Fabrication, Optoelectronic and Photocatalytic Properties of Some Composite Oxide Nanostructures

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This is an overview paper reporting our most recent work on processing and microstructure of nano-structured oxides and their photoluminescence and photo-catalysis properties. Zinc oxide and related transition metal oxides such as vanadium pentoxide and titanium dioxide were produced by a combination of magnetron sputtering, hydrothermal growth and atmosphere controlled heat treatment. Special morphology and microstructure were created including nanorods arrays, core-brushes, nano-lollipops and multilayers with very large surface area. These structures showed special properties such as much enhanced photoluminescence and chemical reactivity. The photo-catalytic properties have also been promoted significantly. It is believed that two factors contributed to the high reactivity: the large surface area and the interaction between different oxides. The transition metal oxides with different band gaps have much enhanced photoluminescence under laser stimulation. Use of these complex oxide structures as electrodes can also improve the energy conversion efficiency of solar cells. The mixed oxide complex may provide a promising way to high-efficiency photo emitting materials and photo-catalysts.

Keywords: Zinc oxide, Vanadium pentoxide, Titanium dioxide, Processing of composite oxides, Nanostructure, Photoluminescence, Photocatalysis

1. INTRODUCTION

Functional one-dimensional metallic oxides have attracted much attention because of their potential use in electronic, optical and spintronic devices [1]–[4]. Among them, zinc oxide (ZnO), titanium dioxide (TiO₂), and vanadium pentoxide (V₂O₅) nanostructures including nanowires, nanobelts and nanorods have been extensively studied due to their special electronic, chemical and optical properties [5]–[11]. Incorporating these metallic oxide materials into an integrated structure with nanoscale dimension is of great interest because the resulting hierarchical nanostructures often possess much large surface areas and improved physical and chemical properties, providing potential applications for sensing, light emission and photocatalysis [12]–[16].

It is known that ZnO material can be made with the most diverse and abundant configurations of nanostructures such

as quantum dots, rods, wires, belts, springs, bows, helices and prisms [12]–[22]. Accordingly, ZnO based composite nanostructures are easily built up combined with other metallic oxides [23]–[25]. The outside metallic oxides layers can be deposited onto the surfaces of the ZnO nanostructure substrates by different ways including sputtering methods or vapor deposition, and then the so-called “hierarchical nanostructures” are formed. Some interesting configurations or morphologies can be obtained for these combined nanomaterials. Special and improved optical or electronic properties are often reported [14], [26]–[29]. Currently, the typical composite nanomaterials such as core-shell nanostructure formed by the inside nanorods with the outside covered layers. Examples including TiO₂/ZnO, ZnO/MgO and ZnO/Er₂O₃ core-shell structures have been fabricated [30]–[33]. Increase in light emission or efficiency enhancement for dye-sensitized solar cells based on those core-shell structures are observed, which certainly proves that these types of composite nanostructures have enhanced optical and electronic properties that may have practical applications.

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In the current review, we summarize our recent work on the ZnO nanorod based composite nanostructures including the fabrication processes, microstructure characterization and the related photocatalytic applications. We would also like to discuss the current research status on these composite nanostructures and demonstrate the promising photocatalytic applications through the way of incorporating these metallic oxide materials into an integrated structure.

2. FABRICATIONS AND MICROSTRUCTURE

The microstructure and properties of metallic oxide are very sensitive to the processing techniques and parameters. In our study, we mainly use ZnO nanorods as the nano-template; some other oxides such as V_2O_5 and TiO_2 were then deposited onto ZnO nanorods by magnetron sputtering to form controllable composite structure [34], [35]. Combined with annealing treatment under controlled atmosphere at suitable temperature, novel hierarchical nanostructures can be obtained, with much improved optical or electronic properties than simple ZnO, V_2O_5 , or TiO_2 nanostructures.

2.1 Simple nanorods array template

For the composite nanostructure preparation, ZnO nanorods and V_2O_5 nanorods are selected as the basic templates since these two metallic oxides have stable characters; and the nanorods structure can be prepared in a well controllable and effective way [34]–[38].

2.1.1 ZnO nanorods array

Aligned ZnO nanorods have been successfully synthesized by catalyst-assisted vapor phase synthesis and catalyst-free metal-organic chemical vapor deposition [39]–[43]. We use a relatively simple method, template-assisted hydrothermal growth based on wet chemical reaction [35], which provide a low-cost, low-temperature, and environmental friendly way for highly ordered ZnO nanorods array preparation.

The template-assisted hydrothermal growth method includes two steps: first a thin ZnO seeds layer (~100 nm) was sputtered onto glass or silicon substrates, and then the coated substrates were suspended vertically in a sealable glass bottle filled with aqueous solutions of zinc nitrate and hexamethylenetetramine for ZnO growth. Diluted nitric acid or ammonia hydroxide solution was used to adjust the pH values. The sealed bottle was put into an oven at 95°C for several hours for the ZnO nanorods to grow. ZnO nanorods with different surface distribution densities can be successfully obtained by controlling the initial pH value of the growth solution, as shown in Fig. 1. The ordered ZnO nanorods have a preferential growth direction of [002], and the rod formed is a single crystal. Furthermore, the morphologies of the nanorods array including the length, radius and orientation can also be controlled to certain extent by adjusting the solution concentration, thickness of the seed layer, growth temperature and growth time. Obviously, this facile preparation method provides a feasible way for the basic ZnO nanorods

Fig. 1. Zinc oxide nanorod arrays with different surface distribution densities prepared by low-temperature template assisted growth in solutions: (a) sparse and (b) dense rods grown in solutions with low and high pH values, respectively.

array preparation, thus supplying good templates for the following oxide composite structure fabrication.

2.1.2 β - V_2O_5 nanorods

Vanadium oxides have several stoichiometries including VO, V_2O_3 , VO_2 , and V_2O_5 , among which vanadium pentoxide, V_2O_5 , is the most stable oxide and show semiconductor property with an energy gap of ~2.2 eV at room temperature [44]–[49]. Due to its layered structure and special characteristics including chemical sensing, multi-colored electrochromism and photochromism, V_2O_5 has attracted much interest, and has been considered to be a promising material for applications in Li-ion battery electrode, optical-electrical switches and color memory devices [50]–[54].

Several approaches have been reported to synthesize nanostructured vanadium oxides including hydrothermal method, sol-gel method and vapor phase epitaxy growth method [37], [55]–[60]. Recently an alternative approach to produce single crystalline β - V_2O_5 nanorods has been developed in our labs [36], [61]. The sputtered amorphous V_2O_5 films on glass substrate showed a temperature-sensitive crystallization behavior and transferred to β - V_2O_5 nanorods or β phase nanoslices with highly oriented structure after an annealing in O_2 atmosphere at 500–550°C as shown in Fig. 2. The related X-ray diffraction (XRD) spectra indicate that the β - V_2O_5 nanorods obtained after an annealing at 500°C possess a highly ordered crystal structure.

Fig. 2. (A) The temperature sensitive crystallization process of vanadium pentoxide (V_2O_5): (a) the as-prepared amorphous V_2O_5 film; (b) annealed at 450°C; (c) β - V_2O_5 nanorods formed after annealing at 500°C and (d) flat-lying nanoslices formed at 550°C. The inserts show the related cross-section morphology for each sample. (B) X-ray diffraction patterns for the as-prepared and annealed samples.

Based on this temperature sensitive crystallization, V_2O_5 can be made to complex composite nanostructures. Interesting morphologies and hierarchical structures can be achieved after suitable annealing treatment, which will be shown below.

2.2 Composite nanostructures

By using the ZnO nanorods array as the basic template, different composite nanostructures can be effectively fabricated with large-scale production. In the following part, we introduce one of these fabrication progresses: producing ZnO based composite nanostructures combined with magnetron sputter method.

2.2.1 ZnO/TiO₂ core-brush array

ZnO and TiO₂ nanowires have been extensively studied due to their potential use in solar cells and as photocatalysts [62]–[65]. The principles of these applications are quite similar: based on their light absorption, light-electron conversion and electron transportation properties. To enhance the light conversion efficiency and improve the performance of the solar cells or photocatalysts, it is necessary to achieve high external quantum yields across a broad visible light spectrum, to

Fig. 3. (a) Zinc oxide (ZnO) nanorods array before titanium dioxide (TiO₂) deposition; (b) ZnO/TiO₂ bottlebrush nanostructures after 90 min deposition; (c) transmission electron microscopy images of ZnO/TiO₂ bottlebrush nanostructures with deposition time of 60 min and 90 min; (d) the insert shows the enlarged image; and (e) schematics for the formation of ZnO/TiO₂ nanobrush.

increase the diffusion length of electrons within the nanocrystalline materials, and to increase the speed of the electron transport process [30]. As TiO₂ and ZnO materials have different band gaps, their composites should cover a broader light absorption spectrum than the individuals can cover. Furthermore, it is known that the electron transport rate in ZnO nanowires is much faster than in TiO₂ due to its higher electrical conductivity [66].

Based on the above factors, ZnO/TiO₂ composites, or core-shell nanostructures, have attracted much attention for solar cell and photocatalyst applications [11], [30], [66]–[68]. Currently we use two-step process to prepare ZnO/TiO₂ heterostructured bottle brush. Firstly, ZnO nanorods arrays are synthesised on glass substrates by the seed-assisted low temperature (95°C) hydrothermal method as described previously [35]. TiO₂ layers are then deposited on the top and side-surfaces of ZnO nanorods by using magnetron sputtering with low deposition rate at room temperature. Pure TiO₂ is used as the target and Ar as the working gas. The deposition time is controlled to be 30 min and 60 min.

The obtained ZnO/TiO₂ nano-bottlebrush structures are shown in Fig. 3. It is clear that a TiO₂ shell has been coated on the surfaces of ZnO nanorods, and the initial ZnO nanorods became the torch-shaped microstructure from the scanning electron microscopy (SEM) images. To further investigate the bottlebrush nanostructure, transmission electron microscopy (TEM) was used for more detailed microstructure of the obtained bottlebrushes. It can be seen that fine TiO₂ nanowires are just like “hairs,” and orderly grown on the top and side surfaces of ZnO nanorods. With longer deposition time, the TiO₂ hairs grow longer on the ZnO nanorods surfaces. Finally, the initially bare ZnO nanorods became bottlebrush-like nanostructures. A schematic drawing of formation mechanism is shown in Fig. 3(e).

The crystal structures of the ZnO/TiO₂ bottlebrush nanostructures were investigated by X-ray diffraction, which shows

Fig. 4. (a) Photoluminescence (PL) spectra at room temperature from zinc oxide (ZnO) nanorods sample and ZnO/titanium dioxide (TiO₂) bottlebrush samples with deposition time of 60 and 90 min; (b) the curve fitting of the PL spectra for the sample of 60 min deposition; (c) schematic illustration of the enhanced PL process from the ZnO/TiO₂ bottlebrush nanostructures with resonant effect. Two excitation channels are shown in the figure.

the basic ZnO nanorods array has good crystalline structure with the preferred oriented growth direction of [002], while the outside-covered TiO₂ layer shows several peaks with the rutile (110) dominant peak. From the current XRD, however, it is difficult to determine the individual TiO₂ nanowires deposited on the ZnO nanorods are polycrystalline or single crystalline, though they look much like single crystals. Further high-resolution TEM (HR-TEM) is needed to confirm the microstructure and crystallinity of the covered TiO₂ nanowires.

The growth mechanism for the TiO₂ nanowire coating is suggested to be in two stages. The first stage is that the initial nucleation of TiO₂ nanocrystals on the ZnO nanorods surfaces. For this stage, it should be attributed to the heterogeneous nucleation, in which the interfacial energetics plays a key role. After the nucleation stage, the TiO₂ nanowires will grow along the preferential [110] direction of rutile phase, which is the second stage of TiO₂ nanowire formation. For the second stage, surface energetics should dominate the crystal growth mechanism to minimize the surface energy [20].

It should be noted that the relatively low depositing rate under a low sputter power in the magnetron sputter is another key point that favors the TiO₂ nanowires growth. If a high sputtering power and high bias voltage were applied, the Ti⁴⁺ and O²⁻ ions will have much higher kinetic energy, which tends to form an amorphous TiO₂ film at room temperature.

The composite ZnO/TiO₂ nano-bottlebrush structures exhibited a much enhanced optical properties as shown in Fig. 4(a). The photoluminescence (PL) emission for the initial ZnO nanorods show a strong UV light emission peak at ~379 nm (curve a), and no other visible light emission peaks can be seen, evidence of the good crystalline quality of the ZnO nanorods prepared by hydrothermal method. After TiO₂ deposi-

tion for 60 minutes, the PL peak from ZnO at the UV range reduced dramatically, and the TiO₂ related PL peaks in the visible light range appeared (curve b). After 90 minutes deposition, the ZnO related PL peak at 379 nm disappeared entirely, and the TiO₂-related PL peaks became weaker (curve c) compared to the sample with 60 minutes deposition. The detailed PL analysis of the 60 minutes deposited ZnO/TiO₂ bottlebrush sample is shown in Fig. 4(b). The peak at 379 nm is the UV peak from the ZnO nanorods and the other peaks at 415 nm, 437 nm, 469 nm and 497 nm are from the TiO₂ nanowires. The peak at 415 nm is likely to come from the self-trapped excitons localized at TiO₆ octahedral sites, and the other longer wave peaks could be attributed to the oxygen vacancies on the surface area of TiO₂ nanowires [69]–[71].

From the different PL spectra, it is interesting to discuss the origin of the enhancement of light emission from the integrated composite nanostructures. Obviously, the disappearance of the ZnO related ultraviolet (UV) peak for the bottlebrush of 90 minutes should be due to the relatively thick and dense TiO₂ nanowire layer, thus the laser source has low penetration intensity to excite the inner ZnO nanorods. For the 60 minutes deposited ZnO/TiO₂ bottlebrush sample, PL came from both the core part of ZnO and the shell part of TiO₂ hairs by the laser excitation. Thus both the UV peak from ZnO and peaks from TiO₂ appeared in the PL spectra. At the same time, a coupling mechanism may have taken place between the ZnO and TiO₂ nanostructures: Some UV photons from ZnO may have been absorbed by the outside TiO₂ nanowires, and the outside TiO₂ hairs were excited by both the laser light and UV emission from the inner ZnO nanorods, as illustrated by the schematic in Fig. 4(c). These two excitation mechanisms may have formed a so-called resonant effect for the PL process, and may have been the reason that the intensity of the TiO₂-related PL peak has been enhanced significantly [34].

2.2.2 ZnO/V₂O₅ bilayer

Our experimental results indicated that V₂O₅ films prepared by magnetron sputtering on glass substrates have temperature sensitive crystallization behavior within a narrow annealing temperature range from 450°C to 550°C [36], [61]. Especially, when annealed at 500°C, highly ordered β-V₂O₅ nanorods will form.

According to the previous research, V₂O₅ material always shows visible light PL, and the emission intensity strongly depends on their microstructure [72]–[74]. However, V₂O₅ has hardly been considered as a candidate for light emitting due to the unsatisfying emission intensity. Recent papers reported that GaN based light emission diodes capped by ZnO layer or nanostructures showed enhanced light emission, which may provide an effective way to increase the light emission efficiency of luminescence materials [75], [76]. Thus it is interesting to investigate the light emission of V₂O₅/ZnO bi-layer composites in an effort to obtain enhanced light emission from ZnO incorporated V₂O₅ nanostructures.

V₂O₅ films capped by a thin ZnO layer were prepared by magnetron sputtering method at room temperature. The microstructure of the post-annealed samples was characterized by SEM and XRD as shown in Fig. 5. It can be observed

Fig. 5. (a) Surface morphology of as-deposited vanadium pentoxide/zinc oxide (V_2O_5/ZnO) samples, the insert shows the cross-section image; (b) sample annealed at 400°C; (c) sample annealed at 450°C; (d) sample annealed at 500°C; (e) X-ray diffraction spectra for V_2O_5/ZnO bi-layer composite samples before and after annealing with different temperatures; and (f) a schematic drawing to show the changes of the microstructure.

that the as-deposited V_2O_5/ZnO sample has a quite smooth surface comprising compact particles with small grain size. The cross-section (the insert image) shows a clear interface between the V_2O_5 amorphous film (~350 nm) and the capped ZnO layer (~120 nm).

After an annealing in O_2 ambience at 400°C, the ZnO small grains grew up and became larger particles at the top surface as shown in Fig. 5(b). When the annealing temperature increases to 450°C, the surface grains grew further larger, Fig. 5(c). After an annealing at 500°C, the samples show very different surface microstructures as in Fig. 5(d). Clusters and nanorods with porous structures clearly appear on the sample surface. Combined with the XRD spectra in Fig. 5(e), it can be seen that those nanorods (slices) grew from the interstices of the porous particles are β - V_2O_5 crystals. The annealed composite samples here show similar β - V_2O_5 nanorods comparing with those pure V_2O_5 films after annealed at 500°C, since V_2O_5 compound always show strong temperature sensitive crystallization. At the same time, the top-layer continuous ZnO thin film transferred into porous particles. This situation is understandable considering the interfacial interaction such as the effects of strain and stress during the annealing process. The capped ZnO layer on V_2O_5 films tends to depress the crystallization process of V_2O_5 to form standing β - V_2O_5 nanorods. However, due to the strong temperature sensitive crystallization behavior, the crystallization of V_2O_5 may not be suppressed by the covered ZnO layer. As a competition reaction, the annealed V_2O_5 became ordered β - V_2O_5 nanorods and the continuous ZnO layer was tore into

Fig. 6. (a) and (c) Photoluminescence (PL) spectra for vanadium pentoxide/zinc oxide (V_2O_5/ZnO) samples, (b) the integrated intensities for the different samples, and (d) PL spectrum and corresponding second-derivative spectrum for a V_2O_5/ZnO sample annealed at 500°C.

porous particles because of the interfacial strain. The porous ZnO particles were therefore dispersed to cover the β - V_2O_5 nanorods surfaces with an amorphous-like state. This process is schematically illustrated in Fig. 5(f). The XRD spectra showing the absence of ZnO related diffraction peaks give direct evidence for the above mechanism. Furthermore, the change of surface morphology for the samples annealed at 500°C is unlikely caused by the solid-state reaction between V_2O_5 and ZnO according to the binary phase diagram of V_2O_5 and ZnO [77].

The optoelectronic properties of V_2O_5/ZnO samples are characterized by PL at room temperature with a 325 nm He-Cd laser source. From Fig. 6(a), it is clear that the broad green light emission from the V_2O_5/ZnO sample and pure V_2O_5 sample after an annealing at 500°C is much stronger than other samples. A great enhancement for the light emission has been observed, especially for the V_2O_5/ZnO sample after annealing. The main peak is centered at 560 nm, which is quite consistent with the reported band gap of crystal V_2O_5 of 2.2 eV, confirming that the enhanced light emission should be mainly generated from the near band edge emission of crystal V_2O_5 nanostructures.

Figure 6(b) shows that annealing temperature has a very strong effect on the integrated intensity of light emission. It can be seen that the intensity enhancement is not significant when the annealing temperature is below 500°C. After an annealing at 500°C, however, the visible light emission increased dramatically. The enhancement for the pure V_2O_5 sample is ~8 times, while for V_2O_5/ZnO composite sample, the enhancement reaches ~25 times compared with the as prepared samples. This tremendous enhancement was attributed to the coupling between V_2O_5 nanorods and ZnO nanoparticles as well as the improved V_2O_5 crystallinity. From the SEM images of Fig. 5(d) and the schematics of Fig. 5(f), the originally continuous ZnO layer becomes individual (amorphous) particles that surrounded the V_2O_5 nanorods, forming a porous surface. As a result, the V_2O_5 nanorods well embed into those amorphous ZnO nanoparticles. Thus, the

absorption for the excitation laser beam is much enhanced for the annealed composite sample via the coupling with the surrounding ZnO particles. Accordingly, the light emission from V_2O_5 will be greatly improved, as the UV emission from ZnO particles (~ 3.4 eV band gap) acts as another exciting source, added to the laser source to excite V_2O_5 nanorods, resulting in a much higher light emission efficiency for the composite V_2O_5 /ZnO sample compared to the pure V_2O_5 or ZnO.

More detailed PL information is shown in Fig. 6(c). It can be seen that the ZnO related peaks at ~ 392 nm is quite clear for the as-prepared V_2O_5 /ZnO sample and the annealed samples below 500°C . The enhanced ZnO peak for the sample annealed at 450°C should be due to the improved ZnO crystallinity. The V_2O_5 /ZnO samples annealed at 500°C show decreased ZnO UV-peak and prominent blue shift to 380 nm. The obvious near-band-edge blue shift of ZnO is considered to come from the phase and microstructure variation of ZnO layer after annealing, since the blue shift of ZnO UV emission was reported to be associated with small particle size and amorphous state [78], [79]. Obviously, the observed blue shift of ZnO UV peak also provides a strong support for the above explanation that the capped ZnO layer becomes porous particles due to the interfacial strain after an annealing at 500°C .

Figure 6(d) shows the PL spectra for the V_2O_5 /ZnO sample annealed at 500°C with the corresponding second-derivative PL spectrum. Vibrational PL is clearly observed, characterizing a fine structure. The related peaks positions are labeled in the figure. According to previous literatures [80], [81], the vibrational fine structures are usually caused by the $V = O$ vanadyl group involved in a tetrahedral coordination. Previous studies reported that the fine features of PL spectra for V_2O_5 were prominent at low temperature experiment. For the current samples, vibrational fine structures can be observed clearly at room temperature, which should be due to the high ordered structure of V_2O_5 nanorods.

V_2O_5 /ZnO composite nanostructures show greatly enhanced visible light emission after an annealing at suitable temperature due to the coupling between V_2O_5 nanorods and ZnO nanoparticles. The improved V_2O_5 crystallinity after suitable annealing may have been another reason. This composite structure with significantly enhanced light emission suggests its potential applications as new luminescence or phosphorescence materials. Further work on other similar oxide pairs may discover more promising light emission systems.

2.2.3 ZnO/ V_2O_5 nano-“lollipop” array

ZnO/ V_2O_5 bi-layers showed strong photoemission due to the temperature sensitive crystallization of V_2O_5 material and interaction of V_2O_5 with ZnO. What will happen if the ZnO layer is replaced by ZnO rods? This session reports our work on the ZnO nanorods based ZnO/ V_2O_5 composite nanostructures and their properties. ZnO nanorods arrays were synthesised on glass substrates ($25\text{ mm} \times 10\text{ mm}$) by using the seed-assisted low temperature (95°C) hydrothermal method described above [35]. V_2O_5 shell layer was then deposited onto the surfaces of ZnO nanorods by using magnetron sputter at room temperature. High purity V_2O_5 ($\sim 99.9\%$) was used as the

Fig. 7. (a) Scanning electron microscopy cross-section and top surface images for as-prepared zinc oxide (ZnO) nanorods array; (b) ZnO nanorods array covered by vanadium pentoxide (V_2O_5) layer with deposition time of 60 minutes; (c) cross-section sample of the annealed ZnO/ V_2O_5 composite nanorods arrays; (d) transmission electron microscopy (TEM) image for the annealed ZnO/ V_2O_5 composite nanorods; (e) The high-resolution TEM (HR-TEM) images for the ZnO nanorods as the stem; (f) HR-TEM images for the V_2O_5 crystal ball as the head; (G) a schematic to show the growth process of the “lollipop” structure during annealing.

target and Ar as the working gas. The base vacuum of the sputtering chamber was lower than 4×10^{-6} torr. The working pressure and the flux were controlled to be 10 mtorr and 10 sccm, respectively. After above preparation, the samples were annealed under oxygen ambience at different temperatures.

The morphologies of ZnO/ V_2O_5 composite nanorods arrays are shown in Fig. 7. It can be observed that a V_2O_5 shell has been coated on the top and side surfaces of ZnO nanorods. After deposition, the initial ZnO nanorods became a torch-shaped core-shell structure according to the SEM images. After an annealing at 500°C in oxygen ambience, the ZnO/ V_2O_5 core-shells changed their morphologies to the interesting heterogeneous nano-lollipops array, as shown in Fig. 7(c). Comparing with the microstructures of as-deposited ZnO/ V_2O_5 core-shell samples, the annealed samples show heterogeneous nano-lollipops shape with the top heads of V_2O_5 crystal balls and the stems of ZnO nanorods.

Figures 7(d)-(e) shows the TEM images for the ZnO/ V_2O_5 nanolollipop structure. The lattice image for the ZnO nanorods as the stem can be clearly observed in HR-TEM image,

which indicates the growth direction of the ZnO nanorods prepared by hydrothermal method. The lattice structure of V_2O_5 crystal is revealed in Fig. 7(f). The lattice distance is about 0.72 nm, which is close to the (200) inter-plane distance of V_2O_5 single crystal.

Figure 7(g) illustrates the microstructure change from the as-deposited samples to the annealed composite samples. It is believed that this phenomenon is related to the temperature-sensitive crystallization behavior of V_2O_5 material which was discussed in details in one of our previous reports [61]. The surface diffusion of V_2O_5 at 500°C may also play an important role in the formation of nano-lollipops array based on ZnO/ V_2O_5 core-shell structure. The initially covered V_2O_5 particles with amorphous state have diffused along the surface of ZnO nanorods, and aggregated together during the heat treatment process, forming ball-shape V_2O_5 nanocrystals on the top of the ZnO nanorods.

3. PHOTOCATALYTIC APPLICATIONS

It can be observed that the metallic oxides composite nanostructures including TiO_2/ZnO and ZnO/V_2O_5 nanostructures show much enhanced PL emission as well as broadened PL spectra. Accordingly, these composite nanostructures may have potentials for photocatalysis or dye sensitized solar cell applications due to the broadened spectra, which covers the spectra band from ultraviolet to visible light band.

3.1 ZnO/ TiO_2 composite nano-brush for decomposition of Bromo-Pyrogallol red dye

ZnO/ TiO_2 composite nano-brush show enhanced photo emission for the TiO_2 covered “brush-hair,” which should have good photocatalytic ability. Here the photocatalytic performance of as formed ZnO/ TiO_2 composite nano-brush was studied by decomposition of Bromo-Pyrogallol red (Br-PGR) dye under UV-radiation.

The decomposition tests of Br-PGR dye aqueous solution were conducted as follows: 1×1 cm of the ZnO/ TiO_2 composite sample was immersed into 2 ml Br-PGR solution with a concentration of 0.02 mg/L in a photoreaction chamber. A mercury tube lamp (25 W) was used as a UV irradiation source with centre wavelength at 254 nm. The lamp was located 10 cm away from the reaction chamber. Before exposure the sample to the UV light, the dye solution with catalyst slide was stirred thoroughly in the dark for 30 minutes to reach the adsorption equilibrium of the dye on the catalyst. The change of Br-PGR concentration in accordance with the irradiation time was measured using a UV-Vis spectrophotometer (Agilent 8453 UV/Visible [Vis] Spectrometer). The Br-PGR decomposition was recorded at the absorption band maximum (546 nm) in the UV-Vis spectrum. Pure TiO_2 thin film and TiO_2/ZnO bi-layer film were used as reference catalysts in order to study the effect of microstructure on the catalytic behaviour. They were prepared on clear glass substrates with pre-deposited ZnO seed layer by using the identical sputtering parameters as those of the ZnO/ TiO_2 composite nano-brush. The tests of photocatalytic decomposition of Br-PGR dye

Fig. 8. (a) Photo-degradation of Bromo-Pyrogallol red (Br-PGR) using zinc oxide/titanium dioxide (ZnO/ TiO_2) composite nano-brush sample sputtered for 90 minutes; (b) temporal degradation rate of Br-PGR with ZnO/ TiO_2 composite nano-brush film (90 minutes), compared with the performance of sputtered TiO_2 film and TiO_2/ZnO bi-layer film.

solution using these reference catalysts were conducted under the same experimental conditions as did with ZnO/ TiO_2 composite nano-brush samples.

Figure 8(a) shows the temporal evaluation of UV-Vis spectrum changes accompanying the photo-degradation of Br-PGR using the ZnO/ TiO_2 composite nano-brush sample sputter deposited for 90 minutes. The Br-PGR dye initially showed a major absorption band at 546 nm, gradually decreased in absorption and slightly shifted the band to the short wavelength with increasing irradiation time under the UV light. Fig. 8(b) shows the temporal degradation rate of Br-PGR over ZnO/ TiO_2 composite nano-brush (90 minutes) compared with TiO_2 thin film and TiO_2/ZnO bi-layer film. C_0 and C are the equilibrium concentration of Br-PGR before and after UV irradiation, respectively.

As can be seen in Fig. 8(b), for the ZnO/ TiO_2 composite nano-brush sample, the concentration of Br-PGR is reduced to 19% after UV irradiation of 210 minutes, whereas the degradation effectiveness of the TiO_2 film and TiO_2/ZnO bi-layer film are 68% and 64%, respectively. It is obvious that ZnO/ TiO_2 composite nano-brush structure has a better photocatalytic property than TiO_2 thin films coated either on glass substrate or on ZnO seeds layer. In addition, the blank Br-PGR sample without any catalyst shows almost no decomposition under the same UV irradiation condition.

An important factor contributing to the enhanced photocatalytic activity of ZnO/ TiO_2 composite nano-brush nanos-

structure is that the special structure has obviously a much larger specific surface area compared to the simple layer deposited films. The large surface area comes from ZnO nanorods array and the covered nanosized TiO₂ “hairs,” which can supply a very high density of active site for surface reactions as well as a high interfacial charge carrier transfer. These factors are believed greatly beneficial for the enhancement of photocatalytic performance. In addition, the coupling of TiO₂ and ZnO nanostructure could induce an extension of the light wavelength range, which increases the light absorption and decrease the photocatalytic reaction energy, therefore improving the photocatalytic activity [7], [29].

Another advantage of using the ZnO/TiO₂ composite nano-brush structure as catalyst is from the unique hierarchically core-brush structure, which can immobilize the TiO₂ nanostructures on the surface of ZnO nanorods. Accordingly, there will be less separation and recovering issues when utilize ZnO/TiO₂ composite nano-brush in water or air purification process, which are currently a major obstacle that limited a wider application of nanostructured photocatalysts. So the ZnO/TiO₂ composite nano-brush structure may be used as an effective and recyclable photocatalyst for practical applications in the near future.

3.2 ZnO/V₂O₅ composite nano-lollipop array for 2,6-dichlorophenol degradation

Session 2.2.3 reported that ZnO/V₂O₅ composite core-shell nanostructures convert to the ordered ZnO/V₂O₅ composite nano-“lollipop” array after annealing treatment. Tests also conducted to investigate the photocatalytic properties of this heterogeneous nanostructure.

The UV-Vis absorption property of the V₂O₅/ZnO composite nano-lollipops array was investigated by UV-Vis spectroscopy as shown in Fig. 9(a). The absorption of pure ZnO nanowire array shows a sharp edge at ~380 nm, which obviously correspond to its band edge absorption since the band gap of ZnO material is about 3.3 eV. For the as-prepared V₂O₅/ZnO composite core-shell structure, the absorption edge has a clear shift towards the long wavelength direction. While for the annealed sample with the nano-lollipops shape, the absorption edge becomes ambiguous. The average absorption for UV light weakens a little while the absorption in the range of visible light strengthens greatly, indicating the potential for the photocatalytic applications with visible light or natural sunlight.

Accordingly, we tested the photocatalytic activity of these V₂O₅/ZnO composite nanostructures by examining the decay reaction of 2,6-dichlorophenol (2,6-DCP) under the radiation of 420 nm light source. The initial concentration of 2,6-DCP solution was fixed at 10 mg/L with an initial pH at 7.0. The results are shown in Fig. 9(b). It can be observed that the photocatalytic activity of these V₂O₅/ZnO composites is quite good in terms of the degradation of 2,6-DCP. After 6 hours, more than 60% removal of 2,6-DCP was achieved while without the catalysts, less than 5% decomposition of 2,6-DCP could be observed.

It is interesting to note it appears that the annealing temperature has little effect on the photocatalytic performance of the V₂O₅/ZnO composite. The UV-Vis spectra in Fig. 9(a)

Fig. 9. (a) Ultraviolet visible spectra for pure zinc oxide (ZnO) nanowire array, as-deposited vanadium pentoxide (V₂O₅)/ZnO core-shell sample and the V₂O₅/ZnO nano-lollipops array after annealed at 500°C; (b) The concentration of 2,6-dichlorophenol solution as the function of irradiation time by using V₂O₅/ZnO composite nanostructures as catalyst.

show the annealed sample has a relatively high absorption over the visible light range from 500 to 800 nm. The photocatalytic light spectra centered at 420 nm, however, contain mainly photos with wavelength ranging from 400 to 500 nm (data are not shown). Thus the annealing treatment could not demonstrate much influence on the photocatalytic activity of these V₂O₅/ZnO composites. We believe that the annealed samples may have better performance under the visible light at the wavelength longer than 500 nm.

Furthermore, we found that the annealed composite samples are much more stable and strong than those as-deposited samples. The as-deposited V₂O₅ layered samples with amorphous state are easily to flake off in solution from the substrates or from the surface of ZnO nanorods. Thus the as-deposited samples are not suitable for long-term use or re-use, while the annealed V₂O₅/ZnO lollipop-array sample are quite strong and stable after several times tests. The next step we will test the photocatalysis performance for the annealed heterogeneous nano-lollipops V₂O₅/ZnO array under visible light with longer wavelength or even with natural sunlight.

4. CONCLUSIONS

We have reviewed our recent work on ZnO, TiO₂ and V₂O₅

related composite nanostructural materials including the preparation, characterization, microstructure and the possible photocatalytic applications for decomposition of organic chemicals. Combined with hydrothermal growth, magnetron sputtering and thermal treatment, different and complex integrated hierarchical structures at nanoscale and low dimension have been prepared. These processing techniques are relatively easy and cheap, providing a convenient route for various composite nanostructures fabrication in the future. It is interesting to see that these composite samples show much improved optoelectronic properties and superior photocatalytic performances compared to the single oxide or simple layered oxide films.

Transition metal oxides with semiconductor nature attract great attention in recent years due to their special electronic and chemical properties. These oxides can often be made as low dimensional nanostructured composites such as nanowires, nanorods and core-shell structures. These types of nanostructures frequently show much improved and/or special electronic and optical properties because of the coupling effect between the different compounds as well as the enlarged surface areas. The mechanisms of these coupling effects are far from well understood. Research in this area is of both scientific and applied significance.

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