Research Article

Fabrication of Core-Shell Structural $\text{SiO}_2@\text{H}_3[\text{PM}_{12}\text{O}_{40}]$ Material and Its Catalytic Activity

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Through a natural tree grain template and sol-gel technology, the heterogeneous catalytic materials based on polyoxometalate compounds $\text{H}_3[\text{PM}_{12}\text{O}_{40}]$ encapsulating SiO_2 : $\text{SiO}_2@\text{H}_3[\text{PM}_{12}\text{O}_{40}]$ ($\text{SiO}_2@\text{PM}_{12}$, $M = \text{W}, \text{Mo}$) with core-shell structure had been prepared. The structure and morphology of the core-shell microspheres were characterized by the XRD, IR spectroscopy, UV-Vis absorbance, and SEM. These microsphere materials can be used as heterogeneous catalysts with high activity and stability for catalytic wet air oxidation of pollutant dyes safranin T (ST) at room condition. The results show that the catalysts have excellent catalytic activity in treatment of wastewater containing 10 mg/L ST, and 94% of color can be removed within 60 min. Under different cycling runs, it is shown that the catalysts are stable under such operating conditions and the leaching tests show negligible leaching effect owing to the lesser dissolution.

1. Introduction

Polyoxometalates (POMs) constitute a large class of inorganic compounds with considerably potential applications in catalysis, medicine, and material sciences [1–3]. Owing to their unique structural versatility and electronic properties, the self-assembly of such POMs building blocks to produce multifunctional materials is becoming a rapidly expanding area of research. Though POMs have high catalytic activity, due to their low-surface area and high solubility in polar solvent, the application of POMs as catalyst is restricted in many conditions. So, there has always been a demand for making high-surface area and insoluble POMs by means of incorporation into pillared clays of layered double hydroxides and on molecular sieves MCM-41, silica or silica nanoparticles, and polyaniline and polypyrrole films [4]. Gao et al. and coworkers have reported layer-by-layer assembly of polyoxometalates into the shell of the microcapsules, with POMs maintaining individual unique properties which can be used in medicine and inorganic chemistry [5]. Many efforts have been made to solve the leaching and solubility

problem by modifying, doping, or exchanging with different metal ions [6]. Pollen is a ubiquitous and inexpensive material with a high degree of species-specific morphological complexity, of which the tough outer shell is amenable to inorganic mineralization without consequent loss of its fine structure [7]. Hall et al. described fabricating porous micron-sized particles of silica using pollen grain templates [8], which is a facile method for replicating the complex surface morphology of tree pollen grains, in the case of silica productions complex colloidal materials with surface areas higher than $800 \text{ m}^2 \text{ g}^{-1}$. This material has a potential application as a drug or catalyst carrier. The synthesis of heterogeneous catalyst based on polyoxometalates impetus us to use this porous particle of silica to fabricate POMs micron-sized core-shell porous materials, which is suitable for catalysis design and industrial preparation. This way is suitable for large scale and industrial preparation.

Catalysis is one of the most important applications of POMs [2, 3, 9, 10]. As green photocatalysts, polyoxometalates (POTs) have been extensively studied for the degradation of organic pollutants in water [11, 12]. Recently, the H_2

evolution activity of a few POTs has also been investigated [13]. However, few studies have been made to develop polyoxometalates catalyst for direct activation of molecular oxygen in degradation of organic pollutants. H_2O_2 , O_3 , and air have been widely used as green oxidants in organic synthesis and environmental remediation because of their green byproduct, high content of active oxygen species [14]. 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 [15–17]. Compared with H_2O_2 , air is cheaper agent in industrial use which exhibits academic value as well as commercial value.

ST is a well-known textile colorant, which is harmful to human beings. A favored, promising, cleaner, and greener technology for the removal of this pollutant from water and wastewater has attracted considerable attention. By now, photochemical degradation of the hazardous dye ST using TiO_2 catalyst has been carried out by Gupta group [18]. We synthesized the core-shell structural $\text{SiO}_2@\text{PM}_{12}$ heterogeneous oxidative catalyst in order to develop a new technique to completely degrade organics into water and CO_2 , without generating any harmful byproducts, which has popularized its role as a wastewater purifier.

In this paper, we described a facile method for assembly hollow inorganic porous polyoxometalates hybrid catalysts $\text{SiO}_2@\text{PM}_{12}$ ($\text{M} = \text{W}$ and Mo) using pollen grains as template and demonstrated their potential applicability in degradation of dye ST catalyzed by these hollow core-shell $\text{SiO}_2@\text{PM}_{12}$ materials using molecular oxygen as oxidation agent. The catalytic activity of POMs in the hybrid catalysts was improved by the physical and chemical properties and the unusual core shell with higher surface areas. Moreover, the separation and recovery of the POMs from the reaction became easy. These catalysts are proved to be available heterogeneous catalysts to degrade the dye when using molecular oxygen as oxidant.

2. Experiment

2.1. Materials. All chemicals (Sinopharm Chemical Reagent Beijing Co., Ltd.) were of analytical reagent grade. All the aqueous solutions were prepared using ultrapure water (Milli-Q 18.2 MX cm, Millipore System). Pollen grain was bought from company Yi Yuan in Beijing. Other reagents were of AR grade and used without any treatment. $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 23\text{H}_2\text{O}$ (PW_{12}) and $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 23\text{H}_2\text{O}$ (PMo_{12}) were prepared following a typical method [19], respectively, and identified by IR spectra.

2.2. Physical Measurements. IR spectra ($2000\text{--}400\text{ cm}^{-1}$) of the microspheres were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. Absorption spectra were recorded on a UV-Vis spectroscopy was performed with a UV-2550 spectrophotometer (Shimadzu, Japan) at room temperature. Electron micrographs were recorded on a Hitachi H-800 scanning electron microscope (SEM) at 200 kV. The X-ray powder diffraction (XRD) patterns of the samples were collected on a Japan Rigaku D/max 2500 PC X-ray diffractometer equipped with graphite monochromatized

$\text{Cu-K}\alpha$ radiation 40 kV/40 mA ($\lambda = 0.15406\text{ nm}$). Elemental analyses of materials were carried out using a Leeman Plasma Spec (I) ICP-AES.

2.3. Preparation of Silica Covering Pollens. The preparation of silica covering pollens was followed by a previously reported method [8]. The typical process is as follows: 0.5 g powder of pollen was soaked in a solution of silicic acid sol ($\text{Si}(\text{OH})_4$, 5 mL, $\text{pH} = 7$) for about 24 h. The silicic acid sol was prepared by passing a sodium silicate solution through an acidified cation-exchange column that was charged by flushing with hot distilled water, 2 M HCl aqueous solution, and then cold distilled water. And the final pH is 7. The soaked powder of pollen was centrifuged to remove the excess silicate. The resulting silica-coated pollen grains were decanted, washed with distilled deionized water, and dried in baking oven.

2.4. Preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Core-Shell Hollow Spheres. 4.85 mmol $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 23\text{H}_2\text{O}$ (PW_{12}) was dissolved in 20 mL distilled water to form a clear solution. The upper prepared silica-coated pollen grains were soaking into the PW_{12} solution for about 24 h to induce polyoxometalate PW_{12} reacting with $\text{Si}(\text{OH})_4$ forming PW_{12} coated pollen grains. The powder was throughout washed with water and ethanol in order to remove the PW_{12} compound, which did not attach to the silicate pollen. Then the PW_{12} coated pollen grains were dried by airflow and then were calcined from ambient temperature to 350°C at rate of 1°C min^{-1} overnight to remove the original pollen grains. The greenish-yellow hollow $\text{PW}_{12}/\text{SiO}_2$ replicas of individual pollen grains were obtained with yield of 3 g. The preparation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ core-shell hollow spheres ($\text{PMo}_{12}/\text{SiO}_2$) is the same as that of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ core-shell spheres except $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ that was used instead of $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

2.5. Catalytic Procedure. The stoichiometry of reaction was determined by allowing 10 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 $\text{SiO}_2@\text{PM}_{12}$ was suspended in a fresh aqueous dye solution ($C_0 = 10\text{ mg/L}$). The air was inputted into the bottom of the suspension with the flow $0.08\text{ m}^3/\text{h}$. At given intervals of illumination, a sample of suspension was taken out by filter. The clear filtrate solution was tracked by UV-Vis spectroscopy using a 756 CRT UV-Vis spectrophotometer at 532 nm.

3. Results and Discussion

3.1. Preparation. As shown in Scheme 1, the assembly of core-shell POMs hybrids contains two main processes. Firstly, porous silica replicas of pollen grains were achieved. Secondly, using these silica replicas of pollen grains as template fabricated POMs coating materials. Then the obtained materials were calcined to remove pollen grain formed hollow core-shell $\text{SiO}_2@\text{PM}_{12}$ hybrid catalysts.

3.2. Spectra. The IR spectrum of the $\text{SiO}_2@\text{PW}_{12}$ was given in Figure 1 which showed several strong bands at 1080, 986,

FIGURE 1: The IR spectra of core-shell hybrid materials ((a) PW_{12} , (b) $\text{SiO}_2@\text{PW}_{12}$).

FIGURE 2: The IR spectra of core-shell hybrid materials ((a) PMo_{12} , (b) $\text{SiO}_2@\text{PMo}_{12}$).

SCHEME 1: The formation of $\text{SiO}_2@\text{PM}_{12}$ core-shell hybrid materials.

889, and 800 cm^{-1} . It has been widely reported that H_3PW_{12} with Keggin structure gives four characteristic peaks which reflected the different vibrations of oxygen atoms at 1080, 960, 869, and 780 cm^{-1} , being attributed to the asymmetry vibrations P-Oa, W-Od, W-Ob-W, and W-Oc-W. The bands of the hybrid $\text{SiO}_2@\text{PW}_{12}$ at 986, 886, and 799 cm^{-1} were attributed to the asymmetry vibrations W-Od, W-Ob, and W-Oc, confirming the existence of PW_{12} in $\text{SiO}_2@\text{PW}_{12}$ core-shell hybrid. It should be noted that the P-Oa band of PW_{12} fully overlapped with the band of Si-O-Si at $1030\text{--}1250\text{ cm}^{-1}$ [20]. The high-energy shift of the W-Oc vibration peaks of the Keggin anion before (780 cm^{-1}) and after (800 cm^{-1}) the adsorption to the silica supports the strong chemical interaction between silicate and heteropolyanion [21].

The IR spectrum of the $\text{SiO}_2@\text{PMo}_{12}$ was given in Figure 2. It is well known that the IR spectrum of PMo_{12} gives four strong typical IR bands at 1079 cm^{-1} (P-Oa), 988 cm^{-1} (Mo-Od), 889 cm^{-1} , and 973 cm^{-1} (Mo-Ob-Mo and Mo-Oc-Mo), respectively. The IR spectrum of the $\text{SiO}_2@\text{PMo}_{12}$ gave

three bands at 1080, 964, and 806 cm^{-1} . The bands at 959 and 797 cm^{-1} were attributed to the asymmetry vibrations W-Od and W-Oc of Keggin structure polyoxometalate, indicating the presence of PMo_{12} in $\text{SiO}_2@\text{PMo}_{12}$ core-shell hybrid. It is also found that the P-Oa band of PMo_{12} fully overlapped with the band of Si-O-Si at $1030\text{--}1250\text{ cm}^{-1}$. The high-energy shift of the Mo-Oc vibration peaks of the Keggin anion before (793 cm^{-1}) and after (800 cm^{-1}) supports the strong chemical interaction between silicate and PMo_{12} anion [20].

In the UV-Vis spectrum (Figure 3(a)) of $\text{SiO}_2@\text{PW}_{12}$ core-shell hybrid, two characteristic absorbance bands at 203 nm and 260 nm, corresponding to oxygen-to-tungsten charge transfer $\text{Od} \rightarrow \text{W}$ and $\text{Ob/Oc} \rightarrow \text{W}$, respectively, verify the presence of PW_{12} in the shell. The same phenomenon was also observed in the UV-Vis spectra of $\text{SiO}_2@\text{PMo}_{12}$ (Figure 3(b)) with two characteristic absorbance bands at 205 nm and 260 nm.

The XRD pattern of $\text{SiO}_2@\text{PW}_{12}$ and $\text{SiO}_2@\text{PMo}_{12}$ was shown in Figures 4(a) and 4(b), respectively. From Figure 4(a), the reflections are known to represent $\text{PW}_{12}\text{O}_{40}$ compared with the standard PDF card (JCPDS number 41-0369). And all the diffraction peaks in Figure 4(b) could be readily indexed to tetragonal $\text{PMo}_{12}\text{O}_{40}$ phase (JCPDS number 75-1588). The XRD results corresponding to Keggin unit in the $\text{SiO}_2@\text{PW}_{12}$ and $\text{SiO}_2@\text{PMo}_{12}$ particles implied their homogeneous dispersion in the silicate.

3.3. Morphology of the Material. The morphology and microstructure of the native pollen grains and prepared hollow core-shell $\text{SiO}_2@\text{PM}_{12}$ particles (Figure 5) were investigated with SEM. The native pollen grain (Figure 5(a)) was ca. $21\text{ }\mu\text{m}$ in length and exhibited a characteristic ellipsoidal morphology consisting of four longitudinal segments with foam-like surface structure. The SEM image of pollen grain covered by SiO_2 and POMs (Figure 5(b)) showed that SiO_2 and POMs form a denser shell covering the pollen grain. After

FIGURE 3: The UV-Vis spectra of core-shell hybrid materials ((a) $\text{SiO}_2@\text{PW}_{12}$, (b) $\text{SiO}_2@\text{PMo}_{12}$).

FIGURE 4: The XRD pattern of $\text{SiO}_2@\text{PM}_{12}$ hybrid materials ((a) $\text{SiO}_2@\text{PW}_{12}$, (b) $\text{SiO}_2@\text{PMo}_{12}$).

the above materials were calcined, the obtained $\text{SiO}_2@\text{PM}_{12}$ particles (Figures 5(c) and 5(d)) with ellipsoidal morphology were replicated from native pollen grain structure. The $\text{SiO}_2@\text{PW}_{12}$ particles and $\text{SiO}_2@\text{PMo}_{12}$ particles are ca. $18\ \mu\text{m}$ in length and ca. $17.2\ \mu\text{m}$ in width, respectively.

3.4. The Catalytic Results. In order to test the potential application of these hollow core-shell $\text{SiO}_2@\text{PM}_{12}$ particles as heterogeneous catalysts for the degradation of dyes, the oxygenation degradation reaction of ST with molecular oxygen (air) catalyzed by $\text{SiO}_2@\text{PM}_{12}$ particles was examined. As shown in Scheme 2, the structure of ST was provided, which is shown as a mixture by these two compounds.

3.5. Degradation of ST. On flowing air into the aqueous solutions of ST without any catalyst, ST did not degrade. Figure 6 showed the results of UV-Vis spectra of degradation

SCHEME 2: Molecule structure of ST.

of ST with different time by $\text{SiO}_2@\text{PM}_{12}$ hybrid materials. Despite the absorbance of POMs at UV area, the peaks of ST were covered, and the absorbance of ST at visible area can reflect the degradation clearly. From Figure 6, the intensity of absorbance of ST decreased accompanied with the addition

FIGURE 5: The typical SEM image of the $\text{SiO}_2\text{@PMo}_{12}$ hybrid materials ((a) the original pollen, (b) the pollen covering with $\text{SiO}_2\text{@PW}_{12}$, (c) $\text{SiO}_2\text{@PW}_{12}$ core-shell particles, and (d) $\text{SiO}_2\text{@PMo}_{12}$ core-shell particles; scale bars were all $1\ \mu\text{m}$).

of reaction time. The ST can be degraded by $\text{SiO}_2\text{@PW}_{12}$ and $\text{SiO}_2\text{@PMo}_{12}$, respectively. In comparison, when the pure PW_{12} and PMo_{12} were added as catalyst, after 60 min, the conversion of ST only reached 74% and 78% (Figures 7(a) and 7(b)). However, apparent discolor of ST was observed when the $\text{SiO}_2\text{@PMo}_{12}$ hybrid catalysts were introduced (Figures 7(a) and 7(b)); that is, the conversions of ST reached 91% and 94% corresponding to $\text{SiO}_2\text{@PW}_{12}$ and $\text{SiO}_2\text{@PMo}_{12}$, respectively, after flowing air for 60 min. Compared with the catalytic activity of their parents (PMo_{12}), $\text{SiO}_2\text{@PMo}_{12}$ hybrids exhibited much higher activity. The result suggested that when forming core-shell hollow structure, the BET surface area was augmented and the activity of which was improved. It also could be seen that $\text{SiO}_2\text{@PMo}_{12}$ showed higher catalytic activity than $\text{SiO}_2\text{@PW}_{12}$ did.

3.6. Mechanism of Degradation. Generally, organic degradation by wet air oxidation was recognized as a free-radical mechanism and hydroxyl radical is an extremely potential

oxidizing agent with a short life which is able to oxidize organic substrates and generate other free radicals [22]. So the mechanism of degradation can be deduced as a mainly two-stage redox cycle.

Firstly, the oxidized form of $\text{SiO}_2\text{@POM}_{\text{ox}}$ interacts with organic dye ST(s) (as an electron donor), leading to product(s) P and reduced form of catalyst $\text{SiO}_2\text{@POM}_{\text{red}}$, which is the formation of the heteropoly blue on the surface of SiO_2 . The latter stage is thought to be the rate-determining step throughout POM-catalyzed oxidation:

Thereafter, the catalytic cycle is completed by reoxidation of the reduced catalyst by molecular oxygen:

FIGURE 6: Monitor process of degradation of ST with different catalyst ((a) $\text{SiO}_2@\text{PW}_{12}$, (b) $\text{SiO}_2@\text{PMo}_{12}$); the reaction time was 0, 5, 10, 20, 30, 40, 50, and 60 min, respectively (orientation of arrow).

FIGURE 7: Degradation of ST under different catalyst ((a) $\text{SiO}_2@\text{PW}_{12}$, (b) $\text{SiO}_2@\text{PMo}_{12}$).

3.7. Separation and Recovery of the Catalysts. After finishing the reactions, the suspensions were centrifuged, and the catalysts were collected. Separation and recovery of the hybrid catalysts were easy. The amount of W determined by ICP-AES in the resulting clear solution was less than 1.2%, which confirmed the less solubility of the catalysts during the reaction process and also showed the chemical bond between PW_{12} and SiO_2 preventing the removal of POMs molecules from it. The catalyst was reused for 4 times (Figure 8), during which the catalytic activity of $\text{SiO}_2@\text{PW}_{12}$ in the degradation of ST was maintained efficiently with slight decrease owing to the lesser dissolution. The results (Figure 8) show that the catalysts are stable under such operating conditions and

the leaching tests show negligible leaching effect owing to the lesser dissolution.

4. Conclusion

The research shows that $\text{SiO}_2@\text{PM}_{12}$ with core-shell structure could be prepared using native pollen grains as templates associated with surface sol-gel method, which is a unique, convenient, low-cost, and green chemical pathway. We can prepare samples with different types of catalytic activity (such as acid, redox) by this method using different types of POMs. The results of catalytic reactions suggested that these samples

FIGURE 8: Cycling runs in the oxidative degradation of ST in the presence of SiO₂@PM₁₂ hybrid materials under airflow.

are very active in degradation of organic dye and insoluble in water aqueous during the catalysis. This catalytic process is a green chemical pathway which exhibits potential industrial application in degradation of organic dye.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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