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Degradation of dye on polyoxotungstate nanotube under molecular oxygen

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Abstract

A facile process to prepare polyoxometalate $Zn_{1.5}[PW_{12}O_{40}]$ nanotube is presented. The structure and morphology of this nanotube were characterized using IR, elemental analyses, X-ray powder diffraction, ^{31}P MAS NMR and transmission electron microscopy. This nanotube material has a self-supporting tube structure that can be used as a heterogeneous catalyst for the degradation of safranine T (ST) using molecular oxygen (air) as oxidant and can be easily separated from the aqueous phase, thus enabling it to be used several times.

Keywords: Polyoxometalate; Nanotube; Synthesis; Catalyst; Degradation of organic dye

1. Introduction

Polyoxometalates (POMs) constitute a large class of inorganic compounds with considerably potential applications in catalysis, medicine and material sciences [1–3]. The self-assembly of such POM building blocks to produce multifunctional materials is becoming a rapidly expanding area of research [4], owing to their unique structural versatility and electronic properties. By far, the most important application of POMs is the field of catalysis, particularly the selective oxidation of industrial materials and products [2,3]. Recently, they have also been applied as environmental catalysts for the photodegradation of various organic pollutants [5], and also applied for wet air oxidation (WAO) [6] of organic pollutants. However, few studies have been made to develop polyoxometalate catalyst for the direct activation of molecular oxygen in the degradation of organic pollutants.

Recently, many efforts have been made using ''advanced oxidation technologies''(AOT) for the treatment of recalcitrant pollutants to more biodegradable molecules or mineralization into CO_2 and other inorganics [7]. So H_2O_2, O_3 and molecule oxygen (air) have been widely used as green oxidants in organic synthesis and environmental remediation because of their green byproduct and high content of active oxygen species [8]. Many POMs have been confirmed to be effective catalysts for activating H_2O_2, O_3 and molecular oxygen in selected oxidation of various organic substrates in dark thermal reactions [8–13]. Compared with H_2O_2, molecular oxygen (air) is cheaper agent in industrial use which exhibits academic value as well as commercial value. The development of an efficient catalytic system for direct activation of molecular oxygen is of great interest.

Because of the high solubility of POMs in aqueous media, some research groups have put forward many efforts for the recovery and reuse of POMs. To achieve this, there are two approaches: one is to implant POMs onto a solid support leading to a catalytic system that may be filtered and reused [14]; the second is to use biphasic liquid–liquid systems, such that at separation temperatures, the catalyst and product phases may be separated by phase separation [15–18]. In the first method, the simple way is to change the soluble catalysts

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into insoluble bulk materials, which in some cases dissolve under reaction conditions. Our group has systematically investigated the synthesis of nanoscale POMs using biological templates such as liposome, or starch microspheres [19,20]. The biological template method is proven to be a flexible way to control the size, structure and higher order organization of inorganic framework [21–23]. As a continuation of our work, we explored to synthesize 1D POM nanotubes using biological template – cellulose fibers associated with surface sol–gel process. This way is suitable for large scale and industrial preparations.

We report here the synthesis of POM $Zn_{1.5}PW_{12}O_{40}$ nanotubes and their application as heterogeneous catalysts for the degradation of safranine T using molecular oxygen (air) as oxidation agent. The structure of ST is shown in Scheme 1, which is a dye mixture of two compounds. Color removal has become a challenging aspect of textile wastewater treatment because of the growing concern about residual color that is closely associated with toxicity and aesthetics of the discharged effluent [24]. Most commonly practiced physical–chemical methods such as coagulation, activated carbon adsorption, membrane filtration and aerobic biological treatment have been proven to be inefficient for decolorization [25] due to dyes' high degree of chemical, photolytic and microbial stabilities.

This is the first report on the synthesis of POM nanotubes using natural cellulose template and is being used as an oxide catalyst for the degradation of organic dyes utilizing molecular oxygen.

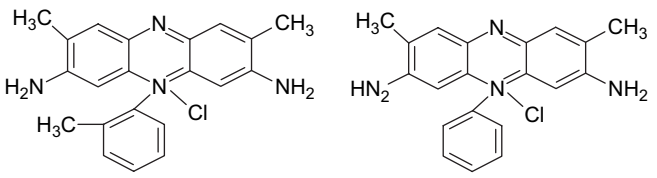
2. Experimental

2.1. Materials

$H_3PW_{12}O_{40}$ was prepared according to literature methods and identified by IR spectra and elemental analyses [26]. Ethanol and zinc acetate were purchased from Aldrich and used without further treatment. All other reagents were of AR grade.

2.2. Physical measurements

Elemental analyses of $Zn_{1.5}PW_{12}O_{40}$ were carried out using a Leeman Plasma Spec (I) ICP-ES. IR spectra (2000–400 cm^{-1}) of the nanotubes were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. The clear filtrate solution of the catalytic process was tracked by UV–vis spectroscopy using a 756 CRT UV–vis spectrophotometer at 532 nm.



Scheme 1. The molecular structure of ST.

Electron micrographs were recorded on a Hitachi H-600 transmission electron microscope. NMR spectra were recorded on a Unity-400 spectrometer at room temperature. The X-ray powder diffraction (XRD) patterns (Fig. 2) of the sample were collected on Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm).

2.3. Preparation of catalyst $Zn_{1.5}PW_{12}O_{40}$ nanotubes

$H_3PW_{12}O_{40}\cdot 23H_2O$ (8 g, 2.4 mmol) was dissolved in 20 mL distilled water to form a clear solution. This solution was added dropwise into 10 mL ethanol solution containing 1.6 g, 7.2 mmol zinc acetate with gentle stirring. The final pH of this mixture was 2. The mixture was continuously stirred for about 30 min, then some pieces of filter paper were dipped into this solution for 15 min and then the filter paper was thoroughly washed with water and ethanol in order to remove the POM complex and zinc acetate which did not attach into the filter paper surface. Then the filter paper coated with $Zn_{1.5}PW_{12}O_{40}$ was dried by airflow. This procedure was repeated for 20 times. The resultant paper/$Zn_{1.5}PW_{12}O_{40}$ complexes were calcined in air to remove the original filter paper. The greenish-yellow powder which was self-supporting was obtained with yield of 40 mg.

2.4. Catalytic procedure

The stoichiometry of reaction was determined by allowing 34.1 mg/L of ST to react with air at room temperature in the presence of the catalyst. A general procedure was carried out as follows: 0.2 g of catalyst $Zn_{1.5}PW_{12}O_{40}$ nanotube was suspended in a fresh aqueous dye solution ($C_0 = 34.1$ mg/L, 200 mL). The air was inputted into the bottom of the suspension with the flow being 0.08 m^3/h. At given intervals of illumination, a sample of suspension was taken out by filtration. UV–vis spectroscopy was used in the experiment to monitor the degradation of ST.

3. Results and discussion

3.1. Preparation

In the previous reports, the POMs with nanostructure were synthesized by carbon-nanotube template, nonionic inverse microemulsion, surfactant template, etc. To the best of our knowledge, there is no report using natural cellulosic substances as template to fabricate nanoscale POMs. The surface sol–gel process could be explained as that a solid substrate with hydroxyl groups on its surface is allowed to react with metal alkoxides in solution to form covalently bound surface monolayers of the metal alkoxides and subsequent hydrolysis. The natural cellulose fibers possess hydroxyl groups on the surface, so the sol–gel process can occur on the surface of cellulose [22,23]. It is known that metal alkoxides are expensive and unstable which the sol–gel process is difficult to be controlled. We attempted using simple inorganic metal salts as a precursor to achieve the sol–gel process. The procedure

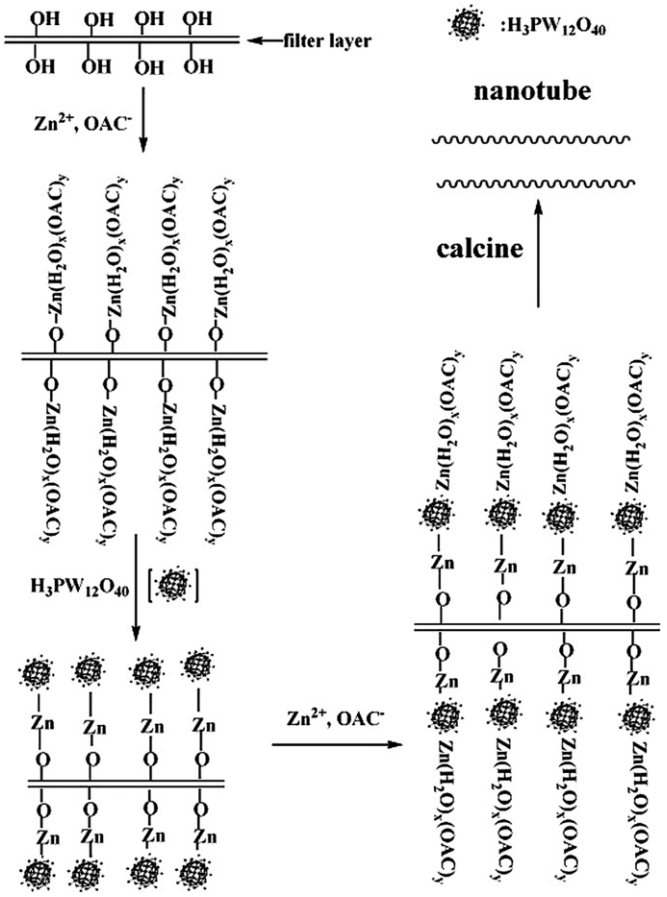


Fig. 1. The formation of $Zn_{1.5}PW_{12}O_{40}$ nanotubes.

of formation of cellulosic fiber covered by $Zn_{1.5}PW_{12}O_{40}$ can be observed in Fig. 1.

3.2. Elemental results

From the result of elemental analysis, the contents of the material are W, 75.9; P, 1.0; Zn, 3.2%, and it can be seen that while the POMs were forming the nanotubes, the ratio of W:P:Zn is 12:1:1.5 corresponding to the formula of $Zn_{1.5}PW_{12}O_{40}$.

3.3. Spectra

The IR spectrum of the $Zn_{1.5}PW_{12}O_{40}$ nanotubes was in good agreement with that of its parent $PW_{12}O_{40}^{3-}$ observed in macro-scale, with the four characteristic peaks reflecting the different vibrations of oxygen atoms of the Keggin-type structure $PW_{12}O_{40}^{3-}$: 1083, 987, 895 and 810 cm^{-1} could be attributed to the asymmetry vibrations P−O_a (internal oxygen connecting P and W), W−O_d (terminal oxygen bonding to W atom), W−O_b (edge-sharing oxygen connecting W) and W−O_c (corner- sharing oxygen connecting W_3O_{13} units.

The XRD of the $Zn_{1.5}PW_{12}O_{40}$ nanotubes is shown in Fig. 2. All the diffraction peaks in Fig. 2 could be readily indexed to tetragonal $PW_{12}O_{40}$ phase (JCPDS no. 41-0369).

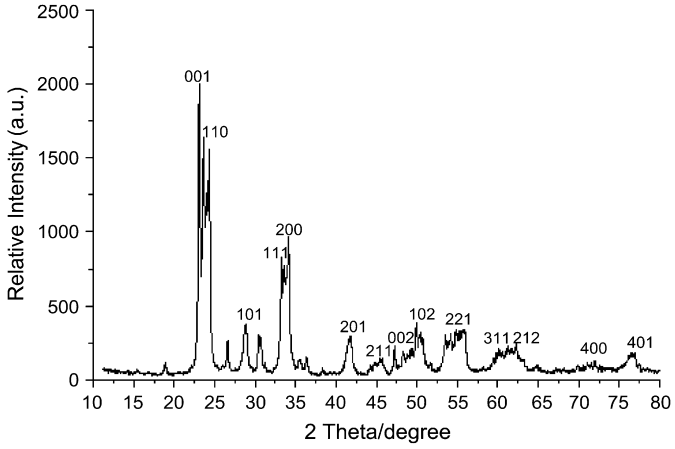


Fig. 2. XRD pattern of the $Zn_{1.5}PW_{12}O_{40}$ nanotubes.

These results indicate that the heteropolyanion in the as-prepared nanotubes retains its original Keggin-type molecular structure.

In order to further confirm the structure of $Zn_{1.5}PW_{12}O_{40}$ nanotubes, the ^{31}P MAS (magic-angle spinning) NMR spectrum of the sample (Fig. 3) was analyzed. It displayed a characteristic peak at −14.9 ppm, which is as same as the starting H_3 $PW_{12}O_{40}$ (−15.0 ppm) [27], suggesting that during the synthetic process, the POMs $PW_{12}O_{40}$ keep its structure. The slight shift may be due to the change of countercations.

3.4. Morphology of the material

The morphology and microstructure of the prepared $Zn_{1.5}PW_{12}O_{40}$ were investigated with transmission electron microscopy (TEM). Typical TEM image (Fig. 4) showed that the sample displayed tube-like shapes. As shown in Fig. 4, some materials have the morphology of tube, in which middle cellulosic fibers have been burnt out to form the hollow tubes. The average length of the tubes is about 150 nm, and the width of the tubes is about 25 nm, the inner width being about 9 nm.

3.5. Degradation of ST

We studied the degradation of ST as a model reaction to investigate the oxidative-catalytic activity of $Zn_{1.5}PW_{12}O_{40}$ under molecular oxygen at room temperature which was

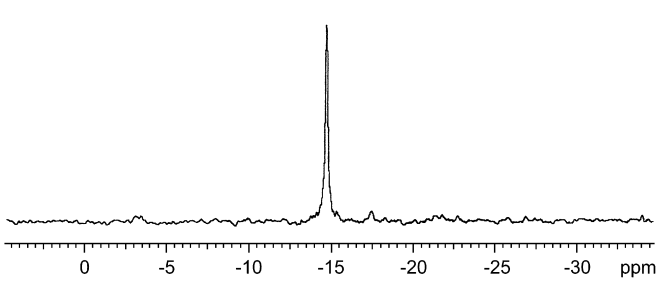


Fig. 3. The ^{31}P MAS NMR of $Zn_{1.5}PW_{12}O_{40}$ nanotubes.

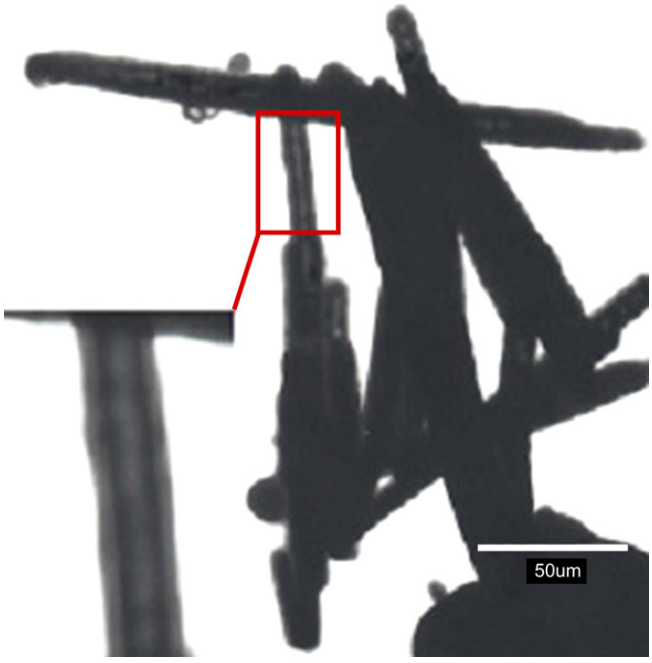


Fig. 4. The typical TEM image of the $Zn_{1.5}PW_{12}O_{40}$ nanotubes.

determined by UV–vis spectra at 532 nm. The concentration changes of ST under different flowing air times are shown in Fig. 5. From Fig. 5, it can be seen that in the presence of catalyst $Zn_{1.5}PW_{12}O_{40}$ nanomaterials, ST dye was decomposed by molecular oxygen. The decomposed rate reached 78% after flowing air for about 4 h.

In order to determine the catalytic effect of $Zn_{1.5}PW_{12}O_{40}$ nanomaterials on dye's decolorization, different experiments were carried out as shown in Fig. 6. It can be seen that on flow air into the aqueous solutions of ST without any catalyst, ST did not degrade in the beginning of 0.5 h. On flowing air for 6 h, the degradation rate of ST only reached 32% (Fig. 6a). However, the conversion of ST was much higher when the catalyst $Zn_{1.5}PW_{12}O_{40}$ nanomaterial was introduced into the mixture, i.e., the conversion of ST reached 80% after flowing air for 6 h. When the polyoxometalate $H_3PW_{12}O_{40}$ without nanostructure was used (0.2 g) as catalyst, the ST

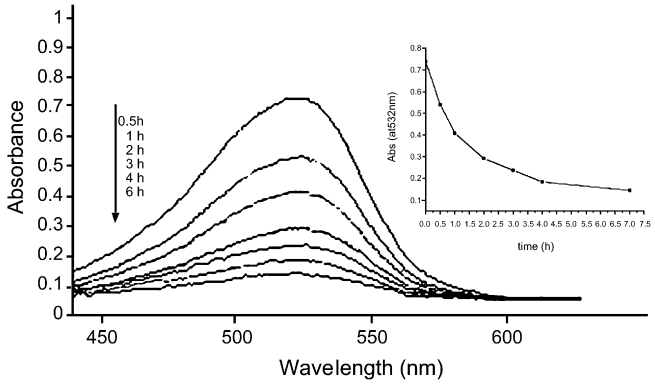


Fig. 5. The UV–vis absorption spectral changes of ST solution under catalyst with different flowing air times.

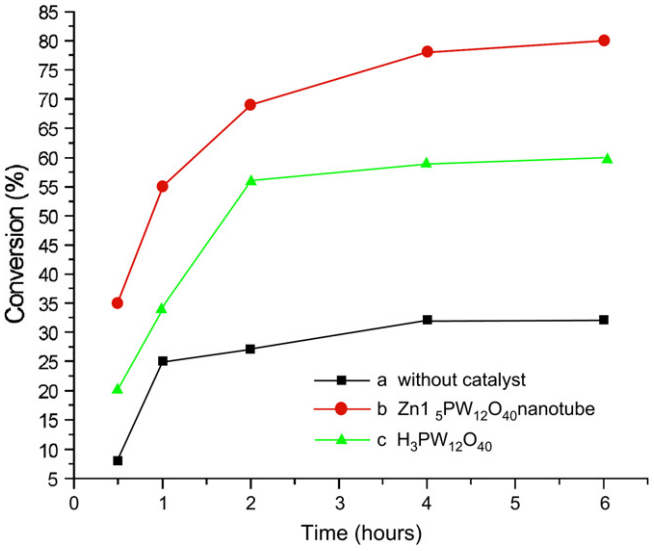


Fig. 6. Degradation of ST under different conditions.

conversion was less than 60% (Fig. 6c) in the same time, which shows that when forming nanotube structure, the BET surface area was augmented and the activity of it was improved.

After the reaction gets completed, the suspension was centrifuged, and the catalyst $Zn_{1.5}PW_{12}O_{40}$ was separated. The amount of W determined by ICP-AES in the resulting clear solution was 0.1%, which confirmed the less solubility of the catalyst during the reaction process. The catalyst was reused for 4 times, during which the catalytic activity of $Zn_{1.5}PW_{12}O_{40}$ in the degradation of ST was maintained efficiently with slightly decrease owing to the lesser dissolution (Fig. 7). And also the catalyst can be easily separated from the mixture.

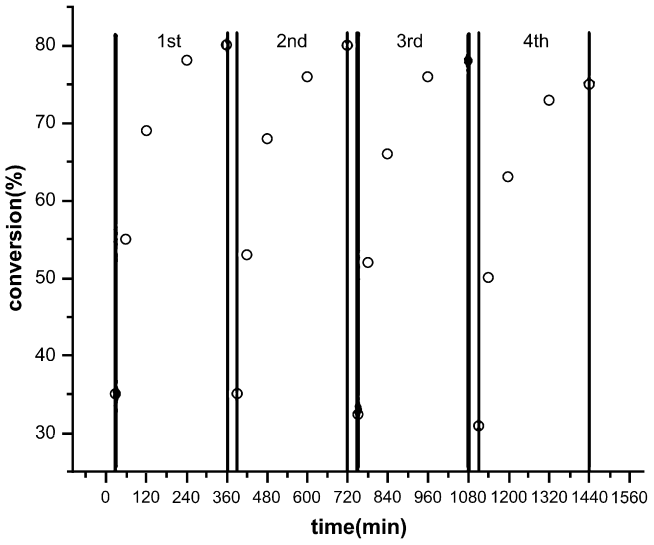


Fig. 7. Cycling runs in the oxidative-degradation of ST in the presence of $Zn_{1.5}PW_{12}O_{40}$ under molecular oxygen.

4. Conclusion

Our ongoing research work shows that $Zn_{1.5}PW_{12}O_{40}$ nanotubes could be prepared using cellulose fiber substance as templates associated with surface sol–gel method, which is a unique, convenient, low-cost and green chemical pathway. This method could be used not only to synthesize other POMs with 1D nanostructure, but also to enhance the surface area of the catalysts to increase the activity. $Zn_{1.5}PW_{12}O_{40}$ nanotube is insoluble in water aqueous and can be used as a as heterogeneous catalyst for degradation of safranine T using molecular oxygen (air) as oxidation agent. This catalytic process is a commercial and green chemical pathway which exhibits potential industrial application in dye's decolorization.

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