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Sunlight highly photoactive TiO_2@poly-*p*-phenylene composite microspheres for malachite green degradation

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ABSTRACT

The TiO_2@poly-*p*-phenylene (PPP) composite microspheres were successfully prepared from the self-assembled PPP microspheres in the tetrabutyl titanate solution *via* the sol–gel method. The morphology and optical properties of the composite microspheres have been characterized by the SEM, EDX, UV–vis diffuse reflectance spectroscopy, and photoluminescence spectra. The presence of PPP changes the band gap of TiO_2, which makes the composite microspheres enhance good photocatalytic activity on the degradation of malachite green (98.2%) under sunlike irradiation. The photo-catalytic reusability was investigated up to five successive cycles and the microspheres still retain their activity about 85.6% of photodegradation ratio. Consequently, the TiO_2@PPP composite microspheres can be employed as the efficient photocatalyst to treat the organic pollutants.

1. Introduction

With the rapid development of economy and industry, environmental deterioration has been a threat to the survival and development of humans. Treatment of wastewater caused by toxic organic compounds has drawn more and more worldwide attention. It is urgent to develop efficient and economically feasible methods for environmental remediation [1]. Photocatalytic process is one of highly promising techniques, because it operates at ambient temperature and pressure, requires O_2 in the ambient air only and no expensive catalysts [2,3].

Because of its thermal and chemical stability and non-toxicity, Titanium (IV) oxide TiO_2 is considered to be an important photocatalyst to decontaminate organic pollutants in dye wastewater. However, the wide band gap of TiO_2 (above 3.2 eV) restricts the excitation to UV light irradiation and greatly decreases the utilization of sunlight [4,5], because UV radiation accounts for only about 4%, compared to more than 50% of visible light in the solar spectrum [5]. Hence, it is very meaningful for practical application to engineer the band gap of catalysts to expand the light absorption area [6,7]. Making full use of solar radiation, not only the use of visible light radiation, but also an adequate overall handling of UV radiation, is the key point for a good photocatalyst performance.

Many developments of visible light-responsive TiO_2 have been reported, such as application of inorganic compounds or noble metals as dopants or surface modifiers [4,8,9]. In recent years, conjugated polymers have been extensively investigated for their remarkable optoelectronic properties. Therefore, the formation of composites by coupling nano-TiO_2 with small band gap conducting polymers is also an alternative technique to enhance the visible photocatalytic performance [10–12]. The polycarbazole/TiO_2 nanohybrids prepared by Riaz et al. exhibited a complete degradation of Amido Black 10B dye in a short span of 60−90 min under UV light [13]. Wang prepared polyaniline/TiO_2 nanocomposites for the degradation of methylene blue (MB) dye with the decolorization efficiency of 80% upon 90 min under natural light irradiation [14]. The polyaniline/TiO_2 nanocomposites were prepared by Salem et al. and showed good degradation with the rate constant of MB degradation of 15.15×10^{-3} min^{-1} after 120 min under visible light [15]. The macro porous polypyrrole/TiO_2 composites for the degradation of Rhodamine B (RhB) showed high photocatalytic performances with rate constant of 14.89×10^{-3} min^{-1} [16]. The visible light photocatalytic behavior of TiO_2/poly(3-hexylthiophene) for methyl orange was found to reach the maximum of 88.5% in 10 h [17].

Because of its excellent blue-light emitting and photoconductivity, poly-*p*-phenylene (PPP) [18] is expected to be used as a stable photosensitizer to improve the photocatalysis of TiO_2 under visible light. Thereby, the TiO_2@PPP composite microspheres were prepared from the self-assembled PPP microspheres [19] in the

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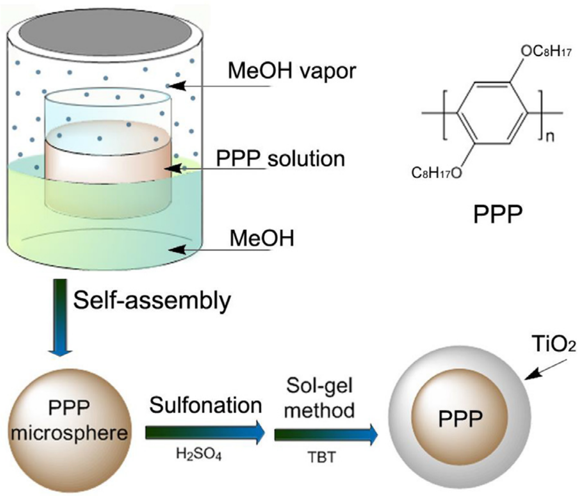

Scheme 1. Preparation of TiO_2@PPP composite microspheres.

tetrabutyl titanate solution *via* the sol–gel method [20]. We propose the composite microspheres presenting high performance for malachite green degradation under sunlike irradiation.

2. Experimental

2.1. Materials

Analytical grade dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrabutyl titanate (TBT), methanol (MeOH), and ethanol (EtOH) were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Malachite green (MG) and Rhodamine B (RhB) were purchased from Tianjin Fuchen Chemical Reagent Factory. All reagents were used without further purification. Demineralized water was used throughout the work. Poly(2,5-dioctyloxy-*p*-phenylene) was synthesized by the solid-state oxidative coupling polymerization using $FeCl_3$ as the oxidative catalyst [21] and its number-average molecular weight and the dispersity were determined to be 7.0×10^3 g/mol and 2.71.

2.2. Preparation of TiO_2@PPP composite microspheres

The process of preparation is shown in Scheme 1. First, the PPP microspheres were self-assembled by the solvent diffusion method [19]. After ultrasonic dispersion in EtOH, the PPP microspheres (0.5 g) were sulfonated by concentrated sulfuric acid of 10 g for 1 h at 40 °C. Then the sulfonated PPP microspheres were collected and dispersed by ultrasonic treatment in 50 mL EtOH, in which, TBT of 50 mL were added and stirred at room temperature for 8 h. After the removal of excess TBT washed by EtOH, the sulfonated PPP microspheres adsorbed TBT were put into the H_2O/EtOH (vol/vol = 1:1) solution and then stirred at room temperature for 4 h [20]. Finally the TiO_2@PPP microspheres were obtained from the mixture after washed by EtOH, centrifugation, and dried in vacuum oven.

2.3. Photocatalytic activity measurement

Photocatalytic activities of the samples were evaluated by measuring the degradation of the organic dyes in aqueous solution under sunlight irradiation. Solar photolysis experiments were carried out on the roof of the Chemistry Building in Fujian Normal University (Fuzhou, China: 26°N latitude) in the mid-September days between 11 AM and 3 PM under clear or partly cloudy sky conditions. For each experiment, 50 mg of photocatalysts was dispersed in 50 mL organic dye solution (3.0×10^{-5} M). At first, the suspensions were magnetically stirred in the dark for 30 min to ensure the adsorption/desorption equilibrium of the dye solution with catalysts. The samples (3 mL) were collected at regular intervals of 15 min. The degradation efficiency was monitored by UV–vis spectroscopy at intervals, respectively.

The percentage of degradation of the dyes was calculated from the following expressions.

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

where C_0 and C are the concentrations of the dye at irradiation times $t = 0$ and $t = t$ respectively. The reaction rate can also be calculated using plots of $\ln(C/C_0)$ *versus* illumination time as follows:

$$-\ln(Ct/C_0) = kt \qquad (2)$$

where t is the irradiation time and k is the first-order rate constant of the reaction [22].

2.4. Characterization

The morphology and the composition of the samples were characterized by a JSM-7500F scanning electron microscope (SEM) equipped with an Oxford Inca energy dispersive X-ray (EDX) analyzer at an accelerating voltage of 20 kV. FT-IR Spectra were recorded on a Bruker Vector 22 Spectrometer. The UV–visible diffuse reflectance spectra were recorded using a PE Lambda850 spectrophotometer. Measurements of photoluminescence (PL) emission spectra were carried out on a Perkin-Elmer LS55. The total organic carbon (TOC) was measured in a Shimazu TOC-L Analyzer. The pH values of the aqueous solutions were measured by PHB-4 Portable pH Meter (Shanghai, China).

3. Results and discussion

The PPP microspheres were self-assembled from the PPP/CH_2Cl_2 solution in a MeOH vapor atmosphere *via* the solvent diffusion method. The polymer microspheres with an undulating filamentous surface can be observed in Fig. 1a. The FT-IR spectrum of the PPP microspheres was shown in Fig. 1b. The breathing modes of the aromatic rings occur at 1640 to 1460 cm^{-1} for the polymeric microspheres. The peak at 860 cm^{-1} assigned to the out-of plane vibration of the isolated C–H in substituted benzene rings indicates the *para*-linkage. The peaks from 2919 to 2851 cm^{-1} assigned to the stretching vibrations of C–H bonds and from 1200 to 1028 cm^{-1} assigned to the stretching vibrations of C–O–C suggest the alkoxy side-chains. These results confirmed the structure of PPP [19]. After the sulfonation of PPP microspheres in concentrated sulfuric acid, the sulfonated PPP microspheres were coated by TiO_2 in the TBT solution by the sol–gel method to prepare the TiO_2@PPP composite microspheres. From Fig. 1c, we can observe the nano-TiO_2 particles covering the surface of the PPP microspheres, which also can be demonstrated by EDX analysis in Fig. 1d.

The absorption wavelength distribution is an important property of photocatalyst. From the UV–vis diffuse reflectance spectra as shown in Fig. 2a, the PPP microspheres show a broad absorbance band in the UV–vis region with the maximum absorbance peak at about 340 nm. The composite microspheres retain the similar absorption spectral pattern, indicating the improved photoactivity of the TiO_2@PPP microspheres than that of the bulk TiO_2. Since photocatalytic activity is related closely to the PL intensity and the recombination rate of photoexcited electrons and holes, the PL measurement was also performed as shown in Fig. 2b. When

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