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Enhanced photocatalytic properties of ZnO/Al₂O₃ nanorod heterostructure

Zhipeng Li*, Ligong Zhou¹, Liying Lu¹, Xiaoguang Xu* and Yong Jiang*

¹ Beijing Advanced Innovation Center for Materials Genome Engineering, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, 100083, People’s Republic of China
² School of Chemistry and Biology Engineering, University of Science and Technology Beijing, Beijing, 100083, People’s Republic of China
* Author to whom any correspondence should be addressed.
E-mail: zplmse@ustb.edu.cn and xgxu@ustb.edu.cn

Abstract

The separation and transfer of the photoinduced charge carriers are essential for the high-efficient photocatalytic materials. Heterostructures which compose of several semiconductors can take advantage of energy level difference to improve photocatalytic properties. However, the fabrication of the related heterostructures normally adopts the physical vapor deposition method, such as atomic layer deposition, hindering the mass production of photocatalytic materials. In this work, ZnO nanorod arrays and ZnO/Al₂O₃ heterostructure were prepared on Si (100) substrates by a cost-efficient method which combines the hydrothermal and photochemical techniques. Microstructure and surface composition analysis on the heterostructure confirm the synthesis of the ZnO/Al₂O₃ core–shell heterostructure. According to the ultraviolet (UV)–visible diffuse reflectance spectroscopy, the band gap of the ZnO/Al₂O₃ heterostructure can be estimated to be 3.25 eV, which is larger than that of pure ZnO nanorod arrays. Moreover, the heterostructure exhibits an obviously enhanced photocatalytic property for photodegradation of methyl orange under UV-irradiation. The energy band diagram of heterostructure shows that the improvement of photocatalytic property can be ascribed to the increase in the electron–hole pair separation rate. This work provides a simple method to fabricate nanoscale semiconductor heterostructures for photocatalytic applications.

1. Introduction

Organic pollutants and toxic water pollutants have become serious environmental problems and attract great attentions. Photocatalytic degradation technique which is an efficient green technique is a desirable solution to deal with the pollutants [1–3]. Among all the photocatalysts, ZnO is one of the most popular ultraviolet (UV) light photocatalyst, owing to its chemically stability, biocompatible, low toxicity, and high-charge transporting abilities [4–13]. Moreover, the photoelectric and photocatalytic properties of semiconductor materials is strongly correlated with their morphology and the surface atomic structures [14]. The one-dimensional ZnO nanorod arrays have attracted considerable attention for their large specific surface area, intrinsic high absorption efficiency and other interesting properties. Semiconductor heterostructures with two or more semiconductor component properties can effectively enhance catalytic activity, since the difference between conduction band and valence band can accumulate photo-generated electrons at the conduction band of one semiconductor, and the photo-generated holes can accumulate at the valence band of the other semiconductor, which can suppress the recombination of the photo generated electrons and holes. Physical vapor deposition method, such as atomic layer deposition (ALD), has been proven to be an efficient way to synthesize heterostructures (e.g. ZnO–CdS and ZnO–Al₂O₃–CdS), the relevant catalytic properties were significantly enhanced [15–17]. The thickness and chemical stoichiometry of semiconductor materials could be well controlled by this method. However, various precursor materials are expensive and high vacuum environment should also be prepared for the growth of heterostructure materials by ALD, hindering its use for mass...
production. In this work, one-dimensional ZnO nanorod arrays on the Si (100) substrates were prepared using a 
hydrothermal method. Based on the one-dimensional ZnO nanorod arrays as prepared, ZnO/Al₂O₃ 
heterostructure was further designed and synthesized by a photochemical method. As compared to bare ZnO 
nanorod arrays, the ZnO/Al₂O₃ heterostructure showed enhanced photocatalytic activity. Moreover, compared 
with the powders, the catalyst growing on the substrate can avoid agglomeration effectively, and it could be easily 
separated from the reaction materials and recycled after being used. The fabrication method is much easier and 
more accessible than using ALD. It is also should be noted that the film deposited by ALD is amorphous and has 
rather flat surface. However, the chemical method can produce ZnO array capped by amorphous oxide with 
large specific area which could enhance photocatalysis properties.

2. Experimental section

2.1. Synthesis of ZnO nanorods and ZnO/Al₂O₃ heterostructures
ZnO nanorod arrays were grown by hydrothermal method on ZnO seed layer prepared by spin-coating. Zinc 
acetate dihydrate was dissolved in ethylene glycol monomethyl ether to prepare 0.5 M solution, followed by 
adding several drops of choline. The solution was stirred to clear homogeneous sol. The sol was spin-coated 
on the Si (100) substrate and annealed at 350 °C for 30 min. ZnO nanorod arrays were grown by placing the 
substrate with ZnO seed layer into a 50 ml Teflon autoclave together with solution of 0.05 M zinc nitrate 
hexahydrate and 0.05 M hexamethylenetetramine, and heating the solution at 90 °C for 10 h. The substrate was 
taken out, rinsed with deionized water and dried in air. The ZnO/Al₂O₃ heterostructure was prepared by 
photochemical method. 7.5 mg of aluminum nitrate was dissolved in 20 ml deionized water. The substrate with 
ZnO nanorod arrays was irradiated in the aluminum nitrate solution by an iodine tungsten lamp for 40 min, and 
then washed with deionized water for several times before dried in the air.

2.2. Characterizations
Crystal structure and morphologies of samples were studied by x-ray diffraction (XRD), field emission scanning 
electron microscopy (SEM) and transmission electron microscopy (TEM). To get the TEM images, the 
ZnO/Al₂O₃ nanorod arrays grown on the Si (100) substrate were mechanically scraped, ultrasonic dispersed 
in ethanol, and deposited on carbon-coated copper grids. Elemental composition and valence states were 
examined by energy dispersive spectrometer (EDS) and x-ray photoelectron spectrometer (XPS). The UV–vis 
diffuse reflectance spectra were measured at room temperature in the wavelength range of 200–800 nm.

2.3. Photocatalytic properties measurements
The photocatalytic activity of the films (20°20 mm²) was evaluated by photodecomposition of 2.5 mg l⁻¹ methyl 
orange solution under irradiation of a 125 W UV lamp with central wavelength of 365 nm. Before irradiation, 
the solution with film was put in darkness for 30 min to achieve adsorption equilibrium. After irradiation, the 
methyl orange solution was collected to measure the absorption spectra using a UV–vis spectrophotometer, so 
as to investigate the photodegradation of the methyl orange solution. In addition, the photocatalyst was recycled 
after photodegradation (180 min) and the photolysis experiments were repeated. The photodegradation time of 
each cycle was set to 180 min.

3. Results and discussion
The XRD patterns for pure ZnO nanorod arrays and ZnO/Al₂O₃ heterostructure are shown in figure 1. The 
pattern was indexed to hexagonal wurtzite structure (JCPDS No. 05-0664). It can be seen that the ZnO nanorods 
had a typical hexagonal ZnO crystal structure and that the ZnO nanorods grew in the [001] direction with high 
orientation in both samples. However, diffraction peaks for alumina are not observed in the ZnO/Al₂O₃ 
heterostructure, which may be caused by its amorphous state and low amount.

In order to obtain detailed information about the microstructure and morphology of the sample, SEM and 
TEM characterizations were carried out. Figure 2(a) are top-view SEM images of the bare ZnO nanorods, the 
inserted in the picture shows the enlarged image of the samples, indicating the nanorods had smooth surfaces. 
The average diameter of ZnO nanorods was approximately 160 nm. The SEM images also indicate that the ZnO 
nanorods were grew vertically in a hexagonal arrangement. Figure 2(b) is top-view SEM image of the 
ZnO/Al₂O₃ heterostructure. The inserted are enlarged image and EDS spectra of the heterostructure, 
respectively. It can be seen that after 40 min of UV-irradiation, the surfaces of the nanorods became rough 
because the alumina grown on the ZnO nanorods. The EDS results indicated that the composite is composed of 
Zn, O and Al elements.
Figures 2(c) and (d) are the TEM images of the ZnO/Al2O3 nanorod heterostructure, which further confirmed the growth of alumina shell on the ZnO nanorods. The TEM image shown in figure 2(c) clearly demonstrates that there was alumina uniformly coated on the surface of the ZnO nanorods. Figure 2(d) shows a high-resolution TEM image taken from a single nanorod. The lattice spacing is 0.26 nm, corresponding to the lattice parameter of the (002) crystal planes of wurtzite ZnO. The ZnO nanorods can be determined to grow along the [001] direction.

To further confirm the growth of Al2O3 on the ZnO nanorod arrays, XPS was performed to analyze the surface composition of the heterostructure. A wide survey scan of XPS spectra taken in the range 0–1200 eV is shown in figure 3(a), and the binding energies are calibrated by C 1 s (284.8 eV). The ZnO/Al2O3 heterostructure only shows emissions of C, Zn, Al and O. The different peaks observed were assigned to Zn 3d,
Zn 3p, Zn 3s, Zn 2p, Al 2s, Al 2p, O 1s, O 2s and C 1s core levels and to Zn LMM and O KLL Auger. The high-resolution XPS spectra for each element are shown in figures 4(b)–(d). The Zn 2p spectrum in figure 3(b) showed two symmetric peaks, the peak centered at 1021.9 eV corresponds to the Zn 2p3/2 and another one centered at 1044.9 eV was signed as to Zn 2p1/2, indicating a normal state of Zn2+ in the ZnO/Al2O3 heterostructures [18].

Figure 3. (a) wide survey scan of XPS spectrum and (b)–(d) high-resolution XPS spectra of Zn 2p, O1s and Al 2p of ZnO/Al2O3 heterostructure, respectively.

Figure 4. Schematic diagram of the growth mechanism of ZnO/Al2O3 heterostructure.

Zn 3p, Zn 3s, Zn 2p, Al 2s, O 1s, O 2s and C 1s core levels and to Zn LMM and O KLL Auger. The high-resolution XPS spectra for each element are shown in figures 4(b)–(d). The Zn 2p spectrum in figure 3(b) showed two symmetric peaks, the peak centered at 1021.9 eV corresponds to the Zn 2p3/2 and another one centered at 1044.9 eV was signed as to Zn 2p1/2, indicating a normal state of Zn2+ in the ZnO/Al2O3 heterostructures [18]. Figure 3(c) shows the XPS high resolution spectrum of oxygen which could be fitted to three peaks centered at 530.8, 531.5, and 532.7 eV. The lower binding energy peak at 530.8 eV is attributed to Zn–O binding [19]. The peak at 531.5 eV could be ascribed to Al–O binding [20]. The peaks at 532.7 eV indicate the presence of...
surface-adsorbed oxygen species such as O\(^2^−\) [21, 22]. The Al 2p spectrum in figure 3(d) showed one symmetric peak centered at 74.5 eV corresponding to Al–O binding in the Al\(_2\)O\(_3\), which indicated a valence state of Al\(^{3+}\) [23]. All these results suggested that the Al\(_2\)O\(_3\) shells were successfully formed on the surface of the aligned ZnO nanorod arrays.

Figure 4 illustrates the possible growth mechanism of alumina shell on the ZnO nanorods by photochemical method [24, 25]. When ZnO nanorod arrays were immersed in the aqueous aluminium nitrate and irradiated by UV light, the electrons in the valence band of ZnO nanorods were excited to the conduction band. Then the photogenerated electrons reacted with H\(_2\)O or dissolved O\(_2\) in the solution and generate OH\(^−\) or consume H\(^+\). As a result, there would be special regions near the surfaces of ZnO nanorods where the concentration of OH\(^−\) anions were much higher than other regions. Al\(^{3+}\) anions could be combined with OH\(^−\) to form [Al(OH)\(_3\)]\(^{2−}\) anions, and Al\(_2\)O\(_3\) formed when [Al(OH)\(_3\)]\(^{2−}\) lost OH\(^−\) and H\(_2\)O. The reactions are as follows:

\[
2Al^{3+} + 10OH^- \rightarrow 2[Al(OH)_3]^{2−} \rightarrow Al_2O_3(s) + 4OH^- + 3H_2O
\]

The UV–vis diffuse reflectance spectrum for the synthesized ZnO/Al\(_2\)O\(_3\) heterostructure is presented in figure 5(a). For comparison, the spectra of pure ZnO nanorod arrays is also plotted. Figure 5(b) is the curve of \((F(R^*)h\nu)^2\) versus photon energy based on the Kubelka-Munk theory, where \(F(R) = (1 - R)^2/(2 R)\) and R is the diffused reflectance. The intercepts of the tangents yielding the band gap energies of the samples [26]. The estimated band gap energies of the ZnO and ZnO/Al\(_2\)O\(_3\) heterostructure were about 3.22 and 3.25 eV, respectively.

The photocatalytic properties of the two kinds of samples were studied by the photodegradation of methyl orange under a UV lamp as a model reaction. Figure 5(c) was the degradation curve of methyl orange (value of absorption maximum normalized by the absorption maximum at 0 min as a function of time) under the UV-irradiation. The Al\(_2\)O\(_3\)/ZnO heterostructure show a considerable increase of photocatalytic activity compared with the bare ZnO nanorod arrays. After 2 h of UV-irradiation, the methyl orange solutions with the ZnO nanorod arrays and Al\(_2\)O\(_3\)/ZnO heterostructure were decomposed by 68% and 86% respectively. With the time of photodegradation going on, methyl orange degradation was approximately complete and the degradation rate decreased. The methyl orange solutions were decomposed by 85% and 92% respectively with degradation time of 3 h. The results represent that by coating Al\(_2\)O\(_3\) shells, the activity of photocatalytic of ZnO nanorod arrays was significantly enhanced. The photostability of the Al\(_2\)O\(_3\)/ZnO heterostructure was also evaluated. Figure 5(d) shows the activity of recycling photocatalysts (degradation time was 3 h). As the times of recycling
increased, the photocatalytic activity of the Al₂O₃/ZnO heterostructure was decreased slightly, so as the ZnO nanorod arrays.

It is generally accepted that the recombination of photogenerated carriers needs to be suppressed to achieve increased photocatalytic efficiency [10]. When Al₂O₃ was grown on the surface of ZnO nanorods, ZnO/Al₂O₃ heterostructures were formed. The band alignment between the core of ZnO and the shell of Al₂O₃ is calculated in the schematic diagram as shown in figure 6, based on the following empirical equation:

\[
E_{VB} = X - E^e + 0.5E_g \\
E_{CB} = E_{VB} - E_g
\]

Where \(E_{VB}\) is the valence band (VB) edge potential, \(E_{CB}\) is the conduction band (CB) edge potential, \(X\) is electronegativity of the material, which is the geometric mean of the electronegativity of the constituent atoms. \(E^e\) is the energy of free electrons on the hydrogen scale (\(\sim 4.5\) eV), \(E_g\) is the band gap of the material. The band gap of the ZnO nanorods was 3.22 eV as evaluated from the diffuse reflectance spectrum. The band gap of the bulk Al₂O₃ was reported to be about 8.8 eV in many experiments and calculation results [27–31], and the value was found often interpreted as a narrowing of the band gap in amorphous Al₂O₃ [32]. In the calculation of band alignment between ZnO and Al₂O₃, the \(E_g\) of the Al₂O₃ was selected as 8.8 eV.

When the ZnO/Al₂O₃ heterostructure catalyst was irradiated by UV light (with central wavelength of 365 nm and photon energy of 3.39 eV), the photon energy is larger than the bandgap of ZnO (3.22 eV), so the electrons in the valance band of ZnO could be excited to the conduction band with simultaneous generation of the same number of holes in the valence band. The ZnO materials have relatively higher CB than Al₂O₃, and the energy difference, \(\Delta E_{CB}\), could be calculated to be about 3.21 eV (smaller than the UV photon energy). It is feasible that the photogenerated electrons in the conduction band of ZnO could be excited again into the conduction band of Al₂O₃ via the interface [33]. Thus, under the UV irradiation, photogenerated electrons at the conduction band of ZnO would migrate to that of Al₂O₃ whereas photogenerated holes could be left in the valence band of ZnO. In this way, photogenerated electrons and holes could be efficiently separated, resulting in an increased lifetime of the charge carriers and an enhanced interfacial charge transfer to adsorbed organic molecules. This transfer mechanism is expected to be the possible reason for the enhanced photocatalytic efficiency of the heterostructure.

4. Conclusions

Both pure ZnO nanorod arrays and ZnO/Al₂O₃ heterostructure were synthesized on Si (100) substrate by a cost-efficient method which combines the hydrothermal and photochemical techniques. The microstructure
characterizations showed the surface composition, microstructure and morphologies of the heterostructure and confirmed the successful growth of Al$_2$O$_3$ shell on the ZnO nanorods. The enhanced photocatalytic property was found in the ZnO/Al$_2$O$_3$ heterostructure under the UV irradiation, which should be ascribed to the increase in the charge separation rate. Photogenerated electrons in the conduction band of ZnO could be excited into that of Al$_2$O$_3$ via the hetero-interface with the UV light, strongly suppressing the recombination of photogenerated electrons and holes, resulting in improved photocatalytic performance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zhipeng Li @ https://orcid.org/0000-0001-7223-9334
Xiaoguang Xu @ https://orcid.org/0000-0002-0972-4641

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