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**Development of High-Performance Photocatalysts
by Using Graphene and AgCl and/or AgBr
Nanoparticles as the Constitutive Elements for the
Decomposition of Chemical Pollutants**

「グラフェンと塩化銀または臭化銀ナノ粒子を素材として用いた環境浄化用高性能光触媒の開発」

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ABSTRACT

Novel Ag@AgX@Graphene (X = Cl, Br) photocatalysts with high-performance decomposition of chemical pollutants in water were developed by using graphene and AgCl and/or AgBr nanoparticles as the constitutive elements. Graphene, a two-dimensional sheet structure patterned with monolayer carbon atoms, has been the subject of intense study due to its unique morphologies and attractive properties. Graphene is the thinnest sheet-shaped nanomaterial with ultralarge surface area, superior mechanical and electronic properties; which facilitate the assembly of Ag@AgX@Graphene photocatalysts adapted for wide applications in environmental remediation.

Large-scale production of high-quality graphene has been the key to achieving the goal of industrialization. The solution-based chemical oxidation of graphite has long been used for the mass production of graphene oxide (GO), a solution-based precursor of graphene. However, a reduction step is required to convert the GO into graphene. Chemical reduction has been commonly used and this is achieved with hydrazine, sodium borohydride, sodium hydrosulfite and L-ascorbic acid as the typical reductants. As the attractive precursor of graphene, the intrinsic hydroxyl, epoxy, carbonyl and carboxylic functional groups of GO sheets could act as active anchoring sites for the heterogeneous nucleation of metal ions and subsequently grown to nanosized photocatalyst

particles via the seeding growth mechanism. In particular, its unique nanostructure and tunable surface properties allow it to be a competitive host substrate for the controlled growth and formation of desired photocatalysts.

The dissertation consists of five chapters. In chapter 1, a brief introduction to the thinnest material ever created with abundant excellent properties was described.

In chapter 2, mass production of GO heavily decorated with oxygen-containing functional groups were introduced by using natural graphite as the starting material. H_2SO_4 as the main intercalating agent separates the layered structure of natural graphite with the aid of ultrasonication. A rapid, cost-effective and safer approach to the facile production of graphene that employs thiourea dioxide (TDO) as the green reductant was described. GO was converted into high quality graphene within 30 min with TDO as the reductant under moderate reaction conditions. The C/O ratio of the TDO reduced graphene was ~ 5.9 with the yield of graphene from GO $> 99\%$. This is better than the reduction efficiency under the identical experimental conditions by using L-ascorbic acid as the reductant which required a reaction time of about 48 hr.

In chapter 3, in order to stabilize the graphene sheets in a single-layered and/or few-layered manner, poly(diallyldimethylammonium chloride) (PDDA), a positively charged polyelectrolyte, was used as the stabilizer to stabilize

graphene sheets in the AgCl/Graphene composites. New insights into the unique photocatalytic properties of the PDDA-stabilized AgCl/graphene hybrid nanoparticles were obtained through analysis of the resultant samples by using X-ray photoelectron spectroscopy together with other suitable analytical methods.

In chapter 4, novel cubic Ag@AgX@Graphene photocatalysts are facilely manipulated by means of a GO sheet-assisted assembly protocol, where GO act as an amphiphilic template for hetero-growth of AgX nanoparticles. A morphology transformation of AgX nanoparticles from sphere to cube-like shape was accomplished by involving GO. With further UV irradiation, the reduction of GO to graphene and the generation of Ag nanocrystals on AgX occur simultaneously. The as-prepared Ag@AgX@Graphene nanocomposites were employed as stable plasmonic photocatalysts to decompose acridine orange as a typical dye pollutant under sunlight. When graphene was employed in the photocatalysts, the decomposition efficiency was enhanced by ~50%. Compared with the bare quasi-spherical Ag@AgX, such graphene-interfaced Ag@AgX display distinctly higher adsorptive capacity, smaller crystal size and reinforced electron-hole pair separation owing to the interfacial contact between Ag@AgX and graphene components, resulting in an enhanced photocatalytic decomposition performance. This study provides new avenues for the assembly of morphology-controlled plasmonic photocatalysts that utilize sunlight as an

energy source.

In chapter 5, the overall achievements obtained in the study were summarized and the prospects of graphene-based photocatalysts in the practical applications of environmental remediation were described.

In conclusion, as the functioning element, graphene oxide, shows a key role in the creation of sunlight-driven Ag@AgX@Graphene photocatalysts. Two kinds of novel Ag@AgX@Graphene photocatalysts display enhanced plasmonic photocatalytic activity toward the chemical pollutants. These new findings reported in this dissertation provide new insights into the environmental remediation.

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List of Acronyms

GO	graphene oxide
TDO	thiourea dioxide
PDDA	poly(diallyldimethylammonium chloride)
PVP	polyvinyl pyrrolidone
CTAB	cetyltriethylammonium bromide
CTAC	cetyltrimethylammonium chloride
ROS	reactive oxidative species
XRD	X-ray diffraction
FT-IR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
TEM	transmission electron microscopic
SEM	scanning electron microscopic
SAED	selected area electron diffraction
EDX	energy dispersive X-ray spectrom
SPR	surface plasmon resonance
FCC	face centered cubic
SERS	surface enhanced Raman scattering

Chapter 1

General introduction

1.1 Recent research on graphene oxide/graphene

Graphene, described as an atomic scale honeycomb lattice made of carbon atoms with a carbon-carbon bond length of 0.142 nm[1], brings people into a newly-discovered field, that is the perfect two-dimensional (2D) materials world. It can be seen a standard building unit for the constitution of all other forms of graphitic materials. For example, graphene can be wrapped into 0D fullerene, rolled into 1D carbon nanotubes and/or stacked into 3D graphite[2]. Until 2004, the argument on the existence of strictly 2D materials stopped. Geim and Novoselov et al. reported a simple approach to get the stable isolated multilayer graphene planes from the pencil graphite by using adhesive tape[3, 4]. Since then, more and more researchers have turned into this new topic and developed enormous applications due to its unique electronic structures.

As shown in Figure 1-1, the number of publications on graphene (according to ISI Web of Knowledge SM) increases dramatically in the recent few years. As a new material, graphene has demonstrated a variety of intriguing properties including high electron mobility at room temperature (250,000

$\text{cm}^2/\text{V s}$)[3, 5], extraordinary thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$)[6] and superior mechanical properties with Young's modulus of 1 TPa and fracture strength of 130 GPa[7]. A wide of potential applications in integrated circuits[8], transistors[9], solar cells[10-12], energy storage devices such as super capacitors and lithium ion batteries[13-16], single molecule gas detection[17], transparent conducting electrodes[12, 18, 19], biomedicine[20], catalysts[21] and nano-composite materials[22-24] have been explored. Graphene has become a rapidly rising star in nanotechnology.

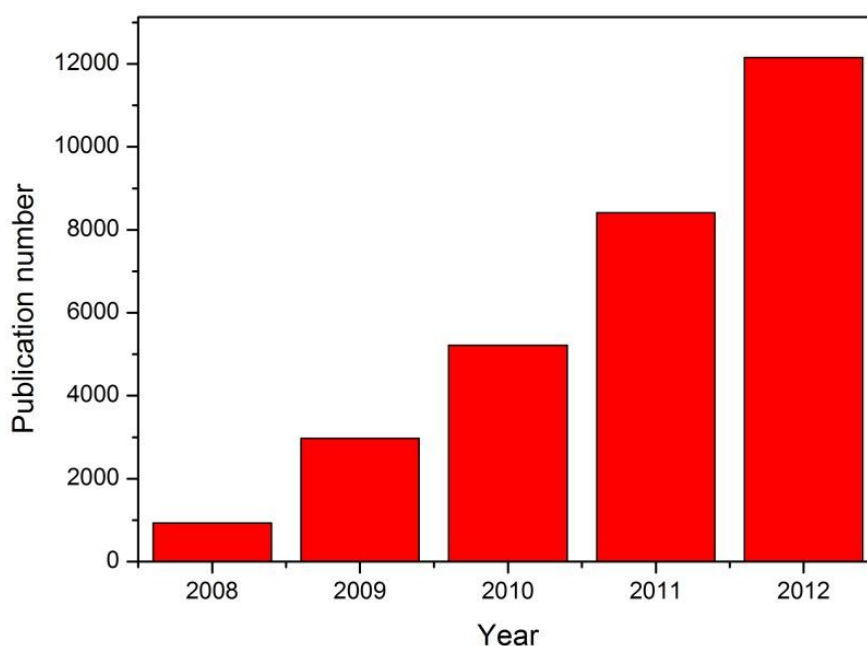


Figure 1-1. Number of publications on graphene during the past five years (according to ISI Web of KnowledgeSM with the topic of “graphene”)

Up to now, versatile methods have been developed for the fabrication or

synthesis of graphene and its derivatives. As we know, the adjacent layers in graphite are bound by weak van der Waals forces. Mechanical exfoliation is a simple peeling approach first used by Geim and coworkers in 2004, while such method is limited by its low production[3]. Alternative methods such as chemical vapor deposition (CVD) of hydrocarbons on transition-metal substrates and epitaxial growth via high-temperature treatment of silicon carbide are capable of producing high-quality graphene[25-28], but these methods are difficult to scale up. Therefore, large-scale production of graphene oxide (GO), a solution-based precursor of graphene, followed by chemical reduction has been a common strategy for the large-scale implementation[29-32]. This is one of the most developed methods in the literature and several kinds of chemical reductants have been reported, such as hydrazine and/or its derivatives[31, 33-37], hydroquinone[38], NaBH_4 [39-42], sodium hydrosulfite[43], L-ascorbic acid[32, 44, 45], amino acid[32], carrot root[46], pyrrole[47], and thiourea dioxide[48]. Besides the reduction methods with chemical reductants, photochemical[21, 49, 50], electrochemical[51-53] and thermal[54-59] reduction methods have also been applied to this procedure.

As the precursor of graphene, GO was produced from natural graphite by using Hummers method via the reaction of natural graphite with a mixture of oxidative agents potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3). The obtained GO sheets were enriched with

abundant of oxygen-containing functional groups, such as hydroxyl, epoxy, carbonyl and carboxyl groups, which can provide large number of active sites for the nucleation of other organic and/or inorganic crystals.

1.2 The role of graphene in environmental remediation

Since the discovery of hydrogen evolution through photoelectrochemical splitting of water on titanium dioxide (TiO_2) electrodes by Fujishima and Honda in 1972[60], the technology of semiconductor-based photocatalysis has attracted great interest in the field of environmental remediation and energy conversion. Some semiconductors such as ZnO [61], WO_3 [62, 63], Cu_2O [64], CuO [65], SnO_2 [66], BaTiO_3 [67], Bi_2S_3 [68] and Bi_2WO_6 [69], etc. can work as efficient photocatalysts for the photon-induced chemical transformation due to the indirect or direct band gap in their electronic structures. With the generation of electron–hole pairs, various kinds of reactive oxidative species (ROS) can be produced during the photocatalytic process. The photogenerated ROS play a important role in the photodegradation of chemical pollutants and solar energy conversion including solar photovoltaic and hydrogen generation.

However, the recombination of electrons and holes easily happens and thus decreasing the quantum efficiency during the transformation from solar energy into chemical energy. During the past 40 years, a variety of strategies have been employed to improve the photocatalytic performance of the photocatalysts, for

example, doping with metallic nanoparticles and/or nonmetal elements[70-73], integration with other types of semiconductors[74, 75], etc.. In particular, numerous attempts have been made to combine graphene or partially reduced graphene with semiconductor photocatalysts to enhance their photocatalytic activities. As shown in Figure 1-2, we can find the growing trend of the publications on graphene-based photocatalysts and the citations in the recent 5 years (according to ISI Web of KnowledgeSM).

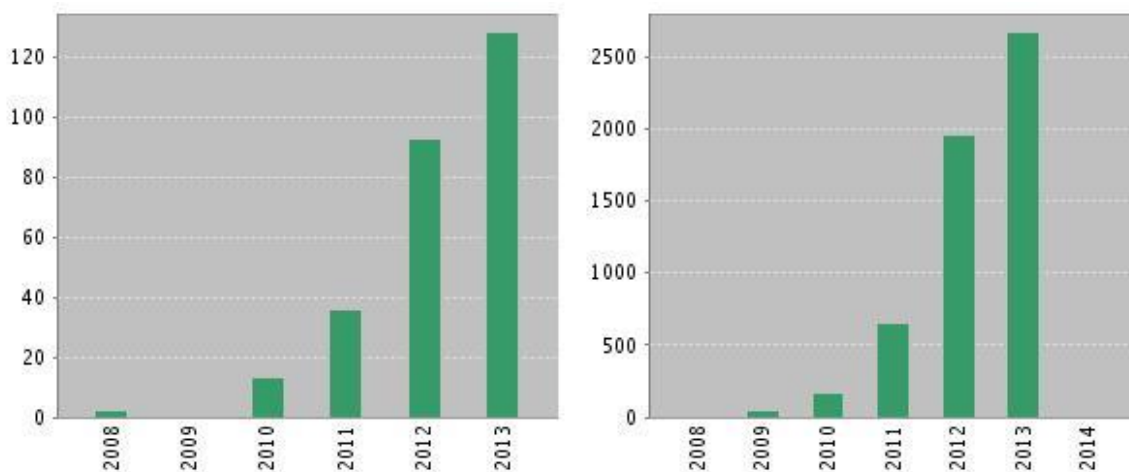


Figure 1-2. Statistic publications (left) of the graphene-based photocatalysts and the citations (right) (according to ISI Web of KnowledgeSM with the topics of “graphene” and “photocatalyst”)

The photoactive materials of graphene-based composite semiconductors mainly include metal oxides such as TiO₂[49, 76-82], ZnO[83-85], WO₃[86-89], SnO₂[90, 91], MnO₂[92, 93], ZrO₂[94], Fe₃O₄[95, 96], etc., metal salts such as CdS[97-101], ZnS[102, 103], Ag₃PO₄[104-108], BiVO₄[109, 110], BiOBr[111,

112], InNbO_4 [113], etc., photoactive organic molecules such as Eosin Y[114], Porphyrin[115-118], Carbon nitride[119, 120], etc. and silver/silver halides such as Ag/AgCl[121, 122-123] and Ag/AgBr[124, 125], etc.. Some selected research results of graphene-based photocatalysts are listed in Table 1-1.

Table 1-1. Recent report of selected graphene-based photocatalysts in environmental applications

Graphene-based photocatalysts	Methods	Experiment conditions	Performances	References
Graphene-TiO ₂	Hydrothermal method	UV light, MB	1.6 times higher than pure TiO ₂	[49, 126]
Graphene-ZnO	Ion exchange	UV and visible, RhB	completely removed in 60min	[127]
Graphene-SnO ₂	Redox reaction	Sunlight, MB	Higher than P25 and SnO ₂	[128]
Graphene-Cu ₂ O	Solution-phase method	UV light, RhB	Higher than Cu ₂ O	[64]
Graphene-ZnS	Hydrothermal method	UV light, Benzyl alcohol	9 times higher than pure ZnS	[97, 103]
Graphene-CdS	Solvothermal method	Visible light, Eosin Y	4.87 times higher than pure CdS for hydrogen production	[129]
Graphene-CdSe	Hydrothermal method	UV and visible, MO	2.4 times higher than pure CdSe	[130]
Graphene-BiVO ₄	Sol-gel method	Visible light, MB	2 times higher than pure BiVO ₄	[131]
Graphene-Ag/AgCl	Solution mixing	Sunlight, AO	1.5 times higher than pure Ag/AgCl and 2 times higher than P25	[21, 132]
Graphene-Ag/AgBr	Solution mixing	Sunlight, AO	1.5 times higher than pure Ag/AgCl and 2 times higher than P25	[21, 124]
Graphene-Ag ₃ PO ₄	Hydrothermal method	Visible light, RhB	1.4 times higher than pure Ag ₃ PO ₄	[133]

Chapter 2

Environmental–friendly production of solution-based graphene using thiourea dioxide as a green reductant

2.1 Introduction

Graphene, a novel two-dimensional structure patterned with sp^2 bonded carbon atoms, has been the subject of intense study due to its unique morphologies and attractive properties[2, 134, 135]. In fact, graphene is the thinnest sheet-shaped molecule with an ultra-large surface area and superior mechanical and electronic properties[136] and holds great promise in applications in electronic devices, sensors, electrodes, and the other graphene-based composite materials.

Large scale production of high quality graphene has been the key to achieving the goal of graphene industrialization[137]. Methods such as chemical vapor deposition (CVD) of hydrocarbons on transition metal substrates and epitaxial growth via high temperature treatment of silicon carbide are capable of producing high quality graphene, but these methods are difficult to scale up. The solution-based chemical oxidation of graphite has long been

used for the mass production of graphene oxide, a solution-based precursor of graphene. However, a reduction step is required to convert the graphene oxide into graphene. Chemical reduction has been commonly used and this is achieved with hydrazine and/or its derivatives[31, 33-37], hydroquinone[38], NaBH_4 [39-42], sodium hydrosulfite[43], L-ascorbic acid[32, 44, 45], amino acid[32], carrot root[46], pyrrole[47], and thiourea[138] as the typical reductants. The thermal reduction[139], microwave irradiation reduction[140], and electrochemical reduction[53] have also been applied to this procedure. Hydrazine or hydrazine hydrate have been used extensively due to their strong reducing capabilities, however, C-N groups were incorporated during the reduction reaction and remained in the resulting graphene, lowering the quality of the product. Furthermore, hydrazine is toxic in nature and also highly explosive and its use should be avoided, especially in reactions that require large-scale implementation. In an effort to replace hydrazine, sodium borohydride (NaBH_4) has been used, but this reductant is readily hydrolyzed and gives rise to an unstable aqueous solution, resulting in low efficiency in the reduction.

Other chemically safe reducing agents, such as amino acids, carrot root, and pyrrole showed some ability to reduce graphene oxide into graphene, but their reduction potential was far inferior to that of hydrazine. L-Ascorbic acid (vitamin C), a green reductant, showed a higher ability for reducing graphene

oxide into graphene, however the reducing procedure is rather complicated and time-consuming (requiring around 48 hours).

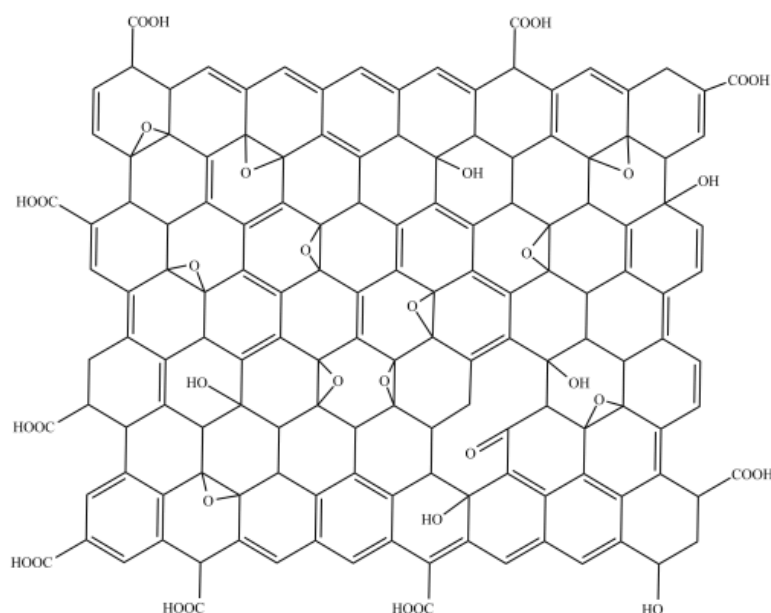
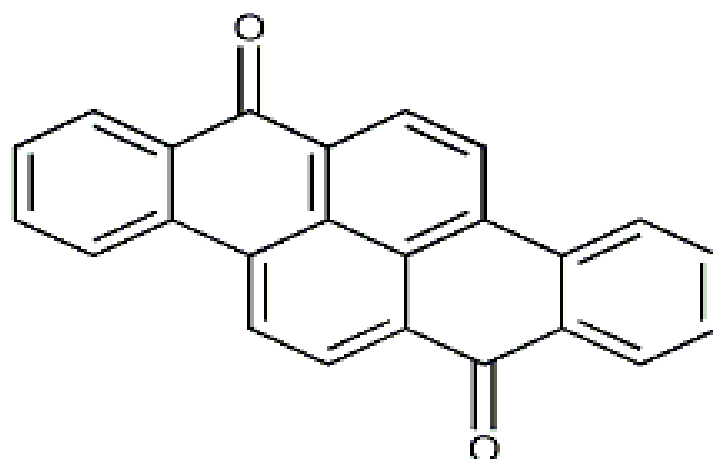


Figure 2-1. Schematic illustrations of the vat dye yellow 4 (upper) used as a dyestuff in the textile industry and the typical structure of GO (down).

Graphene oxide possesses a chemical structure that is similar to that of the vat dyes which have long been used in the textile and paper industry. As shown in Figure 1, graphene oxide can be described as a random distribution of oxidized areas with oxygen-containing functional groups combined with non-oxidized regions where most of the carbon atoms preserve their sp^2 hybridization[41, 137, 141-143]. In this study, inspired by the widespread use of this reductant in the dyeing process of treating cellulosic fibers with vat dyes in the textile and paper making industries, thiourea dioxide (TDO, formamidinesulfinic acid) is used to reduce graphene oxide into graphene. TDO appears terrifically stable at 20 - 30 °C in solution, but when it is heated or catalyzed by alkali, it decomposes rapidly to produce sulfoxylic acid through formamidinesulfinic acid to act as a strong reductant.

We demonstrate in this study that TDO, a traditional yet green reductant, is a highly capable species for chemical reduction of graphene oxide into graphene of high quality. To our best knowledge, this is the first paper reporting the use of TDO as a green reductant for the mass production of high quality solution-based graphene.

2.2 Experimental section

2.2.1 Materials

Purified natural graphite was purchased from Bay Carbon, Inc., Michigan, USA. Other chemicals unless noted were from Wako Pure Chemical Industries, Ltd., or Sigma-Aldrich Inc., Japan.

2.2.2 Preparation of graphene oxide

Graphene oxide was obtained from natural graphite, based on the method proposed by Hummers and Offeman[29]. In a typical treatment, 5 g of the natural graphite was dispersed in 115 mL concentrated sulfuric acid in an ice bath. Approximately 5 g sodium nitrate and 15 g potassium permanganate were slowly added to the chilled mixture, cooled by an ice bath, and stirring was continued for 2 hours. The mixture gradually became pasty and blackish-green.

Then, the mixture was placed in a 35 °C water bath and kept at that temperature for 30 min, followed by the slow addition of distilled water (500 mL) to keep the solution from effervescing. The resulting solution was placed at well below 98 °C for 2 hours. As the reaction progressed, the color of the mixture turned yellowish. The mixture was further treated with 5% H₂O₂ (200 mL), filtered and washed with distilled water several times until its supernatant was without SO₄²⁻, as tested by barium chloride solution (0.2 mM). The purified graphene oxide was finally dispersed in water and ultrasonically exfoliated in an

ultrasonic bath for 1 hour to form a stable graphene oxide aqueous dispersion.

2.2.3 Reduction of graphene oxide using TDO

The solution based graphene was prepared by adding 2.5 g TDO into 100 mL graphene oxide aqueous solution (pH 9.0; 0.2 wt%) at 80 °C for 30 min; sodium cholate was used as a stabilizer to maintain the TDO-reduced graphene with high stability in the aqueous solution. To prepare the TDO-reduced films, the graphene oxide film was first prepared on glass-based substrates through the dropping method and then dried at 80 °C in an oven. The graphene oxide-based films were immersed in the reducing agent aqueous solution containing 25 mg mL⁻¹ of TDO and adjusted to pH 9.0 using NaOH solution (1.0 wt%), followed by a reduction reaction of 30 min in 80 °C. The color of the films changed from yellow-brown to metallic gray.

Finally, the obtained graphene films were washed using distilled water to remove the by-product (urea and sodium sulfite) and the residual reducing agents, and then dried at 80 °C in an oven. Graphene obtained using sodium hydrosulfite and L-ascorbic acid as reductants were also prepared, for the comparison studies.

2.2.4 Characterizations

Atomic force microscopy (AFM) images were acquired using an Agilent Series 5500 AFM instrument. The samples were prepared by casting a highly diluted aqueous graphene oxide aqueous suspension on the surfaces of mica. The images were obtained using the tapping mode at a scanning rate of 0.5 Hz. The X-ray diffraction (XRD) measurements were performed with a Rigaku RINT Ultima diffractometer with Cu-K α radiation (K α 1.54056 Å) and an X-ray power of 40 kV/20 mA at a scan rate of 4 °/min. Fourier transform infrared spectroscopy (FT-IR) was performed over the wave number range of 4000–400 cm⁻¹ with a FT/IR-6100 FT-IR Spectrometer, (JASCO, Japan).

The X-ray photoelectron spectroscopy (XPS, JPC-9010MC, JOEL, Japan) analysis was performed by using an unmonochromated Mg-K α X-ray source (1253.6 eV) with vacuum better than 1×10^{-7} Torr. For the transmission electron microscopic (TEM) analysis, the samples were suspended in water/menthol (0.2 mg/mL) by ultra-sonication for 10 min and then the dispersion was drop-cast on a fresh lacey carbon TEM grid. The beam energy used for TEM analysis was 200 keV. Raman analysis was performed with an Invia Raman Microscope (Renishaw, United Kingdom) with an excitation wavelength at 532 nm. The electrical conductance was tested by a four-point probe resistivity meter (Loresta EP, Model MCP-T360, Mitsubishi Chemical Co., Japan) at room temperature.

2.3 Results and discussion

2.3.1 Characteristics of the TDO-reduced graphene

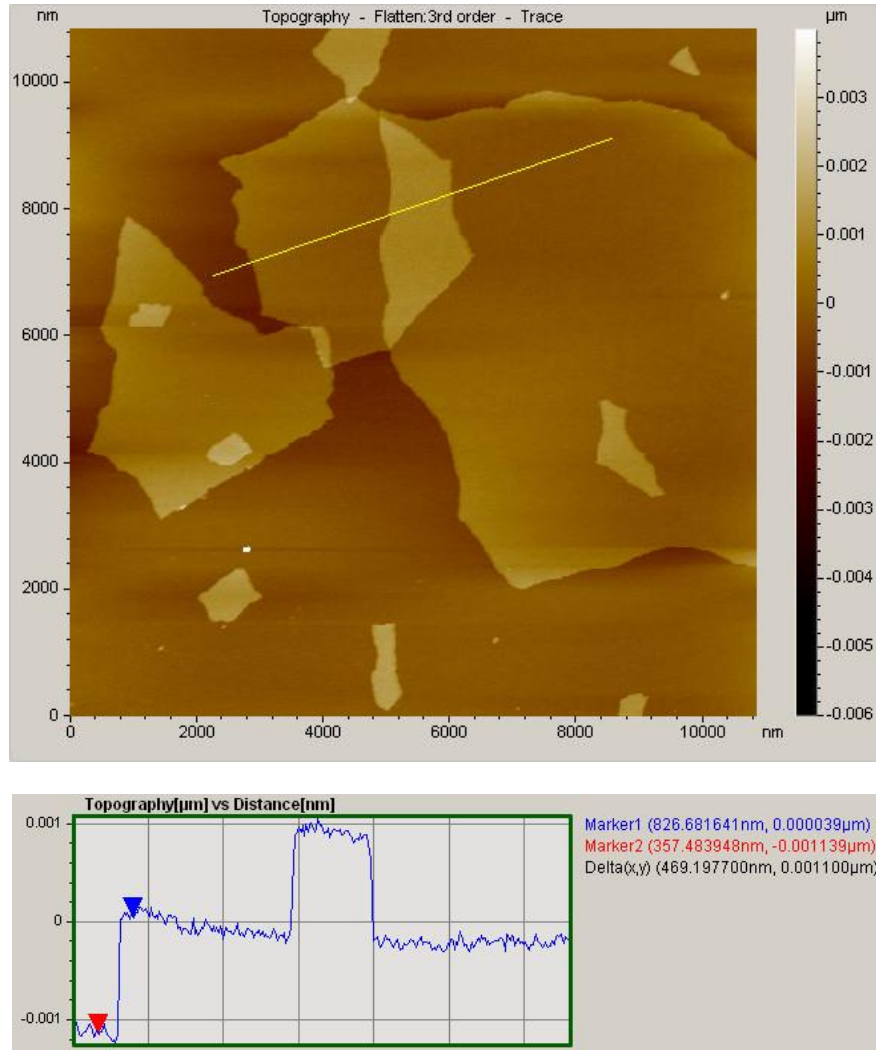
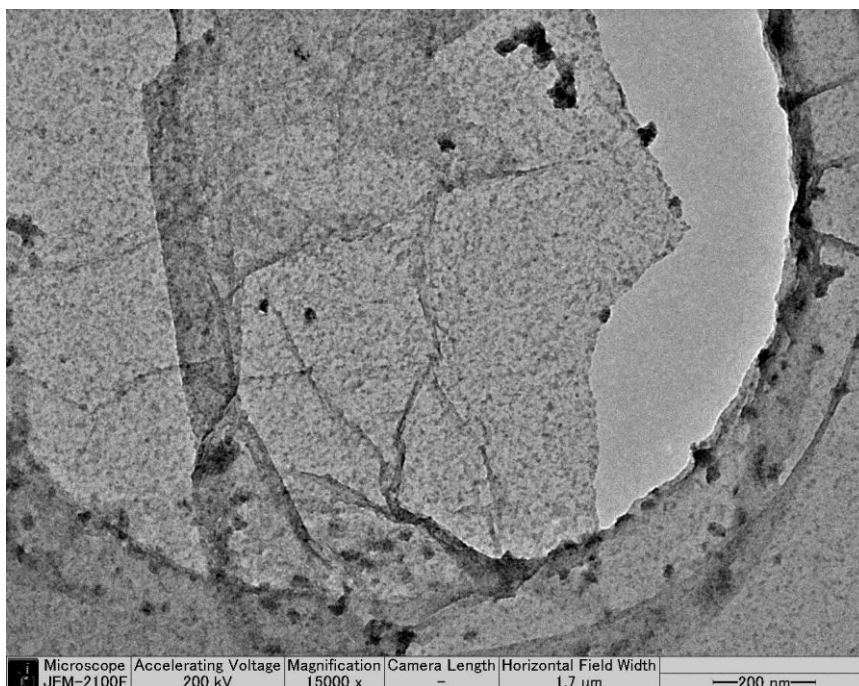


Figure 2-2. A typical AFM image of the graphite oxide on a mica substrate.

The thickness of the graphene oxide was estimated to be 1.1 nm.

In AFM images (Figure 2-2), the graphene oxide produced for these studies exhibited a thickness of ~ 1.1 nm, which indicated that the graphene oxide was exfoliated into single- or a few-layered sheets[141]. The length or breadth of

each of twenty pieces of the graphene oxide was found to be around 1 – 5 micrometers. Through TEM images of the TDO-reduced graphene, we observed sheet-shaped structures with a wrinkled surface (Figure 2-3). In the selected area electron diffraction (SAED) pattern (Figure 2-3) for the TDO-reduced graphene, we observed hexagonal and dodecagonal symmetry diffractions, indicating the TDO-reduced graphene had a well crystallized structure. For the graphene oxide precursor, the oxygen-containing groups as well as defects in the crystal lattice served as strong scattering centers and blocked the π -electrons transfer (data not shown). In contrast, for the TDO-reduced graphene, the oxygen-containing groups were no longer present and also the atomic domain containing defects were converted into long-ranging extended conjugated networks in the graphitic lattice.



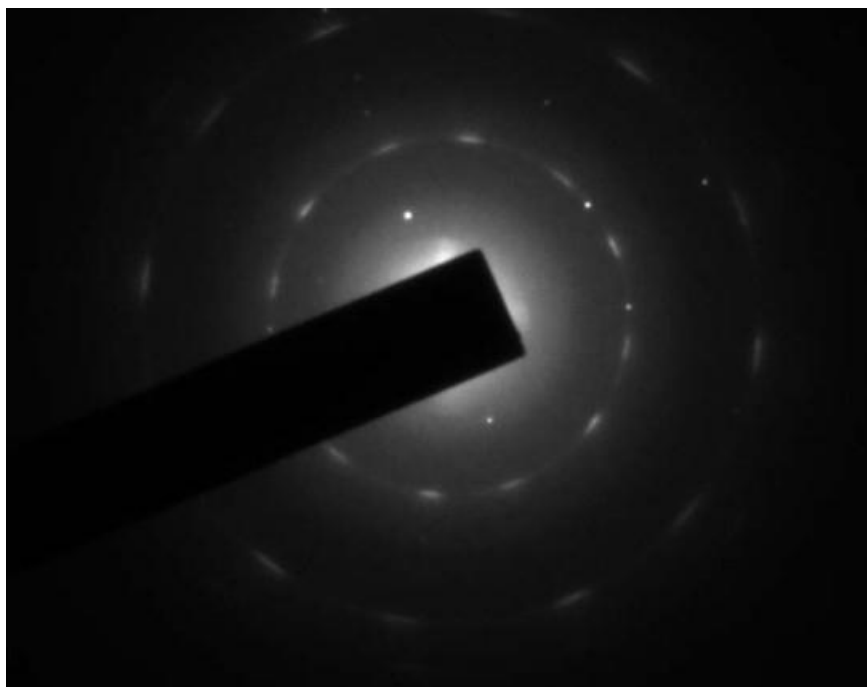


Figure 2-3. TEM image (up) and the relative selected area electron diffraction pattern (down) of the TDO-reduced graphene.

In the XRD patterns of the materials used in these studies (Figure 2-4), pristine graphite exhibited a basal reflection (002) peak at $2\theta=26.44^\circ$ (d spacing = 0.336 nm) due to the tightly packed layers of the graphene[144]. For the synthesized graphene oxide, the 002 reflection peak shifted to a lower angle ($2\theta=12.14^\circ$) and the distance of graphene plates expanded to 0.728 nm. The increase in d spacing is attributed to the intercalation of water molecules and grafting with functional groups, such as hydroxy, epoxy and carboxy groups, between the layers of graphite that occurred during oxidation[145]. For the TDO-reduced graphene, the interlayer distance returned to 0.336 nm; this again indicated that the graphene structure was restored after the removal of most of

the oxygen functional groups[146]. The new broadened diffraction peak at 26.44° and reduced peak intensity demonstrate that graphene was exfoliated into single-layered or few-layered sheets, affording the formation of a new lattice structure which was significantly different from the pristine graphite.

On the contrary, samples obtained using sodium hydrosulfite and L-ascorbic acid as the reductants showed only the 2.14° diffraction peak; this again indicates the poor reduction efficiency of these two reductants.

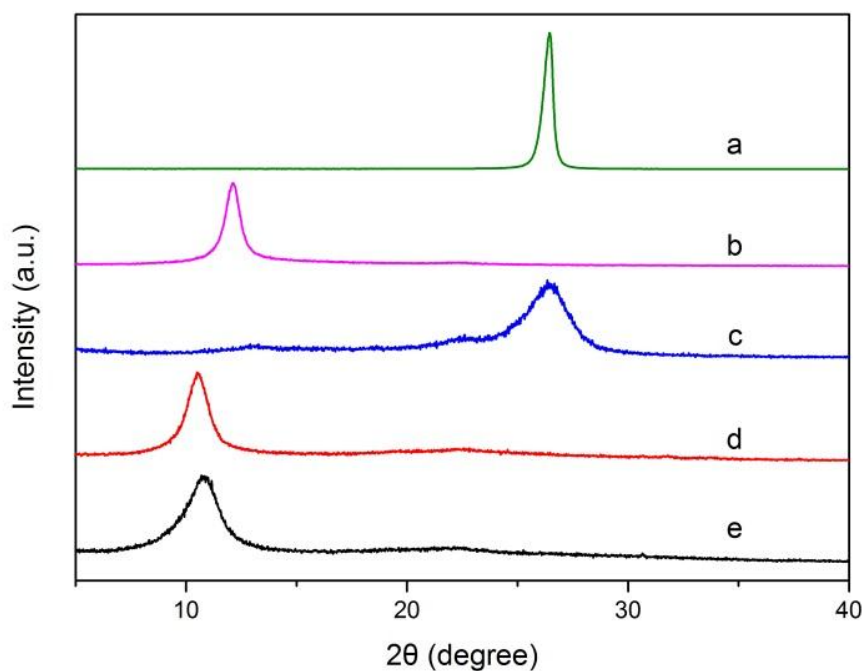


Figure 2-4. X-ray diffraction patterns of (a) the pristine graphite, (b) graphene oxide, (c) reduced graphene with TDO, (d) reduced graphene with $\text{Na}_2\text{S}_2\text{O}_4$ and (e) reduced graphene with L-ascorbic acid.

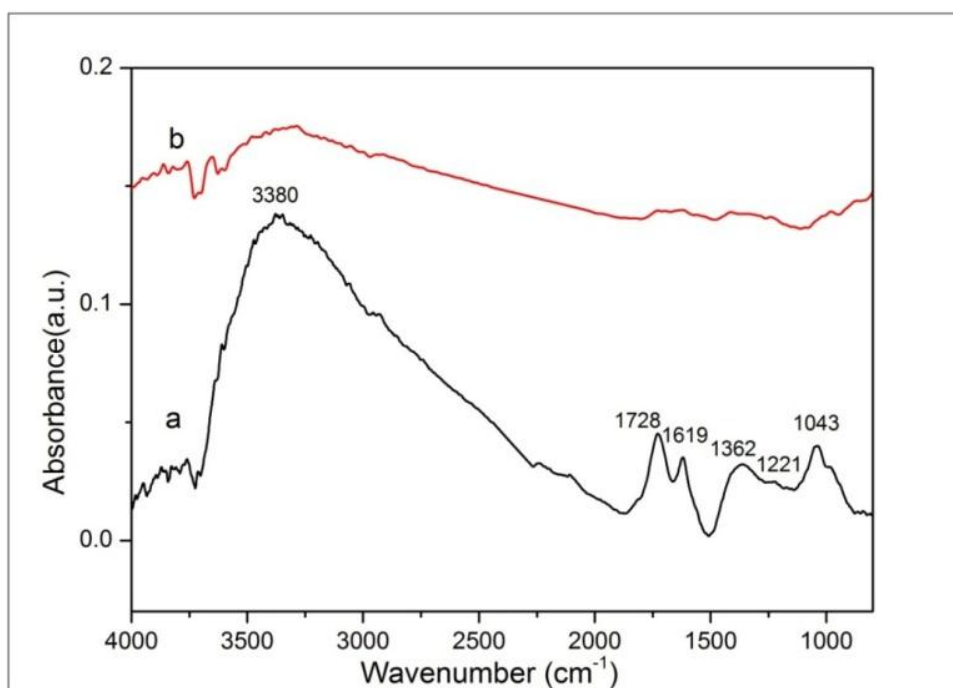


Figure 2-5. Typical FT-IR spectra of graphene oxide (a) and of the TDO-reduced graphene (b).

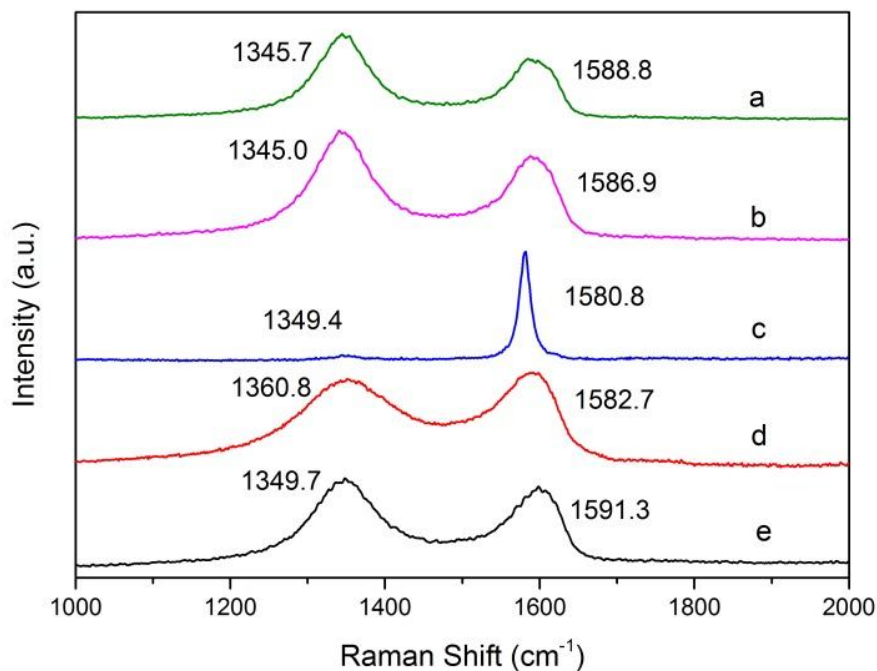


Figure 2-6. Raman spectra of (a) reduced graphene with Na₂S₂O₄, (b) reduced graphene with L-ascorbic acid, (c) graphite, (d) graphene oxide (GO) and (e) reduced graphene with TDO.

The TDO-reduced graphene samples were analyzed by using FT-IR (Figure 2-5). The most characteristic features for the graphene oxide are the vibration and deformation bands of O-H at 3380 cm⁻¹, the stretching vibration band of C=O at 1728 cm⁻¹, and the stretching vibration bands of epoxy and alkoxy groups at 1221 and 1043 cm⁻¹ [44, 147]. In addition, the aromatic C=C (1619 cm⁻¹) stretching vibrations due to the unoxidized graphitic domains and the C-H bending vibration at 1362 cm⁻¹ also appeared in the spectrum. After the TDO-reduction treatment, the FT-IR peaks corresponding to the

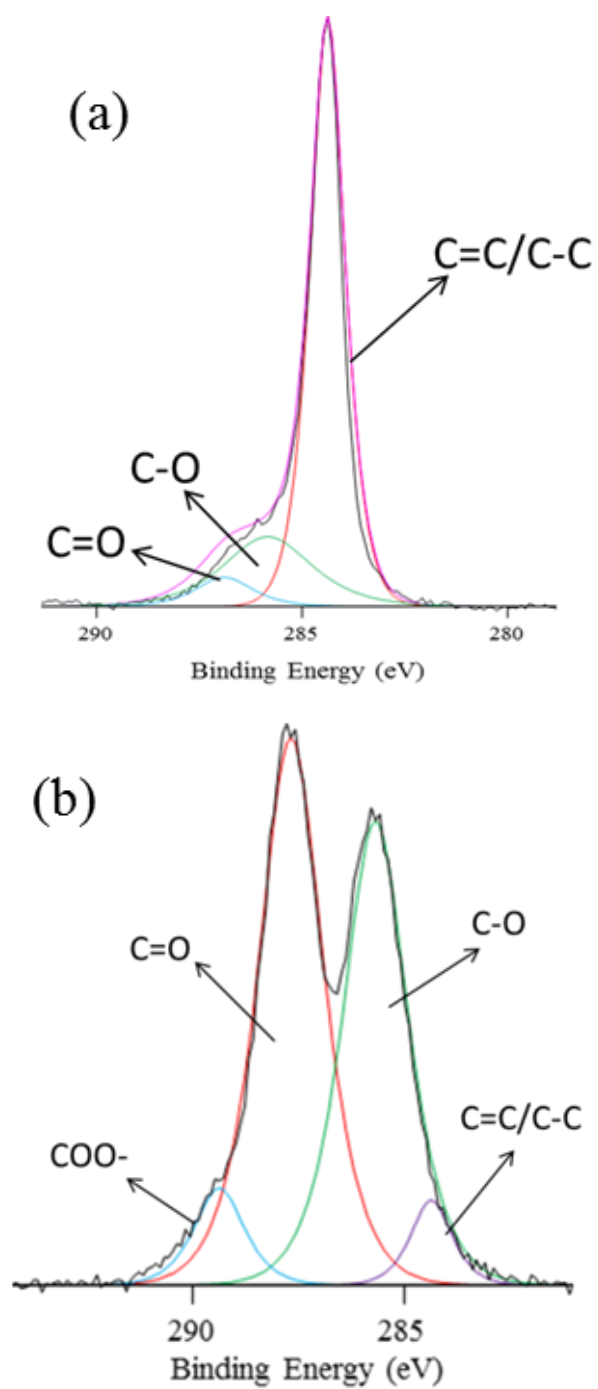
oxygen-containing groups decreased. Pristine graphite was also analyzed under identical experimental conditions, similar spectra to that of the TDO-reduced graphene were observed (data not shown).

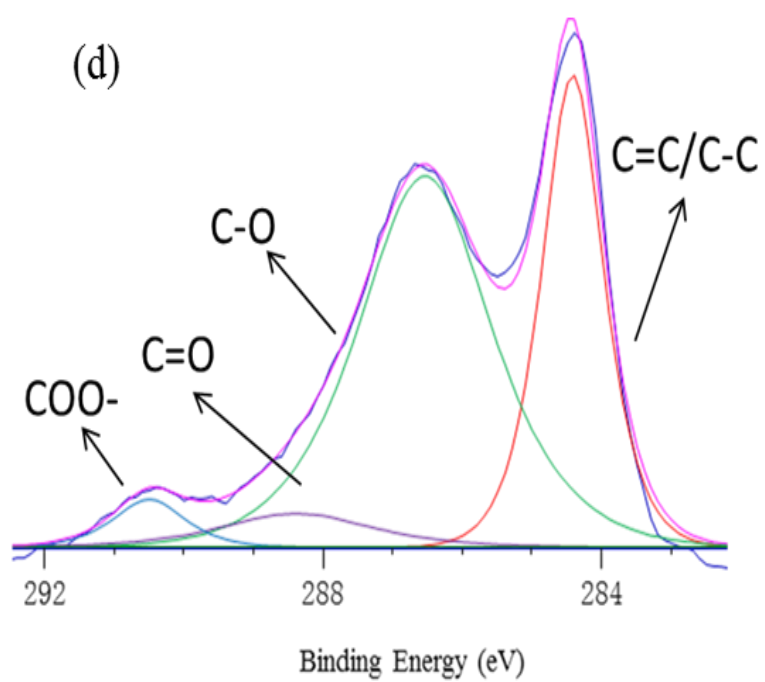
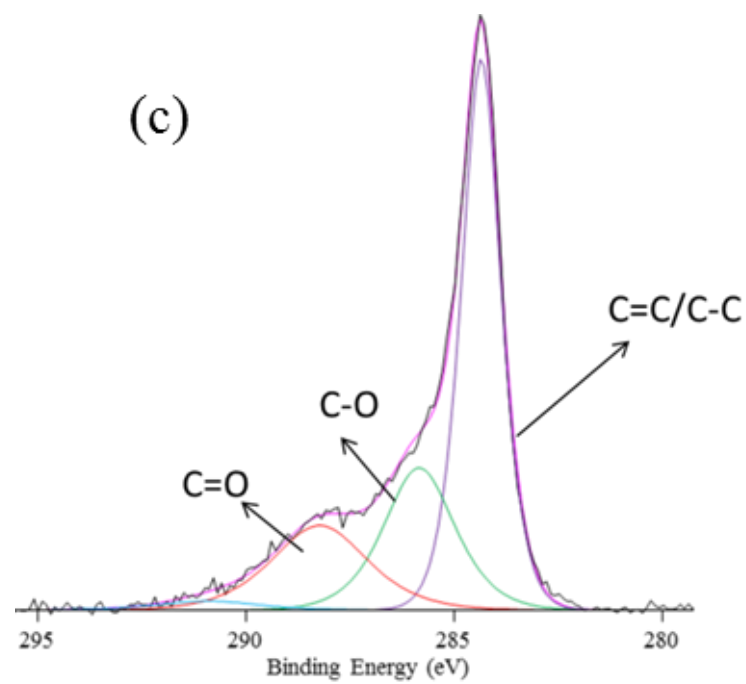
Raman scattering spectroscopy is commonly used to characterize the structural properties of graphite, graphene oxide and graphene, including the degrees of disorder and defect, and/or the doping levels. The Raman spectrum for the pristine graphite showed a strong G band peak at 1580.8 cm^{-1} and a weak D-band peak at 1349.4 cm^{-1} (Figure 2-6). These two main features, the G band and D band, are attributed to the first order scattering of E_{2g} vibration mode of sp^2 -bonded carbon atoms and the breathing mode of κ -point phonons of A_{1g} symmetry[148], respectively.

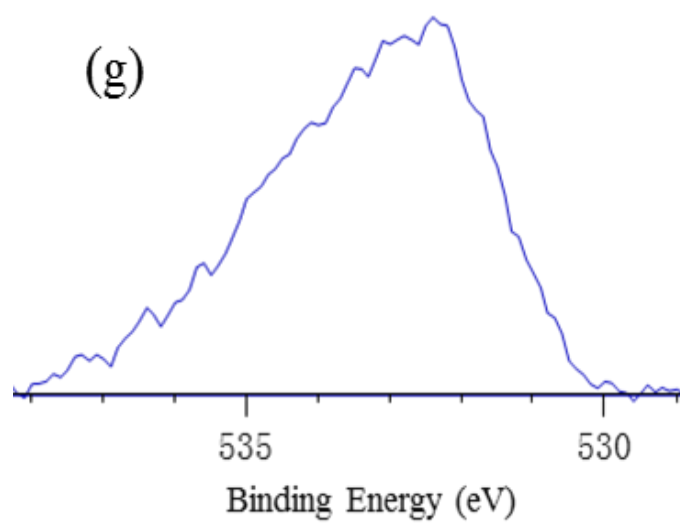
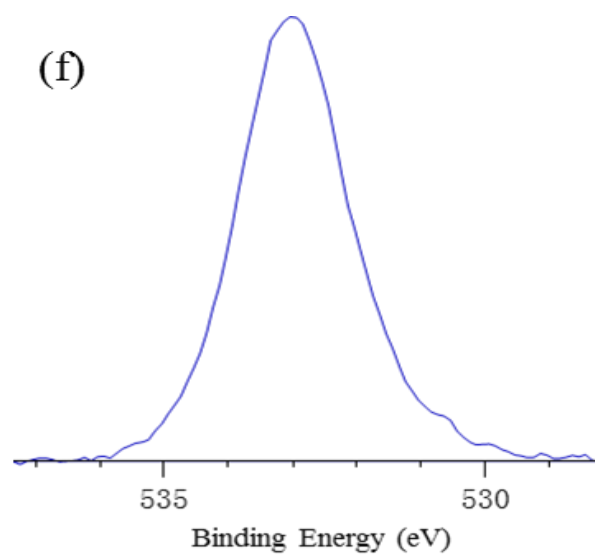
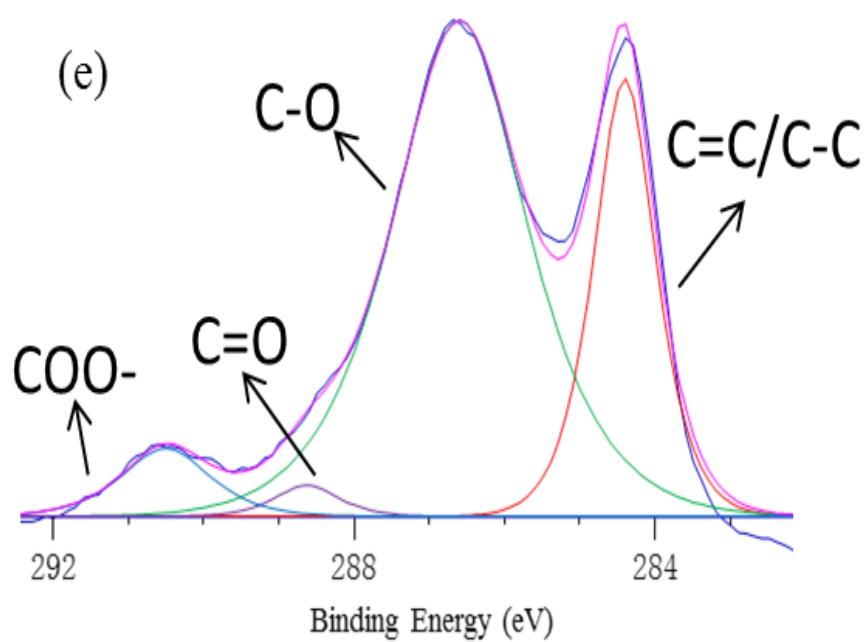
For the graphene oxide, the G band was widely broadened and slightly shifted to 1582.7 cm^{-1} due to the isolated double bonds that resonate at higher frequencies. In contrast, the D band was shifted to a lower region at 1360.8 cm^{-1} and became more prominent, indicating the reduction in size of the in-plane sp^2 domains. After the reduction with TDO, the intensity ratio of D-band to G-band (I_D/I_G ratio) in the Raman spectrum decreased from 2.65 for graphene oxide to 1.81 in reduced graphene. For the samples obtained using sodium hydrosulfite and L-ascorbic acid as the reductants, the I_D/I_G ratios were found to be 2.03 and 2.14, respectively. The large amounts of hydroxy, epoxy and alkoxy groups present in graphene oxide are the key groups responsible for causing the

decrease in the overall amount of the aromatic rings and as a result, diminishing the relative intensity of the G band.

For the TDO-reduced graphene, the residual oxygenated groups and the numbers of the aromatic domains are both important in determining the value of I_D/I_G ratio. In the case that a reductant having a lower reduction ability was used, the reduced graphene contains larger numbers of the smaller sized graphene, thus leading to an increase in the I_D/I_G ratio. In contrast, in a case where a strong reducing agent was used, the graphene was built up by the larger sized aromatic domains and as a result, a smaller value of the I_D/I_G ratio was obtained. The I_D/I_G ratio for the TDO-reduced graphene was almost identical to that for the graphene obtained by reducing graphene oxide using N, N-dimethylhydrazine[149]; this indicated that TDO has a reduction potential which is comparable to that of the hydrazine-based compounds.







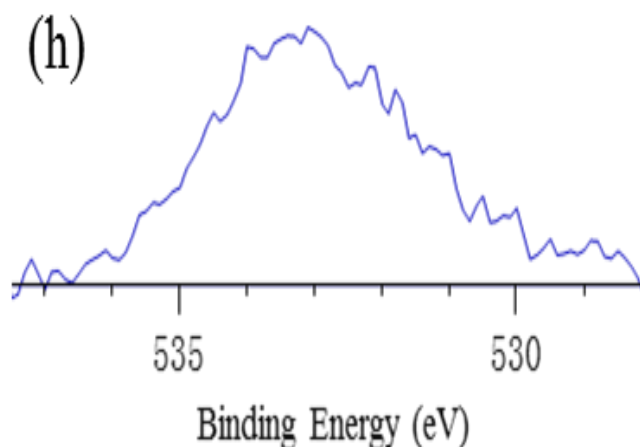


Figure 2-7. High-resolution XPS spectra and curve fitting of C1s spectra of (a) graphite, (b) graphene oxide, (c) TDO-reduced graphene, (d) reduced graphene with $\text{Na}_2\text{S}_2\text{O}_4$, (e) reduced graphene with L-ascorbic acid, (f) the O1s spectra of graphene oxide, (g) the O1s spectra of TDO-reduced graphene and (h) the O1s spectra of graphite.

XPS was used to evaluate the changes on C/O ratios involved in the TDO-reduction of graphene oxide (Figure 2-7). The C1s spectrum for the pristine graphite clearly indicated a lower binding energy feature at 284.4 eV (which is responsible for the C=C bonds), a higher binding energy feature at 285.8 eV (which corresponds to the C-C bonds) and followed by a shoulder at 286.9 eV (which is assigned to the range of C-C sp^3). The C1s XPS spectrum for the graphene oxide shows a considerable degree of oxidation with four components that correspond to carbon atoms involved in different functional groups, namely, the non-oxygenated aromatic C (C=C/C-C), the C in C-O bonds,

the carbonyl C (C=O) and the carboxylate C (-COO-), centered around the binding energies of 284.4, 285.7, 287.7 and 289.4 eV, respectively[32, 150].

After the reduction using TDO, the intensities for all C1s peaks of the carbon-oxygen binding species, especially the peaks of C=O and C-O bonds, decreased rapidly, revealing that most of the oxygen containing functional groups were removed after the reduction; the C/O ratio increased from 1.84:1 to 5.89:1. In previous studies, the C/O ratio for graphene obtained using L-ascorbic acid as the reductant was increased from 2.0:1 to 5.7:1[151] and from 2.7:1 to 10.3:1 using hydrazine as the reductant[152]. However, the reduction with L-ascorbic acid required 48 hours while the reduction with hydrazine required 24 hours. In our method with TDO as the reductant, the reduction was accomplished within 30 minutes. The entire O1s spectrums for the graphene oxide, for the TDO-reduced graphene and for the pristine graphite were also shown in Figure 2-7. The O1s peak intensity at 533 eV for the TDO-reduced graphene was reduced to a value similar to that of the pristine graphite. Table 2-1 summarizes the reduction efficiency of TDO, sodium hydrosulfite and L-ascorbic acid with C/O ratios and the electrical conductance as the indicators.

2.3.2 Proposed reduction mechanism

Table 2-1. Comparison of the reduction efficiency of TDO, $\text{Na}_2\text{S}_2\text{O}_4$ and L-ascorbic acid.

Reductants	Reduction conditions	C/O ratios	Electrical conductance/ S m^{-1}
TDO	80 $^{\circ}\text{C}$ /30 min	5.89:1	$3.205 \times 10^3 \text{ S m}^{-1}$
$\text{Na}_2\text{S}_2\text{O}_4$	80 $^{\circ}\text{C}$ /30 min	3.67:1	$8.454 \times 10^2 \text{ S m}^{-1}$
L-ascorbic acid	80 $^{\circ}\text{C}$ /30 min	3.23:1	$2.958 \times 10^{-2} \text{ S m}^{-1}$

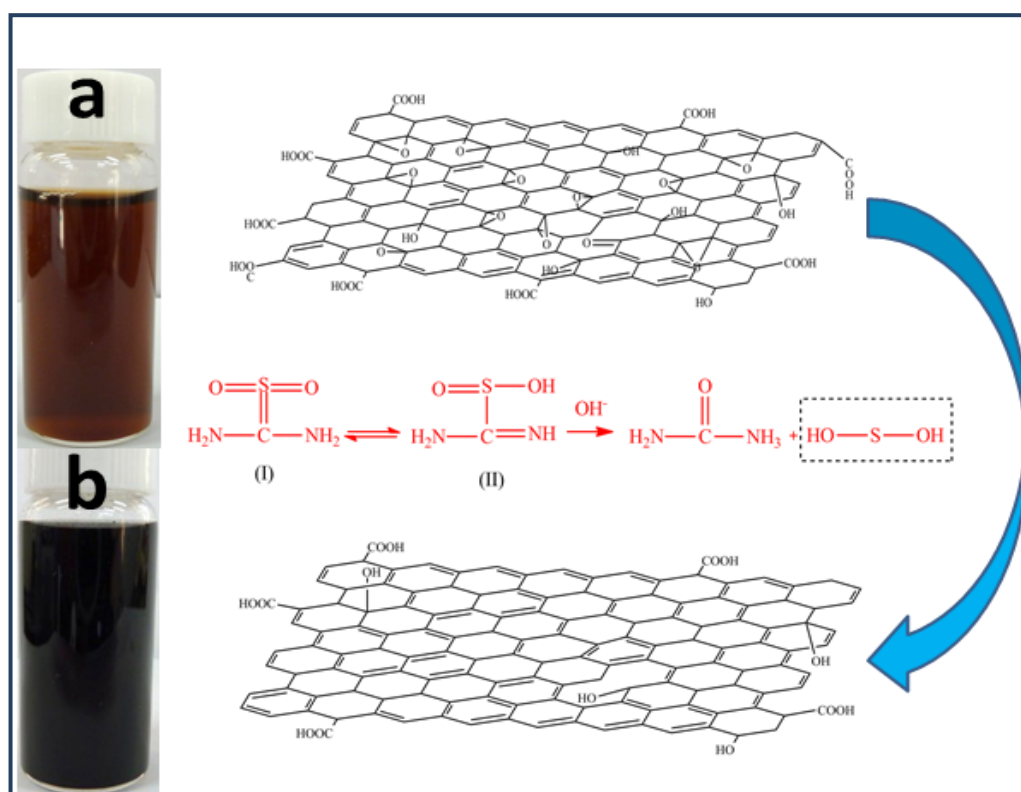


Figure 2-8. Schematic illustration of the reduction, including photographs of (a) the graphene oxide aqueous solution and (b) the reduced graphene sheets in aqueous solution.

The electrical conductance is used as an indicator of the extent to which the electronic conjugation in the graphene is restored after the reduction of the graphene oxide. To evaluate the electrical conductance of the TDO-reduced graphene, graphene-based films were prepared by reduction of 0.015 mm thick graphene oxide-based films with TDO for 30 min. The electrical conductance of the graphene-based film was measured by using a digital four-point probe system at room temperature. Five different sites on each film sample were measured and the results are summarized in Table 2-1. The average value of the electrical conductance of these graphene samples obtained by using TDO, sodium hydrosulfite and L-ascorbic acid were found to be $3.205 \times 10^3 \text{ S m}^{-1}$, $8.454 \times 10^2 \text{ S m}^{-1}$, $2.958 \times 10^{-2} \text{ S m}^{-1}$, respectively. The value of TDO is identical with that of the electrical conductance reported for the graphene films obtained using the hydrazine vapor reduction method [153]. When TDO functioned as the catalyst under alkaline conditions, it decomposed rapidly to produce sulfoxylic acid, which is a highly effective reductant.

After the reduction reaction, the sulfoxylic acid was converted into hydrogen sulfite which is also capable of reducing graphene oxide through a two-step nucleophilic reaction and SO_4^{2-} is believed to be the final product[147, 154-156]. The change in color of the graphene oxide aqueous solution before and after chemical reactions are visible evidence indicating that the graphene oxide was reduced into graphene. Figure 2-8 shows typical photographs for the

graphene oxide aqueous solution and the reduced graphene sheets in aqueous solution together with the schematic illustrations regarding the changes of the functional groups possibly involved in reduction of graphene oxide with TDO.

2.4 Conclusions

TDO is an efficient and nontoxic reductant for the massive production of high-quality, solution-based graphene using graphene oxide as the precursor. The oxygen-containing functionalities have been eliminated and crystalline structures of the aromatic domains have been restored into electronic conjugation states. This green-reduction method should open a new possibility for the mass fabrication of graphene-based functional materials for numerous practical applications.

Chapter 3

A polyelectrolyte stabilized approach to massive production of AgCl/Graphene nanocomposites

3.1 Introduction

Graphene, a novel two-dimensional planar sheets patterned with sp^2 bonded carbon atoms, has been recently highlighted as an intensively studied material due to its unique topological structures and alluring properties[2, 134, 135]. The thinnest known nanosheets with high surface area, superior mechanical and electronic properties hold great promise in applications to electronic devices, sensors, electrodes and other graphene-based materials[136].

Recently, graphene-based functional polar semiconductor photocatalysts have attracted considerable attention because of their practical potentials in environmental and energy applications[157]. As an interesting semiconductor, AgCl has shown important applications in visible light photocatalysis[121, 158, 159]. However, the hydrophobic graphene sheets tend to aggregate irreversibly due to the strong cohesive van der Waals energy of the π - π conjugation in graphene sheets, which makes the dispersion of nanoparticles on graphene

sheets difficult[160]. The superior properties of graphene are only associated with an individual or few-layer sheets forms, such as the optical transparency and extended large surface area in the final products. Therefore, the synthesis of graphene-based photocatalysts with the form of graphene sheets without aggregation is of great significance for many technological applications.

Here we report that a facile method for the preparation of dispersible graphene sheets. Poly(diallyldimethylammonium chloride) (PDDA), an ordinary polyelectrolyte, is able to adsorb on the surface of graphene sheets through π - π interactions and electrostatic interactions, which results in electrostatic repulsion between graphene sheets to prevent them from aggregating together in water solution. To the best of our knowledge, this is the first report on the use of PDDA as the stabilizer for the in situ production of graphene-enhanced AgCl-based photocatalysts.

3.2 Experimental section

3.2.1 Materials

Purified natural graphite (SP-1) was purchased from Bay Carbon, Inc., Michigan, USA. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt % in water, MW = 200000-350000) was purchased from Sigma-Aldrich. Other chemicals unless noted were from Wako Pure Chemical Industries, Ltd., or Sigma-Aldrich Inc., Japan.

3.2.2 Noncovalent functionalization of GO sheets by PDDA

Graphene oxide was obtained from natural graphite, based on the method proposed by Hummers and Offeman[29], as reported previously by the researchers[48, 161]. The procedure for the noncovalent functionalization of GO sheets using PDDA is as follows: 50 μL PDDA was added into 10 mL of GO solution (1 mg mL^{-1}) and then sonicated for 1 hour. Subsequently, the suspension was centrifuged and washed with deionized water. This washing process was repeated three times to remove excess PDDA. Finally, the PDDA-functionalized GO sheets (denoted as PDDA/GO) was dissolved in 20 mL of water.

3.2.3 Synthesis of AgCl/Graphene and AgCl/PDDA/Graphene

In a typical process, 20 mL of prepared PDDA/GO solution was added into 100 mL of ammonia-silver solution (with silver ions concentration of 10 mmol L^{-1}) under vigorous magnetic stirring for 1 hour. Then, 10 mL NaCl solution (0.1 M) was added dropwise into the above solution successively within 10 min under magnetic stirring. The opaque suspension was mixed with 20 mL methanol and irradiated under the UV light (100 W, UVP B-100A). A dark brown suspension was obtained soon after irradiation, which indicated the reduction of graphene oxide. Finally, the suspension was treated by

centrifugation (10000 rpm, 10 min), and collected solids were washed thoroughly with deionized water and dried at 50 °C. In the control experiment, the corresponding AgCl/Graphene nanocomposites were synthesized via a parallel process without any addition of PDDA, and AgCl/PDDA/GO nanocomposites were also synthesized via a parallel process without UV-irradiated reduction.

3.2.4 Characterizations

The morphological observations were carried out using scanning electron microscopy (SEM, JSM-6390, JEOL Co., Japan). Atomic force microscopy (AFM) images were acquired using an Agilent Series 5500 AFM instrument. The samples were prepared by casting a highly diluted aqueous graphene oxide aqueous suspension on the surface of mica. The images were obtained using the tapping mode at a scanning rate of 0.5 Hz. The X-ray photoelectron spectroscopy (XPS, JPC-9010MC, JOEL, Japan) analysis was performed by using an unmonochromated Mg-K X-ray source (1253.6 eV) with vacuum better than 1×10^{-7} Torr. The X-ray diffraction (XRD) measurement was performed with a Rigaku RINT Ultima diffractometer with Cu-K α radiation (K α 1.54056 Å) and an X-ray power of 40 kV/20 mA at a scan rate of 4 °/min.

3.3 Results and discussion

Optical photographs of GO, graphene and PDDA/Graphene sheets in water are shown in Figure 3-1. Homogeneous colloidal suspensions of GO and PDDA/Graphene are easily produced in water, and these colloidal suspensions are stable for more than 3 months at ambient conditions. In contrast, the UV-irradiated reduced graphene sheets solution without any addition of PDDA as shown in Figure 3-1(b), indicates that graphene sheets aggregated together and the precipitate was obtained at the bottom, as reported by other researchers[162]. As evidenced by the AFM image in Figure 3-2, the thickness of exfoliated GO sheets from the height profile is around 1.0 nm, which is consistent with the data reported in the literature[141], indicating the formation of the single layered GO sheets. The heavy oxidation process with oxygen-containing groups grafted onto the graphene planar surface, enabling development of hydrophilic yet thickened GO sheets (over 0.34 nm). As a result, as-synthesized GO sheets were modified with attached groups and lattice defects that serve as strong scattering centers and block the π -electrons transfer.

After the addition of PDDA to GO aqueous solution, the average thickness of GO sheets is 1.3 nm, which is larger than the GO sheets (1.0 nm) or normal single graphene sheet (less than 0.9 nm)[42]. It is reasonable to conclude that positively charged PDDA first absorbs onto the surface of single-sheet GO (negatively charged) *via* electrostatic interaction and increases the thickness of

the obtained GO. During the reduction of GO with UV irradiation, the absorbed PDDA is expected to act as a stabilizer to make hydrophobic graphene stable in water. The reduction of GO is not only concerned with removing the insulting oxygen-containing groups and other atomic-scale lattice defects, but is also aimed at recovering the long-range conjugated network of the graphitic lattice.

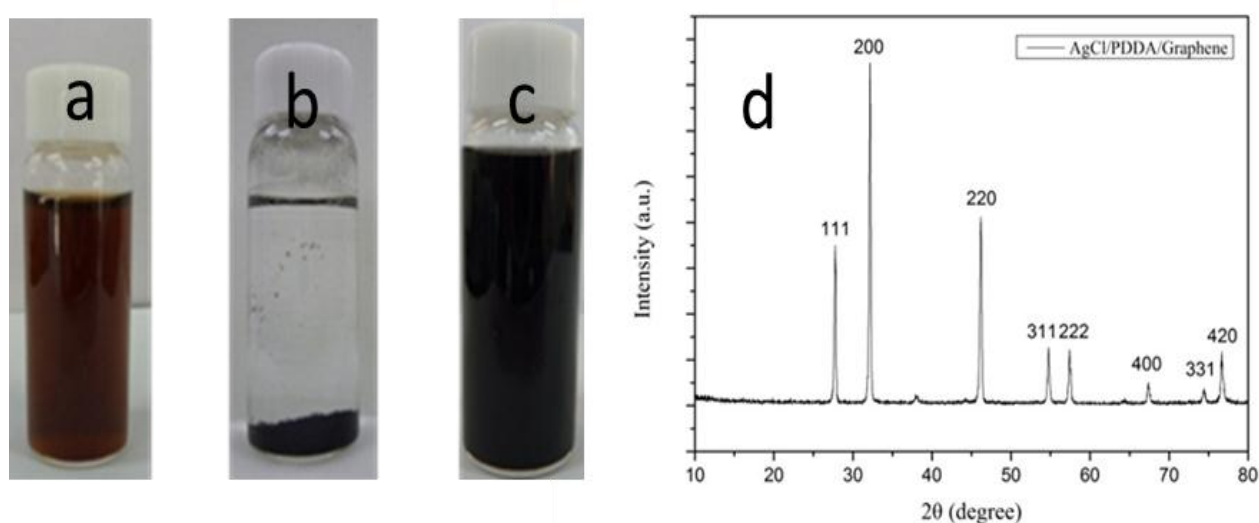


Figure 3-1. Optical photographs of GO sheets (a), UV-irradiated reduced graphene without the addition of PDDA (b) and UV-irradiated reduced PDDA/Graphene (c) in water solution, respectively. X-ray diffraction pattern of AgCl/PDDA/Graphene nanocomposites (d).

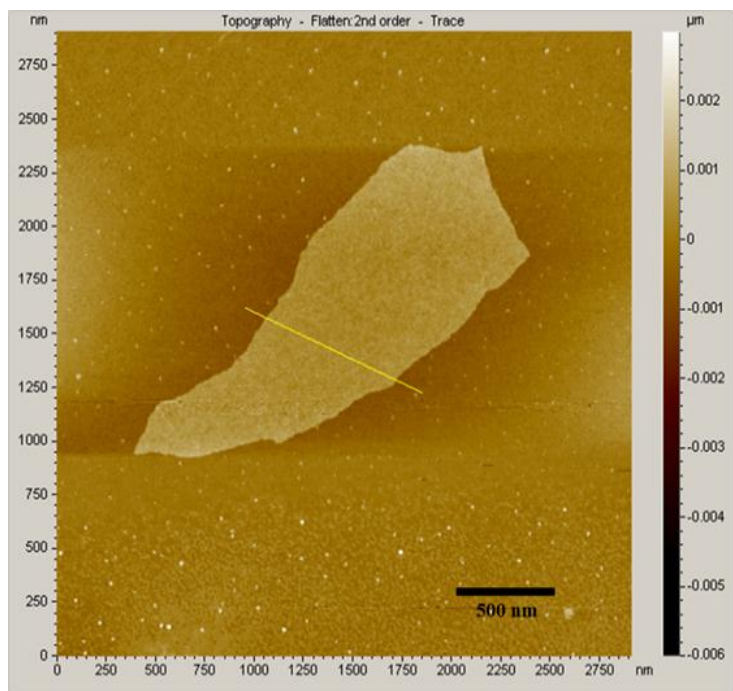
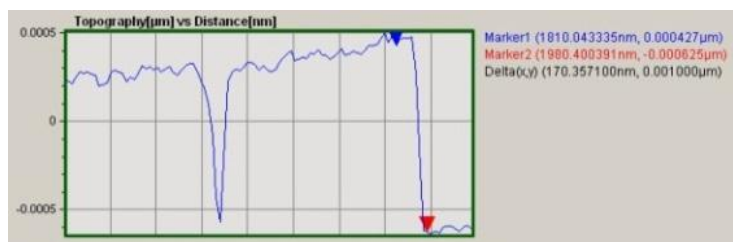
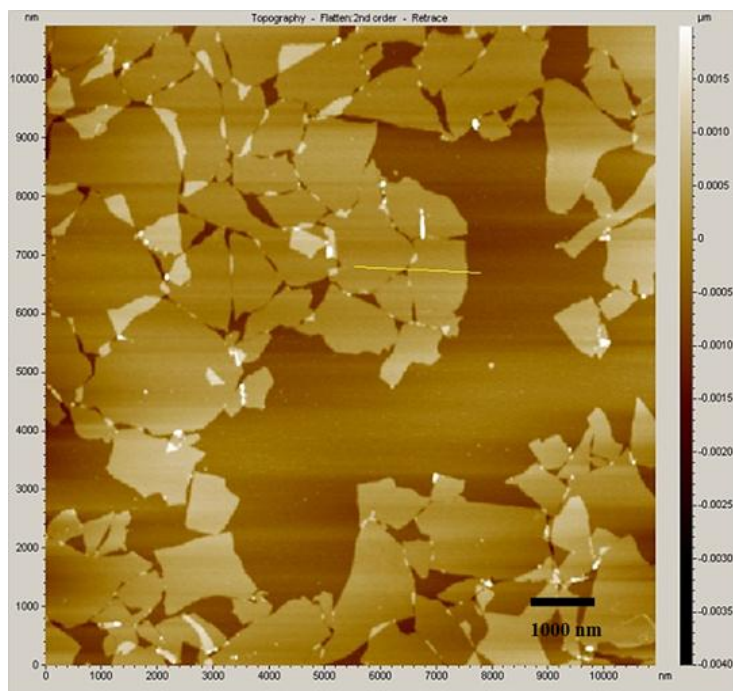




Figure 3-2. Typical AFM images of GO sheets (upper side) and PDDA/GO sheets (lower side) on mica substrate, the thickness of GO sheets and PDDA/GO sheets are estimated to be 1.0 nm and 1.3 nm, respectively.

The morphologies of as-prepared AgCl/Graphene and AgCl/PDDA/Graphene nanocomposites are shown in Figure 3-3. Compared with the AgCl/Graphene prepared without any addition of PDDA, PDDA-involved AgCl/PDDA/Graphene nanocomposites exhibit more uniform distribution and higher dispersibility. This phenomenon may arise from the absorption of long chains of PDDA molecules onto the surface of graphene sheets, which affect the dispersion of the resultant particles[163]. AgCl nanoparticles with sizes of ca. 500 nm are uniformly dispersed on the surface of transparent PDDA/Graphene sheets. SEM images showed the significant high-loading and uniform distribution of AgCl nanoparticles on the surface of PDDA/Graphene sheets, suggesting that our self-assembly method is capable of producing homogeneous high-loading AgCl nanoparticles supported on PDDA/Graphene sheets effectively. Furthermore, the crystal structure of the obtained AgCl/PDDA/Graphene nanocomposites was also characterized by

XRD, as shown in Figure 3-1 (d). The XRD pattern display distinct cubic phase of AgCl with lattice constant $a = 5.5491\text{\AA}$ (JCPDS file: 31-1238).

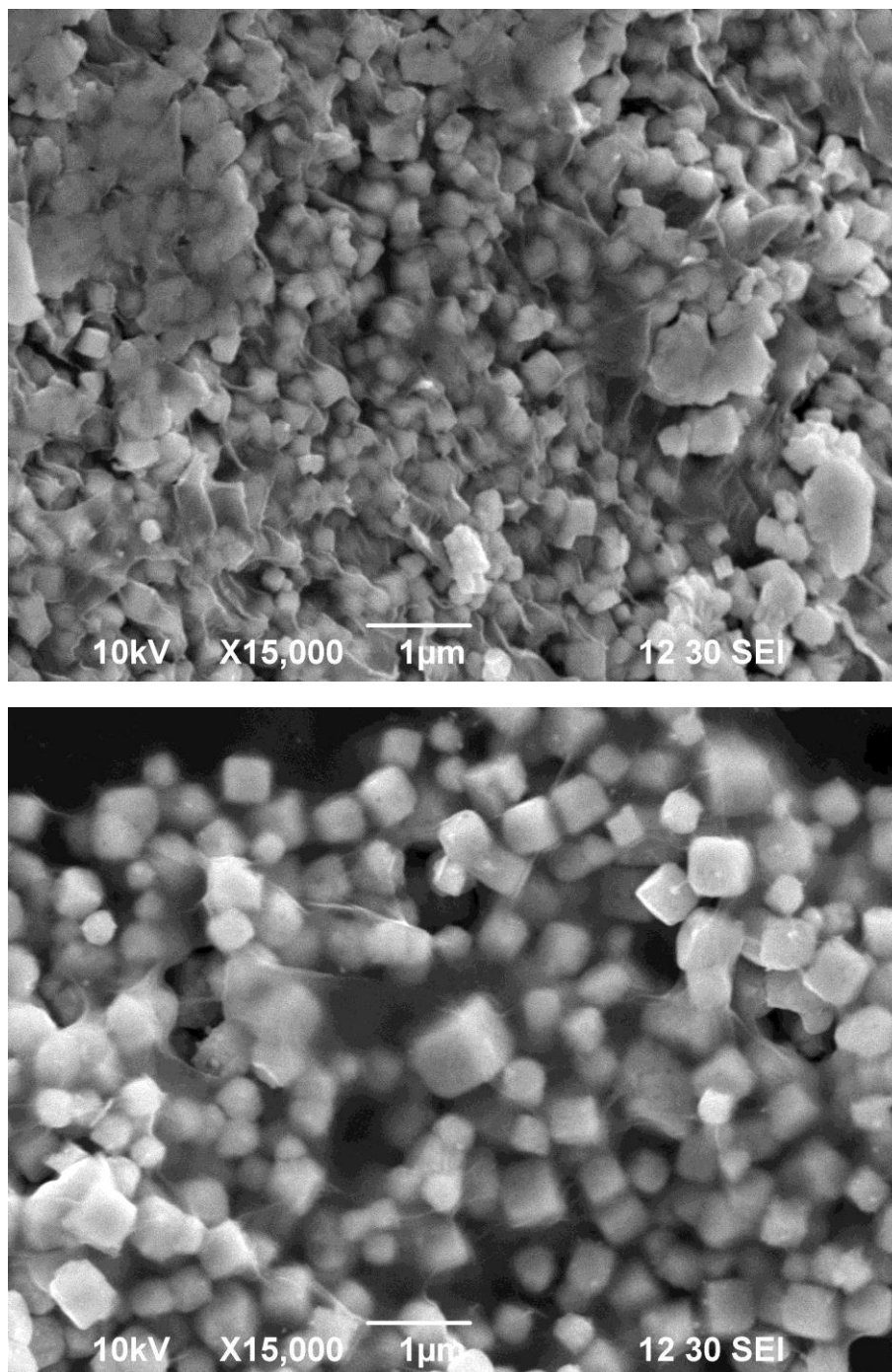


Figure 3-3. SEM images of AgCl/Graphene (upper side) and AgCl/PDDA/Graphene (lower side) nanocomposites.

To illustrate the formation of graphene sheets, XPS was used to characterize the constitutional changes from GO to graphene. Furthermore, XPS spectra give more information on the chemical structures of GO and graphene in the hybrid of AgCl/PDDA/GO and AgCl/PDDA/Graphene systems, respectively. The π electrons sourced from the sp^2 dominate optical and electrical properties of graphene-based materials. Briefly, as shown in Figure 3-4, the C1s XPS spectrum of GO shows a considerable degree of oxidation with four components that correspond to carbon atoms in different functional groups: the non-oxygenated aromatic C (C=C/C-C), the C in C-O bonds, the carbonyl C (C=O) and the carboxylate C (-COO-), centered at around the binding energies of 284.2, 285.7, 287.9, and 289.5 eV, respectively.

After the reduction of GO processed with UV irradiation, the intensities of all C1s peaks of the carbons bound to oxygen, especially the peaks of C=O and C-O bonds decreased rapidly, revealing that most of the oxygen-containing functional groups were removed after UV-irradiated reduction. These results demonstrate that UV irradiation can reduce GO efficiently in our AgCl/PDDA/Graphene system, as indicated by other researchers[164, 165].

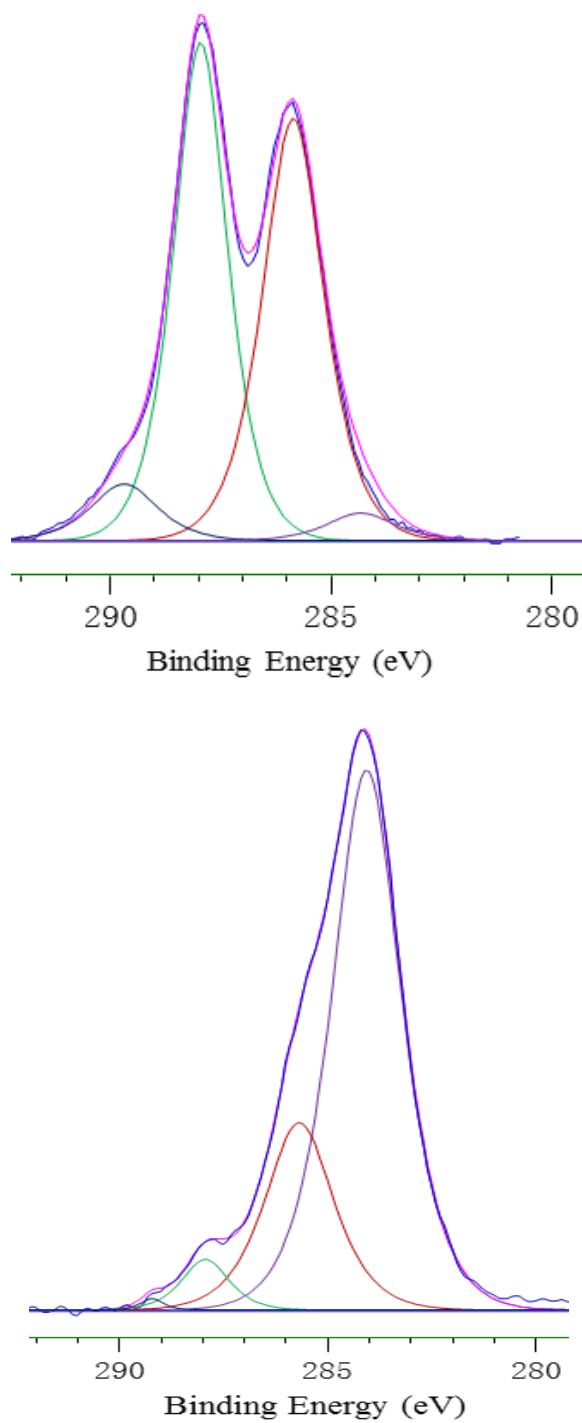


Figure 3-4. High-resolution XPS spectra and curve fittings of C1s spectra of AgCl/PDDA/GO (upper) and AgCl/PDDA/Graphene (lower).

3.4 Conclusions

In conclusion, graphene-enhanced AgCl-based nanophotocatalysts were produced successfully through the approach of in situ stabilization of GO by using PDDA. GO, a highly negatively charged polymer, was firmly stabilized by PDDA, a highly positively charged polymer. The sheet-shaped GO-PDDA complexes retained and stabilized Ag ions on their surfaces; nanosized AgCl particles subsequently formed via the seeding growth mechanism. Under desirable UV irradiation, a certain amount of the Ag ions in AgCl were converted to Ag⁰; Ag⁰ functioned importantly in the simultaneous reduction of GO to graphene. The graphene-enhanced AgCl/Ag nanoparticles functioned as photocatalysts under visible light. The use of the graphene-enhanced AgCl/Ag photocatalysts for the decomposition of toxic organic dyes has been under investigation in our research groups.

Chapter 4

Morphology-controlled synthesis of sunlight-driven plasmonic photocatalysts Ag@AgX (X=Cl, Br) with graphene oxide template

4.1 Introduction

Semiconductor photocatalysis has attracted increasing attention as a green technology to solve the current energy and environmental problems. In recent years we have witnessed the renewed appeal of harvesting and the direct conversion of solar energy into chemical energy by utilizing the sunlight-driven photocatalysts. Although heterogeneous photocatalysts are almost exclusively semiconductors, more recently the plasmonic noble metals (typically gold and silver) have played an important role in the field of photo-driven chemical conversion due to their surface plasmon resonance (SPR). For example, the pioneering work of Awazu and co-workers introduced the concept of SPR into the field of photocatalysts, which is plasmonic photocatalysts[166]. Since the first report on the visible-light Ag@AgCl plasmonic photocatalysts by research group of Huang in 2008[121], a large number of Ag@AgX (X=Cl, Br, I)

plasmonic photocatalysts have attracted much attention. Up to now, various sizes and structures of the new family have been fabricated, which include nanocubic[167, 168], near-spherical[169, 170], rounded triangular pyramid[171], polyhedral[172], heart-like[173], nanocashew[174], hollow-sphere micro/nanostructure[158], etc. In those cases, plasmonic nanostructures have been synthesized via either hydrothermal, ion-exchange method or direct precipitation process, where a subsequent light-, microwave- or heat-induced generation of Ag is required. Similar to the traditional photocatalysts, the quality and morphology of Ag@AgX (X=Cl, Br, I) influence importantly on their photocatalytic activity. Several micrometers sized Ag@AgX cause the recombination of the plasmon-induced electron-hole pairs before they arrive at the photocatalyst surface. The efficient separation of electron-hole pairs is critical for an enhanced plasmonic photocatalyst system. Therefore, owing to their morphology-dependence, one-step synthesis of the metal-semiconductor photocatalysts with high quality and photocatalytic activity is desirable.

To modulate the quality and morphology of plasmonic photocatalysts, since the reports on tailoring nanoscale materials and composites by using various amphiphilic molecules[175], surfactant-based composite systems have been harnessed again recently[125, 143, 157, 158, 168, 176-178]. Shape-directing surfactants or specific surface capping agents such as polyvinyl pyrrolidone (PVP), cetyltriethylammonium bromide (CTAB) and

cetyltrimethylammonium chloride (CTAC) were needed to guide the formation or induce anisotropic growth of different Ag@AgX (X=Cl, Br, I) that are usually synthesized via water/oil or oil/water microemulsions. However, the presence of large amounts of these agents leads to a decrease of active sites, which severely affect their photocatalytic activity[177]. Therefore, it is a significant challenge to develop the morphology-controlled photocatalysts with “clean” surface structure without adding any capping agent. The emergence of single-layer graphene oxide (GO) has received extensive attention, and shows great potential as an ideal additive for controlling the formation of inorganic single crystals owing to its unique two-dimensional (2D) nanostructure, good flexibility and abundant functional groups on its surface[18, 176, 179, 180].

As an attractive precursor of graphene, the intrinsic hydroxyl, epoxy and carboxylic functional groups could act as active anchoring sites for the heterogeneous nucleation of metal ions such as Au^{3+} , Ag^+ , Ti^{3+} , Zn^{2+} , Ca^{2+} , etc. In particular, its large surface and tunable surface properties allow it to be a competitive host substrate for the heterogeneous growth of desired guest materials. Furthermore, the competitive growth of nucleated clusters on GO surface may tailor the size and microstructure of the final particles. For example, very recently, by using monolayer GO sheets as a synthetic template, Huang’s group synthesized exquisite square-like Au nanosheets, which exhibited an edge length of 200-500 nm and a thickness of ~ 2.4 nm[179]. Composite crystals of

calcium carbonate (CaCO_3)/graphene with hexagonal plate, dendritic and rhombohedral shapes were synthesized using GO sheets as the template to precisely control the mineralization process of CaCO_3 [176]. Mesoporous anatase TiO_2 nanospheres/graphene composite photocatalysts by template-free self-assembly were presented, in which the final size and microstructure of TiO_2 could be tailored by the graphene sheets[181]. However, no work related to morphology-controlled plasmonic photocatalysts with GO as the template has been reported. Hence, the development of graphene-based plasmonic photocatalyst system formulates fundamental and practical significance.

In this part, we report our new efforts to synthesize the $\text{Ag}@\text{AgX}@\text{Graphene}$ ($\text{X}=\text{Cl}, \text{Br}$) nanocomposites, where an accelerated GO reduction and generation of Ag nanocrystals occurred simultaneously by photoreducing $\text{AgX}@\text{GO}$ nanocomposites. Interestingly, the cubic $\text{Ag}@\text{AgCl}$ and quasi-cubic $\text{Ag}@\text{AgBr}$ nanoparticles were manipulated by the orientation growth of AgX nanoparticles on the amphiphilic GO template. The obtained hetero-products display enhanced plasmonic photocatalytic activity and good recycling stability toward acridine orange (AO) pollutant under sunlight irradiation, which is ascribed to the synergistic effect of strong SPR excited by Ag nanocrystals and the conductive graphene sheets network for rapid carrier transfer and export between two components in the composite system. It is anticipated to open new possibilities in the application of graphene-based

composites as the photocatalysis in environment remediation.

4.2 Experimental section

4.2.1 Materials

Purified natural graphite (SP-1) was purchased from Bay Carbon, Inc., Michigan, USA. Other chemicals unless noted were from Wako Pure Chemical Industries, Ltd., or Sigma–Aldrich Inc., Japan.

4.2.2 Preparation of GO aqueous solution

GO was obtained from natural graphite, based on the method proposed by Hummers and Offeman, as reported previously by our group[161]. In a typical treatment, 5 g of the natural graphite was dispersed in 115 mL concentrated sulfuric acid in an ice bath. Approximately 5 g sodium nitrate and 15 g potassium permanganate were slowly added to the chilled mixture, cooled by an ice bath, and stirring was continued for 2 hours. The mixture gradually became pasty and blackish-green. Then, the mixture was placed in a 35 °C water bath and kept at that temperature for 30 min, followed by the slow addition of distilled water (500 mL) to keep the solution from effervescing. The resulting solution was placed at well below 98 °C for 2 hours. As the reaction progressed, the color of the mixture turned yellowish. The mixture was further treated with

5% H_2O_2 (200 mL), filtered and washed with distilled water several times until its supernatant was without SO_4^{2-} , as tested by barium chloride solution (0.2 mM). The purified GO was finally dispersed in water and ultrasonically exfoliated in an ultrasonic bath for 1 hours to form a stable GO aqueous dispersion.

4.2.3 Synthesis of Ag@AgX, Ag@AgX@GO and Ag@AgX@Graphene

In a typical process, 10 mL aqueous solution of GO sheets (1 mg mL^{-1}) was added into 100 mL of ammonia-silver solution (with silver ions concentration of 10 mmol L^{-1}) under vigorous magnetic stirring for 1 hour. Then, 10 mL NaCl (or NaBr) solution (0.1 M) was added dropwise into the above solution successively within 10 min under magnetic stirring. The vigorous stirring was maintained for 24 hours under ambient conditions to form a light brown homogeneous suspension. The opaque suspension was mixed with 20 mL methanol and irradiated under the UV light (100 W, 365 nm, UVP B-100A). A dark brown suspension was obtained soon. Finally, the suspension was treated by centrifugation (10000 rpm, 10 min), and the produced solids were collected, washed thoroughly with deionized water and dried in 50°C . In the control experiment, the corresponding Ag@AgX nanospecies were also synthesized via a parallel process without GO sheets. Ag@AgX@GO nanocomposites were also synthesized via a parallel process without UV-irradiated reduction. Note

that the abovementioned synthesis works were performed without being protected from ambient light.

4.2.4 Photocatalytic performance

For the photocatalytic degradation experiments that used sunlight as energy source, a photocatalyst sample typically containing 10 mg of the loaded catalysts was dispersed in a 30 mL aqueous solution of AO dye (20 mg L^{-1}) and the illumination intensity of sunlight was 80 mW cm^{-2} to make the experimental results reasonably comparable with those obtained previously. The dispersion was kept in the dark for 60 min for dark adsorption experiment, after which the photodegradation was carried out. The dark adsorption was designed to be 60 min because the adsorption results indicated AO molecules was absorbed to saturation on the surface of catalysts (data not shown). At certain time intervals of sunlight irradiation, reaction solution was taken out from the system for the real-time investigation. The concentration of AO dye was monitored by UV-vis spectroscopy through recording the absorbance of the characteristic peak of AO at 490 nm. For the evaluation of the photocatalytic activity, C is the concentration of AO molecules at a real-time t , and C_0 is that in the AO solution immediately before it was kept in the dark. For comparison, blank experiment without photocatalysts has also been carried out.

4.2.5 Photoelectrochemical test

The photocurrent response tests were measured using electrochemical analyzer (ALS/CH Instruments 852C, ALS) in a standard three-electrode system using the as-prepared samples as the working electrodes with a diameter of ~3 mm, a platinum electrode as the counter electrode, and Ag/AgCl as the reference electrode. 1M Na₂SO₄ aqueous solution was used as the electrolyte. For the working electrodes, 20 mg catalyst was suspended in 1 mL nafion aqueous solution (2 wt%), the mixtures were ultrasonicated for 15 min to disperse it evenly to get a slurry. The slurry was coated onto the glass carbon electrode and dried under ambient conditions. The current-time (*i-t*) curves were collected at 1.0 V vs Ag/AgCl reference electrode. The intensity of sunlight irradiation was 80 mW cm⁻² using super solar simulator with one-sun irradiation.

4.2.6 Characterizations

The morphological observations were carried out using scanning electron microscopy (SEM, JSM-6390, JEOL Co., Japan) and high resolution transmission electron microscopy (HR-TEM, HD-2000, Hitachi Co., Tokyo, Japan). Atomic force microscopy (AFM) images were acquired using an Agilent Series 5500 AFM instrument. The samples were prepared by casting a highly

diluted GO aqueous suspension on the surface of mica. The images were obtained using the tapping mode at a scanning rate of 0.5 Hz. The X-ray diffraction (XRD) measurements were performed with a Rigaku RINT Ultima diffractometer with Cu-K α radiation (K α 1.54056 Å) and an X-ray power of 40 kV/20 mA at a scan rate of 4 ° min⁻¹. Fourier transform infrared spectroscopy (FT-IR) was performed over the wave number range of 4000–400 cm⁻¹ with a FT/IR-6100 FT-IR Spectrometer, (JASCO, Japan). The X-ray photoelectron spectroscopy (XPS, JPC-9010MC, JOEL, Japan) analysis was performed by using an unmonochromated Mg-K α X-ray source (1253.6 eV) with vacuum better than 1×10^{-7} Torr. For the transmission electron microscopic (TEM) analysis, the samples were suspended in water/menthol (0.2 mg mL⁻¹) by ultra-sonication for 10 min and then the dispersion was drop-casted on a fresh lacey carbon TEM grid. The beam energy used for TEM analysis was 200 keV. Raman analysis was performed with Invia Raman Microscope (Renishaw, United Kingdom) with an excitation wavelength at 532 nm.

The photocatalytic performance of the samples under sunlight were evaluated by the degradation of AO dye under super solar simulator with one-sun irradiation (Super Solar Simulator, WXS-156S-L2, AM 1.5GMM, illumination wavelength: 400 nm-1100 nm, Wacom Electric. Co., LTD.).

4.3 Results and discussion

Typically, quasi-spherical Ag@AgCl and Ag@AgBr could be facilely fabricated by adding an aqueous solution of NaCl into a solution of $[\text{Ag}(\text{NH}_3)_2]\text{OH} \cdot x\text{H}_2\text{O}$. Cubic Ag@AgCl@Graphene and quasi-cubic Ag@AgBr@Graphene could also be produced via a similar process when a GO aqueous solution was added to the system prior to the addition of NaCl solution. The hydroxyl, epoxide and carboxylic functional groups on GO sheets could act as favorable anchoring sites for the heterogeneous nucleation and hetero-growth of AgX nanoparticles.

During the growth process, few amount of Ag^+ in AgX are converted into Ag nanocrystals by the ambient light. Whereas under the subsequent UV irradiation, more Ag^+ are converted, simultaneously with the enhanced reduction efficiency of the adjacent GO into graphene within fewer hours, compared with the previous research[137]. Experimentally, an opaque suspension with a light brown was obtained soon after the dropwise addition of the NaCl solution into the aqueous solution of $[\text{Ag}(\text{NH}_3)_2]\text{OH} \cdot x\text{H}_2\text{O}$ and then a much darker brown suspension was obtained after UV irradiation (Figure 4-1).

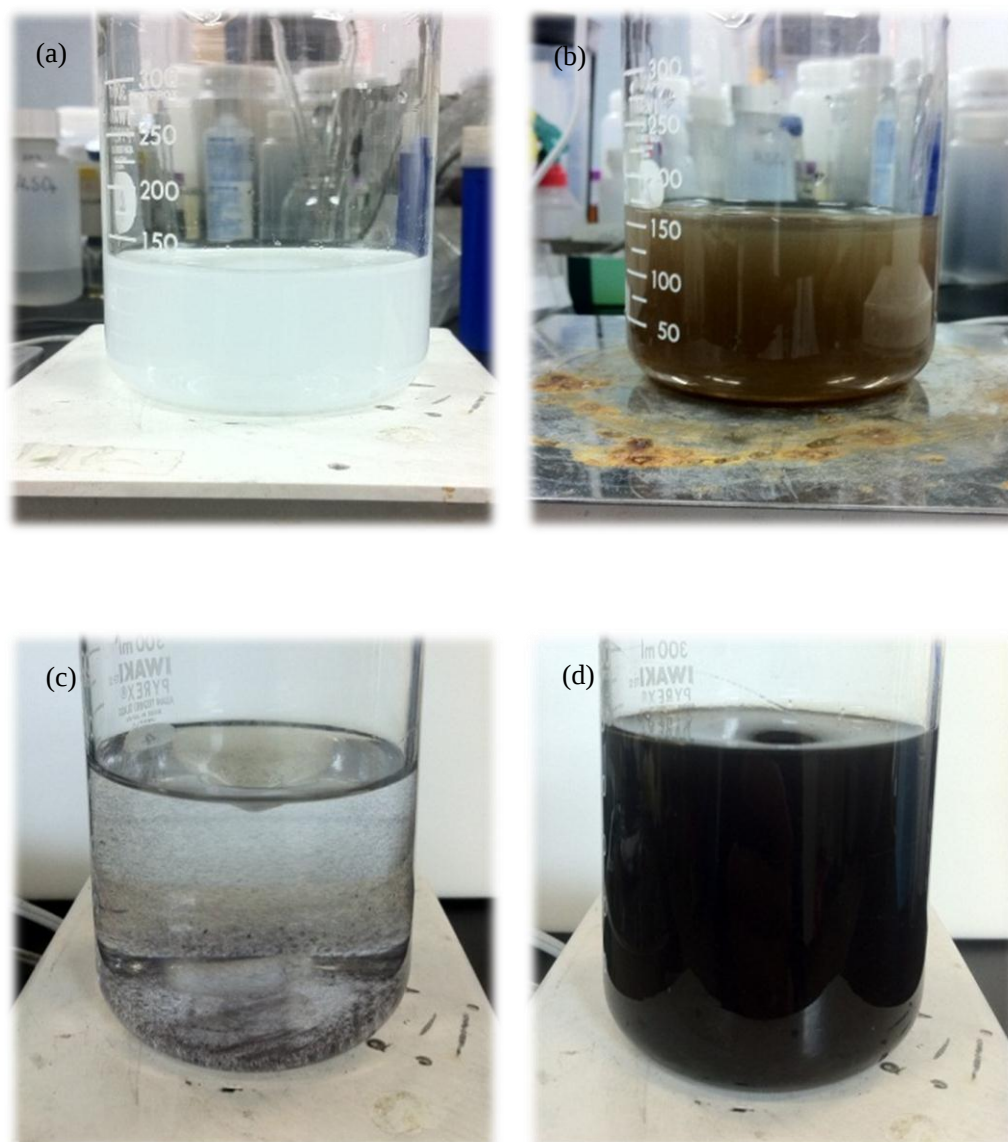


Figure 4-1. Photo images of the synthesis of Ag@AgCl (a, c) and Ag@AgCl@Graphene (b, d) in the process of the addition of NaCl solution and UV irradiation, respectively.

The morphologies of as-synthesized nanostructures are characterized by scanning electron microscopy (SEM), as shown in Figure 4-2 and Figure 4-3. The Ag@AgCl and Ag@AgBr samples exhibit quasi-spherical structures with

sizes of 0.8~1.5 μm as reported previously [121, 182, 183]. While after involving the multifunctional GO, the cubic Ag@AgCl and quasi-cubic Ag@AgBr nanostructures with an average edge length of 400 nm and 200 nm, respectively, were manufactured without the addition of any other surfactant.

After photoreduction, the as-prepared Ag@AgX nanoparticles are distinctly enwrapped with gauze-like graphene sheets, which significantly improve the dispersibility and homogeneity of Ag@AgX. On the other hand, by functioning as “spacer”, these cubic-like nanoparticles attached onto graphene sheets can prevent graphene sheets from aggregation and restacking, and both of the two faces of graphene sheets are accessible in their application.

The transparent gauze-like structure with well restored conjugated networks of the graphene sheets were maintained in the final products, which could promote electron transfer of the catalysts in photocatalytic reaction and favorably improve the adsorption capacity of Ag@AgX@Graphene due to its high surface area.

The ordered structure of the as-prepared Ag@AgX@Graphene compared with the bare Ag@AgX could be attributed to the existence of GO sheets, which play a role as a template modulating the growth of Ag@AgX crystals along certain directions, resulting in a smaller sized of cubic-like products. It has been verified that the multifunctional GO sheets, which could physicochemically and structurally be regarded as an unconventional amphiphilic surfactant[143]. In

that case, GO sheets can work as capping agent or stabilizer to hamper the growth of nanoparticles randomly, which affect the morphology and size of the resultant nanoparticles[124, 125, 168]. The exact role of GO sheets in this process and the formation mechanism of the as-prepared crystals remain to be further studied and established. A representative TEM image of the Ag@AgCl@Graphene nanocomposites further confirms the cubic nanoparticles were uniformly attached to the surface of gauze-like graphene sheets (Figure 4-4).

The full potential of graphene in Ag@AgCl@Graphene is released to the maximum for which the presence form of graphene sheets remains at a single or few layers. Furthermore, the EDX mapping images of Ag@AgCl@Graphene is demonstrated to illustrate the distribution of C, O, Cl and Ag elements (Figure 4-5). Unfortunately, high-resolution TEM image of Ag@AgX@Graphene was not obtained because these nanoparticles were destroyed by the high-energy electron beam during the measurement.

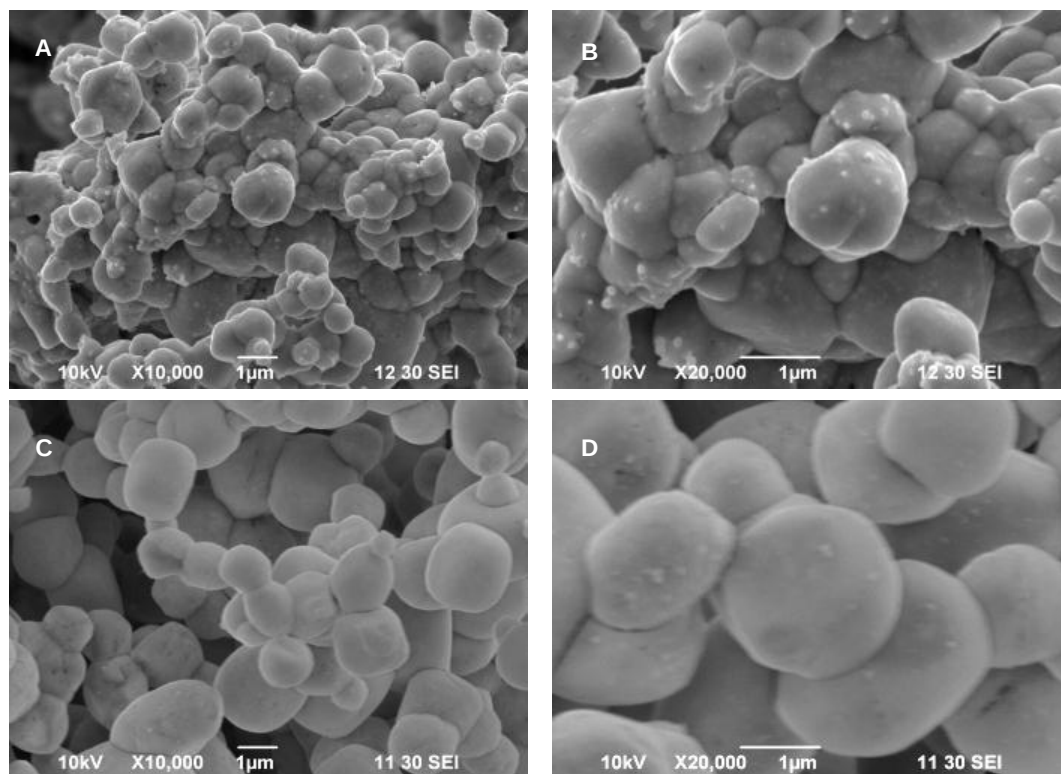


Figure 4-2. Quasi-spherical Ag@AgCl (A and B) and Ag@AgBr (C and D) photocatalysts with inhomogenous particle size.

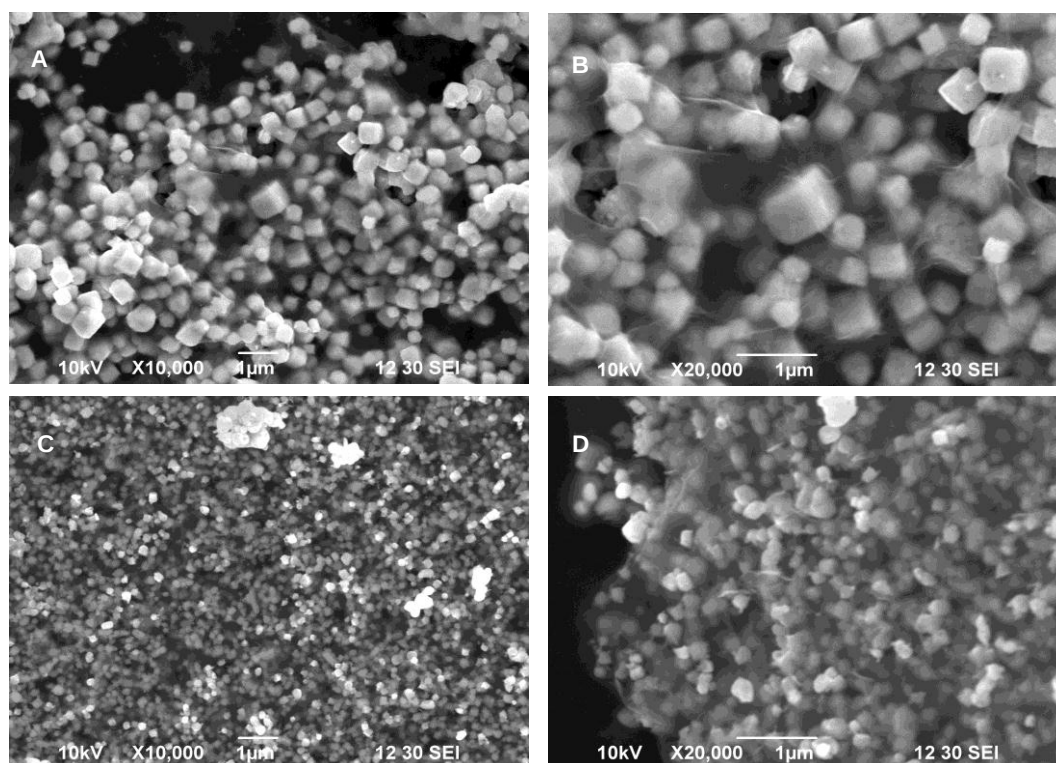


Figure 4-3. Representative SEM images of the as-prepared cubic Ag@AgCl and quasi-cubic Ag@AgBr nanoparticles encapsulated by gauze-like graphene sheets in Ag@AgCl@Graphene (A and B) and Ag@AgBr@Graphene (C and D), respectively.

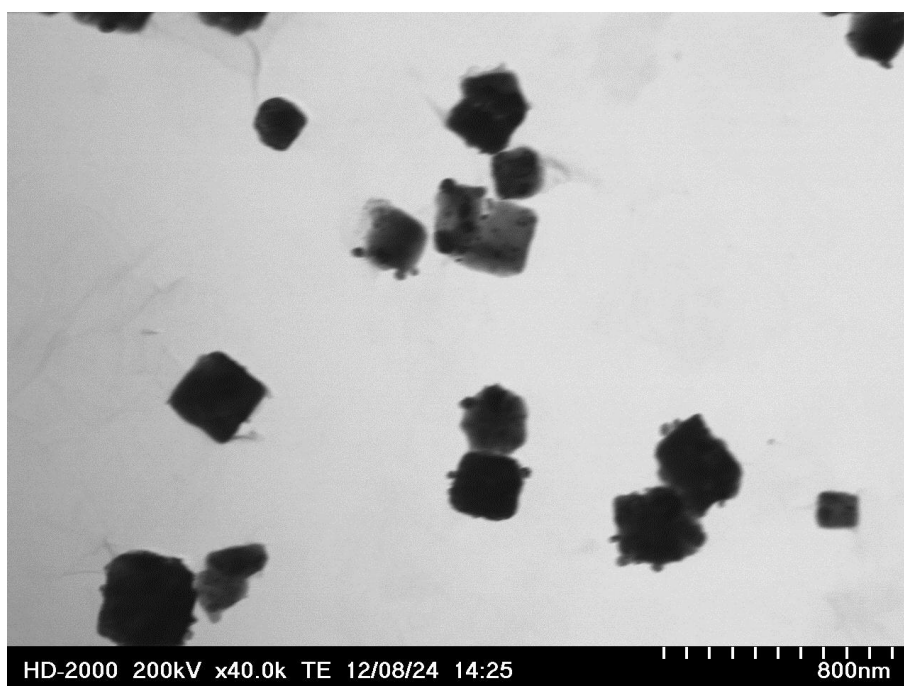


Figure 4-4. Representative TEM image of the as-prepared cubic Ag@AgCl@Graphene nanocomposites.

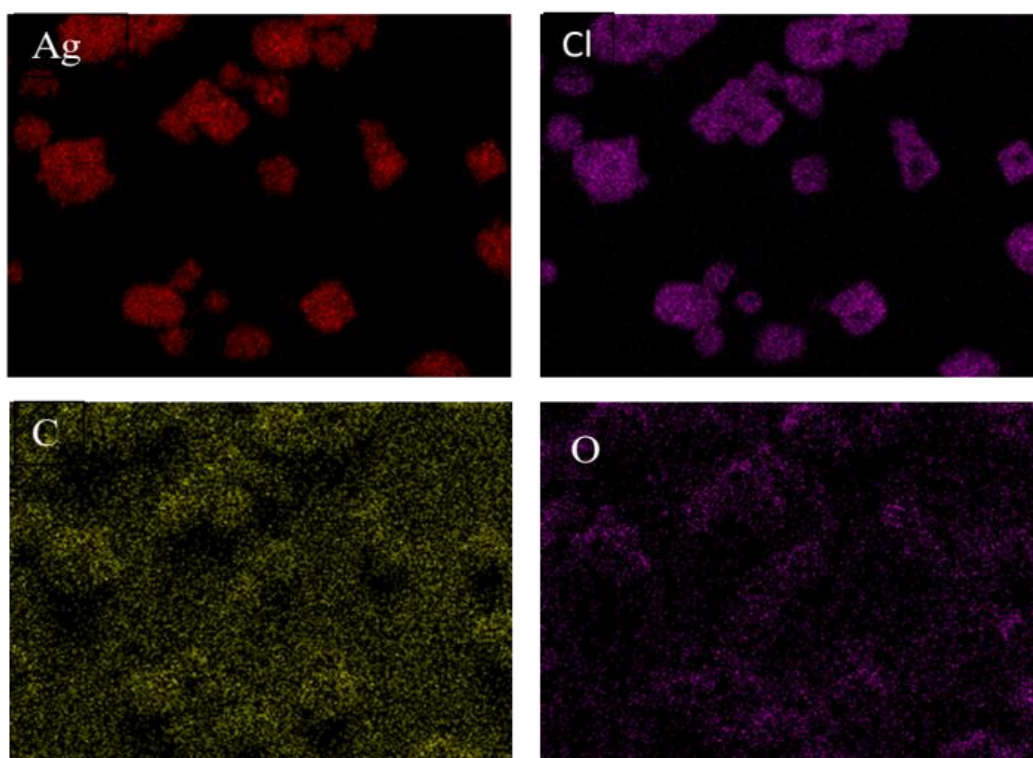


Figure 4-5. Represent EDX mapping images of Ag@AgCl@Graphene.

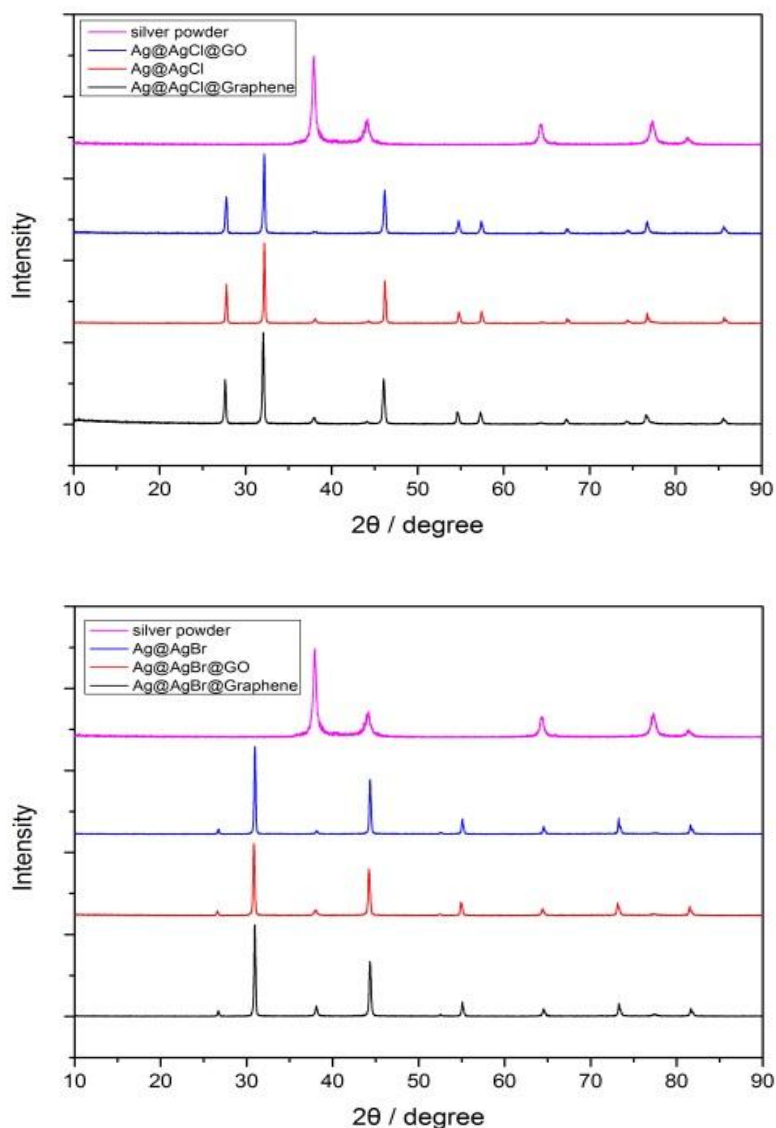


Figure 4-6. XRD spectra of the standard silver powder, bare Ag@AgX, Ag@AgX@GO and the quasi-cubic Ag@AgX@Graphene nanocomposites.

The crystal structures of the obtained Ag@AgX@Graphene (X=Cl, Br) plasmonic photocatalysts are characterized by X-ray diffraction (XRD). As shown in Figure 4-6, the crystalline phase of standard silver powder, bare

quasi-spherical Ag@AgCl, Ag@AgCl@GO and cubic Ag@AgCl@Graphene were investigated. The XRD patterns display distinct diffraction peaks (2θ) at 38.2 (111), 44.6 (200), 67.4 (400), 74.4 (331), 85.6 (422), respectively, which correspond to the typical cubic phase of standard metallic Ag and that of AgCl (JCPDS file: 31-1238). Due to the high photosensitivity of bare AgX, Ag nanocrystals aggregate on the surface of AgX under the ambient light in the cases of Ag@AgX@GO. Compared with Ag@AgX and Ag@AgX@GO, the peak intensity of Ag@AgX@Graphene shows stronger, indicating that simultaneously with the reduction of GO into graphene under UV irradiation more Ag nanocrystals generate, which can be confirmed below by the XPS. These results verify the evident interactions between the generation of Ag nanocrystals and the reduction of GO, as also suggested by other researchers[184].

To investigate the morphology evolution of Ag@AgX@Graphene nanocomposites, the growth process of representative Ag@AgCl@Graphene was further studied by analyzing two intermediate stages as indicated in Figure 4-7. In the first stage, a large amount of irregular AgCl seeds with varying sizes were formed during the initial 4 hours. Due to the complexation of functional oxygen-containing active sites anchoring with Ag^+ , followed by the heterogeneous nucleation process accompanying the addition of chloridion, such a strategy could help put GO into full play with elaborate design, resulting

in reinforced interfacial contact between GO and AgCl nanoparticles[185]. After 12 hours, the AgCl nanoparticles encapsulated tightly by GO tend toward uniformity with size of $\sim 1\ \mu\text{m}$. Meanwhile, a certain amount of quasi-spherical AgCl particles were gradually transformed into AgCl cubes. When the reaction has been performed for 24 hours, the as-prepared cubes were formed finally.

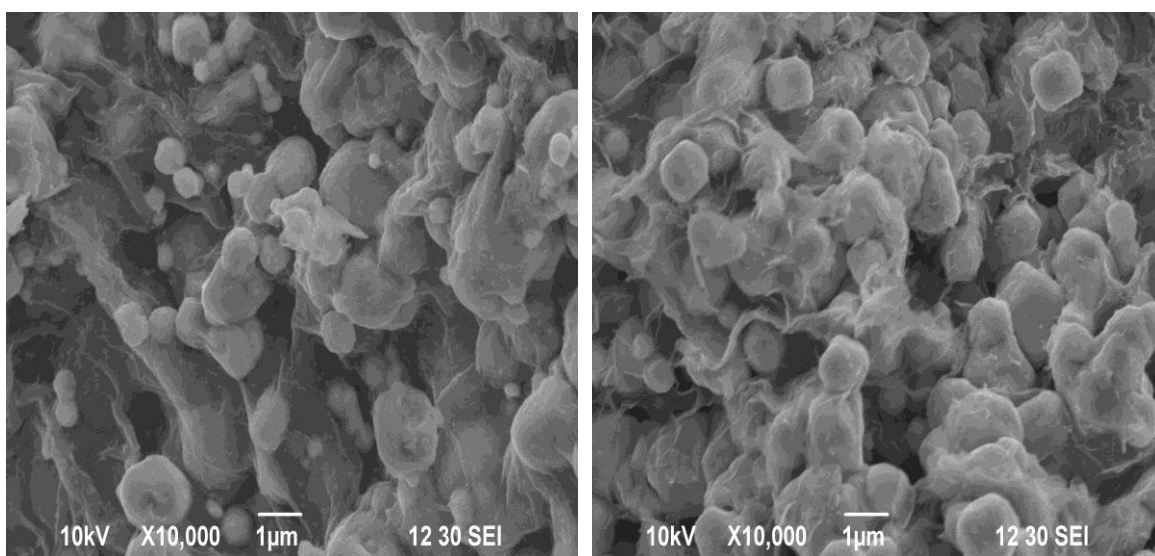


Figure 4-7. SEM images of the shaped evolution of the representative Ag@AgCl@GO samples obtained at different reaction stages: the formed quasi-spherical Ag@AgCl@GO seeds after 4 hours (left) and a certain number of quasi-spherical Ag@AgCl@GO have been transformed into cubes after 12 hours (right).

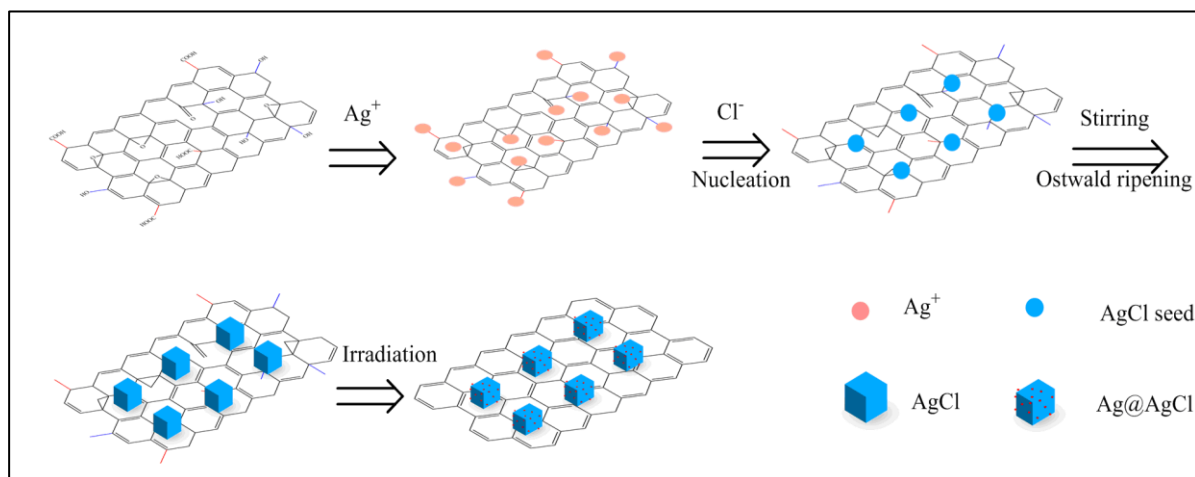


Figure 4-8. Schematic Explanation for morphological evolution of the representative Ag@AgCl@Graphene nanocomposites.

On the basis of the above experimental observations, we proposed a possible fabrication strategy for the cubic Ag@AgCl@Graphene nanocomposites under ambient conditions (Figure 4-8). Chemically derived GO, with a thickness of ~ 1.1 nm and size distribution on the order of micrometers (Figure 4-9), carries abundant functional groups such as the hydroxyl, epoxide and carboxyl on the sheet surface. In GO solution, those active sites are leveraged to stabilize Ag^+ and subsequently grown to the initial AgCl seeds via the seeding growth mechanism. As the time progresses, the functionally layered sheets play a role as surfactant template which makes the AgCl seeds grow along certain directions. For the face centered cubic (FCC) structure in particular, the crystal shape is determined mainly by the function of the ratio R , of the growth rate along the $\langle 100 \rangle$ to that of the $\langle 110 \rangle$ directions. For example,

the cubes bounded by six equivalent[186] facets would form when $R=0.58$ [187]. In this study, rapid nucleation occurred at a very early stage, producing a large amount of irregular AgCl seeds with varying sizes. These nuclei gradually grew along the controlled orientation to form the regular AgCl cubes in the presence of GO, while invariant shape in Ag@AgCl was obtained for comparison in the absence of GO, similarly reported by other researchers[168].

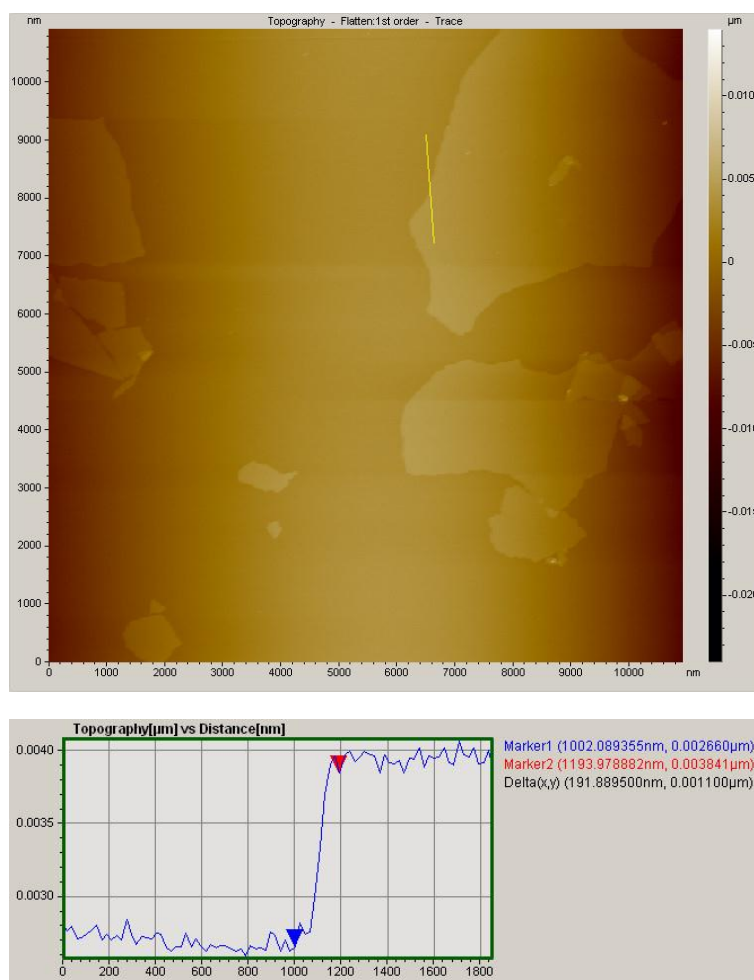


Figure 4-9. A typical AFM image of the GO sheets on a mica substrate.

The thickness of the GO sheets is estimated to be ~ 1.1 nm.

The chemical compositions and surface chemical states of the samples were further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 4-10, the C1s XPS spectrum for the Ag@AgCl@GO indicates a considerable degree of oxidation with four components that correspond to carbon atoms involved in different functional groups, namely, the non-oxygenated aromatic C (C=C/C-C), the C in C-O bonds, the carbonyl C (C=O) and the carboxylate C (-COO-), centered around the binding energies of 284.3, 286.2, 288.1, and 290.1 eV, respectively. After the UV irradiation, the intensities for all C1s peaks of the carbon-oxygen binding species, especially the peaks of C-O and C=O bonds decreased rapidly, revealing that most of the oxygen containing functional groups were removed in the Ag@AgCl@Graphene system after photoreduction; the C/O ratio increased from 2.37:1 to 4.83:1. While for the Ag@AgBr@Graphene system, the C/O ratio increased from 2.49:1 to 4.19:1.

In previous studies, the C/O ratio for graphene obtained by using UV irradiation of GO aqueous solution was increased from 2.20:1 to 5.90:1. However, the reduction process required over 16 hours under 300 W ultraviolet light[184]. It is true that the reduction rate was accelerated in our system, which could facilitate the charge transfer from Ag@AgX to the surface of graphene. Simultaneously, more Ag nanocrystals were obtained with the photoreduction of GO under UV irradiation, which is also confirmed by the XPS spectra of Ag 3d

(Figure 4-11).

For the bare Ag@AgX samples, two bands at 367.5 and 373.6 eV corresponding to the binding energies of Ag 3d_{5/2} and Ag 3d_{3/2}, respectively, are observed. These two bands could be further divided into two groups of peaks 367.5, 368.4 eV and 373.6, 374.3 eV, where the peaks at 367.5 and 373.6 eV are attributed to Ag⁺ in AgX, whereas those at 368.4 and 374.3 eV are attributed to the Ag nanocrystals. The calculated surface mole ratio of the Ag nanocrystals to Ag⁺ for Ag@AgCl and Ag@AgBr is ca. 1:24 and 1:13, respectively.

In the cases of graphene-involved Ag@AgX@Graphene nanocomposites, the Ag 3d_{5/2} and Ag 3d_{3/2} peaks shift to a higher binding energy to 368.2 and 374.1 eV, respectively. The two bands also yield four peaks at 368.2, 369.2 eV and 374.1, 374.8 eV, respectively. The peaks at 368.2 and 374.1 eV could be ascribed to Ag⁺, and those at 369.2 and 374.8 eV are attributed to the Ag nanocrystals. It is interesting that compared with the bare Ag@AgX, these peaks shift to higher binding energies in Ag@AgX@Graphene with a value of ca. 0.6 eV.

In addition, the calculated surface mole ratio of the Ag nanocrystals to Ag⁺ for Ag@AgCl@Graphene and Ag@AgBr@Graphene increases distinctly to ca. 1:10 and 1:4, respectively. In the XPS spectra of Cl 2p and Br 3d of the samples (Figure 4-12), the observed peak could be fitted with two peaks corresponding to Cl 2p₃ (197.7 eV), Cl 2p₁ (199.5 eV) and Br 3d_{5/2} (67.8 eV), Br 3d_{3/2} (68.8

eV), respectively, in good agreement with that of AgCl[158] and AgBr[188].

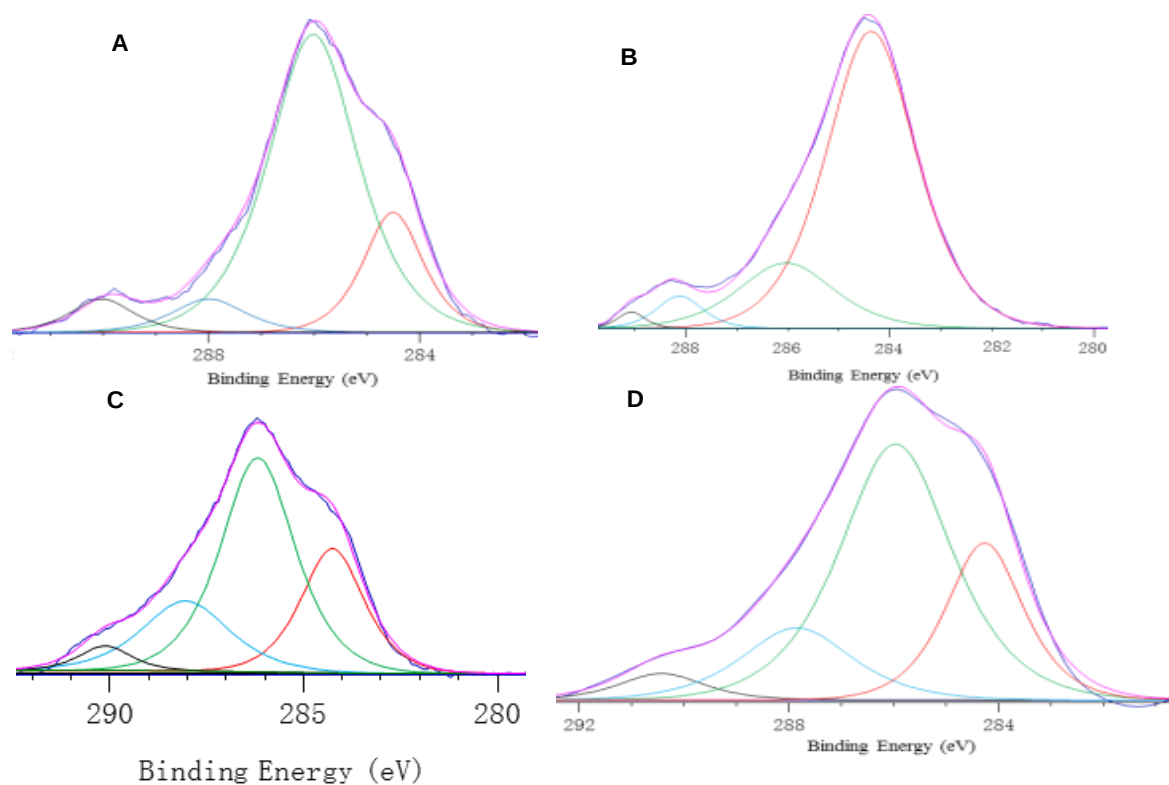


Figure 4-10. C1s XPS spectra of (A) Ag@AgCl@GO, (B) Ag@AgCl@Graphene, (C) Ag@AgBr@GO and (D) Ag@AgBr@Graphene nanocomposites.

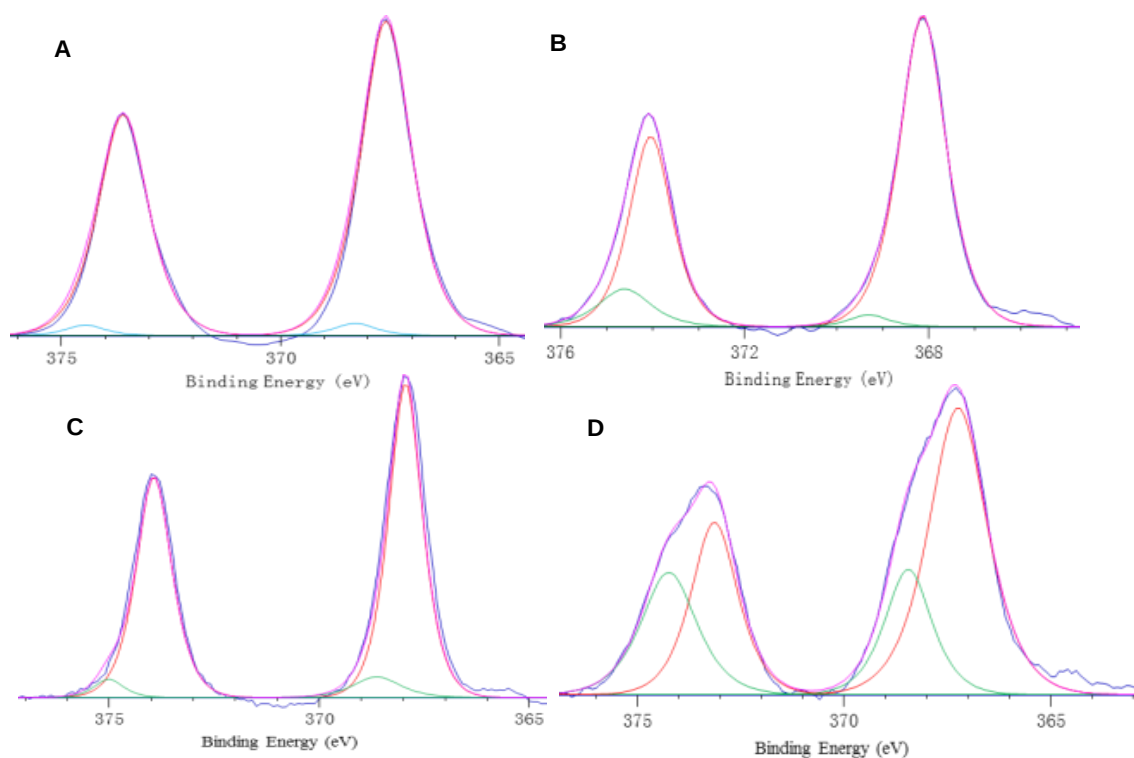
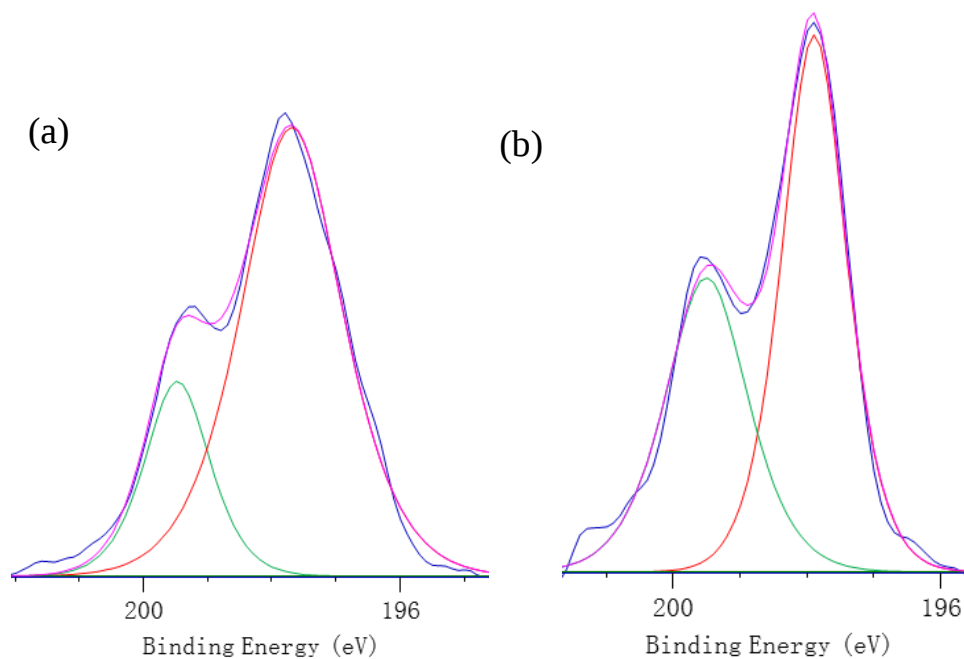


Figure 4-11. XPS spectra of Ag 3d of (A) bare Ag@AgCl, (B) Ag@AgCl@Graphene nanocomposites and (C) bare Ag@AgBr, (D) Ag@AgBr@Graphene nanocomposites.



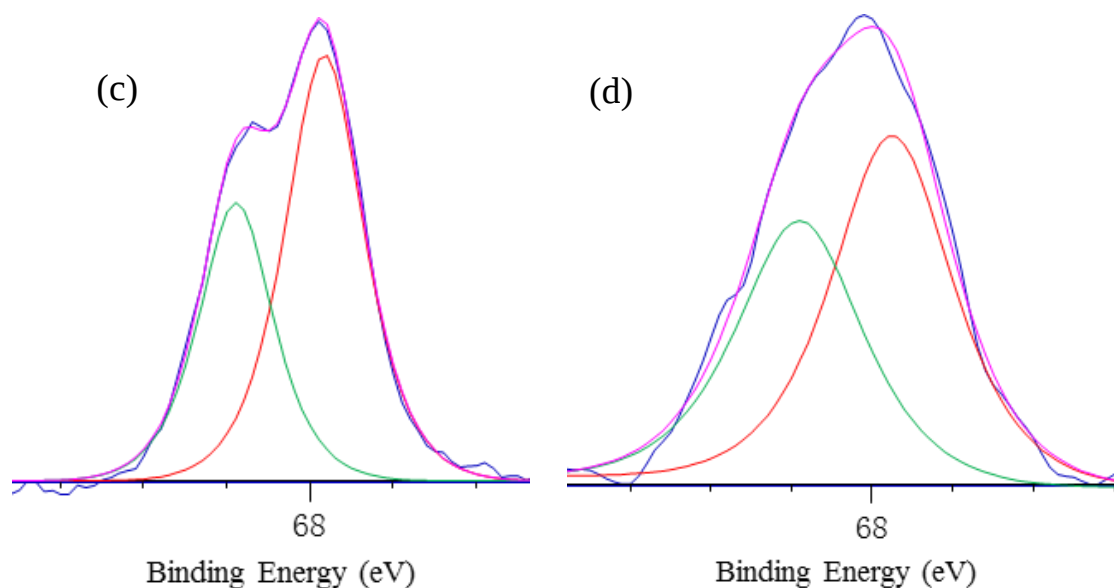
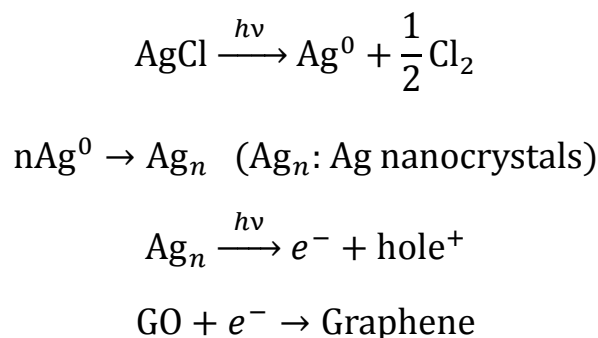


Figure 4-12. XPS spectra of Cl 2p of (a) bare Ag@AgCl, (b) Ag@AgCl@Graphene and Br 2p of (c) bare Ag@AgBr, (d) Ag@AgBr@Graphene nanocomposites.

The formation of Ag@AgX@Graphene nanocomposites by photoreduction in our system can be explained based on the following proposed mechanism. The first step involves the heterogeneous nucleation process of AgX seeds on the surface of GO via the electrostatic interaction between Ag^+ and negatively charged groups on GO surface. Then, the AgX nanoparticles undergo an orientation growth whose surface is encapsulated with functional GO. Subsequently, the AgX nanoparticles would decompose and generate more Ag^0 species through photosensitization under the UV irradiation. The Ag nanocrystals are produced depending on the aggregation of the Ag^0 species and deposited on the surface of AgX nanoparticles. Owing to the excitation by UV

irradiation, the Ag nanocrystals photogenerate electrons and holes. Then, the plasmon-induced electrons are injected into the conduction band of adjacent GO, thus causing the reduction of GO, while the produced positive holes are scavenged by methanol. A similar photoreduction mechanism has been observed in the Ag/GO[184] and Ag/TiO₂/GO systems[189]. It is demonstrated that the generation of Ag nanocrystals and the reduction of GO occur in the interactive process. Due to the presence of GO, more Ag nanocrystals can be formed in the Ag@AgX@Graphene system than those without GO sheets, as confirmed by the XPS spectra of Ag 3d. The related reactions are as follows:



To validate the synergistic effect between the Ag@AgX nanoparticles and graphene sheets, the Fourier transform infrared spectrum (FT-IR) of the samples together with that of the original GO and reduced graphene oxide (RGO) with green reductant thiourea dioxide (TDO) as reported previously by our group were investigated. As seen in Figure 4-13, the carbonyl stretching band at 1728 cm⁻¹ exhibited by the original GO and RGO, shifts to a lower wavenumber,

1716 cm^{-1} and 1710 cm^{-1} for the graphene in Ag@AgCl@Graphene and Ag@AgBr@Graphene, respectively. This result verifies the evident interactions between Ag@AgX and graphene sheets, further suggesting the successful hybridization between these two components[125, 190].

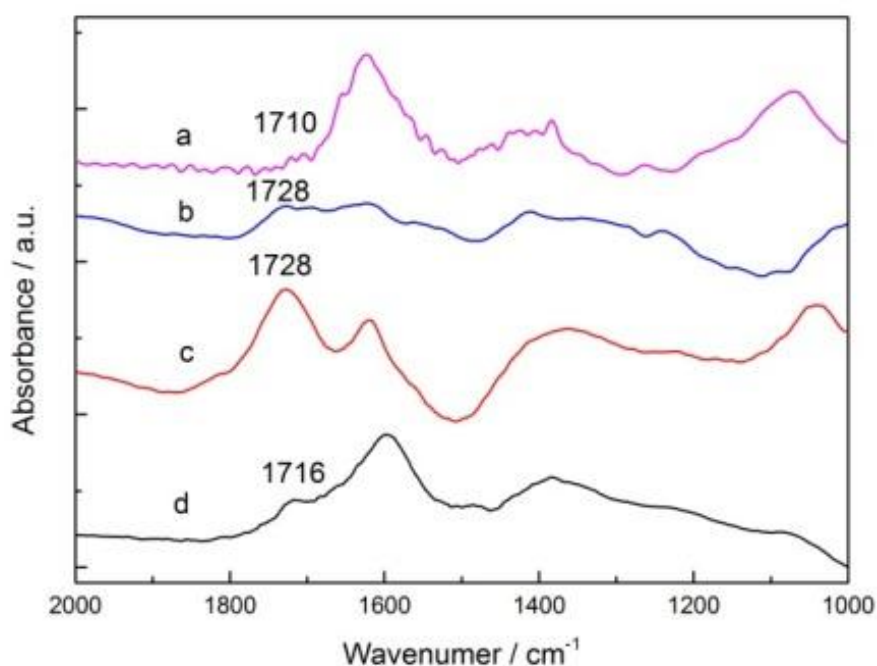


Figure 4-13. FT-IR spectra of (a) Ag@AgBr@Graphene nanocomposites, (b) RGO, (c) GO and (d) Ag@AgCl@Graphene nanocomposites.

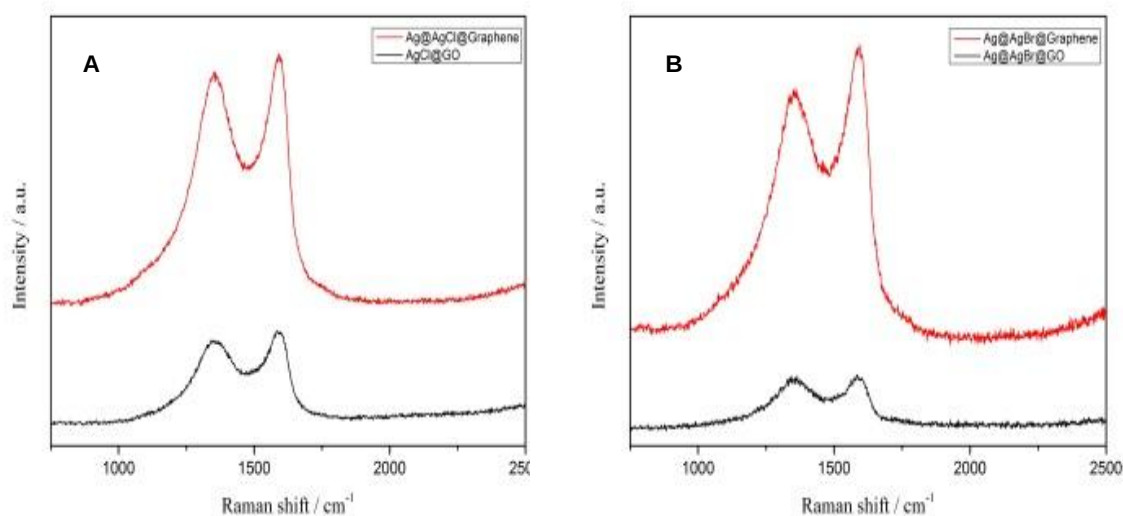


Figure 4-14. Raman spectra of (A) Ag@AgCl@GO, Ag@AgCl@Graphene and (B) Ag@AgBr@GO, Ag@AgBr@Graphene nanocomposites.

Furthermore, the structural change and the interaction effect between Ag@AgX nanoparticles and graphene sheets, could also be disclosed by the Raman spectra, as shown in Figure 4-14. Two characteristic peaks of the graphitic material, namely D and G band, were also observed in Ag@AgX@GO and Ag@AgX@Graphene around 1350 cm⁻¹ and 1590 cm⁻¹, respectively. They are attributed to the breathing mode of κ -point phonons of A_{1g} symmetry and the first order scattering of E_{2g} vibration mode of sp²-bonded carbon atoms. Interestingly, the two bands intensity are significantly enhanced by approximately 3.80 and 5.40 folds in Ag@AgCl@Graphene and Ag@AgBr@Graphene after photoreduction. The strong Raman signal

enhancement that similar to the surface enhanced Raman scattering (SERS) could be attributed to the SPR field induced by Ag nanocrystals in Ag@AgX@Graphene nanocomposites[191]. These results further confirm the occurrence of efficient charge transfer between Ag@AgX and graphene sheets of our graphene-involved nanocomposites, where Ag@AgX and graphene sheets work as electron donor and electron acceptor, respectively. In addition, the intensity ratio of D-band to G-band (I_D/I_G) in the Raman spectrum increased from 2.33 for Ag@AgCl@GO to 3.73 in the photoreduced Ag@AgCl@Graphene, while that from 2.36 for Ag@AgBr@GO to 2.99 in Ag@AgBr@Graphene, indicating a decrease in the average size of the in-plane sp^2 domains of C atoms in the as-prepared Ag@AgX@Graphene nanocomposites, which is similar to that observed in the chemical reduced graphene[148].

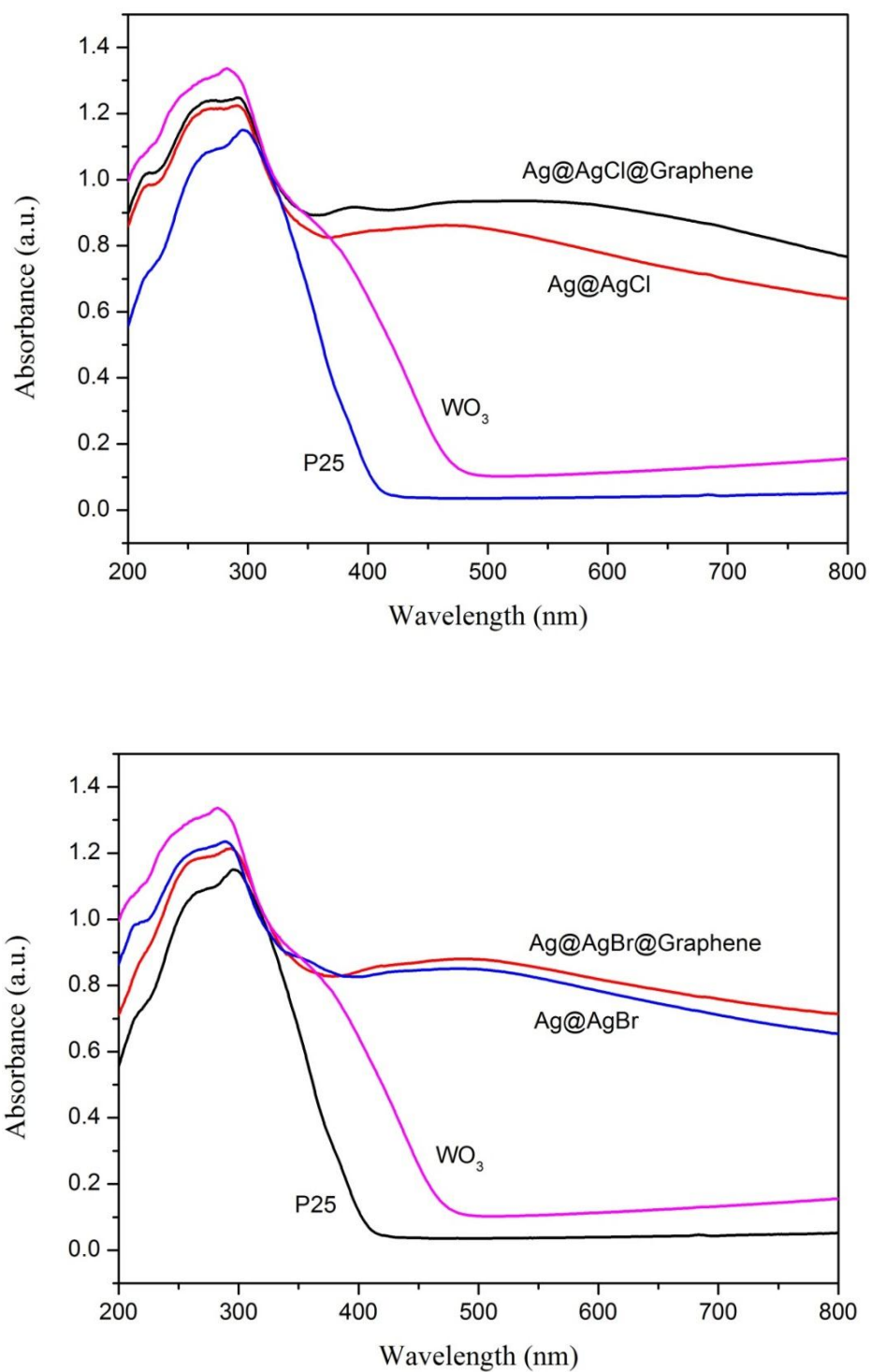


Figure 4-15. UV-vis diffusive reflection spectra of P25 (TiO₂), Ag@AgX and Ag@AgX@Graphene nanocomposites.

For sunlight energized photocatalysts, it is required that they could display distinct absorption in the visible region. The optical properties of plasmonic noble metal are dominated by their SPR when excited by incident light with a specified wavelength. The SPR could interact with the metal particles to establish the photon-stimulated collective oscillations of the conduction band electrons, which occurs with an exciting way of including light absorption in visible, infrared (IR) and NIR regions. As shown in Figure 4-15, the UV-visible diffuse reflection spectra of the synthesized Ag@AgX and Ag@AgX@Graphene exhibit distinct absorption both in the UV and visible regions.

The commercially available TiO₂ (P25) is also employed as the reference photocatalyst. It can be seen that distinct absorption could be detected in the UV region, while negligible absorption could be observed in the visible region. For the visible light-driven tungsten oxide (WO₃) semiconductors, few amount of visible light could be absorbed. In the cases of as-prepared Ag@AgX and Ag@AgX@Graphene, broad and strong absorption both in UV and visible regions could be distinctly detected.

Generally, bare AgX could only show apparent absorption in the UV region but negligible absorption in the visible region. This also suggests the existence of Ag nanocrystals in Ag@AgX and Ag@AgX@Graphene, which could arouse plasmonic resonance absorption in the visible region. Moreover, the obtained

Ag@AgX@Graphene exhibit stronger absorption toward the visible light than their corresponding Ag@AgX@GO precursors without shifted absorption edge. Accordingly, these results further confirm that there indeed exist the synergistic effect between the Ag@AgX component and graphene sheets, as confirmed by the above FT-IR observation.

To investigate the plasmonic photocatalytic activity of the Ag@AgX@Graphene nanocomposites, the photodegradation of AO dye was carried out under sunlight irradiation. Experimentally, 10 mg of the loaded catalysts was suspended in 30 mL AO solution (20 mg L^{-1}) and the intensity of sunlight was 80 mW cm^{-2} to make the experimental results reasonably comparable with those obtained previously. As it is known, the adsorptive ability of photocatalyst for the pollutant molecules is one of the crucial factors to enhance the catalytic property[126, 192]. Dark adsorption experiments were carried out for 60 min to achieve the equilibrium prior to the sunlight irradiation. The graphene-involved samples display distinctly higher adsorptivity for AO than the bare Ag@AgX, WO_3 and P25, which is beneficial for enhancing their photocatalytic activity. The adsorptivity was enhanced $\sim 20\%$, which can be seen from the Figure 4-16. This could be ascribed to the hybridization of graphene sheets, which has been proven to facilitate the adsorption, owing to the noncovalent intermolecular π - π interactions between pollutant molecules and the large graphene sheets area[76, 125, 126].

The normalized temporal concentration changes of AO during the photodegradation process under sunlight irradiation are shown in Figure 4-16. In the blank experiment where no catalysts were employed, negligible photodegradation of the AO was observed, indicating the self-photosensitized decomposition of AO could basically be ignored under our experimental conditions. When the bare Ag@AgX samples were used as photocatalysts, 65% of the AO were decomposed after 25 min. In contrast, when Ag@AgCl@Graphene and Ag@AgBr@Graphene were employed, an approximate 95% and 92% of the AO were decomposed, respectively. It demonstrates that graphene-involved Ag@AgX@Graphene nanocomposites have much higher photocatalytic activity than the bare Ag@AgX, WO₃ and P25. Multifactors, such as the higher adsorptive capacity, the smaller size of Ag@AgX and the reinforced electron-hole pair separation owing to the interfacial contact between Ag@AgX and graphene sheets components, resulting in an enhanced photocatalytic decomposition performance[125, 168, 185]. It has been proven that both for the bare Ag@AgCl and the Ag@AgCl@GO nanocomposites, the cubic-like nanospecies display higher photocatalytic performance than those of the corresponding sphere-like nanostructures under sunlight irradiation[168].

Accordingly, an interesting morphology dependent and enhanced photocatalytic activity could be easily achieved in our system. Moreover, the

photocatalytic stability of Ag@AgX@Graphene nanocomposites were also evaluated by the repeated photodegradation of AO, as those in previous work[121, 158, 182]. After five times recycling experiments, only slight decrease was observed, indicating the good photocatalytic stability. The slight decrease of the activities could be attributed to the loss of the catalysts in every recycling process. These results suggest that Ag@AgX@Graphene nanocomposites are stable under sunlight irradiation and very promising in practical application.

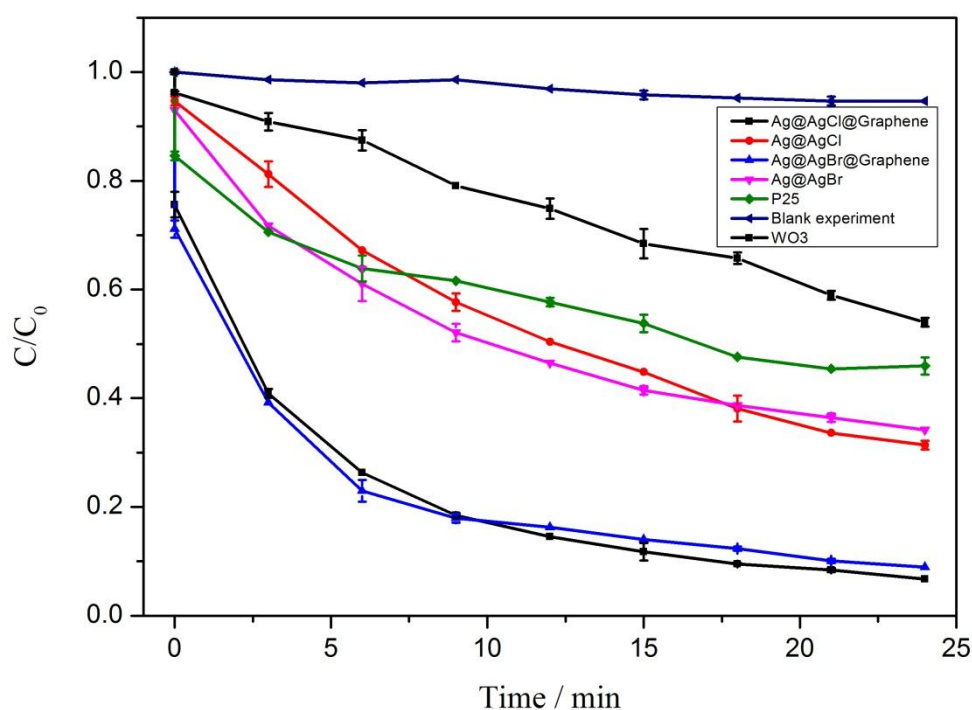


Figure 4-16. Photocatalytic performance of thus-prepared Ag@AgX@Graphene plasmonic photocatalysts for the degradation of AO pollutant under sunlight irradiation.

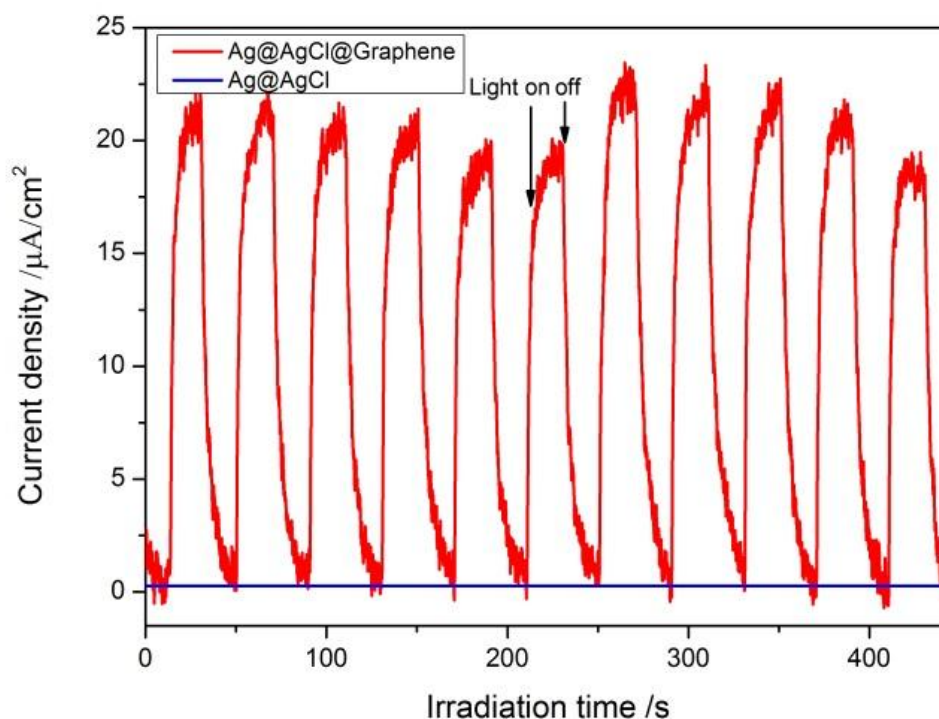


Figure 4-17. Photocurrent response of Ag@AgCl and Ag@AgCl@Graphene nanocomposites in 1M Na_2SO_4 aqueous solution under sunlight irradiation at 1.0 V vs. Ag/AgCl reference electrode.

Furthermore, to confirm the above proposed electron-hole pairs separation in the photocatalytic degradation process, the transient photocurrent response of Ag@AgCl and graphene involved Ag@AgCl@Graphene photocatalysts were recorded as shown in Figure 4-17. Several on-off cycles via intermittent sunlight irradiation were performed. The photocurrent value of Ag@AgCl@Graphene increased rapidly to a comparatively constant value when the light was on, and

the photocurrent value decreased gradually to zero when the light was off. In constant, there scarcely existed any photocurrent density for Ag@AgCl sample. The involvement of graphene supply transport channels for the photogenerated electrons from conduction band of AgCl semiconductor, leading to the gradual decrease of photocurrent to zero. In addition, the fast photoresponse features also exhibited a good reproducibility during the repeated on-off cycles. Based on the above results, the proposed fabrication of heterogeneous components consisting Ag@AgCl and gauze-like graphene sheets is a feasible strategy to develop active photocatalysts under sunlight irradiation.

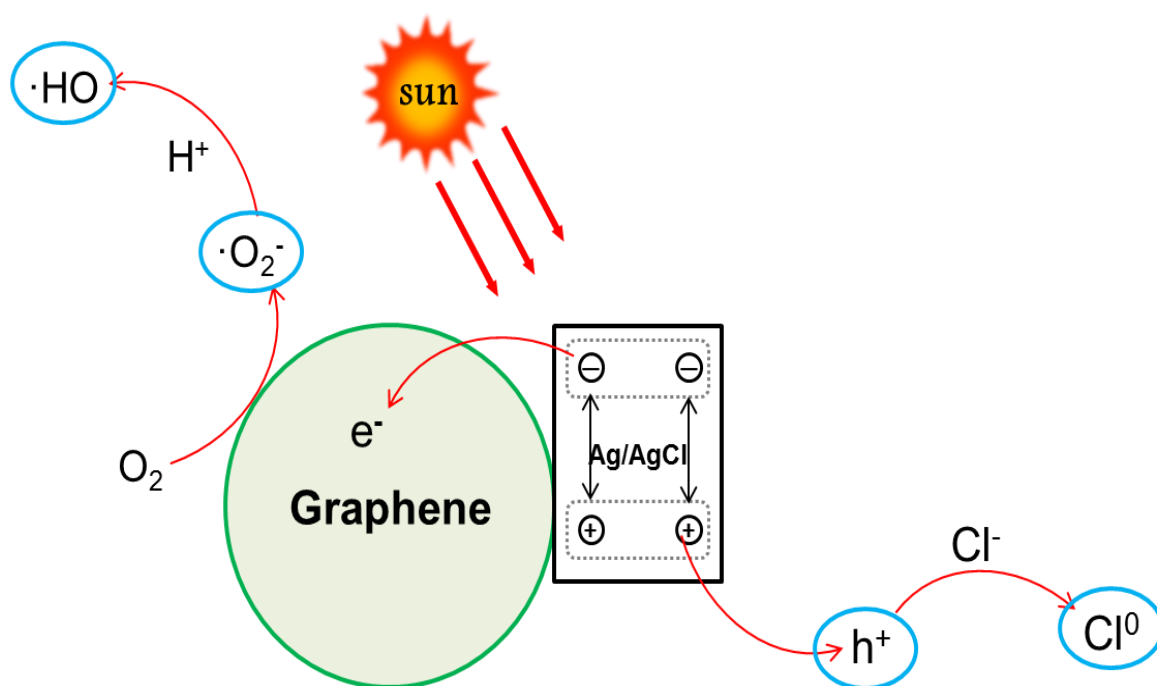
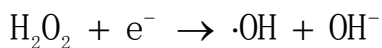
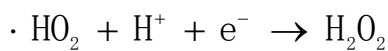
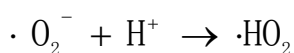
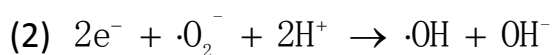
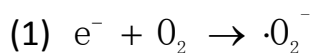


Figure 4-18. Proposed Photocatalytic mechanism and oxidative species in the photodegradation process

In order to illustrate the transportation process of photo-generated electrons, a proposed photocatalytic mechanism in the Ag@AgCl@Graphene was shown in Figure 4-18. When the incident light shines on the surface of the prepared photocatalysts, the electrons are generated and captured by the conductive graphene sheets, which will inhibit the recombination rate of electron-hole pairs. Some kinds of reactive oxidative species will be produced and play an important role in the photodegradation process, as shown below.



(3) Photo-generated h^+

(4) Cl^0

On basis of the above-described experimental facts and analysis, we propose a possible mechanism based on the band structure of metal/semiconductor/graphene heterojunction and plasmon-mediated charge separation. As illustrated in Figure 4-19 and Figure 4-20, the band gap of AgCl and AgBr are 3.25 eV and 2.60 eV, while the work function of Ag is 4.2 eV. Upon illumination by the sunlight, the incident photons could be facilely

absorbed by the Ag@AgCl in terms of their surface plasmonic resonance properties. Through the transportation of generated electrons, several kinds of oxidative species are produced. During the process, the reactive activities of electron/hole pairs could be utilized at the most extent.

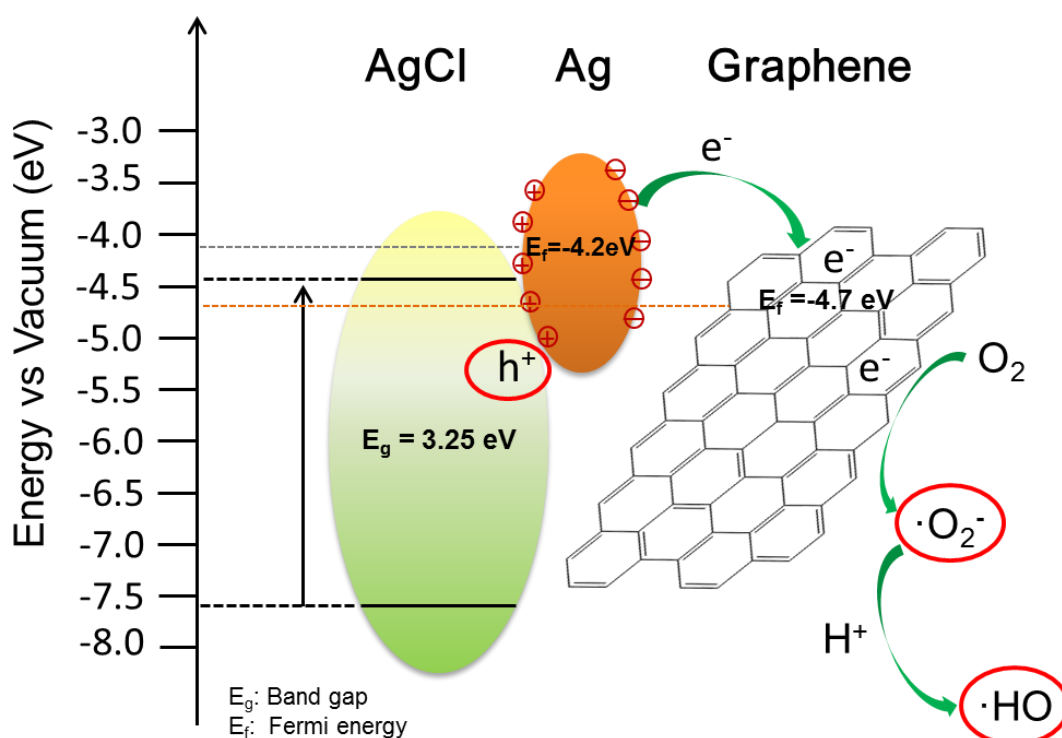


Figure 4-19. A schematic of the energy band structures of Ag@AgCl@Graphene

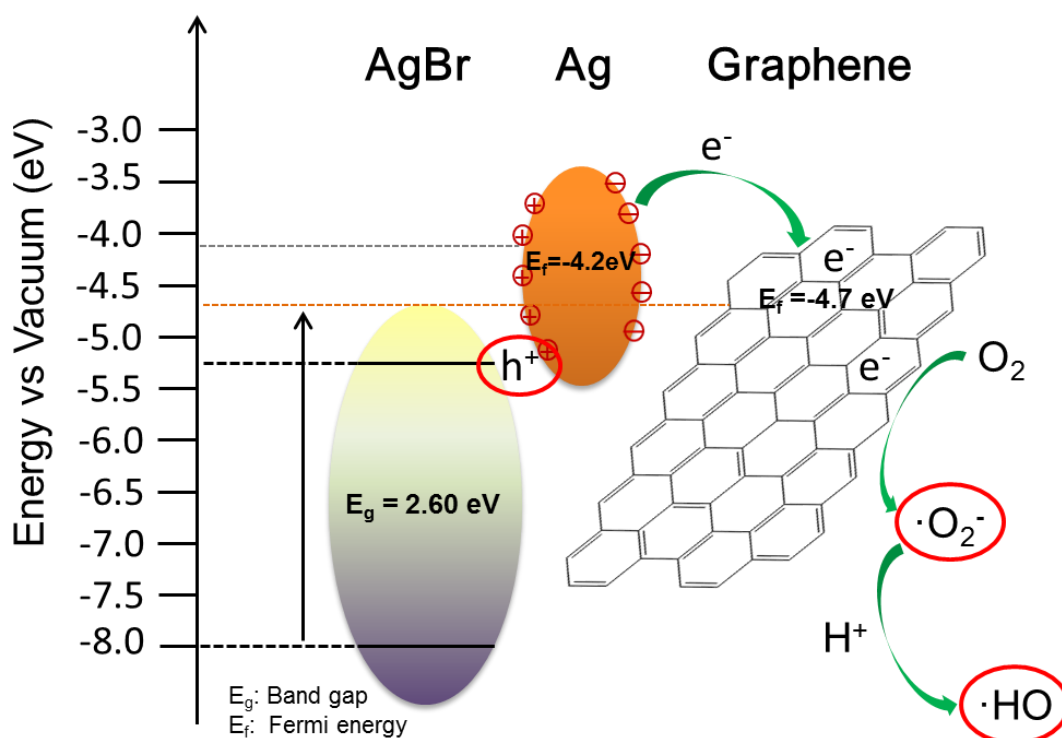


Figure 4-20. A schematic of the energy band structures of Ag@AgBr@Graphene

4.4 Conclusions

We have demonstrated that two kinds of novel Ag@AgX@Graphene heterostructures with high sunlight-driven plasmonic photocatalysis and excellent stability, which could be facilely produced by photoreducing their corresponding AgX@GO precursors under ambient conditions. Unlike the bare spherical Ag@AgX, cubic Ag@AgCl and quasi-cubic Ag@AgBr nanoparticles encapsulated by graphene sheets network are manipulated by controlling the

selective orientation growth of AgX nanoparticles through the abundant active sites on two-dimensional GO sheets, where they function as amphiphilic template. With the unique structure, these nanocomposites could be employed as plasmonic photocatalysts for the efficient decomposition of AO molecules under sunlight irradiation. The graphene-involved Ag@AgX@Graphene nanocomposites have a 50% higher photocatalytic performance than the bare Ag@AgX samples. This study provides a new avenue for the assembly of morphology-controlled plasmonic photocatalysts that utilize sunlight as an energy source in the application of environment remediation.

Chapter 5

General conclusions

Energy crisis as well as environmental problems such as fossil fuel depletion, organic pollutants and global warming have been becoming rigorous menace to modern society. In the field of environmental protection, great efforts have been devoted to develop the green method provided by photocatalysis technology to achieve the photodegradation of hazardous contaminants. In particular, the emergence of single-layer graphene has received extensive attention and shows great potential in the design and/or fabrication of graphene-enhanced photocatalysts.

In chapter 2, it was demonstrated mass production of GO from commercial graphite using the chemically-oxidized protocol was realized. TDO was first used as an efficient and eco-friendly reductant in the reduction of GO that was comparable to other green reductants, such as sodium hydrosulfite and L-ascorbic acid. The oxygen-containing functionalities were eliminated and the crystallized structures of sp^2 domains in the destroyed graphitic sheets were restored into electronic conjugation states. This facile method opens a new avenue for the large scale fabrication of solution-based graphene. However, reduced graphene sheets tend to aggregate irreversibly due to the strong

cohesive van der Waals energy of the π - π conjugation in graphene. The superior properties of graphene are associated with an individual or few-layer sheets forms, such as the optical transparency and extended large area in the final product. Therefore, the synthesis of graphene-based photocatalysts with the form of graphene remains not aggregation is of great significance for their practical applications. Followed by the outline, in the next chapter (chapter 3), during the assembling of graphene-based functional materials, an ordinary polyelectrolyte PDDA was used stabilize graphene sheets by absorbing on the surface of graphene sheets through π - π interactions and electrostatic interactions, which results in electrostatic repulsion between graphene sheets.

In chapter 4, two kinds of novel Ag@AgX@Graphene heterostructures with high sunlight-driven plasmonic photocatalysis and excellent stability, which could be facilely produced by photoreducing their corresponding AgX@GO precursors under ambient conditions. Unlike the bare spherical Ag@AgX, cubic Ag@AgCl and quasi-cubic Ag@AgBr nanoparticles encapsulated by graphene sheets network are manipulated by controlling the selective orientation growth of AgX nanoparticles through the abundant active sites on two-dimensional GO sheets, where they function as amphiphilic template. With the unique structure, these nanocomposites could be employed as plasmonic photocatalysts for the efficient decomposition of AO molecules under sunlight irradiation. The graphene-involved Ag@AgX@Graphene

nanocomposites have much higher photocatalytic performance than the bare Ag@AgX samples. This study provides a new avenue for the assembly of morphology-controlled plasmonic photocatalysts that utilize sunlight as an energy source in the application of environment remediation.

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List of achievements

Publications in international journals:

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