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Photodegradation of phenol via C_3N_4-agar hybrid hydrogel 3D photocatalysts with free separation

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ABSTRACT

The agar-C_3N_4 hybrid hydrogel photocatalysts with 3 dimension (3D) network structure have been prepared via thermoreversible phase transition of agar. The hybrid hydrogels show high efficient pollutants removal ability by synergistic effect of adsorption and photocatalytic degradation. The removal ability of phenol and methylene blue (MB) by hybrid hydrogel is about 1.3 and 4.5 times of pure g-C_3N_4 respectively. The pollution can be degraded continuously via agar-C_3N_4 hybrid hydrogels photocatalysts without separation.

1. Introduction

Recently, the problems of environmental pollution have become increasingly serious, posing a great threat to human health and sustainable development [1–6]. A lot of efforts have been made to remove the organic pollution in water, such as adsorption [7], photocatalytic degradation [8,9], biological treatment [10] and so on. The adsorption is one of the most widely used methods because of the high adsorption efficiency and low cost of the adsorption materials [11–14]. Among all the adsorption materials, the 3D hydrogels have attracted much attention due to their outstanding performance of adsorption and concentration of water pollutants [15–18]. On the one hand, the adsorption materials with three-dimensional network structure avoid aggregation and provide convenient mass transfer channels. On the other hand, the bulk structure can prevent the materials from dispersing in water [19–22]. The operation, collection and separation of the materials from water are simplified by a wide margin. However, the application of 3D hydrogels is limited by their disadvantages. The organic pollutants just can be concentrated rather than degraded to non-polluting molecules by hydrogels. The pollution problem cannot be solved drastically. Besides, only the materials undergo tedious desorption process can they be recycled. Therefore, materials with both ability of pollutants adsorption and degradation are undoubtedly the most advantageous.

Graphic carbon nitride (g-C_3N_4) is an attractive organic semiconductor photocatalyst with visible light activity and excellent thermal and chemical stability [23–25]. It has attracted extensive attention in degradation of organic pollutants, production of H_2 and O_2 from water and photocatalytic conversion of CO_2 under visible light [24,26–28]. However, the catalytic activity of g-C_3N_4 is limited by its poor adsorption ability for some pollutants, such as phenol. Moreover, it is difficult for the nano-sized g-C_3N_4 particles to be separated from water completely. Thus, novel g-C_3N_4 based hybrid hydrogels is not only facile to be separated from water to avoid secondary pollution, but also likely to show improved pollutants removal ability by synergistic effect of adsorption and photocatalytic degradation.

As a biopolymer gel, agar is widely used in the preparation of culture medium and polymeric hybrid hydrogels [29–31]. The application of agar in catalysis field has not been reported yet. In this paper, agar is used to prepare hybrid hydrogels via its thermoreversible sol–gel transition (Scheme 1). Agar and g-C_3N_4 nano-particle hydrosol is transformed into hybrid hydrogel with 3D network structure by a heating–cooling polymerization process. The agar-C_3N_4 hybrid hydrogels show enhanced performance

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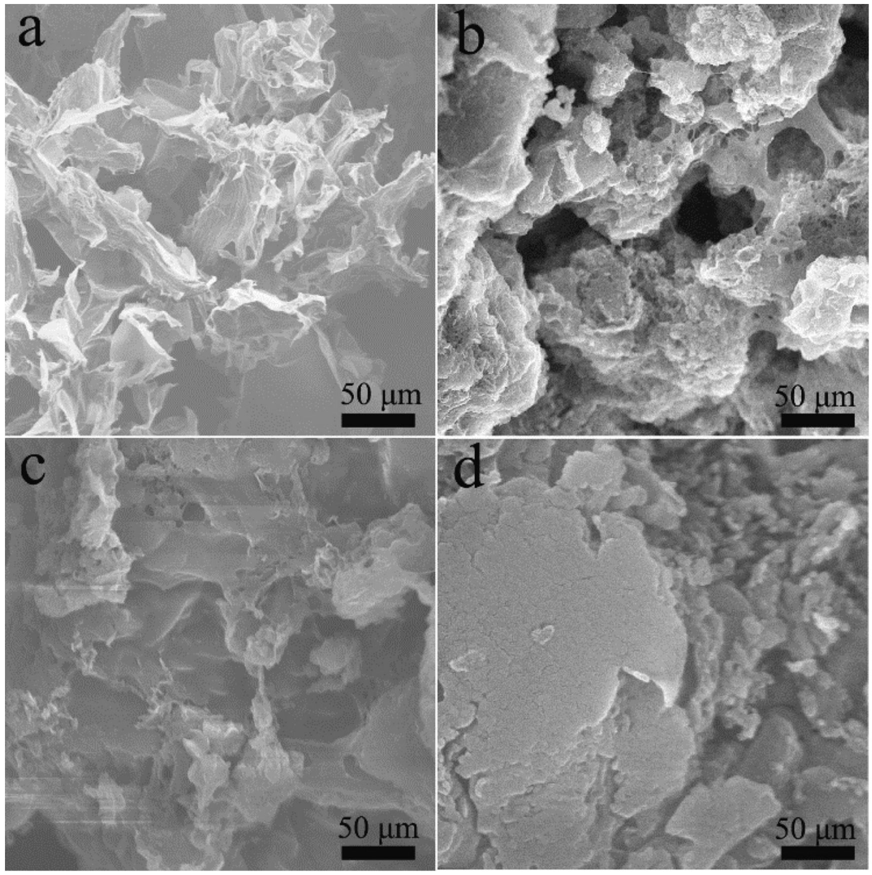

Fig. 1. The SEM images of pure agar (a) pure C_3N_4 (d) and C_3N_4-agar hybrid hydrogels (40% and 90%, b and c).

in photocatalytic degradation of MB and phenol under visible light via synergistic effect of adsorption and photocatalysis. The hybrid hydrogel exhibits excellent cyclic stability and can be used continuously without adsorption saturation. The C_3N_4-agar hybrid hydrogels are promising materials used in the treatment of water pollutants.

2. Experimental

2.1. Preparation of the C_3N_4-agar hybrid hydrogels

Agar and dicyandiamide were purchased from Sinopharm Chemical Reagent Corp., PR China. All other reagents used in this research were analytically pure and used without further purification.

The g-C_3N_4 was prepared by pyrolysis of dicyandiamide in air atmosphere. The typical preparation of g-C_3N_4 photocatalysts was as follows: The dicyandiamide was put in a Muffle Furnace and heated to 550 °C for 4 h to complete the reaction. The yield of the optimum g-C_3N_4 was about 25%.

Agar and g-C_3N_4 nano-particle hydrosol is transformed into hybrid hydrogel with 3D network structure by a heating–cooling polymerization process. The typical preparation process was as follows: A certain proportion of agar and g-C_3N_4 were put in to water and dispersed by ultrasound for 30 min. The hydrosol of mixture was heated up to 95 °C for 5 min and then cooled to room temperature in air to form C_3N_4-agar hybrid hydrogel. The 60%-TiO_2-agar was prepared by the similar method. 300 mg TiO_2 and 200 mg agar were put into water and ultrasound for 30 min. The hydrosol of mixture was heated up to 95 °C for 5 min and then cooled to room temperature in air to form 60%-TiO_2-agar hybrid hydrogel.

2.2. Characterizations

The morphologies and structure of the C_3N_4-agar hybrid hydrogels were characterized by a Hitachi SU-8010 Field Emission Gun Scanning Electron Microscopy and a Hitachi HT 7700 electron microscope operated at an accelerating voltage of 100 kV. UV–vis diffuse reflectance spectroscopy (DRS) was examined by Hitachi U-3010 UV–vis spectrophotometer with $BaSO_4$ as the reference sample. The crystallinity of the hybrid hydrogels were characterized by X-ray diffraction (XRD) on Bruker D8-advance diffractometer using Cu-Kα radiation (λ = 1.5418 Å). Raman spectra were recorded on a microscopic confocal Raman spectrometer (HORIBA HR800) with an excitation of 785 nm laser light. Fourier transform infrared (FT-IR) spectra were carried out using Bruker V70 spectrometer in the frequency of 4000–600 cm^{-1} with a resolution of 1 cm^{-1}. The photocurrents were measured on an electrochemical system (CHI 660B, China). Visible light was obtained from a 500 W xenon lamp (Institute for Electric Light Sources, Beijing) with a 420 nm cutoff filter.

2.3. Photocatalytic experiments

The synergistic effect of adsorption and photocatalytic degradation of the hybrid hydrogels in static systems were evaluated by the decomposition of MB and phenol solution in multi-tube agitated reactor (XPA-7). Visible light source was obtained by a 500 W Xe lamp (Institute for Electric Light Sources, Beijing) with a 420 nm cutoff filter, and the average visible light intensity was 35 mW cm^{-2}. 25 mg photocatalyst was added into prepared 50 mL 3×10^{-5} mol L^{-1} MB solution or 5 ppm phenol solution. The suspensions were magnetically stirred with visible light irradiation. At given time intervals, 3 mL aliquots were sampled and centrifuged