Synthesis, surface modification and photocatalytic property of ZnO nanoparticles


Abstract

ZnO nanoparticles were synthesized by calcination of precursor prepared by the precipitation method. Polystyrene was grafted onto the surface of ZnO nanoparticles to improve the dispersion of the particles and to reduce their photocatalytic activity. The obtained particles were characterized by Fourier transform infrared spectroscopy, X-ray powder diffraction, and transmission electron microscopy. The photocatalytic activity of bare and modified ZnO nanoparticles was studied. The influence of surface modification on the photocatalytic degradation of methyl orange has been analyzed. The composition of residual solution was determined through high performance liquid chromatography. Experimental results show that well dispersed ZnO nanoparticles were obtained after surface modification. ZnO nanoparticles possess high photocatalytic activity, whereas the photocatalytic activity can be significantly reduced when polystyrene was grafted onto the particle surface.

1. Introduction

The nanosized ZnO with the features of large volume to area ratio, high ultraviolet (UV) absorption, and long life-span [1] has been widely used as catalyst [2,3], gas sensor [4,5], active filler for rubber and plastic, UV absorber in cosmetics and anti-virus agent in coating [6–8].

ZnO nanoparticles can be synthesized by various approaches including sol–gel processing [9,10], homogeneous precipitation [11], mechanical milling [12], organometallic synthesis [13], microwave method [14], spray pyrolysis [15,16], thermal evaporation [17] and mechanochemical synthesis [18]. However, ZnO nanoparticles are prone to aggregate due to the large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles. Some researches have revealed several physical and chemical methods for modifying the surface of ZnO nanoparticles. The chemical surface modification, which can be classified as surface grafting and esterification, is the most promising method because of the strong covalent bond between the surface modified particles and polymer chains.

It is reported that some semiconductor, such as nanosized TiO2 or ZnO, has attracted extensive attention as a photocatalyst for the degradation of organic pollutants in water and air under UV irradiation [19–23]. Photocatalyst is also called photochemical catalyst and the function is similar as the chlorophyll in the photosynthesis. In a photocatalytic system, photo-induced molecular transformation or reaction takes place at the surface of the catalyst. A basic mechanism of photocatalytic reaction on the generation of electron–hole pair and its destination is as follows: when a photocatalyst is illuminated by the light stronger than its band gap energy, electron–hole pairs diffuse out to the surface of the photocatalyst and participate in the chemical reaction with the electron donor and acceptor. Those free electrons and holes transform the surrounding oxygen or water molecules into OH free radicals with super strong oxidization [24]. However, for the application of ZnO nanoparticles in cosmetic, the OH free radicals are harmful to human beings due to the super strong oxidization of OH free radicals generated on the surface of ZnO nanoparticles. Therefore, it is necessary to modify the surface of ZnO nanoparticles to obtain well UV shielding ability.

In our previous research, the ZnO nanoparticles were modified by SiO2 [23], PMMA [25] and PST [26], and the influence of particles on the mechanical properties of polymer matrix was studied. In the present investigation, ZnO nanoparticles were first treated with the coupling agent KH-570, and then PST (polystyrene) long chains were anchored on the surface of ZnO nanoparticles through grafting polymerization. The dispersion and photocatalytic activity of the modified ZnO nanoparticles were investigated.

2. Experiments

2.1. Materials

Polyethylene glycol (Mw = 4000, AR), Zn(CH3COO)2·2H2O (AR), (NH4)2CO3 (AR), ammonia solution (AR), anhydrous ethanol (AR),...
ammonium iron (II) sulfate hexahydrate (AR), silver sulfate (AR), potassium dichromate (AR), methyl orange (C₁₄H₁₄O₃N₃SNa, Q/HG22-2406-90), 1, 10-phenanthroline (C₁₂H₁₄N₂H₂O, AR), methyl red (C₁₀H₁₀N₂O₂, HG-958-76), phenolphthalein (C₂₀H₁₄O₄, Q/CYDZ-04-92), xylene (AR), acetonitrile (AR), tetrahydrofuran (THF, AR), styranyl (AR) and azobisobutyronitrile (AIBN, AR) were all purchased from the Sinopharm Chemical Reagent Co., Ltd. KH-570 silane coupling agent (CP) was purchased from Shanghai Yaohua Chemical Reagent Co., Ltd.

2.2. Preparation

2.2.1. Preparation of ZnO nanoparticles

ZnO precursors were synthesized by the precipitation method and then calcined to obtain ZnO nanoparticles. Firstly, polyethylene glycol solution was syringed into a three-neck flask. Then, Zn(CH₃COO)₂·2H₂O and (NH₄)₂CO₃ aqueous solutions were dropped into the flask at the same time with vigorous stirring. After reacting for 2 h at room temperature, the precipitates were washed and filtered with ammonia solution (pH=9) and anhydrous ethanol for several times, and dried under vacuum for 12 h. Finally, the precipitates were calcined in an oven at 450 °C for 3 h and milled, and then ZnO nanoparticles were obtained.

2.2.2. Grafting PSt onto the surface of ZnO nanoparticles

Firstly, the surface of ZnO nanoparticles was activated by KH-570 silane coupling agent. Typical steps were given as follows: 1.0 g of ZnO nanoparticles, 11.6 mL of KH-570, and 41.0 mL of xylene were added into a four-neck flask (ca. 250 mL) and refluxed at 80 °C for 3 h under magnetic stirring and argon protection. After centrifuging and extracting with alcohol for 12 h to remove the residual silane, the precipitate was dried in vacuum for 12 h. From the above treatment, the double bonds were introduced onto the surface of the ZnO nanoparticles. Secondly, the surface activated ZnO nanoparticles were grafted by PSt via a typical solution polymerization. The procedure is described as follows: 1.0 g of modified ZnO nanoparticles and 50 mL of xylene were put in a flask equipped with a reflux condenser. When the temperature reached 80 °C, 160 mg of AIBN was added into the flask, and then 11.0 mL of styrene was added by drip-feeding for 30 min under stirring and argon atmosphere. After 3 h, the resultant suspension was centrifuged and washed with acetone for three times. The dried precipitates were extracted with THF for 24 h to eliminate PSt homopolymers. Then, the grafted nanoparticles were dried under vacuum for 24 h.

2.3. Photocatalytic degradation procedure

Nanosized ZnO particle is a new photocatalyst to degrade organic contaminants, such as MeOr. The photocatalytic degradation of MeOr using nanosized ZnO is investigated with the following process: some ZnO nanoparticles were suspended into MeOr aqueous solution (about 50 mL), and the obtained suspension was kept in a dark environment with stirring for 30 min. Then, the suspension was syringed into a hollow cylindrical reactor made of glass, in which air was bubbling continuously from the bottom of the reactor. Sampling per hour and centrifuging, we measured the UV–vis absorption of the clarified solution at the wavelength from 200 nm to 800 nm. Finally, photocatalytic degradation percentage (PDP) of MeOr was calculated using Eq. (1),

\[
PDP\% = \frac{A_0 - A}{A_0} \times 100\% \tag{1}
\]

where, \( A_0 \) and \( A \) are the UV–vis absorption of original and sampled solutions, respectively.

2.4. Characterization

Surface structure of all samples was characterized by a Nicolet Avatar 360 Fourier transform infrared (FT-IR) spectroscope. Measurements were performed with pressed pellets made using KBr powder as diluent. The FT-IR spectrum was collected between the wave number of 400 and 4000 cm⁻¹.

The bare and modified ZnO nanoparticles were characterized by X-ray diffraction (XRD) (D/Max-IIIC, Japan) using Cu-Kα radiation (\( \lambda = 1.5406 \) Å). Distances between peaks were compared to the JCPDS 5-0664 of the International Center for Diffraction Data to determine crystalline structures.

The morphology of the bare and modified ZnO nanoparticles was determined by transmission electron microscope (TEM, Hitachi H-600-II) with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dropping dilute suspension of ZnO nanoparticles onto copper meshes.

The Perkin–Elmer TGA-7 with variable temperatures from 0 °C to 700 °C was employed to determine the coverage percentage of polystyrene on the surface of ZnO nanoparticles. The test was performed in nitrogen atmosphere with the accelerated speed of 20 °C/min.

The dispersibility of the modified nanoparticles was characterized by the sedimentation test. Typically, the modified nanoparticles (30 mg) and acetone (30 mL) were charged into a scale test tube with a plug, and the tube was required to stand immovably at room temperature. After a definite time, the depth of the suspension was recorded. The less the depth of the suspension is, the better the stability of the modified particles is. The sedimentation percentage of modified particles was determined by the following equation: the sedimentation percentage of modified particles (\( \% \)) = \( H/H_0 \times 100\% \), where \( H \) (cm) is the variable depth of the suspension and \( H_0 \) (cm) is the total depth of the suspension.

The size of the PSt-grafted ZnO particles/aggregates suspended in acetone was determined by Malvern HPPSS001 dynamic light scattering with the scanning range of 0.6 to 6000 nm. The samples were prepared with sonicate before measurement.

The Delta 320 acidimeter (Toledo, America) was used to modulate the pH of solutions. The UV-2812 spectrophotometer (Hitachi, Japan) was used to measure the absorption of azo dyes solution. The high performance liquid chromatography (HPLC, Waters-S10, America) was used to determine the composition of the residual solution.

The chemical oxygen demand (COD) was measured by dichromate method as follows: 10.0 mL of potassium dichromate solution (0.250 mol/L) and 10.0 mL of dye solution before or after treatment were poured into a vessel with a reflux apparatus. After switching on the cooling water, 30 mL of silver sulfate/sulfuric acid was poured into the vessel. Turn on the heater and keep the solution boiling for 2 h. Wash the condenser with 20 mL of deionized water, dilute the solution to 140 mL, and cool it to room temperature. Ammonium iron (II) sulfate was used to measure the residual dichromate quantitatively using 1, 10-phenanthroline as an indicator. The solution quickly turned from yellow to cyan, and to mahogany finally indicating the end of titration. The volume of consumed ammonium iron (II) sulfate was recorded as \( V_2 \). The COD was calculated according to Eq. (2),

\[
\text{COD (mg/L)} = \frac{C(V_1-V_2) \times 8000}{V_0} \tag{2}
\]

where, \( C \) is the concentration of ammonium iron (II) sulfate, mol/L; \( V_1 \) is the volume of consumed ammonium iron (II) sulfate in blank experiments, mL; and \( V_0 \) is the volume of a sample, mL.

Sampling per hour, we measured the UV–vis absorption at the wavelength between 200 and 800 nm. The characteristic absorption
A curve of MeOr aqueous solution was received, as shown in Fig. 1. Comparing the peak positions of those curves, one can find that the peak position was blue-shifted along with reaction time, which is in reasonable agreement with the literature [27] taking account of the experimental errors.

3. Results and discussion

3.1. Characteristics of ZnO nanoparticles

3.1.1. FT-IR spectra

Fig. 2a shows the FT-IR absorption spectrum of ZnO nanoparticles. The peak at 472.54 cm$^{-1}$ is the characteristic absorption of Zn–O bond and the broad absorption peak at 3438.26 cm$^{-1}$ can be attributed to the characteristic absorption of hydroxyls. It is also found that the infrared spectrum of the coupling agent (KH-570) treated ZnO nanoparticles exhibits absorptions at 2951.3, 1716.8, 1169.8, 941.3 and 817.9 cm$^{-1}$ as shown in Fig. 2b, which could be ascribed to the characteristic peaks of $-$CH$_2$– stretching vibration, C=O stretching vibration, $-$SiOH stretching vibration, Zn–O–Si and Si–O–Si symmetrical stretching vibration, respectively. Such results indicate that the active groups have been introduced onto the nanoparticle surface. Fig. 2c shows the FT-IR spectrum of the PSt-grafted ZnO nanoparticles. The absorptions at 1712.9, 1631.9 and 1454.4 cm$^{-1}$, manifest the existence of PSt. Therefore, the polystyrene chains were successfully grafted onto the surface of ZnO nanoparticles.
3.1.2. X-ray diffraction

The XRD spectra of bare and PST-grafted ZnO nanoparticles are shown in Fig. 3. From Fig. 3a, a series of characteristic peaks: 2.814 (100), 2.608 (002), 2.475 (101), 1.911 (102), 1.624 (110) and 1.478 (103) are observed, and they are in accordance with the zincite phase of ZnO (International Center for Diffraction Data, JCPDS 5-0664). No peaks of impurity are observed, suggesting that the high purity ZnO was obtained. In addition, the peak is widened implying that the particle size is very small according to the Debye–Scherrer formula

\[ D = \frac{K\lambda}{\beta\cos\theta} \]

where \( K \) is the Scherrer constant, \( \lambda \) the X-ray wavelength, \( \beta \) the peak width of half-maximum, and \( \theta \) is the Bragg diffraction angle. The average crystallite size \( D \) is 20 nm calculated using the Debye–Scherrer formula.

Fig. 3b illustrates that after modification, the characteristic peaks have broadened and the characteristic peaks are still in accordance with the zincite phase of ZnO, indicating that the grafted polymer does not influence the crystalline structure.

3.1.3. Transmission electron microscope

The transmission electron micrographs (TEM) of the bare and PST-grafted ZnO nanoparticles are shown in Fig. 4. Fig. 4a shows that most of the bare ZnO nanoparticles are quasi-spherical and their diameter is about 20 nm. This result is in accordance with the value calculated from the X-ray diffraction. Due to large specific surface area and high surface energy, some nanoparticles aggregate. The aggregation occurred probably during the process of drying. Fig. 4b shows the TEM of the surface modified nanoparticles, illustrating that aggregation was alleviated and dispersion was improved. Besides, one can also observe that around the ZnO nanoparticles there encircle some shadows, implying the existence of the grafted polymer layers.

3.1.4. TG analysis

Fig. 5 shows the TG curves of the bare and PST-grafted ZnO nanoparticles, and the temperature scale for the measurement is from 50 °C to 700 °C. From Fig. 5a, one can find that about 4.6% of the total weight of bare ZnO nanoparticles is lost. The weight loss of bare ZnO nanoparticles may be due to the evaporation of water adsorbed on the surface of ZnO nanoparticles. Fig. 5b is the TG curve of PST-grafted ZnO nanoparticles and reveals that about 83.3% of the total weight of PST-grafted ZnO nanoparticles is reserved. For PST-grafted ZnO nanoparticles, the weight loss resulted from the evaporation of adsorbed water and the burn-up of grafted polystyrene. Comparing the two TG curves, one can deduce that about 12.1 wt.% of the total weight loss of PST-grafted ZnO nanoparticles is attributed to the grafted polystyrene.

3.1.5. Sedimentation test

To check the effect of surface modification, the dispersibility of PST-grafted ZnO nanoparticles in acetone was compared with that of bare ZnO, as shown in Fig. 6. Results indicate that bare ZnO nanoparticles completely precipitated after 4 h, while PST-grafted ZnO nanoparticles formed a stable dispersion in acetone. This illustrates that the surface modification can increase the compatibility between ZnO nanoparticles and organic solvents. This also shows that the grafted polymer chains on ZnO nanoparticles can result in the steric repulsive forces among particles, preventing the ZnO nanoparticle from aggregation. In addition, the hydrophilicity of the nanoparticle surface changes to extreme hydrophobicity.

3.1.6. Particle size distribution

The particle size distribution of PST-grafted ZnO nanoparticles in acetone suspension is shown in Fig. 7. The number of \( d(0.99) \text{num} \) is 32.07 nm, which means that the median size of 99% particles in volume is 32.07 nm. The core size of PST-grafted ZnO nanoparticles measured by TEM is about 20 nm, which is smaller than that of PST-
grafted ZnO nanoparticles in aqueous suspension measured by a laser particle size analyzer. The enlargement of particle size may be due to the grafted PSt layers. Besides, one can also find that there is only one narrow peak that existed in the figure, implying that after graft polymerization well dispersed ZnO nanoparticles are obtained.

3.2. Photocatalytic activity

3.2.1. Optimal conditions for photocatalytic degradation

A series of experiments were carried out to study the influences of irradiation time, reaction temperature, pH, catalyst concentration, MeOr concentration and airflow rate on the photocatalytic degradation percentage (PDP) of MeOr by ZnO nanoparticles. The results show that the PDP differs very much at different irradiation times and reaction temperatures, and the photodegradation reaction kinetics is approximately the first-order. The degradation of MeOr is favored at higher temperature. However, when the reaction temperature is over 40 °C, the solvent would easily evaporate with air bubbling. The optimal acidity for photocatalytic degradation reaction is at a pH of 7.0. When the pH is below 7.0, the PDP increases quickly with the increasing pH, otherwise, the PDP decreases. The PDP increases with the increasing catalyst concentration. However, at low concentration, the photodegradation is faster than that at high concentration. With the increase of the MeOr concentration, the decolorization efficiency decreases. Experiments performed at different airflow rates from 0 to 100 L/h indicate that the PDP increases from 43% to 90% with the increasing airflow.

Therefore, the optimal conditions for photocatalytic degradation of MeOr using ZnO nanoparticles are reacting for 5 h at a MeOr concentration of 20 ppm, a catalyst concentration of 1.5 g/L, a pH of 7.0 and a temperature of 30 °C.

3.2.2. Comparison of bare and PSt-capped ZnO nanoparticles

The PDP of MeOr solution after UV irradiation using different photocatalysts is illustrated in Fig. 8. One can find that the bare ZnO nanoparticles have much higher photocatalytic activity since almost 80% of MeOr is degraded after 4 h. This may be due to the fact that bare ZnO nanoparticles are hydrophilic. They can absorb more MeOr molecules in water and can contact with air closely. While the PSt-capped ZnO nanoparticles are hydrophobic leading to little photocatalytic activity. This can be explained that the long polymer chains coated on the surface of ZnO nanoparticles interfere with the adsorption of the MeOr molecules and the contact with air. Moreover, the UV absorption of ZnO nanoparticles may be reduced due to the grafted PSt layers. Although the inner of the ZnO nanoparticles is quite active and can produce the electron–hole pairs under UV irradiation, the surface modified ZnO nanoparticles cannot adsorb enough MeOr molecules, and also the contact of PSt-grafted ZnO nanoparticles with air is obstructed by the grafted PSt layers. On the other hand, even if some electrons or holes are produced on the inner surface of ZnO nanoparticles, the electrons or holes cannot reach the outer surface of the modified particles, leading to the failure of photocatalytic degradation of MeOr. So, the PDPs of bare and PSt-grafted ZnO nanoparticles are entirely different under the same condition, and the photocatalytic activity of ZnO nanoparticles is greatly reduced after coating with PSt.

Fig. 5. TG curves of bare (a) and PSt-grafted (b) ZnO nanoparticles.

Fig. 7. Size distribution by volume of ZnO nanoparticles in water.

Fig. 6. Photocatalytic degradation of MeOr using bare and PSt-grafted ZnO nanoparticles.
3.2.3. UV–vis absorption

In order to prove the argument of which the PST layers grafted on the surface of ZnO nanoparticles could reduce the photocatalytic activity of ZnO, the UV–vis absorption of bare and PST-grafted ZnO nanoparticles was measured. Fig. 9 shows the UV–vis absorption curves of bare and PST-grafted ZnO nanoparticles. It is found that the UV–vis absorption of ZnO nanoparticles is reduced after grafting PST layers, especially at the wavelength from 250 nm to 400 nm. That is to say, the UV absorption of the modified ZnO is reduced after the surface is modified by PST. It could at a certain extent explain the reduction of photocatalytic activity of PST-grafted ZnO nanoparticles. Moreover, PST-grafted ZnO nanoparticles were laid on a supporter under continuous irradiation of UV light for different time, and the UV–vis absorption measurement for the obtained PST-grafted ZnO nanoparticles with different irradiation time was performed, as shown in Fig. 10. From Fig. 10, one can find that at the first 10 h, the UV–vis absorption of PST-grafted ZnO nanoparticles is almost the same, showing excellent UV light fastness, and then the UV–vis absorption increases. The increase of UV–vis absorption of PST-grafted ZnO nanoparticles may be due to the destruction of PST layers during the UV irradiation.

![UV–vis absorption curves of bare and PST-grafted ZnO nanoparticles.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>PDP</th>
<th>COD&lt;sub&gt;before&lt;/sub&gt;/COD&lt;sub&gt;after&lt;/sub&gt;</th>
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<td>8:6:1</td>
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<tr>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(269, 28)</td>
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<tr>
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<td>(198, 22)</td>
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3.3. By-products analysis

In order to analyze the by-products during the photocatalytic degradation of MeOr, HPLC measurements were performed using water as flow phase. It is observed that there are another four peaks that appeared after MeOr solution irradiated by UV for 4 h, contrast to the original MeOr solution, which indicates that there are mainly four new by-products generated. According to the reported article [28], the possible by-products are as follows:

![By-products](image)

Besides, there are also some weak peaks of other low molecular weight by-products, which is well in accordance with the previous report [29].

3.4. Photocatalytic degradation of other dyes

The degradation of some other azo dyes, such as methyl red, phenolphthalein and 1,10-phenanthroline is also studied, and the results are listed in **Table 1**. From **Table 1**, one can find that the PDP of methyl red, phenolphthalein and 1,10-phenanthroline is lower than that of MeOr, but the ratio of COD before and after photodegradation goes reversely, suggesting that the organic contamination of industrial wastewater can be evaluated by COD more accurately than PDP.

4. Conclusions

ZnO nanoparticles with an average diameter of 20 nm were obtained, and subsequently were grafted by PST. The optimal conditions for photocatalytic degradation of MeOr using ZnO nanoparticles are reacting for 5 h at a MeOr concentration of 20 ppm, a catalyst concentration of 1.5 g/L, a pH of 7.0 and a temperature of 30 °C. The PDP increased with the increasing airflow rate. The photodegradation of MeOr obeyed the rule of a pseudo first-order reaction. The bare
ZnO nanoparticles showed high photocatalytic activity in photodegradation of MeOr under UV irradiation, and mainly produced four by-products. The photocatalytic activity of ZnO nanoparticles for some other azo dyes was also very high, which showed a good application foreground in organic contamination treatment. Surface modification of ZnO nanoparticles by polystyrene can improve the compatibility of the inorganic nanoparticles and the organic matrix, however, the photocatalytic activity of the modified ZnO is reduced.

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