

Effects of noble metal modification on surface oxygen composition, charge separation and photocatalytic activity of ZnO nanoparticles

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Abstract

In this paper, ZnO nanoparticles were modified by depositing different amount of noble metal Ag or Pd on their surfaces with a photoreduction method. The as-prepared ZnO samples were principally characterized by X-ray photoelectron spectroscopy (XPS) and surface photovoltage spectroscopy (SPS), and their activity was evaluated by a photocatalytic degradation reaction of phenol solution. The effects of noble metal modification on surface composition, photoinduced charge transfer behavior and photocatalytic activity of ZnO samples were mainly investigated. The results show that, after an appropriate amount of Ag or Pd is deposited on the ZnO surfaces, the O 1s XPS spectrum shifts to higher binding energy, indicating that the content of surface hydroxyl oxygen (O_H) increases. And the SPS intensity greatly decreases, indicating that the photoinduced electrons are easily captured by adsorbed oxygen via noble metal clusters so that the recombination of photoinduced electron and hole pairs is effectively inhibited. These are responsible for the enhancement in the photocatalytic activity. Moreover, the effects of Pd modification on photocatalytic activity is greater than that of Ag, which can be explained by means of surface hydroxyl content as well as charge separation situation.

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1. Introduction

Recently, nanosized semiconductor materials have attracted increasing attentions to a wide range of possible applications such as solar energy cells as photoelectric energy conversion materials [1–3] and water or air purification as friendly environmental photocatalysts [4–6]. The foundations and significant applications of semiconductor photocatalytic oxidation have been extensively documented [7–10]. The schematic diagram of photocatalytic reaction on an illuminated semiconductor particle is showed in Fig. 1 [7,9]. When a semiconductor particle is irradiated by the light with equal to or higher than the bandgap energy, an electron from the valence band (VB) is excited to the conduction band (CB) with simultaneous generation of a hole (h^+)

in the VB. The e_{cb}^- and h_{vb}^+ can recombine on the surface or in the bulk of the particle in a few nanoseconds, or can be separated under the built-in electric field to transfer to different positions on the surfaces, further being trapped to react with donor or acceptor species adsorbed on or close to the surfaces. The separation and recombination of photoinduced charge carriers are in competition process, and the photocatalytic reaction is effective only when photoinduced electrons and holes are trapped on the surfaces, respectively. Thus, subsequent redox reactions can be initiated. In general, during the photocatalytic reactions, photoinduced holes can be easily captured by chemisorbed surface hydroxyl, while the electrons can be trapped by adsorbed O_2 . Therefore, the surface oxygen species can play important roles in photocatalytic reactions. To further improve activity of semiconductor photocatalysts, noble metal deposit is taken as an effective modification method [10]. Among many noble metals, Pt is often employed [10,11]. It is known that the noble metal modification can improve the photocatalytic activity. However,

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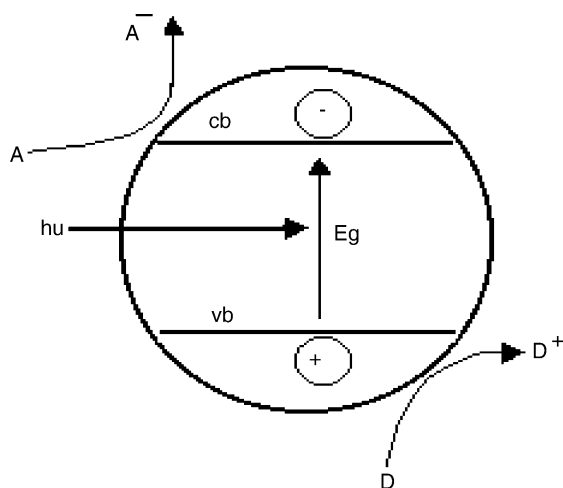


Fig. 1. Schematic diagram of photocatalytic reaction on an illuminated semiconductor particle.

few papers are involved with modification mechanisms of noble metal deposit from the point of surface oxygen composition and charge transfer, and a comparative study of different noble metal modifications is seldom reported. Moreover, Pt is too expensive, while Ag and Pd are relatively cheap. Thus, Ag [12] and Pd [13] modification is of great significance for industrial practice.

X-ray photoelectron spectroscopy (XPS) is a kind of surface testing technique, with high sensitivity, which can provide some important information about surface compositions and chemical states [14,15]. The surface photovoltage (SPV) method with much higher sensitivity is a well-established contactless and nondestructive technique for semiconductor characterization, which relies on analyzing photoinduced changes in the surface photovoltage. The surface photovoltage spectroscopy (SPS) is an effective tool to investigate the photophysical process of excited states, and can disclose some information about charge transfer in photo-stimulated surface interaction, dye sensitization process, and photocatalysis [16–18].

ZnO is close to being one of ideal photocatalysts, due to being relatively cheap, nontoxicity and its holes of strong oxidizing power. ZnO has been proved to be very active in the photocatalytic oxidation of different pollutants [19,20]. Recently, we have reported that Pd deposit could obviously improve the activity of ZnO nanoparticles during the photocatalytic degradation of gas phase $n\text{-C}_7\text{H}_{16}$ [21]. In this work, the modification mechanisms of noble metal deposit were disclosed from the point of surface oxygen composition and charge separation mainly by means of XPS and SPS methods, and a comparative study of Ag and Pd modifications was emphasized. This paper should be valuable for the practice application of ZnO nanoparticles in the field of environmental photocatalysis as well as photovoltaic conversion and energy storage. And, it also illustrates that the XPS and SPS techniques are of great significance to the research on the surface oxygen composition and charge transfer behavior, which can help understanding the modification mechanisms.

2. Experimental

All substances used in this study were analytical grade and were used without further purification. Deionized water was used in all experiments.

2.1. Preparation of unmodified and modified ZnO nanoparticles

The synthesis procedure of Ag or Pd modified ZnO nanoparticles consisted of two major steps: (i) Preparation of ZnO nanoparticles, which was described in previous papers in details [15,22]. ZnO nanoparticles were prepared by calcining the precursor, zinc carbonate hydroxide, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, at 320°C . Thus, ZnO particle with the size of about 13 nm could be obtained; (ii) Ag or Pd deposited ZnO nanoparticles, which was also described in previous papers in details [21]. The noble metal deposit was performed by a photoreduction method as following. Firstly, 6.91×10^{-3} M of AgNO_3 or 7.06×10^{-3} M of PdCl_2 solution, both containing 1.25% CH_3COOH , were prepared, respectively. The CH_3COOH was regarded as sacrificial organic substance to capture photoinduced holes so as to improve the efficiency for utilizing photoinduced electrons. Then, 20 ml of a mixture consisting of desired amount of AgNO_3 or PdCl_2 solution and CH_3COOH solution was added to a beaker containing 0.5 g of ZnO nanoparticles, which was ultrasonicated for 10 min. Subsequently, the mixture was transferred into a cylindrical quartz tube photoreactor of 300 ml placed horizontally with two mouths at its two ends. The photoreactor was blown with ultrapure N_2 gas for 5 min in order to drive out O_2 gas within the reactor after being sealed. Finally, the photoreactor was submitted to a UV irradiation treatment by a 400 W high pressure mercury lamp ($\lambda_{\text{max}} = 365$ nm) for 6 h. Thus, ZnO nanoparticles with different amount of Ag or Pd could be obtained by centrifugating and rinsing with water and drying at 80°C .

In addition, the concentration of Ag or Pd in the mixture treated by UV light for 6 h was tested by an inductively coupled plasma-atomic emission spectrometry (a PE ICP-AES/1000), demonstrating that the deposit rate of noble metal was more than 90% in our experiments.

2.2. Characterization of the samples

The samples were analyzed by X-ray diffraction (XRD) using a Rigaku D/MAX-rA powder diffractometer with a nickel-filtered $\text{Cu K}\alpha$ radiation source, a scanning rate of $4^\circ/\text{min}$. For XRD measurements, nanoparticles were placed on a glass sample holder. The crystal phase and crystallite size were determined from the X-ray diffraction patterns. The size and morphology of the samples were observed with a JEOL-1200EX transition electric microscopy (TEM). Dispersion of the products in ethanol was conducted in an ultrasonic bath for half an hour. A drop was taken out and put on a copper mesh coated with a carbon film for a moment. Then, the TEM measurement was performed. The surface composition of the samples was examined by XPS using a VG ESCALAB Mg $\text{K}\alpha$ X-ray source. The pressure was maintained at 6.3×10^{-7} Pa.

The binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). Relative quantitative analysis was carried out using the sensitivity factors supplied by the instrument. SPS measurement of the samples was carried out with a home-built apparatus that had been described elsewhere [16,23]. Monochromatic light was obtained by passing light from a 500 W Xenon lamp (CHF XQ500W, Global xenon lamp power made in China) through a double-prism monochromator (Hilger and Watts, D 300 made in England). A lock-in amplifier (SR540, made in USA), synchronized with a light chopper (SR540, made in USA), was employed to amplify the photovoltage signal. It was performed by a photovoltage cell, mainly consisting of two ITO quartz glass electrodes. For a powder experiment, the powder sample was sandwiched between two ITO quartz glass electrodes. The photovoltage generation arises from the creation of electron–hole pairs, followed by the separation under a built-in electric field (the space-charge layer). The difference between the surface potential barrier in the light and that in the dark is the SPS signal.

2.3. Evaluation of photocatalytic activity of the samples

The photocatalytic activity of ZnO samples was tested using phenol solution [24]. The degradation intermediates were not determined. The experiments were carried out in a 500 ml quartz photochemical reactor, open to air, having the shape of a vertical cylinder. The light was provided from a side of the reactor by a 350 W high pressure Hg lamp without filter, which was placed at about 20 cm from the reactor, its strongest emission light is with wavelength of 365 nm. The total treated volume was 300 mL, the initial concentration of phenol was equal to 0.20 mmol/L. Phenol solution was continuously stirred with a magnetic stirrer. The solution was first stirred for 20 min to reach the adsorption equilibrium after 0.3 g of ZnO samples was added into the reaction system, then began to illuminate. The phenol concentrations at different times were measured using the colorimetric method of 4-aminoantipyrine with a model 721 spectrophotometer at the wavelength of 510 nm after centrifugation.

3. Results and discussion

3.1. Structure and morphology

X-ray diffraction is used to investigate the changes of phase structure and crystallite size of the as-prepared ZnO powders before and after noble metal deposit, the unmodified and 0.5 wt.% noble metal modified ZnO samples are examined. Fig. 2 shows the XRD patterns of unmodified, Ag and Pd modified ZnO, which demonstrates that the all ZnO samples are with wurtzite structure attached to hexagonal crystal system [15]. The average crystallite sizes of the samples, evaluated by the Scherrer formular [25], are about 13 nm, indicating that the ZnO crystallinity does not change a little before and after noble metal modification. It should be pointed that the substance phase of noble metal cannot be found, which is possibly because of too less content of noble metal. Moreover, it possibly indicates that

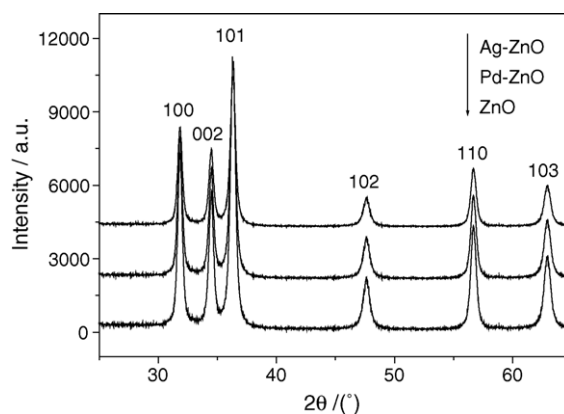


Fig. 2. XRD patterns of unmodified and modified ZnO nanoparticles.

noble metal is dispersed uniformly onto the surfaces of ZnO nanoparticles.

TEM is used to observe the particle size and morphology of the samples. Fig. 3 shows the TEM photographs of the unmodified and 0.5 wt.% noble metal modified ZnO samples. From the TEM micrographs, it can be seen that noble metal Ag and Pd are deposited uniformly on ZnO surfaces, especially much uniformly for Pd deposit, and they both exhibit much black compared with ZnO. The average particle size of unmodified ZnO is about 13 nm, being equal to its average crystallite size, which demonstrates that the unmodified ZnO nanoparticles are easily dispersed. However, the average particle size of noble metal modified ZnO is about 25 nm, being larger than its average crystallite size by the difference of 12 nm, demonstrating that ZnO nanoparticles easily aggregate during the process of photoreduction.

In addition, it has been found by TEM observations that, when the deposited noble metal was Pt, the Pt particles formed clusters with the mean size of 2 nm on TiO₂ surfaces [26]. However, from Fig. 3, Ag or Pd clusters cannot be differentiated, which is possibly attributed to the lower resolving power of the used TEM apparatus. At fact, Ag or Pd clusters can be observed faintly during the TEM testing process. Moreover, with a Pt dose of 10 wt.%, only 6% of the semiconductor surface area is covered, demonstrating that a large surface area of the semiconductor is not still covered by the noble metal [26].

3.2. Surface composition and chemical states

It is well known that material surface composition and chemical states are very important during the process of catalytic reaction since they can strongly affect the catalytic activity. The surface composition and chemical states can be determined by means of XPS spectrum according to the characterizing binding energies of different elements on material surfaces [15]. The XPS spectra of unmodified and 0.5 wt.% noble metal modified ZnO were obtained. Fig. 4 shows the Zn 2p XPS spectra. The peak position of Zn 2p_{3/2} XPS of unmodified ZnO is at about 1021.9 eV, and the Zn 2p_{3/2} XPS peak of modified ZnO has nearly the same position as that of unmodified ZnO. Moreover, the all Zn 2p_{3/2} XPS peaks are sharp. Thus, it can be confirmed

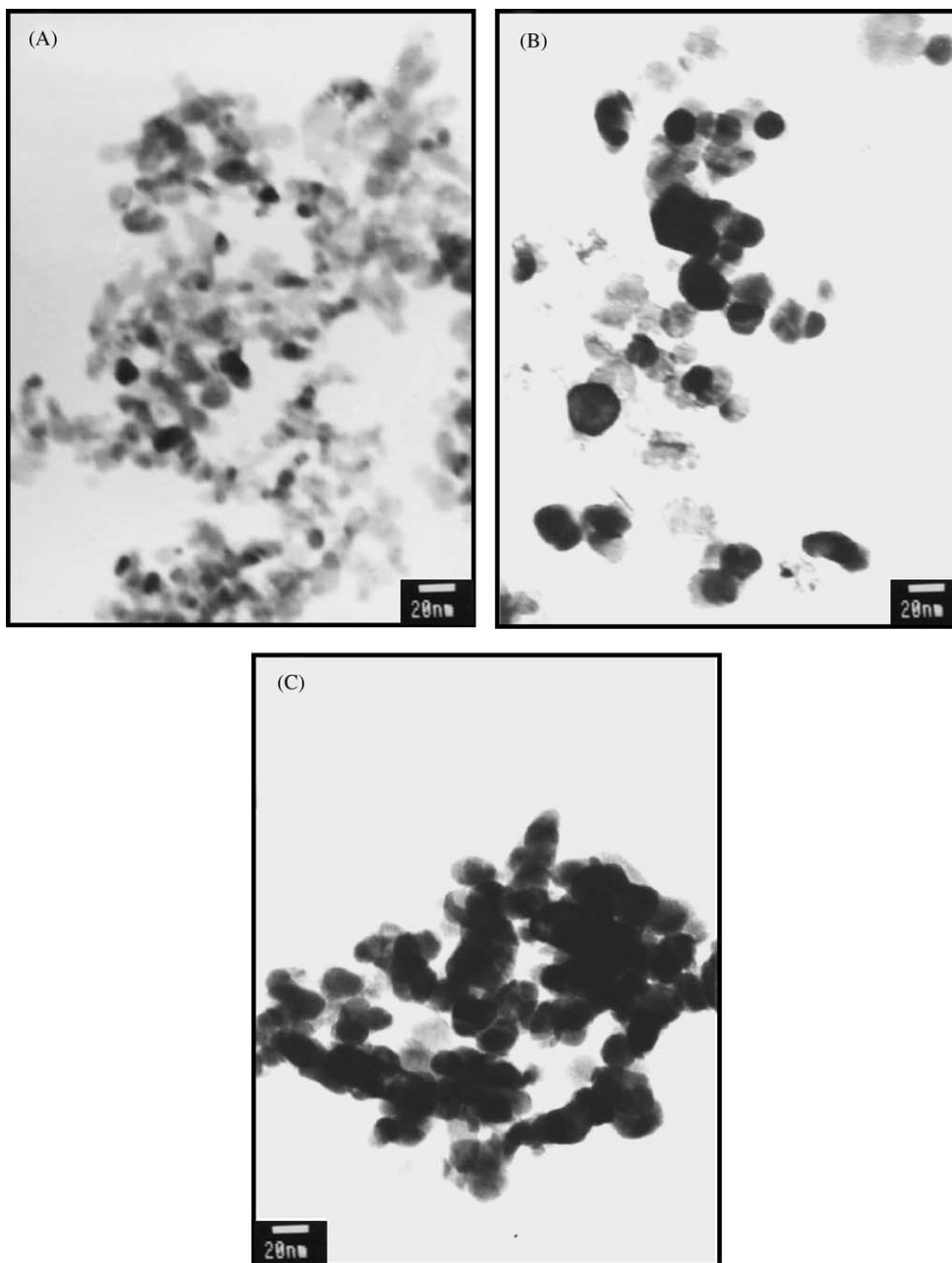


Fig. 3. TEM images of unmodified and modified ZnO nanoparticles: (A) ZnO; (B) Ag-ZnO; (C) Pd-ZnO.

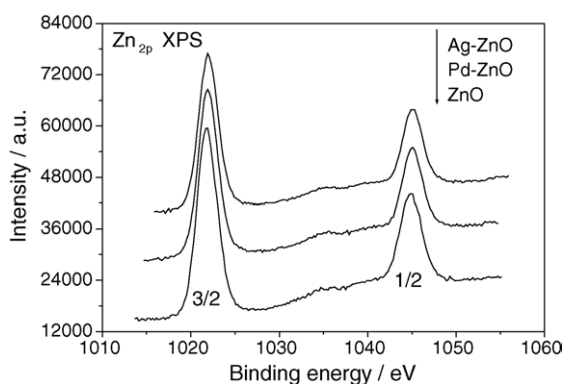


Fig. 4. Zn 2p XPS spectra of unmodified and modified ZnO nanoparticles.

that Zn element exists mainly as the form of Zn^{2+} chemical states on sample surfaces. Fig. 5 shows the Ag 3d and Pd 3d XPS spectra, the XPS peaks both are a little weak, which is possibly because of low content of noble metal. The XPS peak position of Ag 3d_{5/2} is at about 368.1 eV, demonstrating that there is mainly zero-valence Ag [14]. In general, the binding energy of zero-valence metallic atom shows smaller than that of metal cation. However, Ag is exceptionable [14]. According to the binding energy handbook of the XPS apparatus, the binding energy of Ag^+ and Ag^0 is about 367.8 and 368.1 eV, respectively, while the binding energy of Pd^{2+} and Pd^0 is about 336.4 and 335.3 eV, respectively. From Fig. 5, it can be seen that the binding energy of Pd 3d_{5/2} is 335.4 eV, indicating that Pd exists mainly as the form of zero-valence Pd on ZnO surfaces. There-

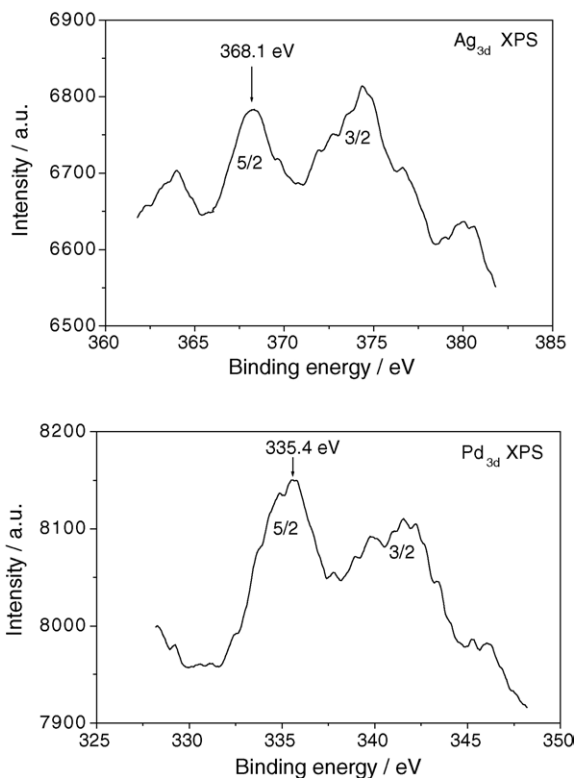


Fig. 5. XPS spectra of Ag 3d and Pd 3d of modified ZnO nanoparticles.

fore, the zero-valence noble metal atoms can easily be deposited on semiconductor particle surfaces via a photoreduction method. Fig. 6 shows the O 1s XPS spectra. It can be seen that the O 1s XPS peaks shift to higher binding energy after depositing noble metal, especially much markedly for Pd deposition. Moreover, the all O 1s XPS are wide and asymmetric, demonstrating that there are at least two kinds of oxygen species according to the binding energy range, including crystal lattice oxygen (O_L) and hydroxyl oxygen (O_H) with increasing binding energy. The O 1s XPS spectrum is fitted to two kinds of chemical states with the Origin software by Gaussian rule. The O_L XPS is attributed to the contribution of Zn–O in ZnO crystal lattice, and its peak position is at about 530.0 eV. The O_H XPS is closely related to the hydroxyl groups resulting from the chemisorbed water, and its peak position is at about 531.5 eV. Although some H_2O and O_2

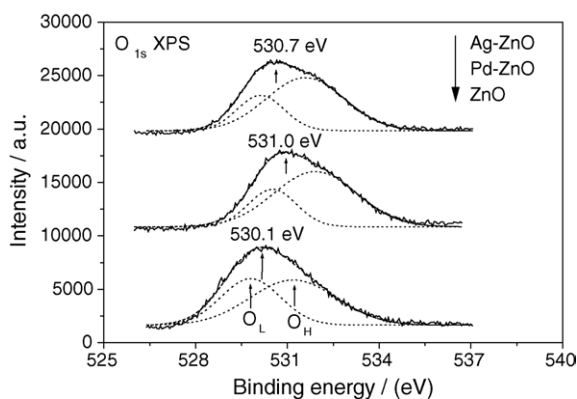


Fig. 6. O 1s XPS spectra of unmodified and modified ZnO nanoparticles.

Table 1

XPS data and the atomic number ratio of Zn to O of different ZnO samples

ZnO sample	E_b of Zn 2p ₃ (eV)	E_b of O 1s (eV)	Atomic number ratio of Zn to O
ZnO	1021.9	530.1	0.65
Ag–ZnO	1022.0	530.7	0.60
Pd–ZnO	1021.9	531.0	0.57

are easily adsorbed on the sample surfaces during preparation process, the physically adsorbed H_2O and O_2 are easily desorbed under the ultrahigh vacuum condition of the XPS system. For a careful XPS analysis, the relatively quantitative analysis is performed according to the following equation:

$$\frac{N_{E1}}{N_{E2}} = \frac{A_{E1}/S_{E1}}{A_{E2}/S_{E2}},$$

where N is the atomic number, A_E the XPS peak area of a kind of element, S the elemental sensitivity factor. Table 1 lists the XPS data and the atomic number ratio of Zn to O. The atomic number ratio of Zn to O decreases after Ag or Pd is deposited, which demonstrates that the total content of surface oxygen species of noble metal modified ZnO is larger than that of unmodified ZnO. Table 2 shows the results of curve fitting of O 1s XPS spectra of different ZnO samples, it can be seen that the surface O_H percentage increases after Ag or Pd is deposited. Thus, the increase in the content of surface total oxygen species and in the percentage of O_H species is responsible for the O 1s binding energy shift to higher edge, especially for Pd deposit. Moreover, the increase in surface O_H content can facilitate photocatalytic reactions since the OH^- groups can easily capture photoinduced holes to produce $\bullet OH$ free radical, which is active groups to oxidize organic substances [9,10]. Therefore, it can be predicted that the photocatalytic activity of ZnO nanoparticles can be enhanced due to the increase in the content of surface hydroxyl group after noble metal deposit, and the effects of Pd deposit are larger than that of Ag deposit on the condition of 0.5 wt.% noble metal.

3.3. Surface photoinduced charge transfer

It is well known that the activity of semiconductor photocatalyst is largely based on the electronic structure and surface or interface charge transfer behavior. Thus, the SPS is used to investigate the effects of noble metal deposit on surface charge

Table 2

Results of curve fitting of O 1s XPS spectra of different ZnO samples

ZnO sample		O_L (Zn–O)	O_H (OH)
ZnO	E_b (eV)	529.8	531.2
	FWHM	2.0	2.8
	r_i (%)	41.4	58.6
Ag–ZnO	E_b (eV)	530.1	531.6
	FWHM	1.5	2.5
	r_i (%)	29.6	70.4
Pd–ZnO	E_b (eV)	530.5	532.0
	FWHM	1.5	2.6
	r_i (%)	28.2	71.8

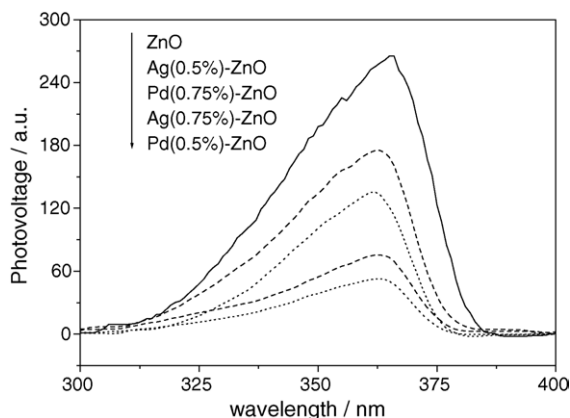


Fig. 7. SPS responses of unmodified and modified ZnO nanoparticles.

transfer. Fig. 7 shows the SPS responses of the unmodified and modified ZnO samples. It can be found that the SPS peak position of ZnO nanoparticles is at about 360 nm with the response threshold of 380 nm, demonstrating that the SPS response of ZnO nanoparticles shifts to the blue due to the quantum size effect since the response threshold of bulk ZnO is 390 nm according to the electronic structure of ZnO. The strong SPS response can be attributed to the electron transitions from the valence band to conduction band ($O_{2p} \rightarrow Zn_{3d}$) [15]. ZnO is a kind of typical n-type semiconductor, its surface band is upward-bent in air, indicating that its built-in electric field direction is from the inner to the outer. Then, the photoinduced holes easily transfer to the particle surfaces, while the photoinduced electrons easily move to the particle inners. The SPV difference before and after illumination, named as SPS signal, can occur. It can also be seen that the SPS response of ZnO nanoparticles becomes weak after the noble metal Ag or Pd is deposited on their surfaces. When a noble metal is deposited on the surfaces of an n-type semiconductor particles, the Schottky barrier at the interface between the noble metal and the semiconductor can occur by charge carrier redistribution since the Fermi level of the n-type semiconductor is higher than that of the noble metal [10]. In general, the Schottky barrier can effectively trap photoinduced electrons to migrate to the surfaces, which not only can effectively inhibit the recombination of photoinduced electrons and holes but also can result into the decrease in the SPV signal. Therefore, the Ag or Pd deposit can make the SPS response decrease, meanwhile the separation rate of photoinduced electron and hole pairs is improved.

Moreover, the amount of deposited noble metal can also strongly affect the transfer behavior of photoinduced charge carriers. From Fig. 7, it can be seen that the SPS response of Ag–ZnO nanoparticles with 0.75 wt.% Ag is weaker than that of 0.5 wt.% Ag, while the SPS response of Pd–ZnO nanoparticles with 0.75 wt.% Pd is higher than that of 0.5 wt.% Pd. In other words, if the amount of deposited noble metal is appropriate, the SPS signal becomes weaker. On the contrary, if the amount of deposited noble metal is excess, the SPS signal increases inversely. This can be explained from the point of the electronic energy level [21,27]. Fig. 8 shows the simplified diagram of electronic energy level of ZnO conduction band (CB) and valence

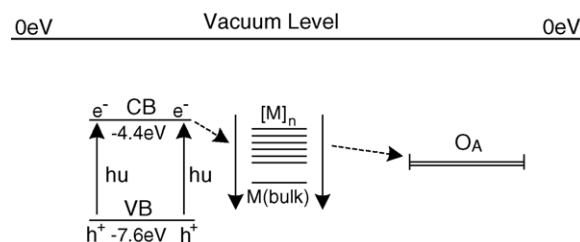


Fig. 8. Simplified diagram of electronic energy level of ZnO conduction (CB) and valence (VB) band, noble metal clusters ($[M]_n$) and O_2 adsorbed on ZnO surfaces (O_A).

band (VB) noble metal clusters ($[M]_n$) and O_2 (O_A) adsorbed on ZnO surfaces. The electronic energy level of noble metal clusters can change to a certain degree with changing noble metal amount due to the quantum size effect, namely, the lower the noble metal amount, the higher the electronic energy level. Thus, if an appropriate amount of noble metal is deposited, the electronic energy level of $[M]_n$ is lower than that of the CB and higher than that of the O_A so that the O_A can easily capture the photoinduced electrons to produce O_2^{\bullet} via noble metal clusters. This is favorable for photocatalytic reactions and results into the decrease in the SPS intensity. However, if too much amount of noble metal is deposited, the electronic energy level of $[M]_n$ will decline to or even lower than that of the O_A . Thus, it is difficult for the adsorbed O_2 to capture the photoinduced electrons via noble metal clusters, and the deposited noble metal will become the recombination centers of photoinduced electron and hole pairs, meanwhile the SPS signal will possibly increase inversely. In addition, the photoinduced electrons will be captured directly by the O_A according to their energy level. However, the step that the O_A captures the photoinduced electrons is actually very slow so as to greatly influence the photocatalytic reaction [28]. The above discussions demonstrate that the appropriate amount of noble metal deposit can promote the O_A capturing photoinduced electrons. Therefore, it can be suggested that the Ag or Pd deposit can make the SPS response decrease, and the weaker the SPS response, the higher is the separation rate of photoinduced electron and hole pairs, the higher will be the photocatalytic performance of noble metal deposited semiconductor.

3.4. Measurements of photocatalytic activity

The activity of ZnO samples can be evaluated by the photocatalytic oxidation reaction of phenol solution. The experiment results show that the phenol concentration changes a little after irradiation for 3 h in the absence of the photocatalyst, indicating that the direct photolysis of phenol can slightly take place in our experimental condition, and the photolysis can be neglected compared with the photocatalysis. Fig. 9 reflects the effects of noble metal deposition on the photodegradation process. It can be seen that the photocatalytic activity of ZnO nanoparticles can be greatly improved by modifying an appropriate amount of noble metal Ag or Pd, which is in good agreement with the above XPS and SPS results. XPS results demonstrate that the noble metal modification can result into the increase in the surface hydroxyl content. The surface hydroxyl groups easily capture

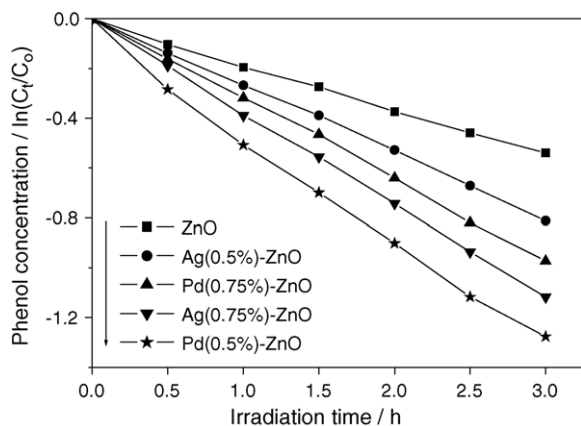


Fig. 9. Evolution curves of photocatalytic degradation phenol on the unmodified and modified ZnO nanoparticles.

photoinduced holes very much to produce $\bullet\text{OH}$ free radicals, which can greatly promote the oxidation of organic substances [9,10]. The SPS results indicate that the noble metal modification can effectively inhibit the recombination of photoinduced electron and hole pairs. And, it can make the O_A capture much easily photoinduced electrons via noble metal clusters to produce $\bullet\text{O}_2$ groups. Therefore, the noble metal modification can enhance the activity of ZnO nanoparticle photocatalysts. From Figs. 7 and 9, it can be found that the orders of photocatalytic activity are opposite to that of SPS intensity, namely, the lower the SPS signal, the higher the photocatalytic activity, which is because that the lower SPS signal corresponds to the higher separation rate of charge carriers. Moreover, according to the XPS results, the content of surface hydroxyl of 0.5% Pd deposited ZnO is larger than that of 0.5% Ag deposited ZnO, which is responsible for the experiment result that 0.5% Pd deposited ZnO exhibits higher activity than 0.5% Ag deposited ZnO. In addition, Fig. 9 demonstrates that the photocatalytic degradation phenol reaction follows the pseudo-first-order kinetics with respect to phenol concentration.

Fig. 10 shows the effects of deposited noble metal amount on the photocatalytic activity of ZnO nanoparticles. It can be seen that the optimized amount of deposited Ag and Pd is 0.75 wt.%

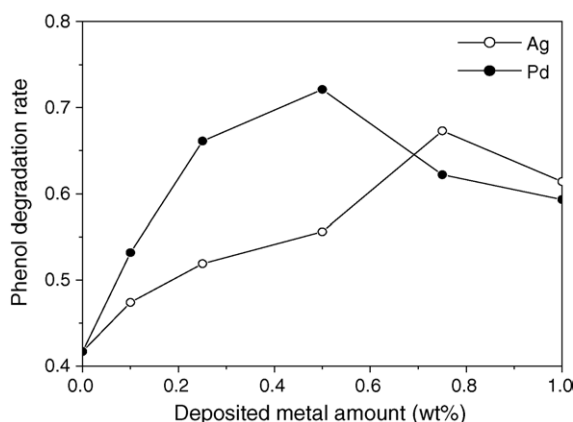


Fig. 10. Photocatalytic degradation rate of phenol on different amount of noble metal Ag or Pd modified ZnO nanoparticles.

and 0.5 wt.%, respectively. If the amount of deposited noble metal is larger than its optimized value, the activity of ZnO nanoparticles begins to go down inversely. This can be explained by the note that an appropriate amount of noble metal may become the center for trapping photoelectrons, while an excess amount of noble metal may become the center for recombining photoinduced electron and hole pairs [10].

4. Conclusions

On the basis of our researches, the following conclusions can be drawn. An appropriate amount of noble metal Ag or Pd modification can greatly enhance the photocatalytic activity of ZnO nanoparticles for degrading phenol solution, which can be explained by means of XPS and SPS measurements. The increase in the surface hydroxyl content and charge carrier separation rate is mainly responsible for the increase in the photocatalytic activity. Moreover, the noble metal modification can promote the adsorbed O_2 capturing photoinduced electrons to produce $\bullet\text{O}_2$ so that the activity is improved. It can also be suggested, for noble metal modified ZnO nanoparticle photocatalysts, the weaker the SPS signal, the higher the activity. In addition, for 0.5 wt.% noble metal deposited ZnO samples, the effects of Pd deposit are greater than that of Ag deposit, which is closely related to the increases in the surface hydroxyl content as well as charge separation rate. The photocatalytic degradation phenol reactions on the unmodified and modified ZnO nanoparticles follow the pseudo-first-order kinetics.

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