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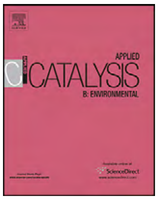

Design of mesostructured $H_3PW_{12}O_{40}$–titania materials with controllable structural orderings and pore geometries and their simulated sunlight photocatalytic activity towards diethyl phthalate degradation

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ABSTRACT

A series of mesostructured $H_3PW_{12}O_{40}$–titania materials with two-dimensional hexagonal, three-dimensional cubic, and three-dimensional interconnected sponge-like pore geometries were developed by using a single step nonionic-surfactant-templating strategy combined with evaporation-induced self-assembly (EISA) or hydrothermal treatment technique. The mesostructure, morphology, porosity, optical absorption property as well as composition and structure of as-prepared materials were well-characterized. Subsequently, the materials were successfully applied to the degradation of an aqueous diethyl phthalate (a kind of endocrine disrupting chemical) under the simulated sunlight irradiation at $\lambda > 320$ nm and $\lambda > 400$ nm region, respectively, and special attention was paid to investigate the influences of the structural orderings, pore geometries, $H_3PW_{12}O_{40}$ loadings as well as calcination temperature on the photocatalytic performance of the $H_3PW_{12}O_{40}$–titania materials to the target reaction.

1. Introduction

The development of efficient TiO_2-based photocatalytic materials still offers unexplored opportunities for total destruction of hazardous organic compounds in polluted air/water with the aid of solar light, owing to their environmental-friendly benefits in the saving of resources [1,2]. Semiconductor TiO_2 has consistently drawn much attention for their fascinating potential in environmental applications [3–5]. However, as a wide band gap semiconductor (3.2 eV), TiO_2 can only absorb UV fraction of solar light (3–5%), which leads to solar light-assisted TiO_2 photocatalytic process performs in very low efficiency [6]; on the other hand, quantum efficiency of TiO_2 is low due to fast recombination of photoinduced electron–hole (h^+–e^-) pairs [7,8]. To overcome the above two drawbacks, extensive research endeavors, therefore, have been devoted to design novel TiO_2-based photocatalysts with high photocatalytic efficiency, by extending the light-response range of TiO_2 to visible-light region and/or by reducing the h^+–e^- recombination probability. To realize this aim, numerous research attempts are currently being employed including crystal growth to tailor phase, shape, defect, and size of TiO_2 together with its crystallinity [9,10]; metal or non-metal doping to modify electronic structure [11–14]; and heterostructuring design of integrated multi-semiconductor systems to promote the separation of h^+–e^- pairs and/or modify electronic structure [15–17].

Additionally, the performance of the heterogeneous photocatalysts is also determined to a great extent by their textural and morphological properties, and fabrication of solid photocatalysts with perfect porous structure including uniform pore channel, large surface area, and larger pore diameter can improve their photocatalytic activity by increase active site numbers and the accessibility of active sites to the substrate [18]. Porous materials, especially mesoporous materials with unique surface physicochemical properties, have been successfully applied in many liquid phase catalytic processes [19–21]. Relying on sol–gel, solution, and surface chemistry, there is great potential to explore novel strategies for mesoporous catalytic materials with controllable wall components and the morphological architectures [22,23].

For the purpose of the improvement of the overall efficiency of TiO_2-based photocatalytic process, herein we developed a series of mesostructured $H_3PW_{12}O_{40}$–titania materials with different textural and morphological properties. $H_3PW_{12}O_{40}$ (12-tungstophosphoric acid), a kind of widely used polyoxometalate (POM) in homogeneous acid- and photocatalytic reactions, is a very strong BrÖnsted acid and efficient electron trap with well-defined Keggin structure [24–29]. $H_3PW_{12}O_{40}$ shares very similar photochemical characteristics of the semiconductor photocatalysts due to their similar electronic attributes. Several group's research has proved the combination of the $H_3PW_{12}O_{40}$ with TiO_2 can enhance the photocatalytic efficiency of TiO_2-

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catalyzed reaction due to the strong electron accept ability of POM and the transfer of electrons from $H_3PW_{12}O_{40}$ to oxygen species present in the reaction medium [30,31]. Our previous studies also found this synergistic photocatalytic effect between POM and TiO_2. POM/TiO_2 materials (POM = $H_3PW_{12}O_{40}$ or $H_6P_2W_{18}O_{62}$) prepared by a sol–gel co-condensation method exhibited higher photocatalytic activity under both UV ($\lambda > 254$ nm) and visible-light ($\lambda > 400$ nm) irradiation towards dye degradation compared with bare TiO_2 [32,33]. More recently, Marcì's group reported that the photocatalytic degradation of 2-propanol under solar simulating Xe lamp irradiation ($\lambda > 320$ nm) occurred successfully by using $H_3PW_{12}O_{40}$–titania material prepared by a post-synthesized method [34]. However, both of the above preparation strategies need to be ameliorated: for the $H_3PW_{12}O_{40}/TiO_2$ materials obtained by a co-condensation method in the absence of any structure-directing agent, its mesostructure was formed due to aggregation among product particles, resulting in the mesophase with uneven pore diameter distribution; in the case of $H_3PW_{12}O_{40}$–titania materials prepared by a post-synthesized method, it suffered from the problems such as the Keggin unit leaching, poor control over $H_3PW_{12}O_{40}$ loading, small specific surface area, and aggregation of the Keggin unit at the composite surface [35–37]. All of these lead to reduced photocatalytic activity of the supported POMs.

In search for new routes to prepare $H_3PW_{12}O_{40}$–titania materials with excellent photocatalytic behaviors, nonionic-surfactant-templating strategy combined with evaporation-induced self-assembly (EISA) or hydrothermal treatment technique were applied in current work. These two strategies can lead to the $H_3PW_{12}O_{40}$–titania materials with different textural and morphological properties, optical absorption properties, crystallinity, and the surface states. All of these factors can affect the photocatalytic activity of as-prepared $H_3PW_{12}O_{40}$–titania materials. Additionally, by using this one-pot preparation process, the interaction between the Keggin unit and TiO_2 matrix is strong, which can avoid the drop of the Keggin unit from the matrix during the preparation and subsequent photocatalytic process.

The photocatalytic activity of as-prepared $H_3PW_{12}O_{40}$–titania ($H_3PW_{12}O_{40}/TiO_2$) was evaluated in terms of the degradation and mineralization of diethyl phthalate (DEP) under solar simulating Xe lamp irradiation in the near UV- ($\lambda > 320$ nm) and visible-light ($\lambda > 400$ nm) region, respectively. DEP is a member of phthalate ester (PAE) family, while PAEs are endocrine disrupting chemicals that have a wide variety of industrial, agricultural, and domestic application, especially for their uses as plasticizers. The release of PAEs into the ecosystem or wastewater effluent has caused many human diseases and pollution. PAEs are rather stable compounds in the natural environment, and they recalcitrate to biodegradation and photolytic degradation owing to the existence of benzene carboxylic group and the lack of light response at wavelengths longer than 300 nm [38]. Therefore, it is urgent to search for alternative and effective treatment processes for such pollutants. In addition, unlike dyes that possess light response in the visible-light area, degradation of DEP due to the sensitization effect can be excluded in current photocatalytic system. During the $H_3PW_{12}O_{40}/TiO_2$-catalyzed DEP degradation process, the influences of $H_3PW_{12}O_{40}$ loadings, mesostructural orderings and pore geometries as well as calcination temperature on the photocatalytic performance were also studied.

2. Experimental

2.1. Chemicals and reagents

Titanium tetraisopropoxide ($Ti(Oi\text{-}Pr)_4$, abbreviated TTIP, 98.0%), 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, 99.9%), P123 ($EO_{20}PO_{70}EO_{20}$, where EO = $-CH_2CH_2O-$, PO = $-CH_2(CH_3)CHO-$), and F127 ($EO_{106}PO_{70}EO_{106}$) were purchased from Aldrich. Titanium tetrachloride (99.0%) and diethyl phthalate ($C_{12}H_{14}O_4$, GC grade) were purchased from Tianjin Guangfu Fine Chemical Research Institute. All chemicals were used without further purification. The double distilled water was used throughout the catalyst preparation and subsequent catalytic test.

2.2. Preparation of mesostructured $H_3PW_{12}O_{40}/TiO_2$ materials with controllable structural orderings and pore geometries

2.2.1. Ordered 2D and 3D $H_3PW_{12}O_{40}/TiO_2$ materials

P123 (1.5 g) was dissolved with ethanol (6 mL) at room temperature. A $TiCl_4$/TTIP solution was prepared by dropping $TiCl_4$ (1.4 mL) and TTIP (2.25 mL) into ethanol (6 mL) under vigorous stirring for 10 min. The desired amount of $H_3PW_{12}O_{40}$ (0.06, 0.12, 0.18, 0.30, and 0.48 mmol) was dissolved in water (5.2 mL). The $TiCl_4$/TTIP ethanol solution and the $H_3PW_{12}O_{40}$ aqueous solution were successively added in the above P123 ethanol solution. After stirring the resulting mixture for 2 h at room temperature, a semi-transparent sol was obtained. The sol was transferred into a Petri dish and aged at 40 °C until a uniform thin layer was formed. After being strengthened at 120 °C for 24 h, the obtained powder was extracted by ethanol at 60 °C for 3 h to remove P123 template (the procedure was repeated twice). Finally, the product was dried at 60 °C for 24 h and crystallized at 350 °C for 1 h. The product was denoted as $H_3PW_{12}O_{40}/TiO_2\text{-}2D_{hex}\text{-}x$, where x represents $H_3PW_{12}O_{40}$ loading in the composite material. For comparison, $TiO_2\text{-}2D_{hex}$ and $H_3PW_{12}O_{40}/TiO_2\text{-}x$ (without template) samples were prepared in the absence of $H_3PW_{12}O_{40}$ and template, respectively; $H_3PW_{12}O_{40}/TiO_2\text{-}2D_{hex}\text{-}x$ (400 °C) and $H_3PW_{12}O_{40}/TiO_2\text{-}2D_{hex}\text{-}x$ (450 °C) materials were prepared under the crystallization temperature at 400 °C and 450 °C, respectively.

The preparation route of ordered 3D $H_3PW_{12}O_{40}/TiO_2\text{-}3D_{cub}$ materials is similar to that of the $H_3PW_{12}O_{40}/TiO_2\text{-}2D_{hex}$ materials by using F127 instead of P123 as a template. Additionally, temperature for the stirring the mixture of $TiCl_4$/TTIP, F127, and $H_3PW_{12}O_{40}$ was set at 40 °C rather than room temperature.

2.2.2. 3D sponge-like $H_3PW_{12}O_{40}/TiO_2$ materials

P123 (1.5 g) was dissolved in ethanol (6 mL) at room temperature. A $TiCl_4$/TTIP solution was prepared by dropping $TiCl_4$ (1.4 mL) and TTIP (2.25 mL) into ethanol (6 mL) under vigorous stirring for 10 min. $H_3PW_{12}O_{40}$ (0.12 mmol) was dissolved in water (5.2 mL). The above $TiCl_4$/TTIP ethanol solution and aqueous $H_3PW_{12}O_{40}$ solution was successively added into the P123/ethanol solution. After stirring the resulting mixture for 2 h at room temperature, a semi-transparent sol was obtained. The sol was subjected to hydrothermal treatment at 150 °C for 48 h at a heat rate of 2 °C/min. The resulting white hydrogel was dehydrated at 60 °C for 24 h until complete gel particulate was formed. After thermal treatment at 120 °C for 24 h, the obtained powder was extracted by ethanol at 60 °C for 3 h to remove template (the procedure was repeated twice). The product was denoted as $H_3PW_{12}O_{40}/TiO_2\text{-}3D_{spo\text{-}1}$.

The preparation route of $H_3PW_{12}O_{40}/TiO_2\text{-}3D_{spo\text{-}2}$ is the same as that of the $H_3PW_{12}O_{40}/TiO_2\text{-}3D_{spo\text{-}1}$ except using F127 instead of P123 as a template agent. Additionally, temperature for the stirring the mixture of $TiCl_4$/TTIP, F127, and $H_3PW_{12}O_{40}$ was set at 40 °C rather than room temperature.

2.3. Characterization

Small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WXRD) patterns were obtained on a D/max-2200 VPC diffractometer using Cu Kα radiation. Transmission electron microscope (TEM), high resolution transmission electron microscope