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Effects of Nanoscale Morphology and Defects in Oxide: Optoelectronic Functions of Zinc Oxide Nanowires

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Oxide nanomaterials have been attracting growing interest for both fundamental research and industrial applications ranging from gas sensors, light emitting devices, to photocatalysts, and solar cells. The optical and electronic properties of oxide nanomaterials are strongly dependent on their surface morphologies as well as defects, such as surface areas, aspect ratios, foreign atom impurities, and oxygen vacancies. In this review, we describe some examples of our recent contributions to the nanomaterials and devices that exhibit remarkable functionalities based on one-dimensional nanostructures of ZnO and their hetero junctions as well as their variants with appropriately incorporated dopants.

Keywords: ZnO nanowires; defects; photodetector; photocatalysis

1. Introduction

Metal oxides are widely used in our society for various applications ranging from pottery to electronics and optical materials/devices. Most of them are insulators or semiconductors, but some of them exhibit high electrical conductivity thus being useful for the applications in flat-panel displays, infrared plasmonic devices as well as in

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electronic devices. Applications in optics and in solar energy conversion are rapidly increasing such as low-emissivity (low-E) heat reflective window coating, fluorescent materials for lighting applications, and photocatalysis. Among them, nanostructured oxide materials such as TiO_2 and ZnO constitute a promising class of materials as they offer a variety of functionalities with controlled surface defects and morphologies. In this article, we select ZnO nanowires (ZnO NWs) as one of the representative oxide nanomaterials that have enjoyed extensive and successful applications in various fields, such as in blue or color-tunable light-emitting devices (1, 2), ultraviolet lasers (3, 4), Schottky diodes (5), ultraviolet photodetectors (6–12), solar cells (13), piezoelectric and pyroelectric nanogenerators (14, 15), and photocatalysis (16–21). The examples introduced here provide some insights on how surface and defect engineering of oxides, as well as the combination with other materials, enables us to achieve the desired functionality.

2. Fabrication of ZnO NWs and their properties: physical vapor deposition and wet chemical growth

2.1. Growth of ZnO NWs by physical vapor deposition

Over the past decade synthesizing and optimizing the growth conditions of ZnO NWs for various applications have been in the forefront of materials science (22). Several methods have been developed to synthesize ZnO NWs (23–26). In solid-state thermal sublimation process, the source materials such as Zn or ZnO powder or a mixture of ZnO and graphite (also called “carbothermal reduction”) are heated above 600 °C. The growth is generally directed by vapour-liquid-solid (VLS) or vapour-solid (VS) mechanism based on the presence or absence of catalyst particles.

In our work (27), we have developed a simple methodology to grow ultralong ZnO NWs with controllable aspect ratio. We have used Zn powder as a source (S.D. fine 99.5%, compact mass of 10 mg) contained in a crucible with Si cap over it and heated above 600 °C. The insolubility of Zn in Si and the use of a Si cap on the Zn source to prevent local source oxidation is the key to growing long nanowires. The quartz boat

with Zn and Si is placed inside the alumina tube on a single zone furnace. The substrate to be grown is placed at a distance of 5 mm from the Zn source and heated to required temperature. The ZnO NWs grown by this method on a glass substrate with Cu doping and on carbon nanotubes are shown in the Figure 1(a)-(d).

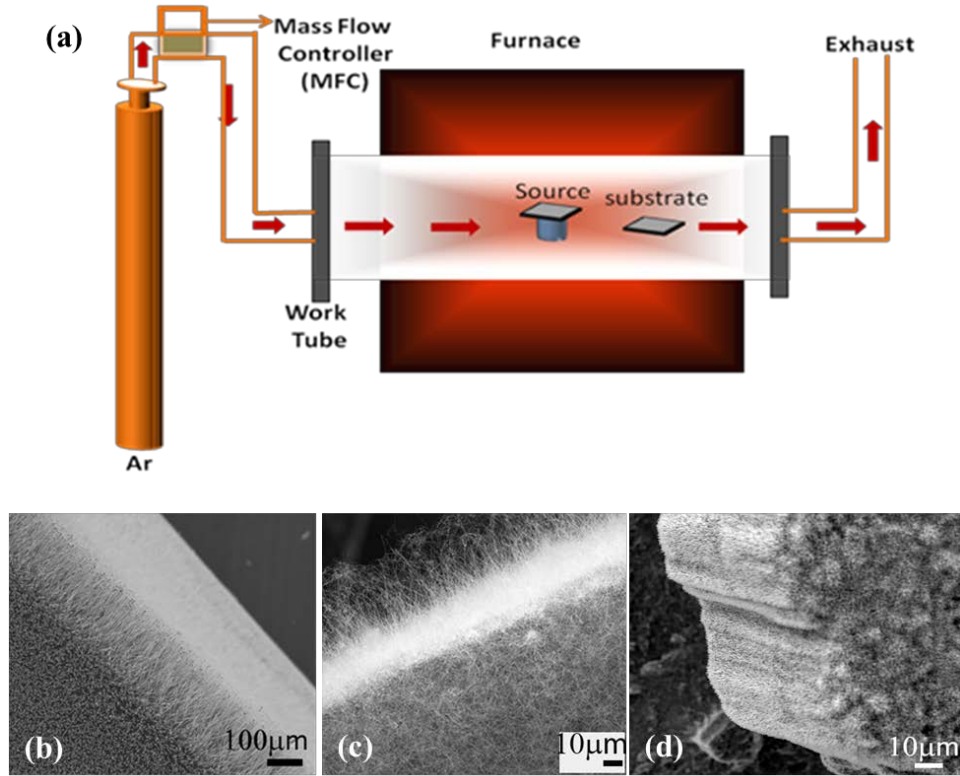


Figure 1. (a) Schematic of the experimental setup. SEM images of (b) ZnO NWs & (c) Cu doped ZnO NWs. SEM image of (d) ZnO NWs on multi-walled carbon nanotube. Reproduced from (27, 28).

2.2. Growth of ZnO NWs by wet chemical growth

The hydrothermal growth of ZnO NWs has gained immense popularity as a simple and efficient alternative method other than VLS and VS methods (29). Figure 2(a)-(c) illustrates the hydrothermal process of growing ZnO NWs on a transparent conductive oxide (TCO) substrate (12). First, a ZnO seeds layer was prepared on top of the cleaned TCO-glass substrate (Figure 2(a)). The mixed solution of zinc acetate dihydrate $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ (0.3 M) and monoethanolamine (MEA) solution (0.3 M) in

ethanol was coated onto TCO-glass substrate three times by spin-coating at 3000 rpm for 30s. The ZnO seeds layer was formed after annealing the dried film in ambient air at 300 °C for one hour (Figure 2(b)). A mixed aqueous solution of zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (0.03 M), hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4]$, HMT (0.03 M) and polyethylenimine (PEI) (0.003 M) was prepared. Then the ZnO seeds coated TCO substrate was dipped into this solution and stirred at 68 °C for 3 hours. The fabricated ZnO NWs array (Figure 2(c)) was then washed in de-ionized water, ethanol and then thermally treated in ambient air.

The structural morphology of the fabricated ZnO NWs array was checked by using scanning electron microscope (SEM, Hitachi S4800, 10 kV operating voltage), transmission electron microscope (TEM, JEOL JEM-2100F, 200 kV accelerating voltage) and X-ray diffraction (XRD, Rigaku Rint 2000, $\text{Cu K}\alpha$) measurements (12). Figure 2(d) shows an SEM image of ZnO nanoseeds formed on a TCO-glass substrate. Figures 2(e) displays an SEM image of the typical ZnO NWs. The fabricated ZnO NWs are oriented nearly vertically with respect to the TCO glass substrate with an average diameter of 50 nm, an average length of 0.8-1 μm , and wire density of $2 \times 10^{10} \text{ cm}^{-2}$. A high-resolution TEM image and a selected-area electron diffraction (SAED) pattern of a single ZnO NW are shown in Figure 2(f) and its inset, respectively, reveals that the fabricated ZnO NW exhibits very high crystalline quality with [0001] orientation. In addition, the XRD patterns of the ZnO NWs grown on TCO substrate (red curve, Figure 2(g)) with respect to the XRD patterns of bare indium tin oxide (ITO) substrate (black curve, Figure 2(g)) reveal a strong peak at 34.39° of ZnO (002) plane, indicating nanowires are well oriented along *c*-axis with high crystallinity (JCPDS card No. 36-1451 of bulk ZnO).

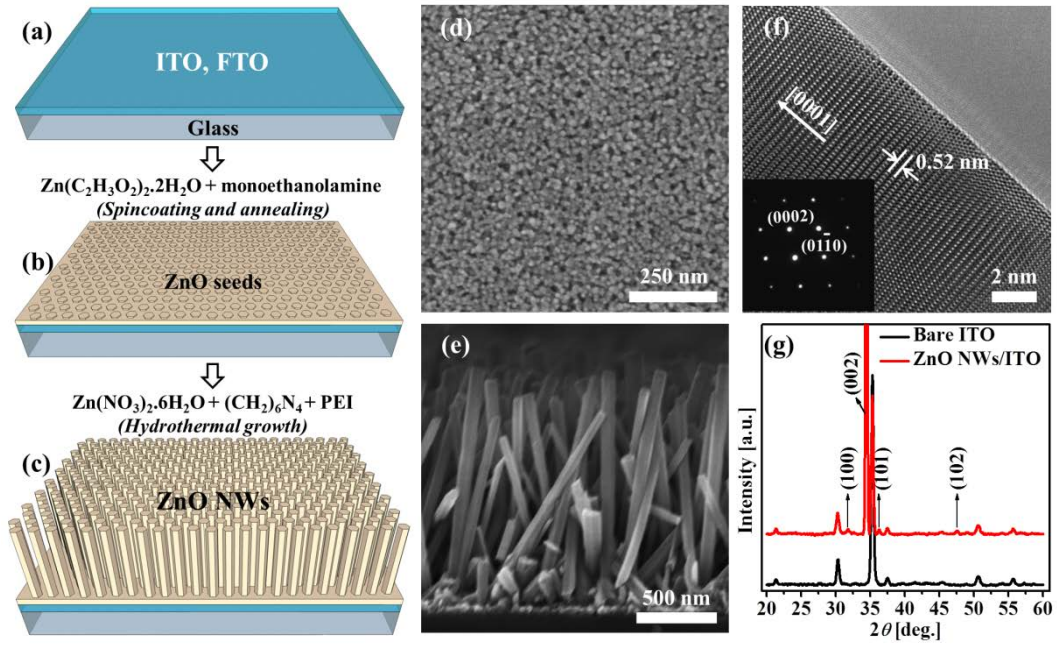


Figure 2. (a-c) Schematic illustration of the hydrothermal growth of ZnO NWs. (d) SEM image of ZnO nanoseeds formed by spin-coating and annealing processes. (e) An SEM image of typical ZnO NWs with averaged diameter of 50 nm and length of about 0.8 – 1 μm . (f) HR-TEM image of a single ZnO NW with [0001] growth orientation. Inset shows SAED of the ZnO NWs. (g) XRD patterns of single crystal ZnO NWs on ITO-glass substrate and bare ITO-glass. Reproduced from (12).

The phonon mode frequencies in ZnO NWs were verified using Fourier-transform infrared spectroscopy (FTIR, Nicolet IS50R-FTIR) and Raman (Micro Raman Witec Alpha 300S) spectrometers. The FTIR spectra of a ZnO NWs array is shown in Figure 3(a) reveal a strong band of Zn-O stretching vibration located at 400 cm^{-1} . Figure 3(b) shows Raman spectra of ZnO NWs with strong peaks located at 99 cm^{-1} , 332 cm^{-1} , 437 cm^{-1} , 481 cm^{-1} , and 572 cm^{-1} , which are attributed to E_{2l} , multiple-phonon scattering, E_{2h} , 2LA and $A_1(\text{LO})$ modes, respectively(30,31). In order to understand the optical properties as well as the defects present in the hydrothermally-grown ZnO NWs, the absorption and photoluminescence spectra of ZnO NWs were carried out using a UV-VIS spectrometer (Jasco V-570) and a fluorescence microscope (Horiba Jobin-yvon, 325 nm He-Cd excitation laser source). Figure 3(c) shows the absorbance of ZnO NWs with a strong absorption peak located at 365 nm, which is attributed to the band gap

absorption of ZnO. Figure 3(d) shows the photoluminescence spectra of ZnO NWs with (red curve) and without (black curve) thermal treatment at 400 °C. Besides a band-edge emission at 384 nm, we observed a broad visible emission around 560nm which can be attributed to the surface oxygen vacancies and other defects such as oxygen interstitials and zinc vacancies (32–36) known as deep donors. However, the visible emission was significantly reduced after the thermal treatment (red curve in Figure 3(d)). This reduction can be attributed to the transformation of the ZnO deep donors into shallow donors by the thermal annealing (33, 37), which significantly improves the transport properties of ZnO NWs (12).

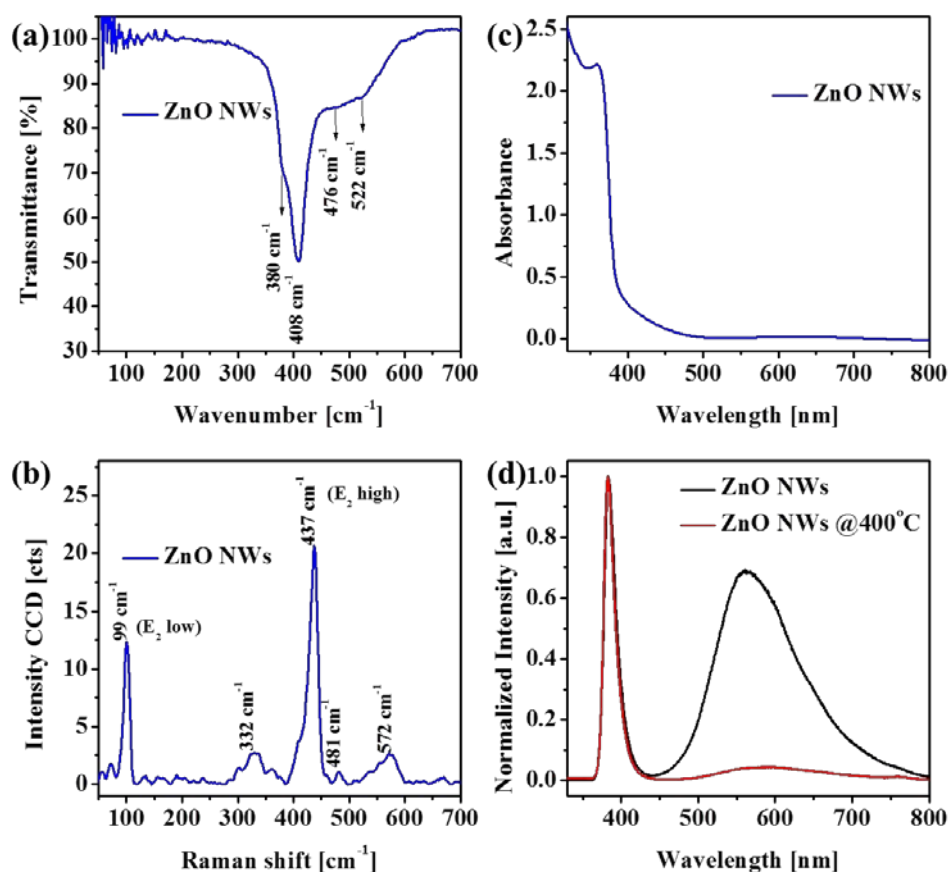


Figure 3. Vibrational spectroscopy of ZnO NWs: (a) FTIR and (b) Raman spectra. Optical properties of ZnO NWs: (c) Absorption and (d) Photoluminescence spectra.

3. Applications for optoelectronics and photocatalysis

3.1. ZnO nanowire (NW)-nanosheets (NSh) dual-band light emitter

Figure 4(a) presents an SEM image of the patterned ZnO nanowires-nanosheets (NWs-NShs) grown on a TCO-glass substrate using the colloidal lithography method and wet chemical ZnO growth (38). Figure 4(b) shows the different photoluminescence property of the ZnO NWs (blue) and ZnO NShs (yellow), which is attributed to the different growth morphology of these two ZnO nanostructures. Within the disk area, one-dimensional ZnO NWs grows with high crystallinity (TEM image in the bottom inset of Figure 4(a) showing a strong band-edge emission (384 nm) and a weak defect emission (590 nm), where the defect emission is mainly contributed by oxygen vacancies defect (34–36, 39, 40). By contrast, between the disks two dimensional ZnO NShs grow with low crystallinity (TEM image in the top inset of Figure 4(a)) exhibiting a strong broad yellow band centered at 547 nm, which is associated to the zinc vacancies (34, 36, 40). A very weak band-edge emission around 400 nm is observed. Therefore, the patterned selective ZnO NWs-NShs arrays show distinctive photoluminescence from the nanowire regions (blue) and nanosheet regions (yellow) (38). Such dual-band nature of the patterned ZnO NWs-NShs arrays enables us to flexibly blend these two emissions to tune the emission color of emitter devices through controlling the disc area and hence the intensity ratio of the two emission bands.

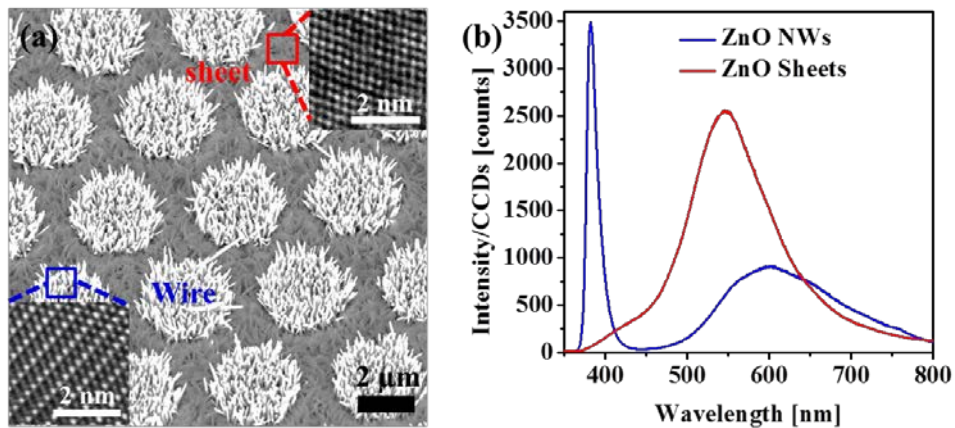


Figure 4. (a) SEM and TEM (insets) images of the patterned ZnO NWs-NShs and (b) Their selective photoluminescence properties. Reproduced from (38).

3.2. ZnO NWs hybrid structures for photodetector devices

ZnO NWs are good candidates for highly responsive photodetectors due to their large surface-to-volume ratio and light scattering (41–44). The generation of a photocurrent in ZnO NWs is attributed to mainly two factors (1) the generation of electrons and holes due to photoabsorption and (2) a surface-related mechanism involving oxygen adsorption and desorption (8, 45–48). The second one has been cited for photoconduction of ZnO in most of the cases. In order to improve the photoconduction in ZnO NWs here we have synthesized Buckled-multiwalled carbon nanotube (BMWCNT)-ZnO nanoheterostructure as shown in the Figure 5(a)-(c) (28). The photoresponse of the MWCNT-ZnO hybrid structures is shown in Figure 5(b). We have found that the photoresponse is mainly due to oxygen absorption and desorption and it could be improved by applying the gate voltage. Furthermore we found that these hybrid structures could be used as high current *p*-type FET as shown in Figure 5(c) which can deliver currents in the mA range and also these structures could be used as a rectifier.

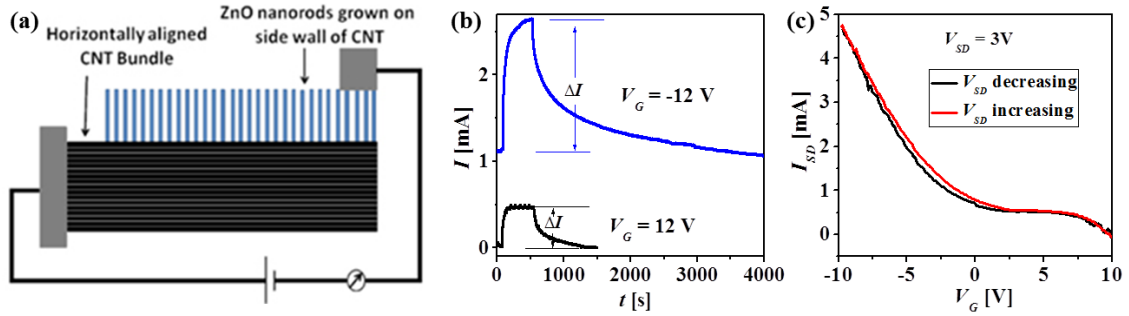


Figure 5. (a) Schematic of the device fabricated for BMWCNT-ZnO hybrid structures. (b) Temporal photoresponse at two gate voltages (12, -12 V). (When illuminated by UV light (wavelength = 365 nm, power = 0.3 mW/cm²) (c) Transport characteristics showing *p*-type FET behavior of a MWCNT-ZnO hybrid structure. Reproduced from (28).

There has been a great deal of interest in ZnO based UV detector in the past, including metal-semiconductor (ZnO)-metal (MSM) (6, 7) and p-n junction (9, 10, 12, 49–51). Similar to ZnO, anatase titanium oxide (TiO₂) is also active in UV region with an indirect band gap of 3.2 eV (52) and p-type TiO₂-based materials can be prepared by doping with Fe (53), Mn (54), Cr (55). By combining these two UV semiconductors, we have fabricated a UV photodiode composed of Cr-doped TiO₂-shell and ZnO NWs-core forming a core-shell p-n heterojunction as shown in Figure 6(a)-(b) (12). ZnO NWs

arrays were grown on a transparent ITO film coated on glass substrate by hydrothermal method. The p-type TiO_2 was prepared by a sol-gel process with Cr as p-type dopant, which was used to completely coat the ZnO surface by single-step spin-coating with thickness in the range of 5 to 10 nm as shown in TEM image (Figure 6(b)). This core-shell nanowire architecture realizes a remarkably enhanced heterojunction area and can swiftly transport photoexcited carriers across a nanometer-thick TiO_2 lamination layer and single-crystalline ZnO NWs. In the photodetection, this device exhibits perfect insensitivity in the visible to infrared regions (i.e. IR-VIS blind) (red and green curves in Figure 6(c)), but extremely high sensitivity in the UV region (purple curve in Figure 6(c)). Figure 6d reveals the power-dependence of the rectification ratio (the ratio between forward current and reverse current at the same bias voltage) and the reverse current under an applied bias of 5 V and excitation of 373 nm. The rectification ratio (black filled squares in Figure 6(d)) evidences that the photodiode works properly under the reverse bias. In addition, the current-power (I-P) characteristic (blue filled cycle in Figure 6(d)) of the device at the same reverse bias (5 V) exhibits a nearly linear response of the reverse current with the increase of the incident power with a responsivity as high as 250 A/W.

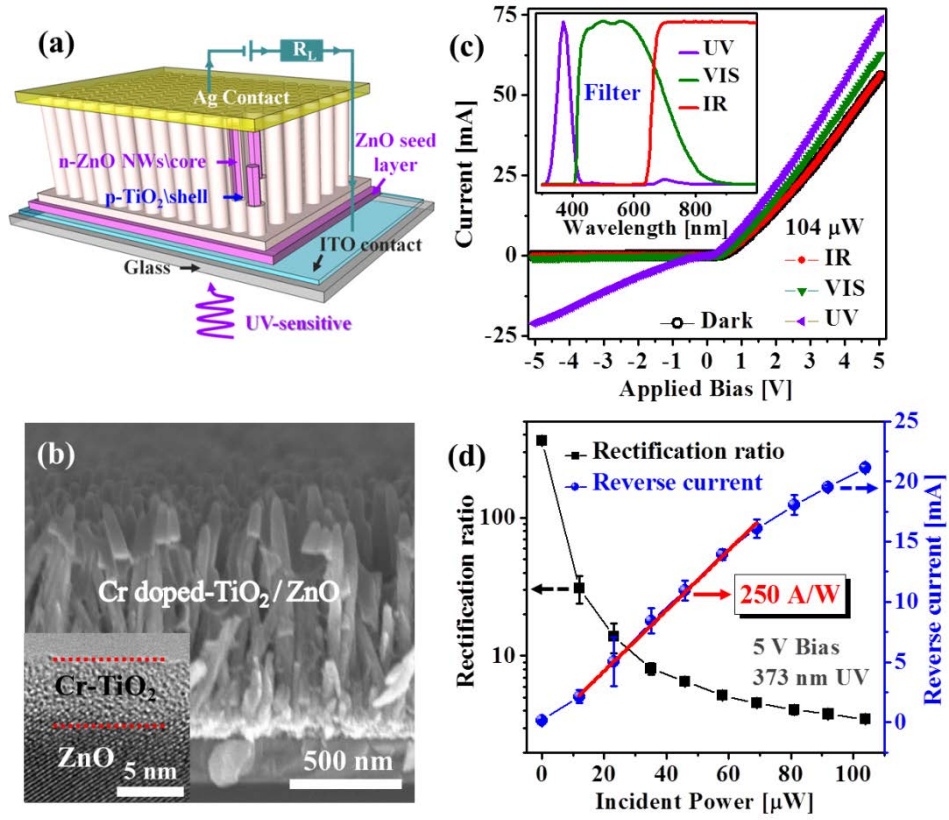


Figure 6. (a) Schematic illustration of the Cr-doped TiO₂-ZnO NWs p-n heterojunction device. (b) Cross-sectional SEM image and TEM image (inset) of the Cr-doped TiO₂-ZnO NWs. (c) IV characteristic of the TiO₂-ZnO NWs photodiode taken under the UV, VIS, IR illumination with the same power (104 μW). The inset shows the transmission characteristics of the filters used in this measurement. (d) Dependence of rectification ratio and reverse current on incident power under 373 nm illumination and 5 V reverse applied bias. Reproduced from (12).

3.3. Plasmon-enhanced photocatalysis of hybrid plasmonic metal-ZnO NWs

Recently, artificial photosynthesis and photocatalysis have become primary research topics in the field of solar energy harvesting. ZnO NWs have been widely studied. This is due to their high surface area, high optical path-length caused by light scattering and interference, and the natural abundance of Zn element and its inexpensive fabrication processes (16–21). However, with a wide band gap of 3.2 eV, the photocatalytic activity of ZnO NWs is limited mainly in UV region, which is not efficient for the solar-photocatalysis application. To improve the efficiency of solar-light driven ZnO NWs

photocatalysts, we have proposed plasmonic metal-ZnO NWs hybrids in which their absorptions in the visible region are highly assisted by plasmonic metals (21). Figure 7(a) shows a SEM image of a proposed plasmon-assisted photocatalyst composed of Au nanoparticles (AuNPs) and ZnO NWs. In this structure, ZnO NWs arrays were synthesized on TCO substrates (1×2 cm) by hydrothermal method. After cleaning with deionized water and ethanol, the fabricated ZnO NWs were then annealed at 400 °C in ambient air for 1 hour to enhance the crystallinity of ZnO crystals. A colloidal suspension of AgNPs (average diameter of 10 nm) and AuNPs (average diameter of 13 nm) solutions were synthesized using wet-chemical methods (21). After drop-casting of metal nanoparticles onto ZnO NWs to form metal NPs-ZnO NWs hybrids, the samples were washed by deionized water and then thermally treated at 150°C for 1 hour to stabilize the metal-ZnO interfaces. As seen in the TEM image (inset of Figure 7(a)), the plasmonic metals are well attached to the ZnO NWs surface wherein they induced absorptions in visible region with a 415 nm peak (for AgNP-ZnO, red curve in Figure 7(b)) and a 550 nm peak (for AuNP-ZnO, blue curve in Figure 7(b)).

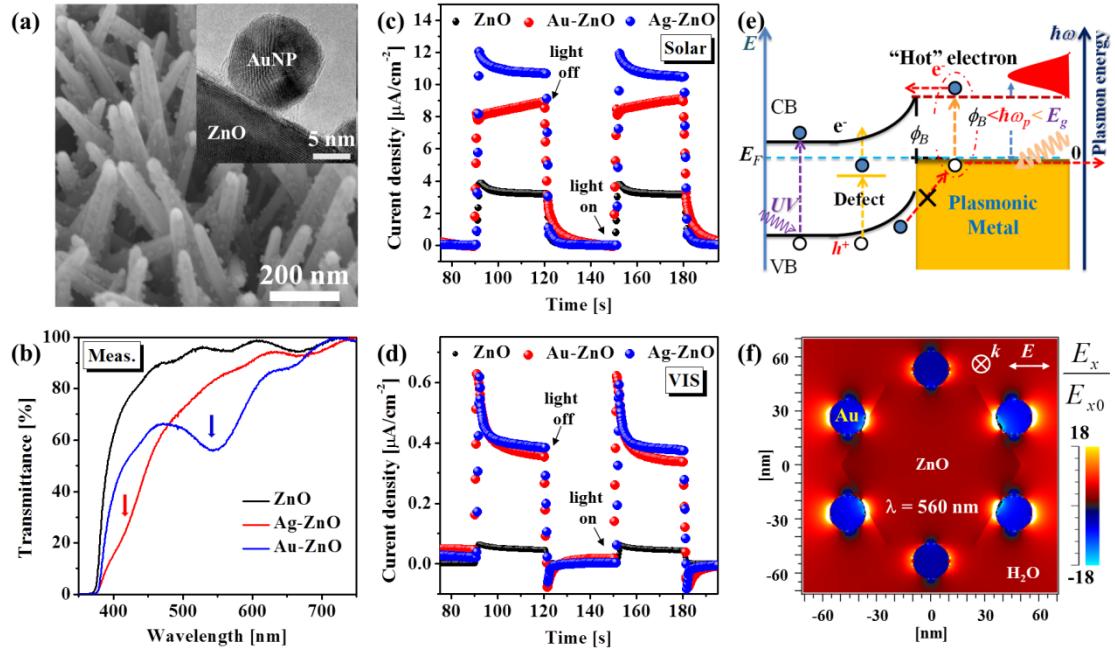


Figure 7. (a) An SEM image of a AuNPs-ZnO NWs array. The inset shows a HR-TEM image of AuNP-loaded ZnO NW surface. (b) Measured transmission spectra of bare ZnO NWs array (black curve), AgNPs-ZnO NWs (blue curve) and AuNPs-ZnO NWs (red curve). Photocurrent density of ZnO NWs and NPs-ZnO NWs hybrid photoanodes: (c) Under solar light illumination with power

density of 100 mWcm^{-2} and (d) Under visible light illumination (wavelength in the range of 400 – 900 nm with power density of 33 mWcm^{-2}). (e) Schematic illustration of plasmon-induced hot-electron injection in plasmonic NPs-ZnO NWs hybrid. (f) Electric field hot-spots at Au-ZnO interface excited at resonant 550 nm of plasmonic AuNPs-ZnO NWs hybrids. Reproduced from (21).

The catalytic activities of the plasmonic metal-ZnO catalysts were examined using a photoelectrochemical (PEC) cell under photovoltaic configuration (without any applied bias) irradiated by a standard solar simulator (AM 1.5G, Jasco Otentosun - IV 5). In this PEC cell, a Pt zigzag wire was used as a photocathode with photoanode made of plasmonic metal-ZnO NWs catalysts. Figure 7(c) reveals the photocurrent density of PEC cell with and without light illumination. Under the illumination of 100 mW/cm^{-2} standard solar light, the averaged photocurrent densities were 8.5 and $11 \text{ } \mu\text{A/cm}^{-2}$ with photoanodes made of AuNPs and AgNPs -ZnO NWs hybrids, respectively, while it is only $3.2 \text{ } \mu\text{A/cm}^{-2}$ with pure ZnO NWs. This result indicates that the plasmonic hybrids exhibit an enhancement of photocatalytic activity, 2.5 - 3.5 times compared to bare ZnO NWs. Besides the plasmon-induced electric field enhancement, the metal NPs can also induce VIS-light catalytic activity in ZnO. To further understand the enhancement mechanism in the plasmonic NPs-ZnO hybrids, we have measured photocurrent of PEC cell under VIS-IR irradiation (400 nm – 900 nm) and the results are shown in Figure 7(d). We clearly observed the photocatalytic activity of plasmonic metals-ZnO NWs hybrids as high as $0.6 \text{ } \mu\text{A/cm}^{-2}$ while only $0.05 \text{ } \mu\text{A/cm}^{-2}$ photocurrent density was observed for pure ZnO NWs. This small current response in pure ZnO NWs might be attributed to the defect-mediated light absorption in ZnO. Here we would like to emphasize that the VIS photocatalysis becomes operative by the combination of ZnO catalysts with plasmonic NPs. The possible mechanism of the VIS photocatalysis of plasmonic NPs-ZnO NWs hybrids is illustrated in Figure 7(e), wherein the plasmon-induced hot electrons or/and plasmon-enhanced defect absorptions of ZnO photocatalyst are shown. As seen in the inset of Figure 7(f), the strong electric-field hot spots under resonant excitation at the metal-semiconductor interface correspond to the generation of high density of excited electrons located at metal-semiconductor interface. With sufficient excitation energy, the excited electrons can overcome Schottky barrier

and jump from metal to semiconductor (56–59). On the other hand, this strong electric field also can enhance the VIS absorption of defect levels in ZnO also contributing to the efficient photocatalytic activity of plasmonic metal-ZnO hybrid in the VIS region.

3.4. ZnO NWs with Cu induced defects for photocatalysis

In addition to increasing the surface area and combining with metal nanoparticles as described above, there are various strategies available to improve the photocatalytic activity of ZnO NWs. One of the most effective methods is the incorporation of selective elements as dopants in ZnO to tailor the light absorption properties (60–64). Here in our work (65) we have incorporated Cu defects in ZnO NWs and found that the Cu defects can enhance the concentration of surface defects and modify the wire growth to increase the surface area in ZnO NWs. This leads to the enhancement of the photocatalytic activity of ZnO, which could be seen from the dramatically improved visible-light emission in the PL spectra and time dependent degradation plot of ZnO NWs as shown in Figure 8(a)-(b).

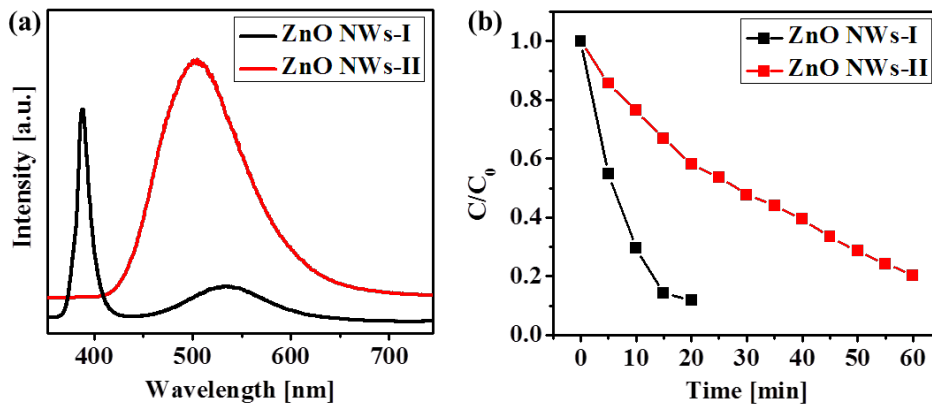


Figure 8. (a) PL spectra of ZnO NWs-I & II. (b) Comparison of the photocatalytic activities of the ZnO NWs-I & II. ZnO NWs –I refers to pristine ZnO NWs. ZnO NWs-II refers ZnO NWs with Cu induced defects. Reproduced from (65).

4. Summary

Several ZnO nanowire-based materials and devices were introduced to demonstrate the tunability of optoelectronic properties of these materials by their nanomorphologies, heterostructures, and defects. Possibility of color-tunable light emission by templated growth of ZnO NWs/NShs, and efficient photoresponsive devices by heterojunction were demonstrated by fabricating ZnO/CNT heterojunction as well as a ZnO/TiO₂ core-shell device with appropriately incorporated dopants. Plasmonic hot-electron injection and Cu doping were also introduced to demonstrate how we can improve a UV-active ZnO NWs catalyst to an efficient solar-driven and visible-active photocatalyst. The methods presented here can be useful for tailoring the functionalities not only for ZnO-based nanomaterials but also for other types of oxides.

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