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Article

Simple preparation of scale-like CuO nanoparticles coated on tetrapod-like ZnO whisker photocatalysts

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ABSTRACT

Scale-like copper oxide (CuO)/tetrapod-like ZnO whisker (T-ZnOw) nanocomposites were fabricated using poly(ethylene glycol) (PEG; $M_w = 400$) as a soft template by a simple and environmentally friendly method without the use of hydroxide reagents at low temperatures. The structures and morphologies of the samples were investigated in detail, and the photocatalytic properties of the samples were determined using photoluminescence (PL) detection and the photocatalytic degradation of cationic pollutant (methylene blue, MB) and anionic pollutant (methyl orange, MO) aqueous solutions under ultraviolet (UV) irradiation. Large numbers of scale-like CuO nanoparticles were deposited on the T-ZnOw surfaces in an ordered fashion; the amount of scale-like CuO nanoparticles increased, and the arrangement became more ordered with increasing PEG 400 content. The PL emission peak intensities of the samples changed with increasing PEG 400 content. All the CuO/T-ZnOw nanocomposites showed excellent photocatalytic activities in the degradation of MB and MO aqueous solutions under UV irradiation when the PEG 400 concentration was less than or equal to 0.60 mol/L. The photocatalytic properties of the samples improved with increasing PEG400 concentration, but deteriorated when the PEG 400 concentration was increased further; this was reflected by the emission peak intensities in the PL spectra. The nanocomposites showed better efficiency for MB degradation than for MO degradation under the same conditions.

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1. Introduction

ZnO, which is an n-type semiconductor photocatalyst, is nontoxic and has attracted much attention for use in the treatment of wastes and pollutants in air and water [1–3]. ZnO has a direct band gap (E_g) of approximately 3.37 eV [4]. It can efficiently absorb ultraviolet (UV) light and then generate numerous photoinduced electrons and holes, and has excellent activity in the degradation of organic pollutants [4–7]. The specific chemical state of a catalyst surface is important in increasing the photocatalytic activity because photocatalytic degradation

reactions occur on the catalyst surface. Compared with conventional ZnO, tetrapod-like ZnO whiskers (T-ZnOw) have higher percentages of exposed (100) to (002) planes and larger specific surface areas and surface traps, which can absorb more dye molecules and active species such as $\cdot O_2^-$, leading to higher photocatalytic activity [8–11]. However, the photoinduced electrons and holes can easily recombine in a single-component catalyst despite the specific surface properties of T-ZnOw. It is therefore important to develop methods for decreasing recombination of electrons and holes. Various methods have been reported for reducing the recombination of photoinduced elec-

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tron–hole pairs, such as noble-metal deposition [4], transition-metal-ion doping [8], and semiconductor coupling [11,12]. Semiconductor coupling is a simple, effective, and low-cost way to improve photocatalytic properties. T-ZnOw are an n-type semiconductor photocatalyst and can couple with a p-type semiconductor photocatalyst to form a p–n heterojunction at the interface of two semiconductors; this can effectively separate photoinduced electrons and holes and greatly improve the catalytic activity [12].

CuO is an important p-type semiconductor with a narrow band gap ($E_g = 1.2\text{--}1.9\text{ eV}$) [13,14], and CuO nanoparticles have great potential in applications such as superconductors, gas sensors, solar energy transformation, and gas catalysts [14–17]. Most importantly, they can be used to improve the photocatalytic activity of ZnO through the coupling method. Several synthetic approaches for CuO/ZnO composites have been proposed [18–22]. However, most of them are complicated, laborious, multistep methods, which require high temperature or alkaline conditions for long periods of time, and/or expensive, complicated equipment. Zhang et al. [18] synthesized CuO/ZnO composite hollow spheres via a reaction in a Teflon-sealed autoclave at 180 °C for 24 h, followed by calcination of the precipitates at 500 °C for 4 h. Wei et al. [19] fabricated CuO/ZnO composite films using cathodic co-electrodeposition; the composite films had higher photocatalytic activities in Cr(VI) reduction than did pure ZnO. Saravanan et al. [20] synthesized ZnO/CuO nanocomposites using a new thermal decomposition method (annealing in an alumina crucible at 350 °C for 3 h); the photocatalytic activities of the nanocomposites in methylene blue (MB) and methyl orange (MO) degradation were better than those of ZnO. Liu et al. [21] prepared CuO/ZnO nanocomposites at a high calcining temperature (up to 350 °C) for a certain amount of time; they found that the nanocomposites had good photocatalytic properties in MO degradation. Li et al. [22] used homogeneous coprecipitation at 80 °C for 24 h, with NaOH as the precipitating agent, to synthesize ZnO/CuO nanocomposites; they exhibited appreciable photocatalytic activity in rhodamine B degradation.

In this work, a simple and environmentally friendly method was developed for depositing CuO nanoparticles on the surfaces of T-ZnOw, which were synthesized without the use of hydroxide ions. The photocatalytic activities of the CuO/T-ZnOw composites in the photodegradation of MB and MO were investigated, and the nanocomposite formation mechanism was explored.

2. Experimental

2.1. Sample synthesis

The T-ZnOw were synthesized using the previously reported equilibrium gas expanding method [23]. Poly(ethylene glycol) (PEG, $M_w = 400$, analytical grade) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (PA 99%, analytical grade) were purchased from the Kelong Chemical Co., Ltd. (Chengdu, China). All the analytical-grade reagents were used without further purification. Distilled water was used to prepare solutions and the oxygen reagent, and PEG 400

was used as the template for preparing CuO/T-ZnOw nanocomposites. The synthesis was performed as follows.

For the pre-treatment of T-ZnOw, neat T-ZnOw were dissolved in water and alcohol for 1 h each. The mixture was filtered, and the upper suspension was dried at 90 °C in an ambient atmosphere for 8 h and collected for further use.

For the composite synthesis, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.15 g) was added to PEG 400 solutions of different concentrations; the mixtures were stirred constantly for 30 min. The pretreated T-ZnOw were added and the solutions were stirred for 1 h. The mixed suspensions were heated using a water bath from room temperature to 65 °C and kept at 65 °C for 3 h. Finally, the precipitates were washed with distilled water and alcohol and dried in an oven at 50 °C for 8 h. Nanocomposites were synthesized using PEG 400 concentrations of 0.30, 0.45, 0.60, 0.75, 0.90, and 1.05 mol/L.

For comparison, we carried out similar experiments without either PEG 400 or T-ZnOw in the reaction system. The blue aqueous Cu^{2+} ions did not react to form black CuO in these reaction systems.

2.2. Sample characterization

Wide-angle X-ray diffraction (XRD; X'pert PRO diffractometer with Ni-filtered $\text{Cu } K_\alpha$ radiation, PANalytical, the Netherlands) was used to investigate the crystalline structures of the nanocomposites. The continuous scanning angle range used was 20°–65° at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600 multitechnique system, with a monochromatic Al K_α X-ray source. All core-level spectra were referenced to the C 1s neutral carbon peak at 284.8 eV. The nanocomposite morphologies were studied using scanning electron microscopy (SEM; Fei Quanta 200, USA) at an accelerating voltage of 20 kV. Energy-dispersive X-ray spectroscopy (EDS; combined spectrometer/SEM instrument) was used to determine the chemical compositions of the photocatalysts. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES; IRIS 1000, Thermo Elemental, USA) was used to determine the CuO contents of the CuO/T-ZnOw composites. Photoluminescence (PL) spectra were obtained using an Edinburgh F900 instrument at room temperature with a He–Cd laser as the excitation source at a wavelength of 325 nm, to characterize the properties of the photoinduced electron–hole pairs in the photocatalyst indirectly. A UV-vis 2550 spectrophotometer (Shimadzu 2550, Japan) was used to determine the photocatalytic activities of the composite catalysts in the degradation of different dyes.

2.3. Photocatalytic tests

The photocatalytic activities of pure T-ZnOw and the CuO/T-ZnOw composite materials were investigated using the photodegradation of MB and MO; the reaction conditions were 0–50 min for MB and 0–100 min for MO at 25 °C under UV light irradiation. MB and MO were used to simulate different wastewaters.

A nanocomposite sample (50 mg) was suspended in a

beaker filled with an aqueous solution (50 mL 10 mg/L) of MB or MO, and then stirred for 30 min in the dark. The mixture was then stirred continuously and simultaneously irradiated using a UV lamp with an emission wavelength of 254 nm (Hangzhou, China) for 50 min (MB) or 100 min (MO). The distance between the UV tube and the solution surface was 26 cm. The solution was sampled periodically during irradiation to monitor photo-degradation of the dye aqueous solution; the main absorbance peaks at 665 nm (MB) and 466 nm (MO) of the samples were measured using a UV-vis spectrophotometer. The temperature was fixed at 25 °C throughout the photocatalytic experiments.

3. Results and discussion

3.1. Sample structures

The crystal structures and phase compositions of the prepared nanomaterials were determined using XRD. Figure 1 shows the XRD patterns of pure T-ZnOw, CuO, and samples prepared using different PEG 400 concentrations. It shows that pure CuO has two characteristic diffraction peaks at $2\theta = 35.50^\circ$ and 38.71° , which correspond to the (002) and (111) crystal-line planes, respectively, of monoclinic CuO (JCPDS 80-1917). The diffraction peaks at $2\theta = 31.88^\circ$, 34.41° , 36.26° , 47.52° , 56.62° , and 62.99° of pure T-ZnOw and the prepared nano-composite samples correspond to the (100), (002), (101), (102), (110), and (103) crystalline planes, respectively, of the wurtzite ZnO structure (JCPDS 36-1451). The peaks of crystal-line CuO are not clearly observed in the nanocomposite samples; this may be because the content of CuO nanoparticles on the T-ZnOw surfaces is relatively low, or the characteristic dif-

Fig. 1. XRD patterns of pure T-ZnOw, CuO, and CuO/T-ZnOw nanocomposite samples prepared using different PEG 400 concentrations.

fraction peaks of T-ZnOw are too strong for the diffraction peaks of CuO to be visible [24]. The prepared nanocomposite samples were further characterized using XPS and ICP-AES.

3.2. XPS and ICP-AES results

XPS can be used to obtain surface information based on the characteristic binding energies of different elements and their chemical states on catalytic surfaces [25]. XPS was performed to further clarify the presence of CuO in the nanocomposite sample prepared using 0.60 mol/L PEG 400; the results are shown in Fig. 2(a)–(d). For comparison, the Zn and O XPS spectra of pure T-ZnOw are shown in Fig. 2(e) and (f), respectively.

Fig. 2. XPS spectra of the CuO/T-ZnOw nanocomposite sample prepared using 0.60 mol/L PEG 400. (a) Full spectrum; (b–d) Spectra for Zn, O, and Cu species, respectively; (e) Zn species in pure T-ZnOw; (f) O species in pure T-ZnOw.

The results show the surface elements and their valence bonding states for the nanocomposite sample prepared using 0.6 mol/L PEG 400 and pure T-ZnOw. Figure 2(a) shows the full XPS spectrum of the nanocomposite sample. All the peaks are attributable to Zn, O, Cu, and C, and no peaks from other elements are present. The C mainly comes from the vacuum treatment before XPS, and the C 1s (284.8 eV) peak is used for calibrating the binding energies of in the XPS spectra. It can therefore be concluded that the prepared sample contains only three elements (Zn, O, and Cu).

Figure 2(b)–(d) shows the high-resolution XPS spectra of Zn, O, and Cu, respectively. The Zn 2*p* XPS peaks, centered at 1044.38 and 1021.25 eV, correspond to the binding energies of Zn 2*p*_{1/2} and Zn 2*p*_{3/2}, respectively. The Zn 2*p* peaks are symmetrical at nearly the same positions as those for pure T-ZnOw (Fig. 2(e)). This confirms that Zn is present mainly as Zn²⁺ ions on the sample surface. As shown in Fig. 2(c) and (f), the broad O 1s core-level spectrum can be Gaussian fitted to two symmetrical peaks. The peak at the lower binding energy (530.17 eV) in Fig. 2(c) corresponds to the lattice oxygen in metal oxides such as CuO, Cu₂O, and T-ZnOw [26–29], and is nearly the same as that for pure T-ZnOw (Fig. 2(f)). The peak at 531.73 eV in Fig. 2(c) is attributed to chemisorbed oxygen and/or hydroxide oxygen [26,29,30], and the peak position is higher than that for pure T-ZnOw; this is because the surface structure of T-ZnOw is changed by deposition of CuO nanoparticles, and this affects the oxygen-adsorption abilities of the surface. No signals from PEG 400 molecules are found in the XPS spectra, indicating that the sample is devoid of PEG 400. In Fig. 2(d), the peaks at 932.91 and 952.64 eV correspond to the Cu 2*p*_{3/2} and Cu 2*p*_{1/2} binding energies of CuO [22,28]; the core-level Cu 2*p*_{1/2} and Cu 2*p*_{3/2} spectrum is symmetric. Figure 2(a) shows that Cu²⁺ comes from CuO crystals. The peaks at 941.91 and 961.82 eV are satellite peaks of CuO, and this confirms the presence of CuO [22,26,30]. It is therefore confirmed that the sample consisted

Fig. 3. Effects of PEG 400 concentration on CuO particle loadings of the CuO/T-ZnOw samples determined using ICP-AES.

of CuO and T-ZnOw crystals.

ICP-AES was performed to determine the CuO particle loadings on the T-ZnOw surfaces of nanocomposites prepared using different PEG 400 concentrations; the results are shown in Fig. 3. The figure shows that the Cu content increases with increasing PEG 400 concentration, confirming that the Cu comes from CuO crystals. However, the amount of CuO deposited on the T-ZnOw is relatively low, which further explains why CuO is observed in the XPS spectra but not in the XRD patterns of the samples.

3.3. Sample morphologies and microstructures

As discussed above, we confirmed the presence of CuO. SEM was then performed to determine the location and morphology of CuO. The SEM images of the samples prepared using 0.30, 0.45, 0.60, 0.75, 0.90, and 1.05 mol/L PEG 400 are shown in Fig. 4. It shows that there are many CuO nanoparticles on the T-ZnOw surface. In Figs. 4(b)–(f), it can be seen that many

Fig. 4. SEM images of CuO/T-ZnOw composites prepared using different PEG 400 concentrations (mol/L). (a) 0.30; (b) 0.45; (c) 0.60; (d) 0.75; (e) 0.90; (f) 1.05.

scale-like CuO crystals are deposited on the surface of T-ZnOw in an ordered fashion. We also found that Cu^{2+} ions could not form CuO without the presence of PEG 400 or T-ZnOw. We can therefore conclude that the PEG 400 molecules and T-ZnOw had a synergistic effect in the reaction system.

Figure 4 also shows that the amount of scale-like CuO crystals on the T-ZnOw surface increases with increasing PEG 400 concentration, and that the CuO morphology changes with the difference of PEG 400 concentration. PEG 400 plays a decisive role in the yields and morphologies of CuO nanoparticles [31]. When the concentration of PEG 400 is low (0.3 mol/L), the amount of CuO nanoparticles dispersed on the T-ZnOw surface is low, and the CuO morphology is irregular (Fig. 4(a)). This may be because lack of PEG 400 molecules to act as a soft template or insufficient PEG 400 coverage of the T-ZnOw surface leads to fewer self-assembled CuO crystals. If the PEG 400 concentration is increased, the PEG 400 molecules can be more uniformly and densely adsorbed on the active sites on the T-ZnOw surface, and the generated CuO crystals will self-assemble on the T-ZnOw surfaces, in a scale-like morphology, leading to more ordered and uniform packing (Fig. 4(e)). On further increasing the PEG 400 concentration, increasing numbers of PEG 400 molecules are adsorbed on the T-ZnOw surfaces, and CuO crystal nucleation increases; however, the Cu^{2+} is constant, so the CuO nanoparticles become smaller (Fig. 4(f)). In our research, we found that PEG 400 served as a soft template in the growth of CuO nanoparticles, which is consistent with previous research [32].

EDS was performed to determine the exact compositions of the nanoparticles on the T-ZnOw surfaces. The EDS spectrum in Fig. 5 shows the chemical composition of the area indicated by the white circle in Fig. 4(c). In Fig. 5, the peaks correspond to Zn, O, Cu, Al, and Au, respectively. The Au comes from the pre-treatment of samples for the SEM and EDS tests, and Al comes from the sample loading platform. The sample in the detection area therefore contains Zn, O, and Cu. XRD and XPS results show that this sample is composed of T-ZnOw and CuO, so it can be deduced that these nanoparticles consist of CuO crystals.

3.4. UV-vis diffuse reflectance spectroscopy (UV-vis DRS)

Figure 6 shows the UV-vis DRS spectra of pure CuO, pure T-ZnOw, and CuO/T-ZnOw nanocomposites prepared using

Fig. 5. EDS spectrum of the CuO/T-ZnOw sample prepared using 0.60 mol/L PEG 400.

Fig. 6. UV-vis DRS spectra of CuO, T-ZnOw, and CuO/T-ZnOw nanocomposites prepared using 0.30, 0.60, and 0.90 mol/L PEG 400.

different PEG 400 concentrations. It shows that pure T-ZnOw has a strong absorption in the UV wavelength region 300–400 nm, and pure CuO has a wide range of absorptions at 400–700 nm. However, the CuO/T-ZnOw nanocomposites have strong absorptions in the UV region ($\lambda = 300\text{--}400$ nm) and a wide range of absorptions ($\lambda = 500\text{--}700$ nm) in the UV-vis DR spectra; these can be assigned to the characteristic absorptions of T-ZnOw and CuO, respectively. The wavelengths of the absorption edges can be determined from the curves by extrapolating the horizontal and sharply rising portions of the absorption curves, and the intersection wavelengths are used to define the sample edges [11,31]. The photocatalyst band gaps corresponding to pure T-ZnOw and the CuO/T-ZnOw nanocomposites prepared using 0.30, 0.60, and 0.90 mol/L PEG 400 were estimated to be 3.180, 3.177, 3.171, and 3.171 eV, respectively, using the equation $E_g = 1239.8/\lambda_g$ [11]. The band gaps of CuO/T-ZnOw were slightly lower than that of pure T-ZnOw; this was attributed to the p–n heterojunction formed at the CuO–T-ZnOw interface.

3.5. Optical properties of samples

In this work, an n-type semiconductor, T-ZnOw, was combined with a p-type semiconductor, CuO, to form a p–n heterojunction at their interface. The recombination of photoinduced electron–hole pairs at a heterojunction can be determined using PL. Figure 7 shows the room-temperature PL spectra of pure T-ZnOw and the nanocomposite samples prepared using different PEG 400 concentrations. A strong UV emission at 382.0 nm and a broad green emission at 517.2 nm are clearly observed. The strong UV emission originates from radiative recombination of excitons, and the primary origin of the green emission is radiative recombination of photogenerated holes with electrons occupying singly ionized oxygen vacancies in the catalyst [33]. If electrons are transferred from one catalyst to another, indicating separation of photoinduced electrons and holes, the PL quantum yield decreases abruptly, and the intensity of the visible emission peak in the PL spectrum also decreases [34–36]. The easier the recombination of photoinduced

Fig. 7. PL spectra of pure T-ZnOw and CuO/T-ZnOw nanocomposite samples prepared using different PEG 400 concentrations.

electron-hole pairs is, the higher the intensity of the visible emission peak, and the lower the photodegradation activity of the catalyst.

In Fig. 7, the visible emission peaks of the CuO/T-ZnOw composites, centered at around 517.2 nm, are clearly lower than that of pure T-ZnOw, and the order of the intensities of the visible emission peaks of the samples prepared using different PEG 400 concentrations (mol/L) is $0.60 < 0.75 < 0.45 < 0.90 < 1.05 < 0.30 < \text{pure T-ZnOw}$. This suggests that separation of photoinduced electron-hole pairs occurs more easily in the CuO/T-ZnOw composites, meaning that the lifetimes of the photoinduced electrons in the composites were extended, enhancing the photocatalytic activity of T-ZnOw.

3.6. Photocatalytic performance of samples

The photocatalytic activities of the CuO/T-ZnOw photocatalysts under UV irradiation were determined by measuring the photodegradation of MB and MO aqueous solutions (10 mg/L). MB and MO dyes have different molecular structures and different functional groups (Fig. 8). The former is a cationic dye with a methyl nitride group $[(\text{CH}_3)_2\text{N}^+]$, and the latter is an anionic azo dye with sulfonate groups (SO_3^-) [37,38]. The characteristic peaks are therefore located at different wavelength and have various intensities, and can be used to monitor the rate of photodegradation.

Figure 8 shows the relationship between absorbance and reaction time for photocatalytic degradation under UV irradiation of MB and MO aqueous solutions by the CuO/T-ZnOw nanocomposite prepared using 0.6 mol/L PEG 400. It was shown that the maximum absorbance bands of MB ($\lambda = 665$ nm) and MO ($\lambda = 466$ nm) both decreased gradually with increasing irradiation time. The absorbance peaks of MB and MO disappeared after irradiation for 50 and 100 min, respectively, indicating that the dye molecules had been degraded and decomposed in the presence of the CuO/T-ZnOw composite under UV irradiation [37,38]. A clear hypsochromic shift in the MB absorbance spectrum can also be seen, with the maximum absorption wavelength at 665 nm shifting to 640 nm after UV irradiation for 30 min; this may be caused by mineralization of

Fig. 8. UV-vis absorption spectra of MB (a) and MO (b) aqueous solutions in the presence of CuO/T-ZnOw composite prepared using 0.60 mol/L PEG 400 at different irradiation times.

MB [39]. Decomposition of MO is caused by demethylation and hydroxylation during photodegradation [12]. The final products of MB and MO photodegradation are CO_2 , H_2O , and other inorganic molecules [40,41]. The degradation efficiency of MB or MO is calculated using the equation $D = (A_0 - A_t)/A_0 \times 100\%$, where D is the degradation rate of the dye solution, and A_0 and A_t are the initial maximum absorbance of the dye solution and the maximum absorbance after irradiation for t min, respectively.

Figure 9 shows that blank tests with only UV irradiation gave decomposition rates of only 9.54% for MB after 50 min and 2.23% for MO after 100 min. Pure T-ZnOw significantly increased degradation of dyes solutions, giving rates of 90.76% for MB and 56.72% for MO. It can be seen that the photodegradation rates of MB and MO with a mechanical mixture of CuO and T-ZnOw (89.01% and 50.83%, respectively) are inferior to those with pure T-ZnOw. This is because of the inferior photocatalytic properties of pure CuO and the failure to form a heterojunctions between CuO and T-ZnOw [31]. The results also show that the degradation rates of MB and MO with the CuO/T-ZnOw composites are higher than those with pure T-ZnOw. Moreover, when the PEG 400 concentration used in the composite preparation is less than or equal to 0.60 mol/L, the photocatalytic activity increases with increasing PEG 400 concentration, leading to degradation rates of 98.38% after UV irradiation for 50 min for MB and 96.46% after UV irradiation for 100 min for MO. On further increasing the PEG 400 concen-

Fig. 9. Photodegradation curves of aqueous dye solutions in the presence of pure T-ZnOw, mechanical mixture of CuO and T-ZnOw (CuO + T-ZnOw), and CuO/T-ZnOw composites prepared using different PEG 400 concentrations. (a) MB; (b) MO.

tration, the photocatalytic activity decreases slightly, and the degradation rates of the sample prepared using 1.05 mol/L PEG 400 decrease to 96.54% (MB) and 86.70% (MO). For samples prepared using PEG 400 concentrations higher than 0.60 mol/L, the decreased activity is attributed to recombination of the created charges and/or light scattering caused by an excess of CuO nanoparticles [31].

As shows in Fig. 9, the improvement in MB photodegradation is more noticeable than that in MO photodegradation; this is because the stability of MO is higher than that of MB. The self-degradation of MB aqueous solution is 9.54% after UV irradiation for 50 min, but that for MO is only 1.36% under the same conditions. In contrast, pure T-ZnOw gives significant degradation of the MB solution (up to 90% at 50 min), higher than that of the MO solution (56.72% at 100 min); all the nanocomposite samples gave higher photodegradation rates for MB and MO than did pure T-ZnOw, although the MB degradation rate was not significantly improved.

The improved CuO/T-ZnOw photocatalytic activity can be attributed to the p–n heterojunction formed between CuO nanoplates and T-ZnOw surfaces; this favors the separation of photogenerated electrons and holes and increases photon harvesting by the CuO nanoplates [20,31].

Fig. 10. Photocatalytic degradation of MO in recycling tests with the CuO/T-ZnOw sample prepared using 0.60 mol/L PEG 400.

3.7. Potential sample recycling and possible photodegradation mechanism

Photocatalytic recycling experiments were performed with CuO/T-ZnOw prepared using 0.60 mol/L PEG 400. Figure 10 shows the results for photocatalytic degradation of MO under UV irradiation. The photocatalytic activity decreased slightly after the third cycle; the MO degradation rate was 96.46% at the end of the first cycle and 90.30% after the third cycle, showing that the photocatalyst has excellent stability.

The enhanced activities of the CuO/T-ZnOw nanocomposites can be explained based on the schematic diagram of the energy band structure of the CuO/T-ZnOw p–n heterojunction, shown in Fig. 11. The valence band (VB) edge of ZnO is -0.99 eV on the absolute vacuum scale (AVS), which is higher than that of CuO (-3.26 eV). The conduction band (CB) edges of ZnO and CuO are located at -4.19 and -4.96 eV (vs AVS), respectively [31]. A possible mechanism of photodegradation by CuO/T-ZnOw nanocomposites is as follows. When the composite is irradiated with UV light, both T-ZnOw and CuO are activated for photogeneration of electron–hole pairs (Fig. 11, processes (1) and (2)). The photogenerated holes are transferred from the VB of T-ZnOw to that of CuO, and the photogenerated electrons in the CB of CuO then migrate to the T-ZnOw CB (processes (3) and (4)) [35]. Increasing numbers of photogen-

Fig. 11. Schematic representation of excitation and separation of electrons and holes for CuO/T-ZnOw heterojunction under UV irradiation.

erated electrons are therefore gathered by T-ZnOw, and the holes mostly aggregate on CuO in the p–n heterojunction. At the same time, photoinduced holes (h^+) react with H_2O to produce hydroxyl radicals ($\cdot OH$; process (5)), and electrons (e^-) can react with dissolved oxygen to give superoxide anions ($\cdot O_2^-$; process (6)) and ultimately generate $\cdot OH$.

The photodegradation of dyes is mainly governed by direct oxidation of photoinduced holes, which can reduce H_2O molecules to $\cdot OH$, and $\cdot OH$ is a strong oxidizing agent for organic pollutants and electrophilic reagents [40]. According to the principles of dynamics, cationic MB pollutant molecules can react faster with $\cdot OH$ than with anionic MO contaminants, resulting in a higher photodegradation rate for MB than for MO. However, the stability of MO is higher than that of MB. As confirmed by Fig. 9, the self-degradation of MB aqueous solution is 9.54% after UV irradiation for 50 min, but that of MO is only 1.36% under the same conditions. These results indicate that the photodegradation activities of the CuO/T-ZnOw composite catalysts for cationic pollutants are significantly higher than those for anionic pollutants. This will be useful in future industrial applications.

4. Conclusions

CuO/T-ZnOw nanocomposites were prepared by a simple chemical method without using any OH^- reagents. PEG 400 molecules and T-ZnOw have a synergistic effect in the synthesis of CuO nanoparticles by depositing Cu^{2+} on the surfaces of T-ZnOw. The PEG 400 molecules serve as a soft template for the growth of CuO nanoparticles. There are numerous scale-like CuO particles regularly arranged on the T-ZnOw surfaces. All the CuO/T-ZnOw nanocomposites exhibit excellent activity in the decomposition of MB and MO organic dyes, and the photodegradation activities of the CuO/T-ZnOw composite catalysts for cationic pollutants (MB) are significantly higher than those for anionic pollutants (MO) under the same conditions. This will be useful in future industrial applications. The enhanced photocatalytic activity is attributed to the p(CuO)/n(T-ZnOw) heterostructure, which favors charge

transfer and inhibits recombination of photoinduced electron–hole pairs, increasing the photon-harvesting ability of the photocatalyst.

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Graphical Abstract

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Simple preparation of scale-like CuO nanoparticles coated on tetrapod-like ZnO whisker photocatalysts

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Poly(ethylene glycol) (PEG 400) molecules and tetrapod-like ZnO whisker (T-ZnOw) had a synergistic effect in the synthesis of CuO nanoparticles by depositing Cu^{2+} on the T-ZnOw surface. The PEG 400 molecules serve as a soft template for the growth of CuO nanoparticles.

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简单低温水浴法合成鳞片状氧化铜/四针状氧化锌晶须复合光催化剂

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摘要: 以硝酸铜为原料, 聚乙二醇(PEG, $M_w = 400$)为稳定剂和模板剂, 采用简单的低温水浴合成法成功合成了四针状氧化锌晶须(T-ZnOw)表面负载鳞片状CuO的纳米复合光催化剂, 系统研究了复合催化剂样品的晶体结构和形貌, 通过荧光发光光谱(PL)和紫外光照射的条件下样品对阳离子污染物(亚甲基蓝, MB)和阴离子污染物(甲基橙, MO)的光催化降解效率表征了样品的光催化性能, 同时采用ICP-AES详细分析了PEG 400浓度对T-ZnOw表面负载CuO纳米颗粒数量的影响。结果表明, T-ZnOw表面有序地沉积了大量鳞片状CuO纳米颗粒, 随着PEG 400浓度增加, T-ZnOw表面沉积的CuO纳米片数量逐渐增多, 且CuO纳米片在T-ZnOw表面的排列更加有序。同时, PEG 400浓度的变化对合成样品特征发光峰的强度也有一定影响, 当PEG 400浓度小于0.60 mol/L时, 合成样品特征发光峰强度随着PEG 400浓度增大而减小; 当PEG 400浓度大于0.60 mol/L时, 样品的特征发光峰强度随之有所增加。在紫外光照射条件下, CuO/T-ZnOw纳米复合催化剂样品对MB和MO水溶液的降解均表现出优异的光催化活性, 当PEG 400浓度 ≤ 0.60 mol/L时, 样品的光催化活性随着PEG 400浓度的增大而增加; 而当PEG 400浓度大于0.60 mol/L时, 样品的光催化活性反而有所降低。此外, 在相同条件下, 所有样品对MB水溶液的降解效率明显高于对MO水溶液的降解效率。

关键词: 鳞片状氧化铜; 聚乙二醇; 氧化铜/四针状氧化锌晶须; 光催化降解; 亚甲基蓝; 甲基橙

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For Author Index:

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