



Keggin type of cesium phosphomolybdate synthesized via solid-state reaction as an efficient catalyst for the photodegradation of a dye pollutant in aqueous phase



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ABSTRACT

Here the potential use of cesium phosphomolybdate salt as a photocatalyst for the photodegradation of dye pollutants was studied. Polyoxometalates salts, having Keggin structure with large cations like Cs⁺, are porous materials. Cs₃PMo₁₂O₄₀ salt was prepared by solid-state method with a much higher surface area than the original Keggin-type heteropolyacids (H₃PMo₁₂O₄₀). The morphological and structural studies of synthesized nanoclusters were carried out using field emission scanning electron microscopy and transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, energy dispersive analysis by X-ray and Brunauer–Emmett–Teller.

UV–vis diffuse reflectance spectroscopy determined the absorption edge and band gap energies of the prepared salt as a direct semiconductor. The optical energy gap was calculated equal to 2.35 eV. The cesium phosphomolybdate nanocluster exhibited high photodegradation ability for basic red 46 (BR46) under the simulated sunlight. The trapping experiments indicated that the photogenerated hydroxyl radicals and holes were the main responsible for the BR46 photodegradation. The presence of H₂O₂ significantly improved the photocatalytic activity of cesium phosphomolybdate. The Cs₃PMo₁₂O₄₀ catalyst was very stable and easily separated from the reaction media for reuse.

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1. Introduction

Among various physical, chemical, and biological technologies used in pollution control, the advanced oxidation processes (AOPs), including the Fenton reaction, photocatalysis, sonolysis, ozonation, and combinations of these methods, are increasingly adopted in the destruction of organic contaminants, due to their high efficiency, simplicity, good reproducibility, and easy automation and control [1–5]. The AOPs are based on the in situ generation of hydroxyl radicals (•OH), highly powerful oxidizing agents, and are effective in treatment of persistent organic pollutants in aqueous solutions until their overall mineralization [6,7]. Among the most promising AOPs for wastewater treatment, using photocatalytic reaction in an aqueous system is particularly attractive and has been investigated in numerous studies [8,9]. The photocatalytic water purification has proven to be an efficient, green and promising remedial technology, which can degrade a wide variety of organic pollutants

into innocuous products (e.g., CO₂, H₂O) utilizing the inexhaustible and clean solar energy [10,11]. In AOPs, the heterogeneous photocatalysis is an emerging technique valuable for water purification and remediation using semiconductors as environmental photocatalysts. Fundamental and applied research on this subject has been performed extensively during the last 20 years all over the world [12–15]. Illumination of semiconductors such as ZnO and TiO₂ with photons of energies greater than the band gap energy promotes electron transition from the valence band to the conduction band, leaving behind positive holes. The valence band potential is positive enough to generate hydroxyl radicals at the semiconductor surface and the conduction band potential is negative enough to reduce molecular O₂. The hydroxyl radical and positive hole (h⁺) are powerful oxidizing agents and attack organic pollutants present at or near the surface of semiconductor photocatalysts, resulting usually in their complete oxidation to CO₂ [16–20].

One of the most interesting characteristics of polyoxometalates (POMs) is that they can act as electron relays, i.e. they can undergo stepwise multielectron redox reactions whilst their structure remains intact. Based on this property, POMs have been widely studied as photooxidation catalysts for organic and inorganic

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pollutants [21–25]. Two catalytic reaction pathways have been proposed: (i) OH[•] attack mechanism [23,26], (ii) precomplexation and subsequently electron or proton transfer between the excited catalysts (POMs^{*}) and substrates [27,28]. The electron transfer between the excited states of POMs^{*} and the ground states of organic compounds can result in the formation of reduced POMs and the radical cations of substrates, and then, the organic substrates are oxidized by oxygen species or hydroxyl radicals. POM anions have also been demonstrated to undergo photochemical reduction with water as an electron donor [29]. On the other hand, a major drawback to the acidic form of POM system is its high water solubility, which impedes recovery and reuse of the catalyst [30]. The acid form has low surface acidity (the number of acidic sites on the surface) because of the low surface area (~5 m²/g) and is highly soluble in water [31]. Various approaches were proposed to solve the problem of low surface areas of POMs. The precipitation of partially saturated Cs⁺, K⁺, (NH₄)⁺ or Rb⁺ salts of POMs results in materials with very high surface areas (more than 100 m²/g) where the unreacted acidic clusters are deposited on the surface, and stabilized by interactions with the cations [32,33]. The salts of POMs are considered to be insoluble and they have been studied as photocatalysts for photodegradation of dye pollutants due to their effectiveness and stability [34–36]. We have recently found that cesium phosphomolybdate (CsPM) salt is an effective heterogeneous photocatalyst for the photooxidation of BR46 in aqueous condition under simulated sun light irradiation. In this paper, the CsPM photocatalyst with changed surface properties were synthesized by solid-state method. Based on the systematic analysis, a mechanism for the formation of CsPM was proposed. The physicochemical characterizations of the as-prepared CsPM were investigated by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen sorption, energy dispersive analysis by X-ray (EDAX) and UV–vis diffuse reflectance spectroscopy (DRS). The photocatalytic activity of the prepared CsPM photocatalyst was evaluated towards BR46 under simulated solar irradiation. Furthermore, the mechanism of the CsPM photocatalytic activity was investigated by adding the corresponding scavengers of reactive species. To the best of our knowledge, the CsPM nanocluster photocatalyst with excellent photocatalytic activity is reported for the first time, here.

2. Experimental

2.1. Materials and the synthesis of CsPM

There are two methods to synthesize cesium polyoxometalate salts: (i) Solid state method [37] and (ii) Ion exchange method [38]. In our work, the one-step solid-state method was used to synthesize CsPM. The scheme of synthesis of CsPM is shown in Fig. S1 in the Supporting Material. The investigated titanium dioxide, Degussa P25 (having 80% anatase and 20% rutile), was kindly supplied by Degussa Co. (Frankfurt, Germany). The structure and characteristics of BR46 are given in Table S1 in Supporting material [39].

2.2. Photocatalytic experiments

The photocatalytic activity of the prepared CsPM was measured by photodegradation of BR46. Experiments were carried out in a photochemical reactor made of Pyrex glass with the capacity of 50 mL equipped with a magnetic stirring bar. Artificial irradiation was provided by a 300 W Xenon lamps (HID, the P.R.C) as the simulated solar light. IR radiation and short wavelength UV radiation ($\lambda < 380$ nm) were eliminated by outer jacket of arc tube. Fig. S2 shows the spectra of the xenon lamps (according to

the technical report on HID-Xenon 300). The distance between the lamp and the reactor was maintained as 15 cm. In a typical experiment, 100 mg photocatalyst was added into 50 mL of 10 mg/L BR46 aqueous solution. Prior to illumination, the suspensions were magnetically stirred for 30 min in dark to achieve an adsorption–desorption equilibrium. Then the suspension was exposed to irradiation under magnetic stirring. At certain intervals, aliquots of the suspension (3 mL) were sampled and centrifuged. 3 mL samples were withdrawn at predetermined time intervals. After measuring the concentration of residual BR46 in the solution by UV–vis spectroscopy (PerkinElmer 550 SE) at λ_{max} equal to 531.0 nm, the sample was immediately returned to the reactor. The photocatalytic efficiency was calculated according to the following equation:

$$\text{Degradation Efficiency (\%)} = ((C_0 - C)/C_0) \times 100 \quad (1)$$

where C_0 is initial concentration of dye (mg/L) in the solution before adding the CsPM, and C is final concentrations of dye (mg/L) in the solution after adding the CsPM at time t .

2.3. Analytical procedures

The morphology of the CsPM was observed using field emission scanning electron microscopy (FESEM Model MIRA3/Tescan-Czech Republic) with an accelerating voltage of 3 kV after sputter coating with gold under vacuum. The samples were also subjected to energy dispersive analysis by X-ray (EDAX) unit coupled with the above microscope. Transmission electron microscopy (TEM) analysis was performed using a Zeiss-EM10C electron microscope operated at 80 kV with a point-to-point resolution better than 3.0 nm. For TEM observations, the samples were ground in an agate mortar and placed on amorphous carbon-coated copper grids. Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Quantachrome instrument, Belsorp mini II (Japan) series to determine the specific surface area, S_{BET} , average cylindrical pore diameters, d_p and adsorption pore volume, V_{PN2} .

To determine the average crystal size of CsPM, X-ray diffraction (XRD) measurements were carried out at room temperature by using Siemens X-ray diffraction D5000, with Cu-K α radiation ($\lambda = 1.5416$ Å). The accelerating voltage of 40 kV and emission current of 30 mA were used. The average crystal size of the CsPM was calculated according to Debye–Scherrer formula [40]. The chemical structures of the CsPM were confirmed using Fourier transform infrared spectrometry (FT-IR, Bruker Tensor 27 spectrometer, Germany). The UV–vis diffuse reflection spectra of heteropoly compound samples were measured on a Lambda 950 PerkinElmer spectrometer with integrating sphere.

3. Results and discussion

3.1. Characterization of CsPM

Morphology and structure of the synthesized photocatalyst was investigated by FESEM and TEM images. Fig. S3 shows SEM images of H₃PMO₁₂O₄₀ (HPM) and CsPM. As can be seen in Fig. S3(b), HPM clusters are quite irregular in size and shape. This non-uniformity can be attributed to the aggregation of HPM clusters and the growth of irregular crystalline grains during synthesis. A simple comparison between SEM images of HPM (Fig. S3(a) and (b)) and CsPM (Fig. S3(c) and (d)) reveals that the incorporation of cesium into HPM structure restrains the aggregation phenomenon and subsequently decreases the particle size and solubility in water [41] which improves its active surface and photocatalytic activity. Moreover, the presence of cesium ions in the structure increases the shape and size uniformity of synthesized nanoclusters. To clearly

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