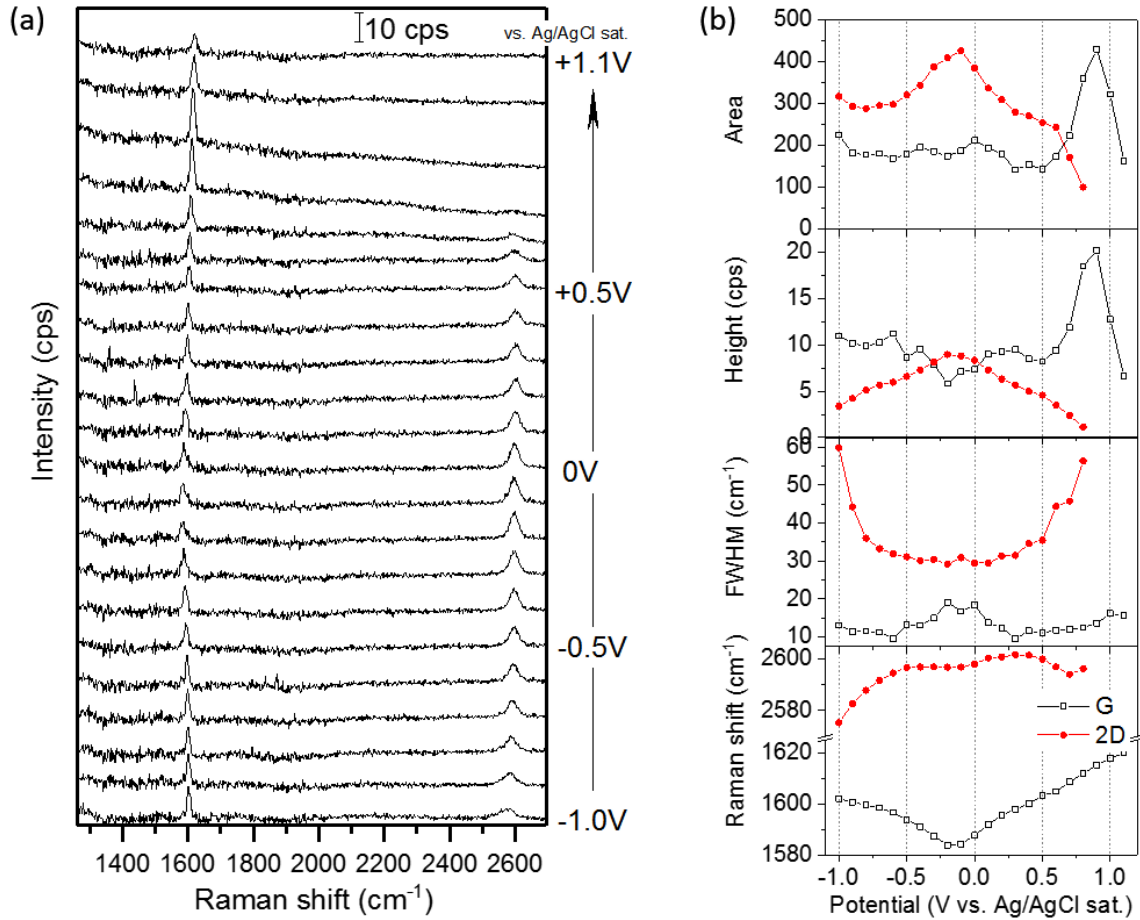


Figure 5.11 (a) Raman spectra of Gr/ITO under potentials from (bottom) -1.0 V to (top) $+1.1$ V vs. Ag/AgCl sat. with an interval of 0.1 V. The illumination conditions were 785 nm, 15.76 mW, 120 sec. The grating density was 300gr/mm . The electrolyte solution was

NaClO₄ saturated aqueous solution. (b) Dependence of band position, width, height and area of (squares) G and (disks) 2D bands on electrochemical potentials. Both of G and 2D bands were fitted with Lorentzian functions.

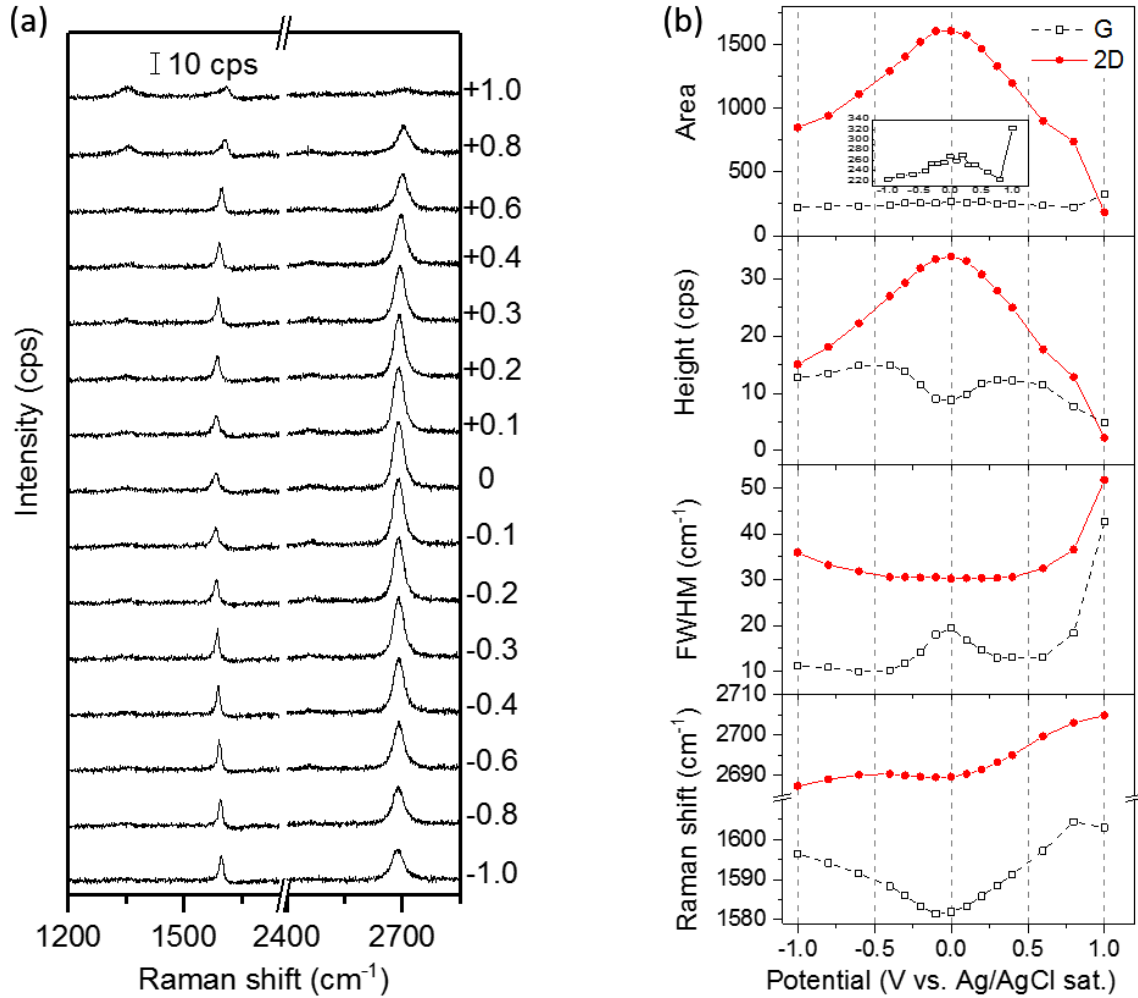


Figure 5.12 (a) Raman spectra of Gr/ITO under potentials from (bottom) -1.0 V to (top) $+1.0$ V vs. Ag/AgCl sat.. The illumination conditions were 514 nm, 4.0 mW, 60 sec. The grating density was 1200gr/mm. The electrolyte solution was NaClO₄ saturated aqueous solution. (b) Dependence of band position, width, height and area of (squares) G and (disks) 2D bands on electrochemical potentials. Both of G and 2D bands were fitted with Lorentzian functions.

Plasmon modified the G band process and makes the quantum interference effect invalid. As is shown in Figure 5.13, the Dirac point remains at about -0.1 V, according to the 2D band maximum. The G band intensity decreases monotonically as the doping level increases in the p -doping regime. 2D band process is not affected by the plasmon, thus its behavior is the same as that of Gr/ITO in Figures 5.11.

The additional peaks (at 1270 cm^{-1} , 1311 cm^{-1} , 1476 cm^{-1} and 1555 cm^{-1}) at negative potentials, are from by-reaction under illumination of strong near-field. The reaction is reversible and localized within the laser spot, but it leads to potential loss. It makes the doping level of the graphene layer could not be tuned as effective as in positive range. This could be seen from the G band position and 2D band intensity as functions of potential.

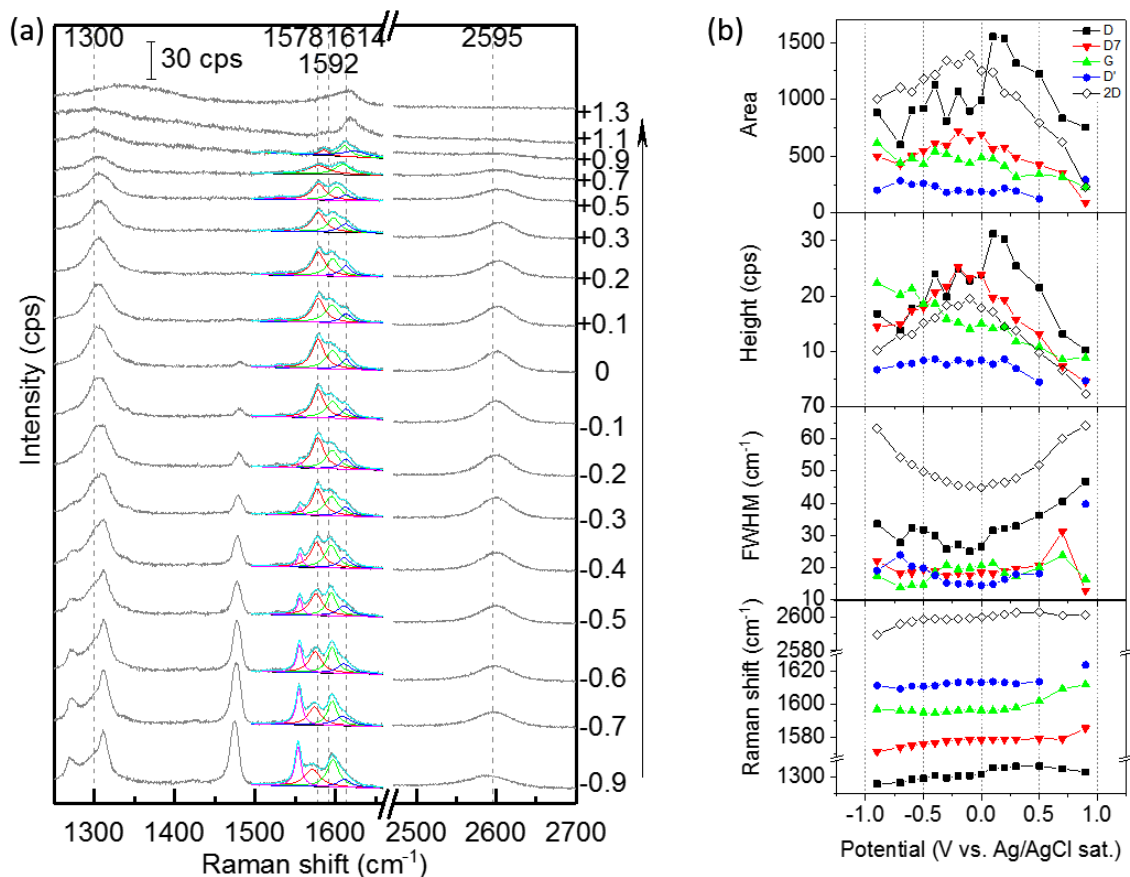


Figure 5.13 (a) Raman spectra of Au/Gr/ITO under potentials from (bottom) -0.9 V to (top) $+1.3$ V vs. Ag/AgCl sat.. The illumination conditions were 785 nm , 0.78 mW , 30 sec .

The grating density was 1200gr/mm. The electrolyte solution was NaClO₄ saturated aqueous solution. The colorful lines are the Lorentzian fits of band around 1600 cm⁻¹. (b) Dependence of band position, width, height and area of D, D7, G, D' and 2D bands on electrochemical potentials. All of the bands were fitted with Lorentzian functions.

Finally, oxidation of graphene under illumination of laser at high positive potentials could be seen from the Raman spectra. As is shown in Figures 5.12 and 5.13, at high positive potentials, D band appears for Gr/ITO under illumination of 4 mW 514 nm laser; and the D band and G bands significantly broaden for Au/Gr/ITO under illumination of 0.78 mW 785 nm laser. These irreversible change of Raman features indicates the oxidation of graphene.

5.4 Conclusion

In conclusion, plasmon-induced Raman bands of defect-free single-layer graphene were studied. The influence from LSPR was investigated in detail via the electrochemical SERS. The multiple bands around 1600 cm⁻¹ observed in SERS were assigned to the G band, D' band and D7 band. Models of plasmon-mediated Raman scattering processes were proposed. It was found that the broadening of wavevector distribution of incident and emitted light by spatial confinement, and the destroying of bilateral symmetry of by strong field gradient cause the breakdown of selection rule in Raman spectroscopy. The plasmon-modified G band process remove the quantum interference effect at high doping levels.

These findings demonstrate the modification of photoexcitation by LSPR. The non-vertical electronic transitions have potential to change the energy distribution of hot electrons and holes. Under the standard selection rules for optical electronic transitions, the electrochemical potentials of hot electrons and holes are specified by the excitation photon energy. In the presence of LSPR, the non-vertical transitions broaden the energy distribution of hot carriers; and the energy range is expected to be tuned by both the Fermi energy and the excitation photon energy.

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Chapter 6.

General Conclusion

In this thesis, I investigated the photo absorption, scattering, and hot carrier generation in the presence of LSPR under electrochemical circumstances, defined as the plasmonically-powered processes. The systems showing the plasmon-induced exotic electronic transitions were designed, constructed, and interrogated to realize the formation of hot carriers with very characteristic electrochemical potential for chemical reactions.

First, I studied the effects of longitudinal plasmon modes of Au nanorods on the electrochemical polymerization of pyrrole. The charge transfer efficiency is found to be dependent on the shape of metal nano-structures. The findings demonstrate the relation between plasmon mode, excitation wavelength and the shape of metal. It shows the possibility to carry out chemical reactions on a specific metal structure with a variety of photon energies and remotely control the reaction sites with nanometer preciseness.

Then, in chapter 3, the plasmon thermal effects on the excitation process is investigated. It is found that the intense pulse laser leads to the shape transformation of Au nanorods and further peeled off the TiO₂ substrate under resonance condition. The findings show that the stability of plasmonic metal nanostructures is critical in plasmon-induced chemical reactions.

In chapter 4, the Raman spectra of Au-covered graphene under resonance illumination were measured with increasing laser power. The D-to-2D band intensity ratio in the lower power regime suggests the reshaping of Au nanodimers; while the ratio in the higher power regime indicates the irreversible oxidation of graphene. Thus, attention should be to the chemical stability of target materials for the plasmonically-powered processes.

In chapter 5, plasmon effects on the Raman spectra of graphene were investigated. A single G band around 1600 cm⁻¹ split into three bands when the laser frequency is in resonance with the localized surface plasmon. According to their distinct behaviors under electrochemical control, the appearance of new bands in a defect-free single-layer graphene is ascribed to the plasmon-assisted electronic transition, in which confined photons have large enough wavevectors to excite non-zero momentum transitions. Furthermore, Raman

spectra of graphene at electrochemical high doping proved the suppression of the quantum interference of electronic excitation by LSPR. The finding proves the non-vertical electronic transitions have potential to change the electrochemical potentials of hot electrons and holes.

In conclusion, this thesis proves plasmon effects on the photoelectrochemical processes. The spectral range of photo-response of material could be extended via excitation of different plasmon modes. Most importantly, new photoexcitation pathways are enabled by LSPR effect. This not only changes the optical response of the target materials but also tunes the electrochemical potentials of hot electrons and holes. Therefore, drastic improvements in the efficiency and the diversity of photoelectrochemical reactions could be realized by the newly developed method based on the present finding.

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