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Study of the preparation of CdS on the surface of geopolymer spheres and photocatalyst performance

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HIGHLIGHTS

- Chemosynthetic geopolymer sphere (GS) is prepared by a suspension solidification.
- A photochemical growth method is used to grow CdS crystals on the GS surface.
- The CdS-GS exhibited good adsorption and photocatalytic degradation performance.
- The CdS-GS photocatalytic degradation efficiency to methyl orange is about 92.57%.
- The CdS-GS degradation kinetics meet with the pseudo-second-order rate equation.

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ABSTRACT

Geopolymer spheres (GS) made of chemosynthetic geopolymers are prepared through a suspension solidification method. Cd^{2+} ions can easily absorb on the surface of the GS via van der Waals forces and ion exchange interactions. A photochemical growth method is used to grow CdS crystal particles homogeneously on the GS surface. The CdS-GS exhibited good adsorption and photocatalytic degradation performance in the decolourisation of methyl orange (MO) with a degradation efficiency of approximately 92.57%. The analysis of the CdS-GS degradation kinetics of MO indicated that it is corresponding to the pseudo-second-order rate equation. The repeating degradation experimental results indicated the CdS-GS photocatalyst had relatively stable photocatalytic performance.

1. Introduction

Geopolymers, first named and identified by Joseph Davidovits in 1978, are non-crystalline or quasicrystalline gels manufactured with three-dimensional network structures on the alkaline activator used for their manufacturing and reaction conditions [1]. Their framework consists of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons linked by shared oxygen atoms with the negative charge balanced by cations such as Na^+, K^+, and Ca^{2+}. The negatively charged three-dimensional network is also balanced by extra-framework cations that can participate in the immobilization of heavy metal ions and ion exchange, which is a result of the presence of ring forming cationic sites for bare cations [2–7].

A study of geopolymers as photocatalysts for the degradation of methyl blue from waste water has recently been reported, revealing a novel photocatalyst that showed an excellent synergetic performance in the process for the degradation waste water [8].

Semiconductor photocatalysts, which possess strong oxidation ability and better stability, have attracted considerable interest in the treatment of waste water. CdS is an effective photocatalyst [8–11]. Currently, most studies regarding the treatment of waste water have reported on the direct applications of pure CdS nanoparticles, which have two disadvantages: (1) CdS is not easily isolated from the treatment liquid, making it difficult to run a treatment plant using CdS nanoparticles; (2) it does not allow the continuous treatment of industrial waste water leading to low treatment efficiency. To solve these defects, many articles in the literature [10–13] have reported a method to load these CdS nanoparticles onto a polymer matrix. However, this method leads to a large amount of CdS sealed in the matrix and decreased

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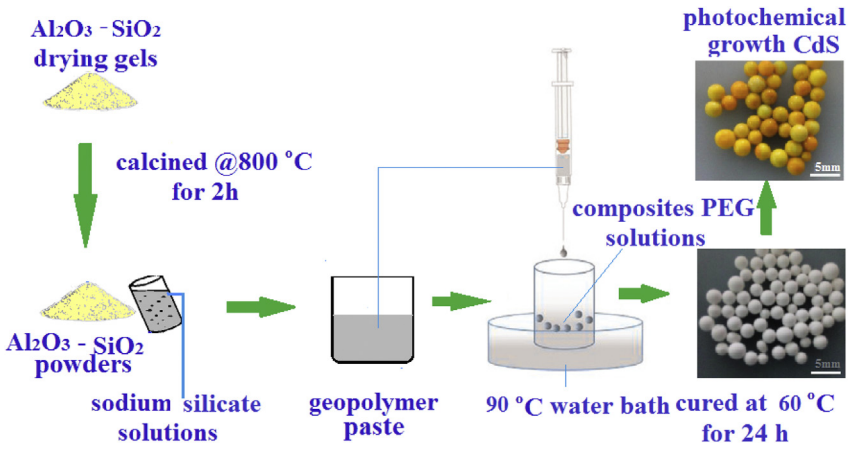

Fig. 1. The sketch of preparation of geopolymer sphere (GS) and CdS-GS by suspension solidification method combined photochemical synthesis process.

degradation efficiency. Furthermore, active biopolymer matrices have low intensity and easy decomposition defects, which tremendously reduce the life of the photocatalyst as well as reusability. According to recent study [4,5,7], millimeter-sized geopolymer spheres can be easily handled solve these defects. More importantly, they can be used in columns for catalysis or for the continuous treatment of industrial waste water [7].

Based on the above research, we utilized geopolymer spheres loaded with CdS nanoparticles, with high strength, rapid hardening and excellent synergetic performance, and the transition metal in the degradation process. To prepare CdS directly on the surface of the geopolymers spheres, the suspension and solidification method combined with the photochemical method was studied in this paper.

2. Experimental procedures

The geopolymer slurry (Na_2O:Al_2O_3:SiO_2:H_2O = 1:1:2:10) was first prepared by adding 5 g chemosynthetic Al_2O_3–SiO_2 powders and 2.32 g water into 8.36 g sodium silicate solution (with a molar ratio of SiO_2/Na_2O = 0.9). Subsequently, the homogeneous slurry was continuously injected into a PEG-600 medium in a 90 °C water bath by the suspension solidification method for the preparation of the geopolymeric spheres (GS) [4,5,7].

This suspension solidification process of preparation of geopolymer sphere (GS) was performed in Fig. 1 as follows: chemosynthetic powders were mixed with a sodium silicate solution according to the designed composition, which was stirred uniformly to obtain geopolymer slurry. Then, droplets of the slurry were injected into the PEG-600 medium maintained at 90 °C in a water bath. As the densities of the droplets and PEG-600 are approximately equivalent, the droplets were suspended and retained their spherical shape. Rapid solidification of the spheres facilitated their separation from the PEG-600 medium. Isolated spheres were washed by distilled water to remove excess adsorbed PEG-600. Finally, the geopolymer spheres were obtained by curing at 60 °C for 1 day, which would be applied in next experiment.

The photochemical synthesis process of CdS-GS was shown in Fig. 1. Approximately 5 g of GS was added into the solution of $CdSO_4$ (0.05 M) in a beaker. Subsequently, the beaker was placed on a magnetic stirrer for 2 h at room temperature. The GS were then washed several times with deionized water to remove the unnecessary SO_4^{2-}, and the Cd^{2+}-GS were obtained after drying. Finally, the growth of CdS crystals on the surface of Cd^{2+}-GS was achieved by photochemical synthesis [10–12]. Approximately 5 g of Cd^{2+}-GS was added into the solution of $Na_2S_2O_3$ (0.06 M) in a beaker, which was then placed under a tube-type UV lamp (Philips, 245 nm, 8 W, and 0.734 mW cm^{-2}) in a box. When the lamp was turned on, a photochemical reaction occurred, mainly at the surface of the Cd^{2+}-GS. After 24 h, these spheres turned yellow as CdS crystals formed over the entire surface (Fig. 1). The spheres were then collected and washed several times with deionized water. Finally, the products were collected and dried at 60 °C in atmospheric conditions. After drying for about 24 h, the mass of CdS-GS samples was about 5.67 g, so the load mass ratio of CdS on GM was about 13.25 wt%.

A Hitachi scanning electron microscope S–3400 N was used with an accelerating voltage of 10 kV to observe morphology of the

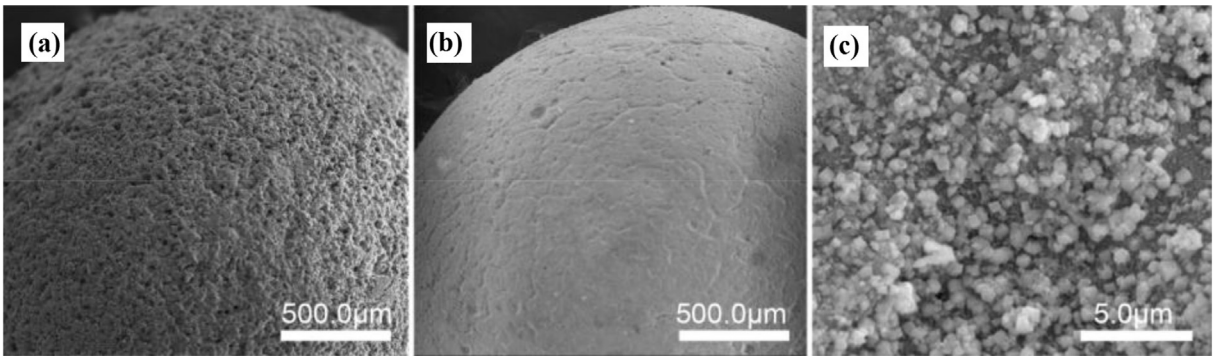

Fig. 2. Surface SEM photos of (a) GS; (b) CdS-GS; (c) enlarged surface image of CdS-GS.