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Article (Special Issue on Photocatalysis)

Synthesis, characterization and photocatalytic performance of rod-shaped Pt/PbWO₄ composite microcrystals

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ARTICLE INFO

Article history:

Received 15 August 2015

Accepted 4 November 2015

Published 20 December 2015

Keywords:

Rod-shaped

Lead tungstate microcrystals

Platinum nanoparticles

Photocatalytic activity

Photocatalytic stability

Surface plasma

Electron-hole separation

ABSTRACT

Rod-shaped PbWO₄ microcrystals of length >1 μm were fabricated by a hydrothermal route and subsequent calcination. Pt nanoparticles (NPs) of different contents (0.5 wt%, 1 wt% and 2 wt%) were subsequently deposited on the PbWO₄ microcrystals, producing robust Pt/PbWO₄ composite microcrystals. The PbWO₄ microcrystals and Pt/PbWO₄ photocatalysts were characterized by X-ray diffraction, N₂ sorption measurements, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron, photoluminescence, Fourier-transform infrared, and ultraviolet-visible diffuse reflectance spectroscopies. The photocatalytic performances of the catalysts were evaluated by the consecutive photocatalytic degradation of acid orange II dye. The Pt/PbWO₄ composite microcrystals exhibited high photocatalytic activity and stability. The deposition of Pt NPs produced surface plasmon resonance (SPR), which induced a large visible light absorption. A Pt NP content of 1–2 wt% resulted in an ~2 times increase in photocatalytic activity, compared with the activity of Pt/PbWO₄. The crystal structure and high crystallinity of PbWO₄ resulted in its favorable photocatalytic property, and the SPR effect of the Pt NPs promoted visible light harvesting. The Pt NPs also enhanced the separation of photo-generated electrons and holes, which further promoted the photocatalytic reaction.

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1. Introduction

Photocatalysis is an environmentally friendly technology, with promising applications in environmental purification and in converting solar energy to chemical energy [1–6]. Under suitable light irradiation, most permanent organic pollutants in wastewater can be rapidly degraded by an appropriate photocatalyst. The main advantage of such process is relatively sim-

ple, and secondary pollution can be avoided. Many semiconductor photocatalysts have been developed, including large band gap semiconductors (e.g. TiO₂ [7], ZnO [8]), narrow band gap semiconductors (e.g. CdS [9], BiOBr [10,11], Ag₂CO₃ [12,13]), plasmonic noble metal (e.g. Au, Ag) nanoparticles (NPs) [14], Au₂₅(SR)₁₈ nanoclusters [15], and metal free photocatalysts (e.g. C₃N₄) [16].

Lead semiconductors are an important solid material. Lead

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This work was supported by the National Natural Science Foundation of China (21067004, 21567008, 21263005), Project of Jiangxi Province Natural Science Foundation China (20133BAB21003), Training Programs of Innovation and Entrepreneurship for Undergraduates of Jiangxi Province (201310407046), The Landing Project of Science and Technology of Colleges and Universities in Jiangxi Province (KJLD14046), and Young Scientist Training Project of Jiangxi Province (20122BCB23015), Yuanhang Engineering of Jiangxi Province.

DOI: 10.1016/S1872-2067(15)61009-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 12, December 2015

tungstate (PbWO_4) has received much recent interest, because it is widely used in inorganic scintillators in high-energy physics. PbWO_4 has favorable properties as a scintillator, including a short decay time (10 ns), high energy density (8.28 cm^3), low light yield (300 photons/MeV), short radiation length (0.9 cm), and high irradiation damage resistance (107 rad) [17]. The excitonic luminescence, thermoluminescence, and other optical properties of PbWO_4 crystals strongly depend on their morphology and nanostructure [18]. PbWO_4 nanocrystals with morphologies of tetragonal-bipyramidal microcrystals [17], microspheres [19], nanorods [19], nanospindles [20], nanobelts [21], and nanodendrites [22] have been reported. PbXO_4 ($X = \text{W}, \text{Mo}$) materials have attracted much recent attention as potential photocatalysts [23–29]. We previously demonstrated that the photocatalytic activity of PbWO_4 was determined by its microstructure and morphology [29]. Hierarchical PbWO_4 microspheres exhibited the highest activity among the morphologies of 14-faceted polyhedrons, hierarchical microspheres and nanoparticles. The PbWO_4 microspheres were also easily separated and recycled. Designing and fabricating high quality PbWO_4 crystals with desired microstructure or morphology is of fundamental and technological interest. Noble metal/composite structures are another strategy for improving photocatalytic performance [30,31]. In noble metal/semiconductor composites, the recombination of photo-generated electrons (e^-) and holes (h^+) is minimized because of efficient charge separation, in which e^- accumulate on the metal and h^+ remain on the photocatalyst surface.

In the current study, we prepared rod-shaped Pt/ PbWO_4 microcrystals (1–3 μm) by a hydrothermal route and subsequent calcination. Pt NPs of different contents (0.5–2 wt%) were then photo-deposited on the PbWO_4 microcrystals. The photocatalytic performances of the resulting catalysts in the degradation of aqueous acid orange II dye were investigated. To the best of our knowledge, such rod-shaped Pt/ PbWO_4 microcrystals have not been previously reported.

2. Experimental

2.1. Catalyst synthesis

Rod-shaped PbWO_4 microcrystals were fabricated by a hydrothermal route with subsequent calcination. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.658 g) was dissolved in 100 mL of deionized (DI) water under stirring, to obtain solution A. 1.056 g of $\text{Pb}(\text{NO}_3)_2$ and 0.8 g of CTAB were dissolved in 40 mL of DI water, and the resulting solution was added dropwise to solution A. After stirring for 30 min, the mixture was placed in a polytetrafluorethylene-lined stainless steel autoclave and maintained at 160 °C for 18 h. The resulting white powder was collected by centrifugation, washed twice with DI water, and dried in an oven at 100 °C. The sample was then calcined in a furnace for 2 h at 400 °C.

The Pt/ PbWO_4 composite microcrystals were prepared by the photo-deposition method. Approximately 1 g of PbWO_4 , 4 mL of methanol and the appropriate amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were added to 40 mL of DI water. The suspension was stirred in a 100 mL Pyrex round bottom flask for 30 min while purging

with a stream of N_2 , and then irradiated with an ultraviolet (UV) lamp ($\lambda_{\text{max}} = 365 \text{ nm}$) for 4 h. After irradiation, the powder was separated by centrifugation, washed with DI water, and dried under vacuum at 120 °C for 10 h. The catalyst loaded with $x \text{ wt}\%$ Pt was denoted $x\%\text{Pt}/\text{PbWO}_4$. The final Pt contents of the Pt/ PbWO_4 composites were determined by X-ray fluorescence analysis (Magix 601) to be ~0.5 wt%, 1 wt% or 2 wt%.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded at a scanning rate of $0.05^\circ/\text{s}$, using a Bruker D8 advance X-ray diffractometer at 40 kV and 40 mA with a $\text{Cu } K_\alpha$ radiation source ($\lambda = 0.15418 \text{ nm}$). Scanning electron microscopy (SEM) images were collected using a SU8000 scanning electron microscope, and were used to investigate sample morphologies. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected using a Tecnai 20 FEG microscope. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS), using a PHI Quantum 2000 XPS system with a monochromatic Al K_α source and a charge neutralizer. All binding energies were referenced to the C 1s peak of surface adventitious carbon at 284.8 eV. Photoluminescence (PL) emission spectra were recorded using a fluorescence spectrometer (Hitachi F-4500, Japan). Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet 470 FT-IR spectrometer (USA). Samples were pressed by a KBr disk preparation apparatus. Ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were recorded using a UV-Vis spectrophotometer (UV-2550, Shimadzu).

2.3. Photocatalytic activity

The photocatalytic activities of the bare PbWO_4 and Pt/ PbWO_4 samples were determined by the degradation of aqueous acid orange II dye. 50 mg of photocatalyst was suspended in 100 mL acid orange II (20 mg/L). A 500 W Xe lamp (CHF-XM-500W) was used as the light source. Before irradiation, the suspension was stirred by magnetic force in the dark for 40 min to ensure sorption equilibrium between the dye and photocatalyst. During the degradation process, the reaction temperature was maintained at 20 °C by the circulation of water. After fixed irradiation intervals, ~2 mL aliquots of suspension were removed, and the solids removed by centrifugation. The acid orange II concentration of the clear upper layer was determined by UV-Vis spectrophotometry, from its absorbance at $\lambda = 484 \text{ nm}$.

3. Results and discussion

3.1. XRD and surface area analysis

The phase composition and crystal properties of the samples were analyzed by XRD. Fig. 1 shows the XRD patterns of the bare PbWO_4 and Pt/ PbWO_4 samples. Similar diffraction peaks at $2\theta = 27.43^\circ, 29.66^\circ, 32.75^\circ, 44.72^\circ, 47.07^\circ, 51.27^\circ$,

Fig. 1. XRD patterns of PbWO₄ and Pt/PbWO₄ containing varying Pt concentrations.

55.34° and 56.58° were observed in the XRD patterns of the four samples. These peaks corresponded to the (400), (211), (410), (212), (511), (402), (013), and (−603) planes, respectively, which were indexed to the monoclinic stolzite phase of PbWO₄, with unit cell constants of $a = 13.525 \text{ \AA}$, $b = 4.968 \text{ \AA}$, and $c = 5.546 \text{ \AA}$ (PDF 16-0156). The space group belongs to P2₁/a(14). The strong and sharp diffraction peaks indicated a high degree of crystallinity. No peaks of any other phases were detected in any of these patterns, because of the small crystallite size and low Pt concentration.

The average crystallite size of the bare PbWO₄ and Pt/PbWO₄ samples was estimated using the Scherrer equation. The strongest diffraction plane of PbWO₄ was the (400) plane, which was used in this calculation. Table 1 shows the average crystallite sizes and surface areas of the bare PbWO₄ and Pt/PbWO₄ composites. The average crystallite size of PbWO₄ was 65–70 nm. While small variations in crystallite size were observed, the Pt loading appeared to have little effect on the crystal properties of PbWO₄. Table 1 indicates that the bare PbWO₄ and Pt/PbWO₄ composites had very small specific surface areas (1.5–1.9 m²/g). The Pt NP loading resulted in a small increase in surface area.

3.2. SEM and TEM analysis

Fig. 2 shows a representative SEM image of the bare PbWO₄, showing well-dispersed rod-shaped particles. The rods were typically ~1–1.5 μm long, consistent with a morphology of rod-shaped PbWO₄ microcrystals.

The morphology and crystallinity of the 1%Pt/PbWO₄ sam-

Fig. 2. SEM image of the PbWO₄ sample.

ple were further investigated by TEM. Fig. 3(a) shows a TEM image of a well-formed PbWO₄ microrod, with a smooth surface, diameter of 100 nm, and length of >1 μm. Some small spherical particles of diameter 1–5 nm were observed on the smooth microrod surface, consistent with Pt NPs deposited on the surface of PbWO₄ microcrystals. Fig. 3(b) shows a high magnification TEM image of a single Pt particle, indicating a particle size of ~6 nm. A close-contact Pt–PbWO₄ interface was produced across the entire Pt/PbWO₄ composite. In this Pt/PbWO₄ system, the recombination of photo-generated e[−] and h⁺ could be suppressed, because e[−] accumulated on Pt NPs which were separation from h⁺.

Fig. 3(c) shows a HRTEM image of a PbWO₄ microrod, in which the crystal face was structurally uniform. The interplanar spacing of ~0.55 nm corresponded to the [001] lattice spacing of monoclinic PbWO₄. The vertical direction of the [001] plane corresponded to the (001) crystal axis (red line). The XRD analysis showed that the PbWO₄ was of monoclinic phase with $\alpha = 90^\circ$, $\beta = 107.7^\circ$, and $\gamma = 90^\circ$ (PDF card No. 16-0156), with an intersection angle of 27.63° between the

Fig. 3. TEM images of the Pt(1%)/PbWO₄ sample Low (a) and high (b) magnification TEM images; (c) HRTEM image; (d) SAED pattern of the PbWO₄ microrod in (a).

Table 1

Crystallite sizes and specific surface areas of the samples.

Sample	Average crystallite size (nm)	Specific surface area (m ² /g)
PbWO ₄	67.9	1.6
0.5%Pt/PbWO ₄	69.7	1.5
1%Pt/PbWO ₄	65.2	1.8
2%Pt/PbWO ₄	65.7	1.9

(001) crystal direction and crystal growth direction. Thus, the growth direction of the PbWO_4 microrods was along the (-102) crystal direction. The selective area electron diffraction (SAED) pattern in Fig. 3(d) recorded from the body of the PbWO_4 microrod showed that it was of high crystallinity.

3.3. XPS analysis

XPS was used to investigate the surface composition and elemental states of 1%Pt/ PbWO_4 . Fig. 4(a) shows the XPS survey spectrum of 1%Pt/ PbWO_4 , showing that the sample mainly consisted of Pb, W, O, and Pt. The mass fractions of Pt, Pb, W, and O on the 1%Pt/ PbWO_4 surface were estimated to be 0.96%, 45.0%, 43.0%, and 14.0%, respectively. High-resolution XPS spectra of the O 1s, W 4f, Pb 4f, and Pt 4f regions are shown in Fig. 4(b), (c), (d) and (e), respectively. The O 1s region (Fig. 4(b)) contained two peaks at 530.3 and 532.1 eV, which were attributed to O^{2-} in PbWO_4 and surface hydroxyl groups, respectively. The W 4f region (Fig. 4(c)) contained two peaks at 35.7 and 37.6 eV, which were attributed to the binding energies of $\text{W } 4f_{7/2}$ and $\text{W } 4f_{5/2}$, and were similar to literature values for W^{6+} [32]. The high-resolution XPS spectrum of the core levels of the Pt 4f region is shown in Fig. 4(e). The binding energies of 74.76 and 71.46 eV corresponded to the Pt $4f_{5/2}$ and Pt $4f_{7/2}$ states, respectively, which were consistent with Pt(0) [33].

3.4. UV-Vis DRS properties

UV-Vis DRS was used to determine the absorption of the samples at different wavelengths (200–800 nm). Fig. 5 shows the UV-Vis DRS spectra of the bare PbWO_4 and Pt/ PbWO_4 samples. Bare PbWO_4 absorbed at ~ 330 nm, which was outside the

Fig. 5. UV-Vis DRS spectra of the bare PbWO_4 and Pt/ PbWO_4 samples.

visible region. Visible light (350–600 nm) absorption was observed for the Pt/ PbWO_4 samples. Pt NPs deposited on semiconductors can reportedly induce surface plasma absorption in the visible range [30]. The visible light absorption of Pt/ PbWO_4 originated from surface plasma absorption, and was consistent with the presence of Pt NPs.

3.5. FT-IR properties

The catalyst surface properties were further analyzed by FT-IR spectroscopy. Fig. 6 shows the FT-IR spectra of the samples. According to the Ref. [34,35], the characteristic absorption band at ~ 700 – 900 cm^{-1} was ascribed to the W–O stretching vibration of WO_4 tetrahedra. Bands at ~ 1625 and ~ 3447 cm^{-1}

Fig. 4. XPS spectra of the 1%Pt/ PbWO_4 sample. (a) Survey spectrum; (b) O 1s; (c) W 4f; (d) Pb 4f; (e) Pt 4f.

Fig. 6. FT-IR spectra of the bare PbWO_4 and Pt/PbWO_4 samples.

were assigned to the OH bending and stretching modes, respectively. A relatively strong intensity of the absorption peak of –OH groups was observed for the Pt/PbWO_4 samples. During photocatalysis, –OH groups can capture photogenerated h^+ and transform to $\cdot\text{OH}$ radicals, which are the main reactive species for the decomposition of organic dyes. Therefore, an increase in the number of surface –OH groups potentially improves photocatalytic activity.

3.6. PL properties

Fig. 7 shows the room temperature PL emission spectra of the bare PbWO_4 and Pt/PbWO_4 samples. All samples exhibited an emission peak at ~ 476 nm. The PL emission of PbWO_4 microcrystals typically consists of two bands, named green luminescence and blue luminescence [36]. The peaks at ~ 470 and ~ 500 nm corresponded to blue and green luminescence, respectively. The emission peak at ~ 476 nm could be attributed to the radiative recombination of self-trapped excitons localized on regular WO_4 complex anions. The intensity of the PL peaks of Pt/PbWO_4 was much weaker than that of PbWO_4 . The PL spectrum of a semiconductor largely results from the radiative recombination of self-trapped excitons. The weak intensity

Fig. 7. PL spectra of the bare PbWO_4 and Pt/PbWO_4 samples.

suggested a low recombination rate of e^-/h^+ pairs, and high photon efficiency for catalysis.

3.7. Photocatalytic performance

Acid orange II was chosen as the photodegradation target under Xe lamp illumination. Fig. 8(a) shows that during irradiation, the photolysis of acid orange II did not occur in the absence of a photocatalyst. Introducing bare PbWO_4 microcrystals resulted in the rapid degradation of acid orange II, suggesting the PbWO_4 possessed high photocatalytic activity. The high crystallinity and UV absorption of the bare PbWO_4 contributed to its high activity. Loading Pt NPs into the PbWO_4 resulted in a large increase in activity, which was closely related to the Pt NP content. Increasing the Pt NP content from 0.5% to 1% resulted in an obvious increase in photocatalytic activity. Further increasing the Pt NP content to 2% resulted in only a small increase in activity. Acid orange II was completely decomposed within 50 min under irradiation in the presence of Pt/PbWO_4 . To evaluate the photocatalytic performance of the Pt/PbWO_4 microcrystals, the activity of the standard photocatalyst P25 (TiO_2 , $\sim 80\%$ anatase 20% rutile, Degussa Co., Dossenheim, Germany) was compared under the same conditions. The

Fig. 8. Decomposition of acid orange II under Xe lamp irradiation. (a) Change in acid orange II solution concentration with reaction time; (b) Kinetics of acid orange II decomposition.

Pt/PbWO₄ microcrystals exhibited higher activity than P25.

The pseudo first order kinetics model expressed by $\ln(C_0/C) = kt$ was used to describe the kinetics of the acid orange II degradation. Fig. 8(b) shows the kinetics of acid orange II degradation in solution, based on the data in Fig. 8(a). The rate constants were obtained from the regression lines in Fig. 8(b). A good correlation to the pseudo first order model ($R^2 > 0.99$) was observed for the four samples. The rate constants over PbWO₄, 0.5%Pt/PbWO₄, 1%Pt/PbWO₄, and 2%Pt/PbWO₄ were calculated to be 0.028, 0.036, 0.051, and 0.054 min⁻¹, respectively. Based on the above surface area data, the apparent rate constants for the degradation per unit surface area of the four catalysts were ~0.0175, 0.024, 0.0283 and 0.0284 min⁻¹m⁻², respectively.

One advantage of the rod-shaped Pt/PbWO₄ microcrystals was their ease of separation and recycling, which resulted from their high density. The stability of the 1%Pt/PbWO₄ catalyst was therefore tested over consecutive reactions, as shown in Fig. 9. The activity of the photocatalyst slightly decreased with increasing recycling number. The degradation rate of acid orange II decreased from 93% in the first reaction to 88% in the fourth reaction. This indicated that the photocatalyst had high photocatalytic stability. The rod-shaped Pt/PbWO₄ microcrystals are therefore promising for practical application.

Based on the characterization and photocatalysis results, a diagram accounting for the high photocatalytic activity of the rod-shaped 1%Pt/PbWO₄ microcrystals was proposed, as shown schematically in Fig. 10.

For the bare PbWO₄ microcrystals under Xe lamp irradiation, UV light excited electrons in the PbWO₄ valence band (VB) to the conduction band (CB), resulting in holes in the VB. The e⁻ and h⁺ could convert to reactive radicals like O₂⁻ and •OH, which decomposed the dye. The fraction of UV light emitted by the source was low, but the high crystallinity and rod-shaped structure of PbWO₄ lead to a high quantum efficiency in the photocatalytic reaction. Two explanations are given for the enhanced photocatalytic performance of the 1%Pt/PbWO₄ microcrystals and the effect of Pt NPs. Pt NPs deposited on the PbWO₄ microcrystals could act as electron traps, promoting e⁻/h⁺ separation, as suggested in Fig. 7. The trapped electrons could react with surface-adsorbed O₂, to generate O₂⁻. On the other hand, holes accumulated in the VB of PbWO₄ could react

Fig. 10. Proposed mechanism for the photocatalytic reaction in the rod-shaped 1%Pt/PbWO₄ microcrystals.

with H₂O to give form •OH radicals. O₂⁻ and •OH radicals were the main active species responsible for the decomposition of the dye. Quenching and radical production experiments were carried out, to confirm the identity of the radicals involved in dye degradation in the presence of Pt/PbWO₄. *p*-Benzoquinone (BZQ) is an O₂⁻ radical scavenger [6]. Fig. 11 shows that adding 2 m mol BZQ rapidly deactivated the Pt/PbWO₄. BZQ could have captured O₂⁻, thus decreasing the amount of O₂⁻ available for photocatalytic reaction. •OH radicals could also have been involved in dye degradation. Coumarin readily reacts with •OH to form the highly fluorescent product 7-hydroxycoumarin. Under irradiation, •OH radicals generated in Pt/PbWO₄ solution in the presence of Fe³⁺ were detected by a fluorescence technique, using coumarin as an •OH trap. Fig. 12 shows PL spectra of coumarin•OH adducts (7-hydroxycoumarin), generated in the irradiated 1%Pt/PbWO₄ suspension. The intensity of the PL peak increased with increasing time, indicating an increase in the amount of generated •OH radicals.

Photocatalysis could also have been mediated by the surface plasmon resonance (SPR) of the Pt NPs [30]. Fig. 5 shows that the presence of the Pt NPs increased the visible light (350–600 nm) absorption of the composite. SPR-mediated photocatalysis could have involved the SPR-induced excitation of noble metal NPs under visible light, and electrons could have transferred from the Pt NPs to the CB of PbWO₄. These electrons could then be trapped by O₂, to form reactive oxygen species like O₂⁻. The

Fig. 9. Stability of the 1%Pt/PbWO₄ microcrystals over consecutive reactions.

Fig. 11. Effect of BZQ on the photocatalytic degradation of acid orange II by 1%Pt/PbWO₄.

Fig. 12. PL spectra of aqueous Pt/PbWO₄-coumarin (1 mmol/L) under irradiation.

resulting positively charged Pt⁺ could also oxidize organic molecules. The BET analysis showed that loading with Pt NPs did not change the surface area of the catalyst. Therefore, the Pt NP content could have influenced the efficiency of e⁻/h⁺ separation. A suitable Pt NP content could provide good particle dispersion on the PbWO₄ surface. Excess Pt NPs would result in large overlapping particles, leading to new recombination centers, and adversely effecting charge separation.

4. Conclusions

Rod-shaped PbWO₄ microcrystals of high crystallinity were synthesized via a hydrothermal route with subsequent calcination. Pt NPs were subsequently deposited on the PbWO₄ microcrystals by a photo-deposition method, producing rod-shaped Pt/PbWO₄ composite microcrystals. Pt/PbWO₄ exhibited high activity and stability in the photodegradation of acid orange II dye. The favorable crystal structure and high crystallinity resulted in the good photocatalytic activity of PbWO₄. The well-dispersed Pt NPs produced a SPR effect that promoted visible light harvesting. The Pt NPs also acted as electron traps to promote electron-hole separation, which fur-

ther promoted the photocatalytic reaction. The rod-shaped Pt/PbWO₄ microcrystals have potential in the degradation of organic pollutants and other environmental purification applications.

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Graphical Abstract

Chin. J. Catal., 2015, 36: 2178–2185 doi: 10.1016/S1872-2067(15)61009-9

Synthesis, characterization and photocatalytic performance of rod-shaped Pt/PbWO₄ composite microcrystals

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A novel Pt NPs deposited PbWO₄ composite microrod was fabricated by a hydrothermal route combination with calcination method. The unique crystal and texture properties lead to the high photocatalytic activity and stability in recycling reactions.

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棒状结构Pt/PbWO₄微米晶的合成、表征及其高光催化性能

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摘要: PbWO₄是一类重要的半导体, 广泛运用于高能物理领域无机闪烁晶体. 它具有许多独特的物理性能, 如衰减时间短(10 ns)、能量密度高(8.28 cm³)、低光产率(300 photons/MeV)、短辐射长度(0.9 cm)和高抗辐射损伤等. PbWO₄纳米晶体的激子荧光、热荧光和其它光学性能主要取决于PbWO₄晶体的形貌和微观结构. 目前已经合成了不同结构的PbWO₄纳米/微米晶体, 如四角双锥微米晶、微米球、纳米棒、纳米纺垂体等. 近年来, PbWO₄的光催化性能也引起人们的重视. 研究发现, PbWO₄晶体的光催化性能和其形貌、微观结构密切相关. 如在不同形貌的十四面体、三维多尺度微米球和纳米颗粒中, PbWO₄微米球表现了极高的光催化活性. 此外, PbWO₄微米球由于密度大, 非常容易分离, 从而有利于其回收利用, 在循环使用时具有很高的稳定性. 因此, 合成具有特殊形貌的PbWO₄纳米/微米晶体具有重要的理论和现实意义. 此外, 合成贵金属/半导体复合纳米结构是提高光催化性能的另一有效策略. 在贵金属/半导体复合纳米结构中, 光生电子(e⁻)和(h⁺)的复合可以在很大程度上得到抑制, 因为光生e⁻可以快速地迁移至贵金属颗粒中心, 从而加速e⁻和h⁺的分离.

本文利用水热结合焙烧法首先合成了长度大于1 μm的棒状PbWO₄微米晶. 然后利用光化学沉积法, 在PbWO₄微米晶表面沉积不同含量(0.5 wt%, 1 wt%, 和2 wt%)的Pt纳米粒子. 利用X射线衍射(XRD)、N₂物理吸附、扫描电镜(SEM)、透射电镜(TEM)、光电子能谱(XPS)、光致发光谱(PL)和紫外-可见漫反射吸收光谱(UV-Vis DRS)等手段对所制PbWO₄和Pt/PbWO₄进行了表征. 表征结果表明, 合成的PbWO₄和Pt/PbWO₄的比表面积很小(1.5–1.9 m²/g), 沉积的Pt纳米粒子为金属态. UV-Vis DRS测试表明, 沉积的Pt纳米粒子在光照下可以产生表面等离子共振, 促进可见光的吸收. 另外, PL的结果则证实Pt纳米粒子的存在还可抑制PbWO₄晶体在光照下产生的光生e⁻和h⁺的分离. 而XRD和高分辨TEM分析表明PbWO₄微米棒的晶体生长方向为(-102)晶体方向. 电子选区衍射表明, 棒状PbWO₄微米晶具有极高的结晶度. 以氙灯为光源进行了光催化降解染料酸性橙II的光催化性能测试. 结果表明, 当沉积1–2 wt%Pt纳米粒子时, 可使光催化活性提高2倍左右. 另外, Pt/PbWO₄微米棒的密度较大, 非常容易进行离心分离催化剂及其循环使用. 在第一次使用时酸性橙II的降解率为93%, 而在第四次使用时酸性橙II的降解率仍维持在88%, 表现出很好的光催化稳定性. Pt/PbWO₄具有很高的光催化活性的原因, 一方面是由于其具有很高的结晶度和独特的棒状结构, 另一方面是由于沉积的Pt纳米粒子在光照下可以产生表面等离子共振, 促进了可见光的吸收和光生e⁻与h⁺的分离.

关键词: 棒状; 钨酸铅微米晶; 铂纳米粒子; 光催化活性; 光催化稳定性; 表面等离子体; 电子-空穴分离

收稿日期: 2015-08-15. 接受日期: 2015-11-04. 出版日期: 2015-12-20.

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基金来源: 国家自然科学基金(21067004, 21567008, 21263005); 江西省自然科学基金(20133BAB21003); 江西省大学学生创新创业训练计划(201310407046); 江西省高等学校科技落地项目(KJLD14046); 江西省青年科学家项目(20122BCB23015); 江西省远航工程.

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).