Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 348–355

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Facile synthesis of $PbWO_4$: Applications in photoluminescence and photocatalytic degradation of organic dyes under visible light

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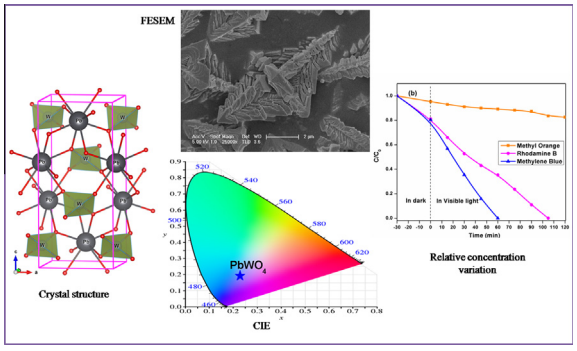
HIGHLIGHTS

- We report stolzite $PbWO_4$ phosphor material by precipitation method at room temperature.
- $PbWO_4$ phosphor revealed broad and intense blue luminescence.
- We achieved 100% MB and RhB dye degradation in 60 and 105 min.
- The photocatalytic degradation was in the order of MB > RhB > MO under visible light irradiation.
- $PbWO_4$ can be a favorable candidate to fabricate blue component in white LEDs and to remove the textile effluents.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 May 2014
Received in revised form 29 August 2014
Accepted 18 September 2014
Available online 6 October 2014

Keywords:
$PbWO_4$
Scheelite structure
Rietveld refinement
Phosphor
Photocatalytic degradation

ABSTRACT

Stolzite polymorph of $PbWO_4$ catalyst was prepared by the facile room temperature precipitation method. Structural parameters were refined by the Rietveld analysis using powder X-ray data. $PbWO_4$ was crystallized in the scheelite-type tetragonal structure with space group $I4_1/a$ (No. 88). Field emission scanning electron microscopy revealed leaf like morphology. Photoluminescence spectra exhibit broad blue emission (425 nm) under the excitation of 356 nm. The photocatalytic degradation of Methylene blue, Rhodamine B and Methyl orange dyes were measured under visible illumination. The 100% dye degradation was observed for MB and RhB dyes within 60 and 105 min. The rate constant was found to be in the decreasing order of MB > RhB > MO which followed the 1st order kinetic mechanism. Therefore, $PbWO_4$ can be a potential candidate for blue component in white LEDs and also acts as a catalyst for the treatment of toxic and non-biodegradable organic pollutants in water.

Introduction

Organic dyes were widely used in the textiles, paper, plastics, leather, food, cosmetic and various other industries to color products. The effluents from these industries were water soluble and causing serious threat to aquatic life and environment. Due to the increase in chemical oxygen demand (COD), reducing light penetration and visibility in the water [1–3]. Since most of them are stable and resistant to bio/photodegradation, the removal of these discharged dyes has been an active area of research. During the last two decades, semiconductor metal oxides and sulfides have been found to possess the ability to decompose organic pollutants. A good photocatalytic material should be cheap and highly effective in utilizing visible light.

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http://dx.doi.org/10.1016/j.saa.2014.09.038
1386-1425/

In recent years, the metal tungstates have been focused due to their structural, optical and photocatalytic properties [4,5]. As a member of the tungstate family, lead tungstate ($PbWO_4$) is an important inorganic scintillating semiconductor. There are two different polymorphs of lead tungstate: stolzite and raspite [6]. At room temperature, stolzite $PbWO_4$ presents a scheelite-type tetragonal structure (space group: $I4_1/a$, with $Z = 4$). On the other hand, dimorphous with the monoclinic form raspite. Stolzite $PbWO_4$, with scheelite structure, is most attractive because of their high density (8.28 g/cm^3), short decay time, high-irradiation damage resistance, interesting luminescence and stimulated Raman scatting behavior [7,8]. $PbWO_4$ exhibits self luminescence in almost entire visible spectrum which could be decomposed in blue, green and red components under UV excitation. The emission in blue region was assigned to the charge transfer transition within WO_4^{2-} group [9].

Several methods have been employed to synthesize $PbWO_4$, such as solid-state reaction [10], flux method [11], Czochralski [12] and Bridgman method [13]. All these methods require high temperature, long processing time and sophisticated equipment with high maintenance costs. However, room temperature precipitation method offers advantages as less time consuming, convenient, economical and environmental friendly.

In the present study, stolzite $PbWO_4$ compound was synthesised by wet chemical approach without using any stabilizing agent or surfactants. The synthesized compound was characterized by using powder X-ray diffraction (XRD), Field emission Scanning electron microscopy (FESEM), BET surface area, Transmission electron microscopy (TEM), Fourier transform infrared (FTIR), UV–Visible and Photoluminescence (PL) spectroscopy. The photocatalytic performance for different organic dyes (MO, RhB and MB) was examined in detail.

Experimental

Synthesis of stolzite $PbWO_4$

All the chemicals of analytical grade were used without further purification. $PbWO_4$ compound was synthesized by the precipitation method at room temperature. In the synthesis process, the stoichiometric amount of $Pb(NO_3)_2$ (0.1 M) and $Na_2WO_4{\cdot}2H_2O$ (0.1 M) were dissolved in 50 ml distilled water separately. The lead nitrate solution was added dropwise to sodium tungstate solution and stirred for an hour. The resulting white slurry was kept for 2 h without disturbing. The chemical reaction between lead nitrate and sodium tungstate in aqueous medium is as follows:

$$Pb(NO_3)_2 + Na_2WO_4 \cdot 2H_2O \rightarrow PbWO_4 + 2NaNO_3 + 2H_2O \quad (1)$$

The resulting white precipitate was filtered and washed with distilled water several times. Then, it was dried at 100 °C in the hot air oven for further characterization. The obtained $PbWO_4$ compound was white in color.

Characterization

The phase purity of $PbWO_4$ compound was examined by powder X-ray diffractometer (XRD) (PANalytical X'Pert Pro) using Cu Kα radiation ($\lambda = 1.5418$ Å) with a nickel filter. Rietveld analysis measurement was performed in a step mode with 2θ varying from 10° to 80° with scanning rate of 0.02 min^{-1}. The structural parameters were estimated by using FullProf Suite-2000 programme. The surface morphology was examined by field emission scanning electron microscopy (FE-SEM, FEI Sirion XL 30) at accelerating voltage of 10 kV. The N_2 adsorption study at 77 K was performed on the Autosorb-1C (Quantachrome corp.). A Fourier transform infrared (FTIR) spectrum was recorded using Perkin Elmer FTIR/FIR Spectrometer, Frontier, and the KBr was used as a reference sample. The UV–Vis absorption spectrum of the powder sample was recorded on Perkin Elmer Lambda 750 spectrophotometer. The photoluminescence studies were performed on a Horiba Flurolog-3 spectrofluorimeter using 450 W Xenon lamp as excitation source. The photocatalytic degradation rates of Methylene blue, Rhodamine B and Methyl orange solutions were analyzed by Perkin Elmer UV–Visible spectrophotometer (Lambda 35) in the range from 200 to 800 nm periodically.

Evaluation of photocatalytic activity

Basic Methylene blue, Rhodamine B dyes and acidic Methyl orange dye were selected as model organic compounds to examine the photocatalytic activity of stolzite polymorph of $PbWO_4$ catalyst. In a typical photocatalytic reaction, about 50 mg of catalyst was added to 50 ml of Methylene blue dye with an initial concentration of 5×10^{-6} M to get a suspension. The suspension was magnetically stirred for 30 min in the dark to establish an adsorption/desorption equilibrium between the dye and the photocatalyst. Then the mixed solution was irradiated with a metal halide lamp (500 W, $\lambda > 420$ nm) for different time. During each photocatalytic experiment, 3 ml of the suspension was collected at predetermined time intervals and centrifuged to remove the catalyst particles for analysis. The supernatants were analyzed by recording variations of the absorption band maximum in the UV–Vis spectra periodically. Similarly, the photocatalytic activity was performed for Rhodamine B and Methyl orange dyes. The stability of $PbWO_4$ catalyst was verified for three cycles. The efficiency of the dye degradation was calculated by the following equation [14]:

$$\text{Degradation efficiency}(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration at 0 min and C is the concentration at certain reaction time t.

Results and discussion

Powder X-ray diffraction

The phase purity of the $PbWO_4$ compound was analyzed by powder XRD. No secondary phase or impurity peaks were observed in the XRD pattern, which confirmed the formation of single phase compound. All observed diffraction peaks were matched with the reported tetragonal stolzite phase of $PbWO_4$, JCPDS card No. 86-0843. The crystallographic structural parameters were refined by the Rietveld refinement method. Fig. 1 shows the observed, calculated and the difference XRD patterns of $PbWO_4$ compound. The difference between XRD pattern profiles experimentally observed and calculated data display near to zero in the intensity scale. Refined structural parameters, selected bond lengths and bond angles were summarized in Table 1. The crystal structure was modeled through VESTA program [15] using lattice parameters and atomic positions obtained from Rietveld refinement analysis. In $PbWO_4$ crystal structure (Fig. 1, see inset), lead (Pb) atom was coordinated to eight oxygen (O) atoms which results in deltahedral [PbO_8] clusters. The tungsten (W) atom was coordinated to four oxygen atoms which form [WO_4] clusters. These [WO_4] clusters were slightly distorted in the lattice due to difference in the O–W–O bond angles. The average crystallite size was estimated using Scherrer's equation [16]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where λ is the wavelength (1.5418 Å) of X-rays, β is the full width at half maximum (FWHM), θ is the diffraction angle, k is the shape