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Short communication

Microwave-assisted synthesis of nanoscale tungsten trioxide hydrate with excellent photocatalytic activity under visible irradiation



Xu–Teng Yu^{a,1}, Heng–Xin Liu^{a,1}, Yanhua Shen^{b,1}, Jian–Ying Xu^a, Feng–Ying Cai^a, Taohai Li^{b,c,*}, Jian Lü^{a,d,**}, Wei Cao^c

^a Fujian Provincial Key Laboratory of Soil Environmental Health and Regulation, College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, PR China

b College of Chemistry, Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, PR China ^c Nano and Molecular Systems Research Unit, Faculty of Science, P. O. Box 3000, University of Oulu, FIN 90014, Finland

^d Samara Center for Theoretical Materials Science (SCTMS), Samara State Technical University, Samara 443100, Russia

GRAPHICAL ABSTRACT

Tungsten trioxide hydrate (WO₃·1/3H₂O) nanoparticles (NPs) were prepared and applied in visible–light–driven photocatalysis for organic dye degradation.



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Keywords: Tungsten trioxide Nanoparticle Photocatalysis Microwave-assisted synthesis Dye degradation

ABSTRACT

Tungsten trioxide hydrate (WO3.1/3H2O) nanoparticles (NPs) were prepared via a microwave-assisted synthetic pathway by using Na2WO4:2H2O and PdCl2 as precursors. Microstructure and morphology of as-prepared WO₃·1/3H₂O NPs were investigated through X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared (FT-IR) spectra, while porosity and bandgap through specific surface area and UV-vis absorption spectroscopy. It was found that Pd^{2+} ions played a crucial role in the formation of WO₃ 1/ 3H₂O NPs, and thus a possible formation mechanism was proposed based on the growth processes. The photocatalytic property of WO3.1/3H2O NPs was evaluated on the basis of Rhodamine B (RhB) degradation in aqueous solutions under simulated visible irradiation. Photocatalytic experimental results indicated that as--prepared WO₃·1/3H₂O NPs exhibited much more superior photocatalytic activity by contrast to that of the commercial WO3.

E-mail addresses: hnlth@xtu.edu.cn (T. Li), jian_lu_fafu@163.com (J. Lü).

¹ These authors contribute equally.

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^{*} Corresponding author at: College of Chemistry, Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, PR China.

^{**} Corresponding author at: Fujian Provincial Key Laboratory of Soil Environmental Health and Regulation, College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, PR China.

Low-dimensional nanomaterials, e.g. nanoparticles, nanorods, and nanotubes, have been within the research focus of functional materials due to their unique physical and chemical properties in comparison with their bulk counterparts. A wide range of advanced applications have been developed based on these novel nano-complexes [1-3]. Many low-dimensional nanostructures can be synthesized through self-assembled growth by means of simple and spontaneous processes, paving a facile route for their applications in large scales. Among the various low-dimensional materials, semiconductor metal oxides have attracted tremendous attentions because of their distinctive utilities in optics and electronics. For instance, the tungsten trioxide (WO₃) in nanoparticle form is an n-type indirect wide band gap semiconductor material [4,5]. Due to its high work function, WO₃ has been employed as a charge injection layer [6], further to the high catalytic activity that enables WO3 to be useful for photocatalytic and electrocatalytic purposes [7,8]. Furthermore, WO₃ is widely used in electrochemical Li ion batteries, electrochromic, thermochromic, and photochromic devices [9–12].

A number of chemical and physical methods have been developed for the synthesis of low-dimensional WO3 nanostructures including hydrothermal/solvothermal synthesis [13-16,9,17], hot-wire chemical vapor deposition [18], spray pyrolysis [19], template mediated synthesis [14], sol-gel method [20-22] and micro-emulsion technique [23]. Among these techniques, the microwave heating route distinguishes itself from other conventional methods with the following features: (i) microwave heating enables a new heating way down to molecular levels, even at small temperature gradient through molecular dynamics; (ii) the adjustable heating characteristics of microwave can precisely tune vapor-phase temperatures, improving selectivity of reactions; (iii) the microwave heating has little residual heat. When power generator is switched off, the microwave immediately stops. The non-delayed effect makes the reactions with higher demand for controlling temperature progress; and (iv) the high-speed heating accelerates the speed of disposing materials, offering a very good efficiency of energy utilization. Thus, microwave-assisted synthesis may result in a high-speed, low-cost, pollution-free and high-efficient method for the preparation of inorganic oxide semiconductor-tungsten trioxide. Several studies have been reported in literatures towards the preparation of WO₃ powders via microwave-assisted methods. Hernandez-Urestia et al. described a hydrothermal method without the use of any additives during the synthesis of WO₃ nanoparticles [24]. The products exhibit either hexagonal or monoclinic structures by varying the time (30 or 60 min) of microwave hydrothermal reactions. Recently, doping of metal ions in WO₃ represents a promising means to enhance their excellent catalytic activities. Hence, various metal ions such as Co²⁺, Cu²⁺, Zn²⁺, Cr³⁺ and Ti⁴⁺ have been tentatively doped into WO₃ nanomaterials [25–29]. For example, Kovendhan reported that 5% Li-doped WO₃ resulted in blue-shift of photoemission and structural change from the orthorhombic to tetragonal phase [30]. Boubaker investigated the Zn/In--doped WO3 and proposed that quantum-linked lattice disorder could influence the final photoresponse [31]. Despite of above achievements, very few investigations have been carried out to study the effect of cation or anion of salts on the formation of WO₃.

In the present work, tungsten trioxide hydrate WO₃·1/3H₂O nanoparticles were synthesized through a facile microwave–assisted hydrothermal method by which the morphology of nanomaterials was controlled. Based on the experimental results, we discovered that Pd^{2+} ions played a crucial role in the formation of the WO₃·1/3H₂O nanostructures, and thus a possible formation mechanism were proposed. In addition, the photocatalytic activity of as–prepared WO₃·1/3H₂O was investigated, which was much superior to that of the commercial WO₃, for Rhodamine B (RhB) degradation in aqueous solutions under simulated visible irradiation. These results indicated that the as–prepared WO₃·1/3H₂O nanostructures possessed great potentials as visible–light–driven photocatalysts.

Sodium tungstate dihydrate (Na2WO4·2H2O), palladium chloride

(PdCl₂), palladium acetate palladium acetate (Pd(AC)₂), cobalt chloride anhydrous (CoCl₂), Rhodamine B (RhB), methyl orange (MO), methylene blue (MB) and absolute ethanol were commercially purchased and used without further purification or modification. Reaction and stock solutions were prepared by using deionized water provided with a UPT–I–5T ultrapure water system.

The X-ray powder diffraction (XRD) was performed by using a MiniFlex II X-ray diffractometer operated at 40 kV and 40 mA to get the Cu K α_1 ($\lambda = 0.15406$ nm) line as the incident source. The XRD data were recorded at the 2 θ range of 5–70° with a scan rate of 0.02° s⁻¹. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100 microscope with a LaB6 filament at an accelerating voltage of 200 kV. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption isotherm obtained at 77 K in a constant volume adsorption apparatus (2020 M). FTIR spectra were recorded in the range of 400–4000 cm^{-1} at a step of 2.0 cm^{-1} and KBr as pellets. The UV–vis absorption spectra were recorded on a Lambda 25 UV-vis spectrophotometer (Perkin-Elmer, USA) in the range of 200-800 nm. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-vis spectrophotometer (UV-2550) with BaSO₄ as the background. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi spectrometer with Al Ka X-ray source (15 kV, 10 mA).

To synthesize WO_3 ·1/3H₂O nanomaterials, 330 mg sodium tungstate dihydrate (Na₂WO₄·2H₂O) and 178 mg palladium chloride (PdCl₂) were dissolved in 10 mL deionized water. Vigorous stirring and ultrasonic disperse were necessary to ensure that starting materials were dispersed homogeneously in the deionized water, and then the mixture was heated under microwave irradiation at different reaction temperatures (140 °C, 160 °C and 180 °C). After cooling down to room temperature naturally, the precipitate was collected by centrifugation, and washed several times with deionized water and absolute ethanol. Finally, the precipitation was dried in a vacuum oven at 50 °C for 12 h.

The photochemical reactor consists of an optical quartz glass beaker surrounded by a water jacket to keep the reaction at room temperature. The photocatalytic activity of as–prepared $WO_3 \cdot 1/3H_2O$ catalysts were evaluated for the degradation of RhB (10 mg L⁻¹) under visible light irradiation (Xe–lamp, 300 W) with the 400 nm cutoff filter. Typically, 50 mg of the catalyst and 100 mL of aqueous dye solution were mixed with stirring. The adsorption–desorption equilibrium of dye molecules on catalyst surfaces was reached by keeping the solution in dark for 30 min. During a catalytic process, 3.0 mL of the suspension was extracted at certain time of reaction to record with UV–vis spectra. The RhB concentrations were evaluated initially and at certain time intervals for kinetics study. The RhB degradation efficiency was calculated using the following equation:

$$\eta = (1 - C_i/C_0) \times 100 \tag{1}$$

where C_0 is the initial concentration and C_i the concentration after a certain time of reaction.

In order to verify the crystalline phases of tungsten trioxides prepared by the microwave-assisted hydrothermal method at different reaction temperatures with the same reaction time of 20 min. The overall crystallinity and purity of the nanomaterials were examined by X-ray diffraction (XRD), as in Fig. 1. All diffraction peaks were indexed to the pure phase of the WO₃·1/3H₂O according to the JCPDS Card no. 35–1001. Fig. 1A, 1B and 1C correspond to the XRD patterns of WO₃·1/ 3H₂O nanomaterials prepared at 140 °C (W–140), 160 °C (W–160) and 180 °C (W–180), respectively. The relative peak intensity of the three materials varied significantly. It was found that the crystallization of WO₃·1/3H₂O samples could be controlled by varying reaction temperatures with a set reaction time (20 min). In general, the WO₃·1/ 3H₂O showed better crystallinity with the increase of reaction temperature. The results illustrated that the increase of temperature by microwave radiation was beneficial for the crystallization of tungsten



Fig. 1. XRD patterns of as-prepared W-140 (A), W-160 (B), W-180 (C) and R3 product (D).



Fig. 2. XPS spectra of WO3·1/3H2O nanomaterials: (A) O1s (B) W4f.

trioxide nanomaterials and the well–crystallized WO₃·1/3H₂O was prepared at 180 °C for 20 min (W–180). The X – ray photoelectron spectroscopy (XPS) technique was applied to reveal surface compositions and valence state of elements in WO₃·1/3H₂O samples (Fig. 2). Taking the XPS spectra of W–160 as a representative, the strong peak at 530.5 eV was attributed to the lattice O atoms of WO₃, and the shoulder peaks at 531.8 eV and 534.1 eV corresponded to the oxygen atoms in chemically adsorbed H₂O and OH groups (Fig. 2A). The doublet peaks at 35.4 eV (W 4f_{7/2}) and 37.5 (W 4f_{5/2}) were characteristics of W(VI) species [14] (Fig. 2B).

It has been recognized that the size and shape of nanoscale photocatalyst particles profoundly affect their reaction performance. Therefore, the microstructure of $WO_3 \cdot 1/3H_2O$ nanomaterials were confirmed through the scanning electron microscope (SEM) and



Fig. 3. Typical SEM (A), TEM (B), high–resolution TEM (C) and SAED (D) images of as–prepared $WO_3 \cdot 1/3H_2O$.

transmission electron microscope (TEM) determinations. Fig. 3A shows the typical SEM morphologic image of WO_{3} ·1/3H₂O nanomaterials (W–160). TEM and high–resolution TEM (HR–TEM) images clearly revealed that the WO_{3} ·1/3H₂O possessed nanoscale structures with particle sizes below 5.0 nm (Fig. 3B and 3C), which also suggested the formation of crystalline hexagonal phase of tungsten trioxide hydrate with crystal plane spacing of 0.203 nm corresponding to the (211) lattice plane (Fig. 3C). The SAED pattern of the sample was highly symmetric (Fig. 3D), indicating single crystal characteristics of single nanoparticles.

The bonding structure of the WO3·1/3H2O samples was studied through the FT-IR spectra. As shown in Fig. 4A a representative, the structure of W-160 consisted of packed corner-sharing WO₆ octahedra that had three vibration modes in the IR region of 900-600, 400-200 and $< 200 \text{ cm}^{-1}$, which corresponded to the O–W–O stretching, bending and lattice modes [32]. Two peaks at 661 and 888 cm^{-1} were assigned as a shortening of the W–O bonds of hex–WO₃. Additionally, a sharp peak was observed at 1617 cm⁻¹, while two narrow bands and a broad band at the range of 500–1000 cm^{-1} . The first groups of bands were caused by air contact (i.e. aging effect), as moisture could be readily absorbed at surfaces. The band in the range of 2800-3650 cm⁻¹ and a peak at 1617 cm⁻¹ belonged to v(OH) and $\delta(OH)$ modes of adsorbed water molecules [33]. The Brunauer – Emmett – Teller (BET) surface areas of WO₃·1/3H₂O with different reaction temperature were examined by the N_2 adsorption/desorption (Fig. 4B), which showed typical type II isotherms. BET surface area of W-140, W-160 and W–180 was calculated to be 73.7 m² g⁻¹, 169 m² g⁻¹ and 176 m² g⁻¹, and Langmuir surface area to be 114 m² g⁻¹, 262 m² g⁻¹ and 271 m² g^{-1} , respectively, which was comparable to WO₃·1/3H₂O samples reported in the literature [14,31]. The N2 adsorption/desorption isotherms also indicated typical adsorption behaviors of nanomaterials. As a result, the $WO_3 \cdot 1/3H_2O$ samples showed considerable surface areas, which could affect their photocatalytic properties.

In general, reaction temperature is a very important parameter determining the phase of low-dimensional nanomaterials produced from the microwave-assisted hydrothermal process. The anisotropic growth of nanoparticles can be explained by the specific adsorption of ions to particular crystal surfaces, inhibiting the growth of these faces by increasing their surface energy. Herein, it was likely that the presence of



Fig. 4. (A) The FT-IR spectrum of the W-160; and (B) nitrogen adsorption/desorption isotherms of as-prepared WO₃·1/3H₂O samples.

Pd²⁺ was responsible for the formation of WO₃·1/3H₂O nanostructures with high aspect ratios [34]. These ions act as capping agents to control the growth rate of different crystal faces through a selective adsorption process. Based on the above experimental results, the PdCl₂ was believed to play a crucial role in the formation of the WO₃·1/3H₂O nanostructures. Formation of WO₃·1/3H₂O nanostructures could be represented as follows [35,36]:Na₂WO₄ + PdCl₂ + (n + 2)H₂O → H₂WO₄·nH₂O + 2NaCl + Pd(OH)

$$H_2WO_4 nH_2O \rightarrow WO_3 + (n+1)H$$
 20

To study the effect of cation and anion of salts on the formation of WO_3 ·1/3H₂O nanostructures, additional syntheses were carried out with Pd(AC)₂ or CoCl₂ as the substitution of PdCl₂. The selected materials and the factors of reactions are summarized in Table 1.

Supernatant liquid, brown mixture and blue blade precipitation were obtained as products from entries R1, R2 and R3, respectively, at the end of reactions. The samples were centrifuged and washed with distilled water and absolute ethanol to remove ions possibly remaining in products, followed by drying at 50 °C in air for 12 h. The brown mixture sample R2 was demonstrated to be an amorphous phase. The XRD analysis of product from sample R3, as shown in Fig. 1D, could not match the pattern of WO₃·1/3H₂O. On the basis of above analysis, we concluded that Pd²⁺ was crucial for the formation of WO₃·1/3H₂O nanomaterials.

The photocatalytic activity of WO₃·1/3H₂O samples were evaluated for RhB degradation as a model reaction under visible light irradiation [37,38], by monitoring the maximum absorbance of RhB at 552 nm (Fig. 5A). The photodegradation of RhB is shown in Fig. 5B for W–140, W–160 and W–180, respectively. Noticeable changes of maximum absorption characteristics were observed upon visible irradiation for 6 h. The photodegradation efficiencies of RhB for W–140, W–160 and W–180 were ca. 82.2%, 92.8% and 89.1%, respectively, whereas commercial WO₃ achieved only 66.1% of RhB degradation under the same conditions (Fig. 5B). By contrast, the W–160 displayed much superior (ca. 1.4 times) photocatalytic efficiency for RhB degradation. To estimate the rate of reactions, kinetic experiments were performed to study the photocatalytic degradation of the RhB. The kinetics equation can be expressed as follows:

$$\eta = \ln (A_0/A_t) = \ln (C_0/C_i) = kt$$
(2)

where A_0 and A_t are corresponding maximum absorption of RhB measured at the initial concentration and at different illumination time, k the reaction rate constant, and t the reaction time. The reaction rate (k) was calculated from all photodegradation experiments by ln (C_0/C_i) versus t, as shown in Fig. 5C. Rate constant (k) were estimated to be 0.721 (commercial WO₃), 0.816 (W–140), 1.81 (W–160) and 1.43 (W–180) min⁻¹. Based on these results, the W–160 sample exhibited the best photocatalytic performance, which was in accordance with BET analyses.

In order to further demonstrate photocatalytic ability of the best--performing W-160 nanomaterial, photodegradation of methyl orange (MO, maximum absorbance at 464 nm) and methylene blue (MB, maximum absorbance at 664 nm) were further studied. As shown in Fig. 5D, the W-160 showed considerable degradation efficiency towards MO (ca. 83.1%) and MB (ca. 97.2%) after illumination under visible irradiation for 6 h. Moreover, it should be noted that the as--prepared WO₃·1/3H₂O was found to be more active in the degradation of the organic pollutants under visible irradiation. Furthermore, UV-vis diffuse reflectance spectra (DRS) was measured to study the photoabsorption behavior of the W-160 (Fig. 6A), which exhibited absorption edges at ca. 662 nm and calculated by the Tauc equation, corresponding to the bandgap energy of ca. 2.32 eV. Mott-Schottky plots were employed to estimate the flat-band potentials (V_{fb}) of the W-160 photocatalyst. As shown in Fig. 6B, the intersection point was independent on frequency and flat band potential (V_{fb}) of W-160, which was estimated form the intersection to be -0.24 V vs. Ag/AgCl (-0.04 V vs. NHE). Therefore, the conduction band (CB) of W-160 was approximately -0.04 V vs. NHE, and the valence band (VB) potentials of W-160 was ca. +2.32 V vs. NHE, calculated by the equation: $E_{VB} = CB + E_{g}$ [39].

For the photodegradation of organic dyes (RhB, MO and MB) shown by WO_3 ·1/3H₂O nanomaterials (the W–160 as a representative), a

Table 1

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Reaction reactants and	Darameters	for the	formation	OF WU2	1/3H ₂ O

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Sample	Reactant (mg)			Temperature	Time	Solvent	pН				
	Na ₂ WO ₄ ·2H ₂ O	Pd(AC) ₂	CoCl ₂			H ₂ O					
R1* R2 R3	330 330 330	0 224 0	0 0 130	160 °C 160 °C 160 °C	20 min 20 min 20 min	10 mL 10 mL 10 mL	8.2–8.2 6.7–5.4 7.0–6.2				

* R represents the experimental entry.



Fig. 5. (A) Typical UV–Vis absorption spectrum of the RhB solution under visible irradiation; (B) decolorization rates of RhB solutions with different materials; (C) plot of $\ln (C_0/C)$ as a function of irradiation time in the presence of various photocatalysts; and (D) photocatalytic degradation of MO and MB with W–160.

possible photocatalytic mechanism of photocatalysis was proposed as shown in Scheme 1. The photocatalysts were activated by visible irradiation to generate pairs of electrons (e⁻) and holes (h⁺) [40–42]. Afterwards, the photogenerated holes reacted with H₂O to form hydroxyl radicals (·OH) and hydrogen ions (H⁺), in which the hydroxyl radicals served as the main oxidant species to degrade the organic pollutants [43], while the generated hydrogen ions as a byproduct and resulted in the decrease of pH in the reactor. On the other hand, the photogenerated electrons consumed oxygen to create other oxidant species, which can be oxidized directly by active radicals to final products as H₂O and CO₂ [44]. For these reasons, the nanomaterial photocatalysts exhibited excellent photocatalytic efficiency. Overall, dye molecules are degraded by the active species as follows:

$$WO_{3} + h\nu \rightarrow h^{+} + e^{-}$$

$$h^{+} + OH^{-} \rightarrow OH$$

$$h^{+} + H_{2}O \rightarrow OH + H^{+}$$

$$e^{-} + O_{2} \rightarrow O_{2}^{-}$$

$$\cdot O_{2}^{-} + H^{+} \rightarrow H_{2}O \rightarrow O_{2} + OH^{-} + OH$$
Organic pollutants + $\cdot OH + O_{2} \rightarrow CO_{2} + H$
20

In this work, nanostructured tungsten trioxide hydrates (WO_3 ·1/3H₂O) were successfully synthesized by a facile and fast microwave–assisted hydrothermal reaction. The structural, physicochemical and photocatalytic property of the nanomaterials were



Fig. 6. (A) UV–Vis DRS and (B) Mott – Schottky plots for W–160.



Scheme 1. Schematic illustration of the photocatalytic mechanism of WO_3 -1/ $3H_2O$ under visible light irradiation.

comprehensively studied. It was concluded that Pd^{2+} cations played a crucial role in the formation of $WO_3 \cdot 1/3H_2O$ nanomaterials. Besides, the photocatalytic property of $WO_3 \cdot 1/3H_2O$ photocatalysts were closely related to the morphology, crystallization and surface modification. The as-prepared $WO_3 \cdot 1/3H_2O$ nanomaterials generally showed excellent photocatalytic ability than that of the commercial WO_3 for the degradation of organic dyes. This work thus provides a viable pathway by using the microwave-assisted hydrothermal method to prepare functional nanomaterials for potential photocatalytic applications.

2. Author statement

All authors discussed the results and provided feedback on the manuscript and gave approvals for submission in the Inorganic Chemistry Communications journal.

Declaration of Competing Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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