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Super-hydrophobic fluorination mesoporous MCF/TiO_2 composite as a high-performance photocatalyst

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ABSTRACT

NH_4F was used instead of conventional organic silylation agent as the hydrophobic modifier to synthesize the super-hydrophobic mesocellular foams (MCF) loaded with nano-sized TiO_2 photocatalysts in its pore channels, which could be considered as an extractant for organics. Compared to organosilane modified catalysts, NH_4F-modified MCF/TiO_2 has a more stable super-hydrophobic property and much higher photocatalytic activity. It was found that only using isopropanol as the solvent, the NH_4F-modified catalyst showed super-hydrophobic property. It is believed that the solvent plays a role in controlling the exchange between surface OH groups and F ions. The special structure of supported mesoporous catalyst greatly facilitated the surface fluorination, which together with the Ti^{3+} generation led to its excellent adsorption capacity and UV/visible light photocatalytic activity. This novel super-hydrophobic mesoporous photocatalyst has a large application potential in the field of photocatalysis, shipbuilding, and other industries.

1. Introduction

As a widely used photocatalyst, TiO_2 is limited by its wide bandgap [1], which greatly restrains its practical applications. Many studies have been done on modifying TiO_2 to improve its visible light photo activity [2], such as doping impurities to narrow its bandgap [3,4]. However, attempts at increasing visible light activity by narrowing the bandgap of TiO_2 through doping have proven difficult, because of defect-induced charge trapping and recombination sites of photo-excited charge carriers [5]. Recently, mesoporous materials are widely used as an ideal adsorbent for the adsorption of organic molecules, due to its large specific surface area [6,7], which has a broad application prospect in the field of photocatalysis. Matthews et al. [8] have found that the adsorbent (silica gel)/photocatalyst (TiO_2) with excellent adsorption capacity of organic impurities, resulting in its enhanced photocatalytic activity. Although mesoporous material as an ideal adsorbent could effectively adsorb organic molecules, its adsorption capacity would be greatly reduced when the concentrations of organic molecules in aqueous solution was very low, because of the presence of competitive adsorption of organic molecules and water molecules.

The promoting performance of semiconductor surface hydrophobic property is considered as an effective way to further improve its adsorption capacity for organic molecules at a very low concentration in an aqueous solution [9]. Hydrophobic materials based on zeolites and mesoporous silicas such as HMS, SBA-15, and MCF could offer excellent ability of adsorption of organic compounds owing to their weak adsorption of water molecules and the large surface areas [9]. Hence, hydrophobic zeolites have a large potential application as supports for TiO_2 photocatalysts to the photocatalysis filed. Conventional hydrophobic modifiers include organosilane coupling agents, and silylation agent contains an inorganic function group such as fluorine [9,10]. The organic functional groups are easily photo degraded by the TiO_2, and most of them are poisonous and costly [9,11]. NH_4F as a cheap and relative low-toxic inorganic compound has a large application potential in the silica hydrophobic modification. In 1996, Adachi et al. [12] have found that the HF- and NH_4F-treated Si(111) surfaces are hydrophobic. And that Nadargi et al. [13] considered the NH_4F being used as a catalyst for the tetraethoxysilane gel formation during the preparation of hydrophobic silica aerogels. Actually, we have found that the choice of solvent is critical for the NH_4F hydrophobic modification in a simple surface fluorination process.

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Though a simple surface fluorination on TiO_2 can induce an enhanced UV light photocatalytic oxidation activity, but it is difficult to improve the visible light photocatalytic activity of TiO_2, owing to the lack of photo-excited holes in the visible light irradiation [14].

We try to find ways to design and prepare a novel hydrophobic TiO_2 photocatalyst, which can enhance visible light response. In our previous work, we have found that the economic vacuum activation method is an effective way to produce much more Ti^{3+} in TiO_2 and enhance its visible light photo activity [15]. Therefore, design and preparation of a new type Ti^{3+} modified mesoporous MCF/TiO_2 photocatalyst with permanent hydrophobic property and enhanced photocatalytic activity has a large potential application to the photocatalysis. Herein, NH_4F is used as the hydrophobic modifier, and isopropanol is used as the solvent to synthesize the super-hydrophobic mesoporous MCF loaded with highly dispersed and Ti^{3+}-self doped TiO_2 nanoparticles, through a simple one-step solvothermal method, followed by a low-temperature vacuum activation process to produce Ti^{3+}. The prepared catalyst exhibits permanent and excellent super-hydrophobic property, high-adsorption capacity, and enhanced photocatalytic activity for Rhodamine B (RhB) degradation.

2. Experimental section

2.1. General information

All chemicals, including pluronic P123 triblock copolymer (EO20PO70EO20, *M*av = 5800, Aldrich), 1,3,5-trimethylbenzene (TMB, AR), ammonium fluoride (AR), tetraethyl orthosilicate (TEOS, AR), hydrochloric acid (36–38%), titanium sulfate (CP), isopropanol (AR), methanol (AR), and ethanol (AR) were used as received without any further purification.

2.2. Preparation of MCF

The purely siliceous MCF sample was prepared as described previously [16]. In a typical preparation, 8.0 g P123 was dissolved in the mixture solution of 40 mL hydrochloric acid and 260 mL distilled water under the 37 °C temperature. 0.1 g NH_4F and 4.0 g TMB were added in the above solution and then stirred for 1 h. At the same 37 °C temperature, 18.3 mL TEOS was added under stirring for 20 h. The obtained slurry was transferred to an autoclave and aged at 100 °C for another 24 h. The solid products were washed by the distilled water and dried overnight at 60 °C under vacuum condition. The occluded surfactant was removed by calcinations at 550 °C for 6 h in air (1 °C/min), yielding the final mesoporous MCF material.

2.3. Synthesis of TiO_2 loaded on MCF

1.2 g $Ti(SO_4)_2$ was dissolved in 25 mL distilled water under stirring for 30 min. 0.8 g MCF was added in the solution and stirred for another 4 h. The solution was transferred to an autoclave and hydrothermal at 120 °C for 7 h. The obtained products were washed and dried at 60 °C for 12 h under the vacuum condition to obtain the catalyst of MCF loaded with TiO_2. The loading concentration of TiO_2 on MCF was 25 wt%, which was calculated from the elemental analysis results. The prepared sample was denoted as MCF/TiO_2.

2.4. NH_4F hydrophobic modification

A certain amount of NH_4F was mixed with 70 mL isopropanol under stirring for 1 h. 0.5 g MCF/TiO_2 was added in the solution and stirred for another 1 h. The above solution was kept under 120 °C for 20 h hydrothermal treatment. The obtained products were washed with distilled water for three times and then transferred to the vacuum oven and activated at 200 °C for 3 h under the vacuum condition. This prepared modified sample was denoted as 0.4-MCF/TiO_2, where 0.4 described the molar ratio of NH_4F to Ti and Si total moles. In addition, the NH_4F-modified MCF/TiO_2 treated with activation in the air at 200 °C for 3 h was denoted as A-0.4-MCF/TiO_2 (F/(Ti + Si) molar ratio is 0.4). The catalyst of MCF/TiO_2 treated with activation in vacuum at 200 °C for 3 h but without the NH_4F modification was denoted as V-MCF/TiO_2. All the above catalysts are used as the references.

In order to investigate the hydrophobic mechanism of NH_4F modification, different dissolvent was used in the process of NH_4F modification. The dissolvent was changed from isopropanol to water, methanol, and ethanol to modify the MCF with NH_4F (F/Si molar ratio is 0.4) using the same above method.

2.5. Trimethyl chlorosilane hydrophobic modification

MCF/TiO_2 was also modified by the organosilane agent trimethyl chlorosilane using the reflux method, which was prepared as a reference. The modification procedures are as follows: 0.2 g MCF/TiO_2 was mixed with 10 mL trimethyl chlorosilane and 15 mL methylbenzene under stirring for 5 min. Mixture was reflux under the 50 °C for 8 h. Powders were washed followed by ethanol and distilled water for three times and then dried under 80 °C for 6 h. The obtained sample modified by trimethyl chlorosilane was denoted as T-MCF/TiO_2. A direct comparison in stability between NH_4F and trimethyl chlorosilane modified catalysts was carried out.

2.6. Characterization details

X-ray diffraction (XRD) patterns of all samples were collected in the range 10–80° (2θ) using a Rigaku D/MAX 2550 diffractometer (Cu K radiation, $\lambda = 1.5406$ Å), operated at 40 kV and 100 mA. The morphologies were characterized by transmission electron microscopy (TEM, JEM2000EX). The instrument employed for XPS studies was a Perkin-Elmer PHI 5000C ESCA system with Al Kα radiation operated at 250 W. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.6 eV as an internal standard. The X-band EPR spectra were recorded at room temperature (Varian E-112). BET surface area measurements were carried out by N_2 adsorption at 77 K using an ASAP2020 instrument. The elemental analysis was carried out on a VARIO EI III, and its measuring range was within 0.3%. Water repellency was checked by the contact angle of a pure water droplet using a contact angle meter Dataphysic OCA20. Catalyst was deposited on the membrane filter to carry out the contact angle measurement. Water adsorption isotherms were measured at room temperature ($\sim$25 °C) using a conventional vacuum system (temperature-humidity test chamber). Before the measurements, the samples (70 mg) were spread and preheated at 373 K for 2 h in the vacuum to remove the surface adsorbed H_2O molecules. The pressure changes were recorded at the appropriate intervals after the adsorption had reached equilibrium. Electronic balance (minimal scale of 0.0001 g) was used to weigh the quality of the adsorbed H_2O molecules. Fourier transform infrared (FTIR) spectra were recorded with KBr disks containing the powder sample with the FTIR spectrometer (Nicolet Magna 550). Residual organic carbon in RhB solution was measured using a total organic carbon analyzer (TOC-VE, Shimadzu).