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A novel strategy to prepare ZnO/PbS heterostructured functional nanocomposite utilizing the surface adsorption property of ZnO nanosheets

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ABSTRACT

To avoid the secondary pollution in the regeneration procedure of conventional water treatment methods with absorbents and develop new functional nanocomposite utilizing the surface adsorption property of ZnO, the ZnO nanosheets prepared via a hydrothermal approach were used to adsorb Pb^{2+} in aqueous solution and then hydrothermally treated in aqueous solution containing sulfur source. The products at different stages were characterized with scanning electron micrographs (SEM), energy disperse spectroscopy (EDS), transmission electron microscopy (TEM), selected area electron diffraction (ASED), X-ray diffraction (XRD), Fourier transform infrared spectroscopy spectra (FTIR), photoluminescence (PL) spectra and atomic absorption spectrophotometer. The results proved that the ZnO nanosheets had sorption capacity for Pb^{2+} due to the role of surface hydroxy groups of ZnO. Enhanced diffraction peaks of PbS were observed after the ZnO adsorbing Pb^{2+} hydrothermally treated. TEM result showed that the ZnO/PbS presents in a nanocomposite heterostructure, in which PbS nanoparticles in a form of single crystal structure were attached to the surface of ZnO proved by selected area electron diffraction. PL spectra indicated that the photoluminescence property in a wide light range was dramatically enhanced and some new peaks clearly appeared. Based on these preliminary experimental results, a simple and environment-friendly strategy to remove toxic heavy metal ions in aqueous solution was proposed. Utilizing the doping effects of nanostructured ZnO, a feasible method to produce the ZnO/PbS nanocomposite with wide range light-responsing property was introduced while the efficient removal of toxic heavy metal ions in aqueous solution was carried out. These resulted multifunctional materials have potential to apply to photocatalytic fields, energy-conversion devices and light-emitting/detecting devices.

1. Introduction

Heavy metal ions have been a major preoccupation because of their toxicity towards aquatic life, human beings and the environment. Many pollutants present a public health problem due to their absorption to cause possible accumulation in organisms. They may affect the organisms' structure as well as their functions. Therefore, the treatment technologies of toxic heavy metal ion pollution have received global attention [1–20]. An efficient, easy and environment-friendly approach to treat toxic heavy metal ions has been strongly required.

Several approches have been developed to remove dissolved toxic metal ions from industrial wastewater, such as chemical precipitation, ion exchange, flocculation, reverse osmosis, membrane filtration and adsorption. Among these methods, the adsorption process is the most promising technique to attract much attention of the researchers in this field [3–20].

Nowadays, the advances in nano-scale science and engineering provide great opportunities to develop cost effective and environmentally acceptable water purification processes [21]. Nanosorbents, including organic [22], inorganic [4–6] and organic–inorganic composite sorbents [7,8], will become critical components of industrial and public wastewater purification systems as more progress is made towards the synthesis of functional materials. The applications of the adsorption properties of different forms of carbon, such as carbon molecular sieves, activated carbon fibers, carbon nanotubes and graphite nanofibers, are intensively explored as well as nanoporous materials, including metal oxide nanomaterials with different morphology and dendrimers.

Nanostructured materials have some important physi-chemical properties to make them particularly attractive as separation media for water purification, such as larger surface area than bulk particles, which making them to be able to functionalize with different

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chemical groups to increase the affinity towards target compounds. Several research groups are exploiting the unique properties of nanomaterials to develop high capable and selective sorbents for toxic metal ions [3,21].

The metal oxides contained in water treatment systems as toxic heavy metal ion adsorbents have to be nontoxic, safe and not expensive. As one of the metal oxides fitting this criteria as well as iron oxides, titanium oxides and aluminum oxides [4,11,13,21], ZnO is an important electronic and photonic material due to its wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV. It has great potential to apply as the functional materials for UV detectors, dye-sensitized photovoltaic cells, piezoelectronic devices, hydrogen storage devices, chemical sensors and biosensors [23–27]. Besides some properties similar to TiO_2, ZnO has many unique advantages, such as simple and cheap to prepare, convenient to tailor morphologically, which can be utilized to enhance the removal efficiency of toxic heavy metal ions and develop some advanced functional composites.

There are many studies focusing on ZnO modification to widen the light response or to enhance photocatalytic activities, including modification with noble metal or organic modifiers, doping with N, S, P, transition metal oxides and sulfides [28–42]. Wang et al. [28] prepared ZnO/Au hybrid nanocomposite using wet-chemical synthesis approach to enhance the photocatalytic performance. It is promising to provide a novel class of multifunctional materials possibly apply on energy-conversion devices, biofunctionalized materials, photocatalytic fields and infrared-emitting/detecting devices. Zhang et al. [32] synthesized zinc oxide composite via hybridization with monolayer polyaniline with dramatic photocatalytic activity. Mapa et al. [33] studied on the electronic, optical and dehydrogenation catalytic characters of $(Zn_{1-z}In_z)(O_{1-x}N_x)$ solid solution. Zheng and Wu [34] synthesized nitrogen-doped ZnO nanocrystallites with one-step approach. Shen et al. [37] prepared S-doped ZnO nanostructures and investigated their optical properties. Lee and Yoon [39] synthesized visible light-sensitive ZnO nanostructures. Zeng et al. [40] prepared rare earth doped ZnO hierarchical microspheres, and studied their photoluminescent properties. Wang et al. [41] synthesized highly photocatalytic ZnO/In_2O_3 heteronanostructures by a coprecipitation method. It is promising to prepare nanocomposites with outstanding properties via some simple approaches. If the ZnO dope could be performed while the toxic heavy metal ions in water are removed, the second pollution of regeneration of absorbents might be avoided. At same time some new functional composites might be formed. Herein, preliminary attempts were carried out in this paper.

2. Experimental details

2.1. Materials

Zinc nitrate (Analytical Reagent, i.e. AR, the purity ≥99.0%), thiourea (AR, the purity ≥99.0%), ammonia (CP, the purity is 25%), lead nitrate (AR, the purity ≥99.5%), were commercially available. Deionized filtered water was used in all studies.

2.2. Preparation of ZnO nanosheets

A mixture was prepared by adding equal zinc nitrate and thiourea in water (0.2 M). Then the above-mentioned mixture was transferred into a Telfon-lined stainless steel autoclave. The pH value of reaction solution was controlled within 10–11 with ammonia aqueous solution. The hydrothermal treatment was carried out at 90–95 °C for 3–10 h. The resulted product was washed with deionized water repeatedly 5–6 times.

2.3. Morphology observations with SEM

The scanning electron microscopy (SEM) observation was performed with FEI Quanta 200 (FEI Company). The sample obtained was washed with deionized water, deposited on a glass substrate, dried at room temperature and then sputtered with a thin layer of gold on the surface for the SEM observation, except for the determination of EDS.

2.4. XRD characterization

The powders' X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max 2550 Pe diffraction device, rotating anode X-ray generator working at 40 kV, 300 mA, with Cu Ka monochromatic radiation. The sample was dispersed in aqueous solution, then casted on a glass substrate, dried for 48–96 at room temperature for determination.

2.5. Removal of toxic heavy metal ions

Pb^{2+} was selected as model toxic heavy metal ion for this study. Firstly, the normal Pb^{2+} solution was prepared with lead nitrate. An appropriate amount of ZnO nanosheets (W) synthesized was added in 200 mL normal Pb^{2+} solution and stirred for several hours. The color of the suspension was changed to grey from white, indicating indirectly that the removal effect of ZnO nanosheets is significant. After filtration, the concentration of Pb^{2+} before (C_0) and after (C) treatment with ZnO nanosheets was determined by an atomic absorption spectrophotometer. The removal capacity of ZnO nanosheets (η) is calculated as follows:

$$\eta = \frac{(C_0 - C) \times 200 \times 10^{-3}}{W}$$

where W represents the weight of ZnO nanosheets, C_0 and C represent the concentration of Pb^{2+} before and after treatment with ZnO nanosheets, respectively.

2.6. Treatment of ZnO nanosheets adsorbing Pb^{2+}

The ZnO nanosheets adsorbed Pb^{2+} were transferred into a Telfon-lined stainless steel autoclave. An appropriate of thiourea in water was added. The hydrothermal treatment was carried out at 120 °C for 12 h. The resulting-product was washed with deionized water repeatedly 5–6 times.

2.7. Measurement of FTIR spectra

The FTIR (Fourier transform infrared spectroscopy) spectra were taken with KBr, and recorded on a Bruker IFS 66 V/s Fourier transform infrared spectrometer (Bruker Optics, USA). ZnO or ZnO adsorbing Pb^{2+} and KBr powders were mixed and pressed into a small slice of sample, and then dried at room temperature for determination.

2.8. Morphology observations with TEM

The transmission electron microscopy (TEM) observation and selected area electron diffraction (ASED) were performed with a JEM-2000CX (JEOL Co., Tokyo, Japan) under an acceleration voltage of 160 kV.

2.9. Measurement of photoluminescence spectra

Photoluminescence spectra were recorded on a 970CRT Laser Micro Raman Spectrometer (Shanghai, China) using the

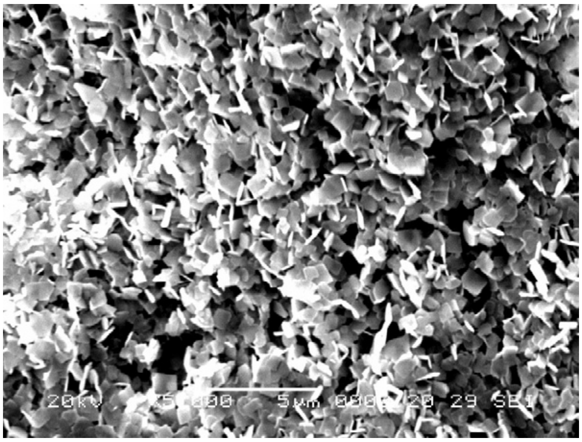

Fig. 1. SEM images of ZnO nanosheets obtained under hydrothermal condition.

325 nm exciton line of the He–Cd laser at room temperature.

3. Results and discussion

A typical SEM image of the morphology of the ZnO nanosheet structure obtained under hydrothermal condition is shown in Fig. 1.

Most nanosheets like a square with sides of about 1 μm, the thickness is in nano-scale. In comparison with conventional ZnO bulk structures, this morphology can provide much more effective surface area for absorption.

The surface of the ZnO nanosheets contains abundant hydroxy groups as shown in Fig. 2A, the shoulder band at wavenumber of 3200–3650 cm^{-1} is corresponding to stretching due to O–H groups. These active groups can react with heavy metal ions in aqueous solution, leading to a large number of adsorption of heavy metal ion. Good removal result was obtained using Pb^{2+} as a model of toxic heavy metal ions. The removal capacity is 6.7 $mg\,g^{-1}$, much higher than the similar results previously reported [21]. It was observed that the color of the ZnO nanosheets was changing from white to grey when adsorbing Pb^{2+}. Fig. 2 shows significantly different spectra of ZnO, Pb^{2+} adsorped ZnO and resulted products after hydrothermal treatment with sulfur-containing source. More adsorption bands (887, 929, 1247, 2190, 2234, 2796 cm^{-1}) and

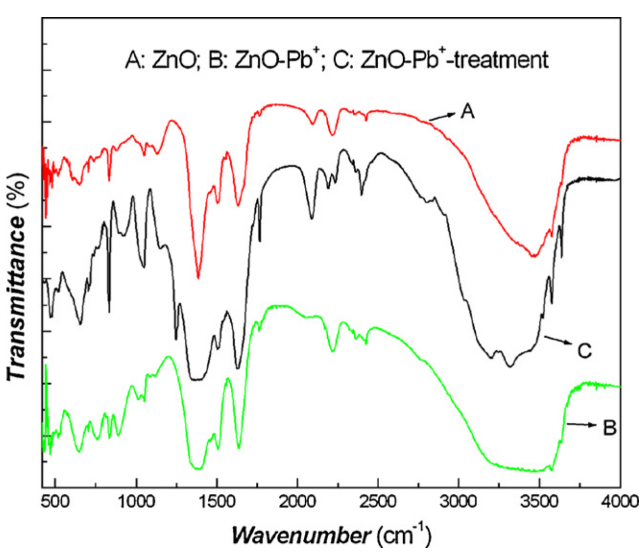

Fig. 2. FTIR of ZnO nanosheets before and after adsorption of Pb^{2+}.

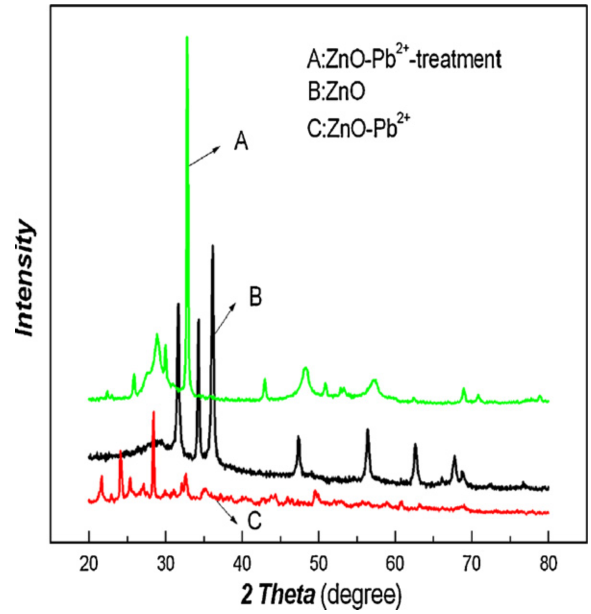

Fig. 3. The XRD result of ZnO after hydrothermal treatment.

widening adsorption bands (2920–3680, 1339–1431 cm^{-1}) appear in the FTIR of ZnO absorbing Pb^{2+}. After hydrothermal treatment with sulfur-containing source, some new bands (753, 887, 1012, 2218, 2770–3708 cm^{-1}) also appear in the FTIR of ZnO composite. This illustrates that the adsorption approach and post-treatment of ZnO nanocomposite increase the infrared adsorption, which would widen the light response properties.

Fig. 3C shows that the Pb^{2+} adsorption mainly exists in a form of lead oxide as well as a little lead sulfide. The diffraction peaks of 2θ of PbS are appeared in 25.43, 30.10, 43.69, 53.02, 68.63, respectively. This is because some sulfur-containing source used for ZnO nanosheet preparation is still remaining.

PbS is a good photoelectron material in near-infrared band, so the combination with PbS may change the photoelectronic property of ZnO. The ZnO nanosheets adsorbing Pb^{2+} were put into a Telfon-lined stainless steel autoclave containing sulfur source to treat at 120 °C for 12 h. The diffraction of PbS increased clearly after the hydrothermal treatment as shown in Fig. 3A. Strong diffraction peaks of 2θ of PbS were clearly appeared in 25.84, 43.08, 53.22, 62.34, 68.83 and 71.06. This indicates that it is feasible to remove toxic heavy metal ions utilizing the doping-effect of ZnO nanocomposite while avoiding the secondary pollution during regeneration of conventional absorption treatments. This phenomenon is very interesting and deserves further investigation.

The XRD of ZnO, ZnO absorbing Pb^{2+} and the products after hydrothermal treatment indirectly illustrates the significant adsorption ability of the ZnO nanosheets, while proving PbO_2 and PbS are the main presenting forms after adsorption. As shown in Fig. 3, though the presence of strong diffraction peak of PbS in the composite, the dominating component of the composite is still ZnO, which can be proved by the EDS results shown in Fig. 4.

It is hardly to observe the peaks of Pb in Fig. 4, which illustrates that ZnO is the main component of composite and PbS is few.

As important functional materials, PbO_2 and PbS can be utilized to avoid disposing to cause the secondary pollution. The idea is also suitable for removing other toxic heavy metal ions, such as Cd^{2+}. Therefore, the nano/micro-structured metal oxides have potential to be functional materials utilizing their active surface and interface to capture harmful heavy metal ions.

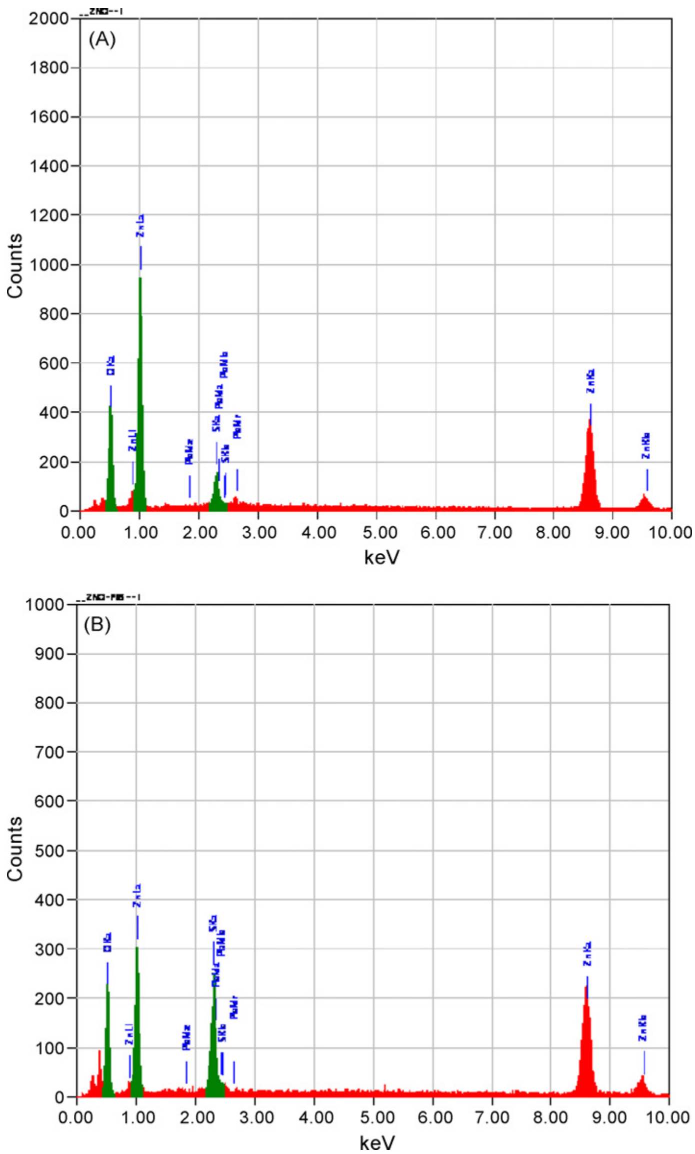

Fig. 4. Results of EDS between ZnO and ZnO/PbS heterostructured nanocomposite (A: ZnO; B: ZnO/PbS heterostructured nanocomposite).

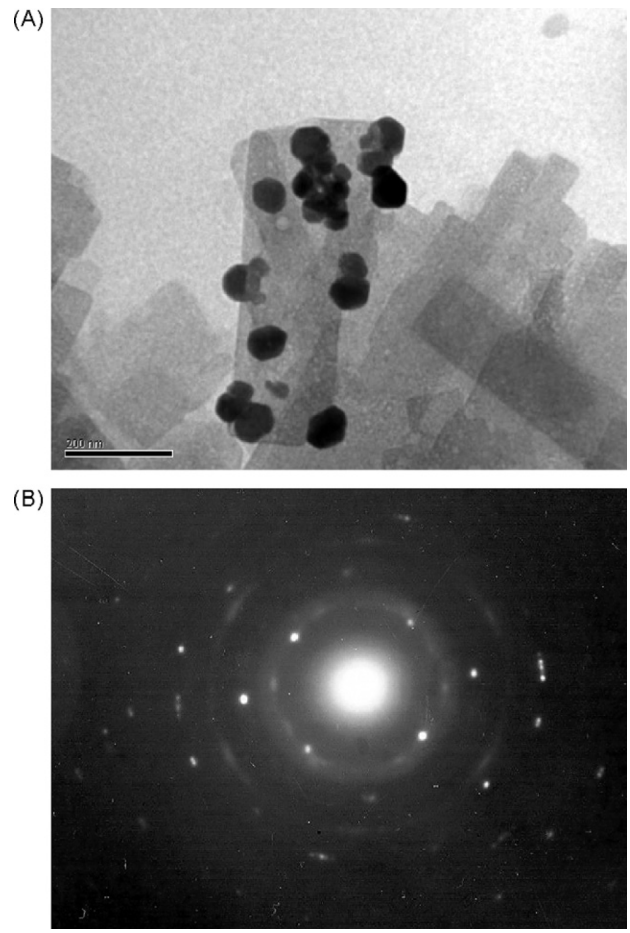

Fig. 5. TEM of ZnO/PbS heterostructured nanocomposite (A: TEM of ZnO/PbS heterostructured nanocomposite; B: images of selected area electron diffraction of nanoparticles attached to the surface of ZnO nanosheets).

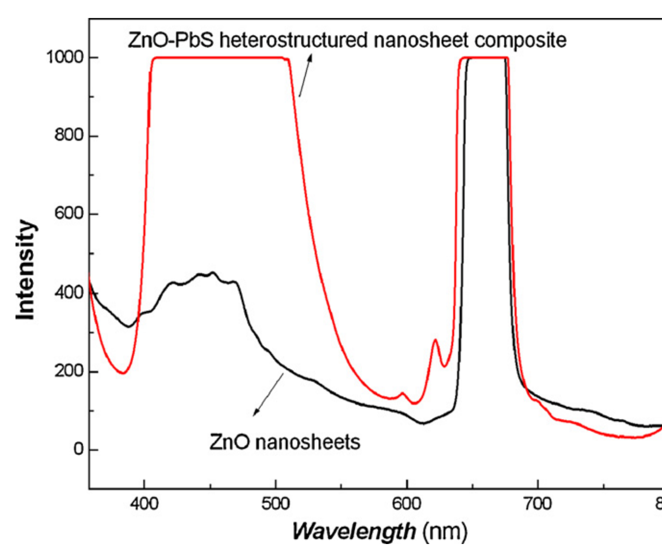

Fig. 6. Photoluminescence spectra of ZnO and ZnO/PbS heterostructured nanosheet composite.

The TEM of the ZnO/PbS heterostructured nanocomposite as the resulted products is shown in Fig. 5. PbS nanoparticles are attached to the surface of ZnO, which is proved by selected area electron diffraction (ASED). The results of selected area electron diffraction (ASED) showed that the particles on nanosheets are single crystal of PbS. Due to PbS possessing good photoelectron properties in near-infrared band [43], it is expected to develop a new ZnO nanocomposite which responding in both visible and near-infrared light ranges [44–46].

As a typical light-emitting material, the light-emitting properties of ZnO might change due to PbS attachment. In order to examine the effect of attached PbS to ZnO, the photoluminescence spectra of both the ZnO nanosheets and the ZnO/PbS nanocomposite are shown in Fig. 6.

In comparison with ZnO nanosheets, a dramatic improvement of photoluminescence property due to the PbS attachment is observed in a wide light range (378–635 nm). Particularly, two peaks around 596 and 622 nm clearly appear. A small amount of PbS endows ZnO with some new functional properties. It is expected to apply to photocatalysts and solar cells.

4. Conclusions

ZnO nanosheets were prepared via a hydrothermal approach. The ZnO nanosheets show good sorption capacities for Pb^{2+} due to the surface hydroxy groups, while forming new functional nanocomposites to avoid the secondary pollution of regeneration procedure caused by conventional water treatment methods with absorbents. It is possible to provide a simple and environment-friendly method to prepare ZnO nanocomposite with wide range light response while removing the toxic heavy metal ions in aqueous solution. This idea is also suitable for other nanostructured metal oxides utilized to remove toxic heavy metal ions while forming some new functional materials for photocatalyst and solar cell applications.

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