



Synthesis of buoyant metal-coated fly ash cenosphere and its excellent catalytic performance in dye degradation

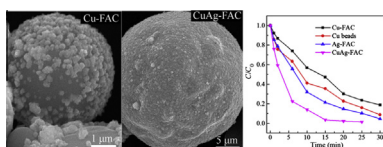


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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, Ag⁺ and Ag⁰ were absorbed onto the surface of 3-mercaptopropyltriethoxysilane modified fly ash cenospheres (FACs) in two Ag activation processes. The activation methods, avoiding traditional surface sensitization by SnCl₂, successfully initiated electroless copper particles deposition for the preparation of buoyant Cu-FAC and CuAg-FAC composites. The CuAg-FAC had a much more uniform morphology than the Cu-FAC. The catalytic performance of the Cu-FAC and CuAg-FAC was examined by the reduction of Orange IV azo dye with the presence of NaBH₄. 98.4% of Orange IV was rapidly reduced within 25 min by the CuAg-FAC, whereas 76.4% of Orange IV was removed by the Cu-FAC. The results reveal that the degradation processes matched well with the pseudo-first-order kinetics model, and rate constants of 0.057 and 0.186 min⁻¹ were obtained for the Cu-FAC and CuAg-FAC, respectively. Moreover, two other dyes of Orange II and Reactive Black 5 were also efficiently reduced by the CuAg-FAC which could be easily recycled and stably reused at least four times. These buoyant metal-coated FAC composites would be very useful in various catalytic reductions.

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1. Introduction

Nowadays synthetic dyes are among the most widely used organic chemicals, and they are of great importance to a variety of industries. However the release of dyes to environment may result in water pollution and health problems due to their toxicity and persistence [1]. Azo dyes, which constitute more than half of synthetic dyes, are always regarded as one kind of stubborn pollutants [2]. Hence decoloring (decomposing the —N=N— bond in azo dye) and remediating wastewater with azo dyes are of consid-

erable significance to environmental safety and human health. Various methods have been reported for the degradation of azo dyes including bacterial degradation [3], reduction by zero-valence metals [4], carbon sorbent absorption [5], and advanced oxidation [6]. Among them, the use of zero-valence metals has been considered as a highly efficient, rapid and low-cost technology [7,8]. As a relatively inexpensive catalyst, copper has been known for its mild hydrogenation property [9]. Recently, copper has been used for the removal of various environmental pollutants such as dichloromethane, carbon tetrachloride, eosin Y, methylene blue, and nitrobenzene, etc. [10–13]. However, there are still some problems with the application of submicron copper particles. They have a strong tendency to agglomerate in solution, which will dramatically

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diminish the catalytic activity. Furthermore, separation of the Cu catalyst from solution after treatment should also be taken into account. The problems of aggregation and separation associated with Cu particles need to be resolved. Stabilizing Cu particles onto supports has been demonstrated as an effective way of avoiding aggregation [14,15].

Fly ash cenospheres (FACs), a by-product generated abundantly in coal-fired power plants, have posed a challenge to waste disposal and environmental management. Accordingly, disposal and reuse of FACs have attracted a great deal of attention. Due to their superior properties of low density, strong filling ability, chemical inertness and thermal resistance [16], FACs have been dispersed in different matrices, such as polyurethane [17], aluminum [18], and cement [19] for fabricating lightweight composite materials. Thus copper particles could be loaded onto the surface of FACs to prepare buoyant composites. This will increase the stability of Cu particles and be convenient for recycling.

In general, coating FACs with Cu can be achieved by electroless plating and magnetron sputtering. Electroless plating is more suitable for the deposition of Cu particles owing to the spherical shape of FACs substrate [20]. The technique of electroless metal plating has been extensively studied [21,22], and has also been used on solid workpieces in industry. Electroless metallization on nonmetallic surface of FACs requires surface catalytic sites which initiate Cu particles loading on FACs surface rather than forming in plating solution. Generally, the pretreatment to anchor catalytic seeds onto surface is carried out in a two-step process. The substrate is first treated in a sensitizer solution (typically SnCl_2) and then in an activator solution (typically PdCl_2 or AgNO_3) [23,24]. But such method involves the use of undesirable Sn (II). Mondin et al. [25] developed a simple process only using polydopamine activator for selective electroless metal deposition. Glickman et al. introduced an ordered monolayer of mercapto- and amino-silanes that were used as coupling agents between silica substrate and nano-sized gold catalysts [26].

Silane coupling agents have two different kinds of functional groups. One is alkoxy moiety that can be hydrolyzed and reacted with surface hydroxyl group, leading to the linkage between silane and FACs [27]. The other is nonhydrolyzable organic moiety which contains ethylene, amine, epoxy, or thiol group, etc. According to the hard-soft acid base (HSAB) theory [28], thiol groups can strongly chelate with Ag^+ , Au^+ and their metallic atoms. Therefore, in this study, 3-mercaptopropyltriethoxysilane (MPTES) was employed to modify the FACs, and then the remained mercapto groups underwent a complexation with Ag^+ and Ag which were used as catalytic seeds for electroless Cu plating. The buoyant metal-coated FAC composites were reported with excellent capability as the catalysts in degrading organic chemicals, by evaluating their decolorizations for Orange IV, Orange II, and Reactive Black 5 azo dyes in aqueous solution.

2. Experimental

2.1. Materials

FACs were supplied by Shanghai Huijing Sub-Nanoseal New Material Co., Ltd, China. The size distribution of FACs varied from 1 to 20 μm . All the major chemicals except 3-mercaptopropyltriethoxysilane (MPTES), i.e. sodium hydroxide (NaOH), hydrochloric acid (HCl), silver nitrate (AgNO_3), ammonium hydroxide (NH_4OH), potassium sodium tartrate tetrahydrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), formaldehyde (HCHO), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), and sodium borohydride (NaBH_4) were of analytical grade, and were used without further purification. MPTES was provided by Hubei Wuhan University Silicone New Materials Co., Ltd. Dithio-

threitol, Orange IV, Orange II, and Reactive Black 5 were obtained from Sigma Aldrich. Deionized (DI) water was used throughout the work.

2.2. Surface activation of FACs

The FACs were treated in 10% HNO_3 solution at room temperature for 12 h and subsequently washed three times with DI water. 0.5 mL of MPTES was added into 166 mL of an ethanol-water mixed solution (95/5 in volume ratio), and the solution was stirred for 5 min. Then 5 g of FACs was added into the MPTES solution and incubated for 40 min under agitation at 50 °C. The modified FACs were rinsed three times with ethanol and dried in a vacuum oven at 80 °C. In order to cleave the possible disulfide bonds on the surface of MPTES modified FACs, the particles were treated with freshly prepared 10 mM of dithiothreitol solution for 20 min. The dithiothreitol solution was made by dissolving 154 mg of dithiothreitol in 100 mL of NaOH solution (pH = 8). After thoroughly rinse, the modified FACs were ready for further Ag activation.

1 g of AgNO_3 was dissolved in 100 mL of DI water, followed by a slow addition of NH_4OH under agitation until the turbidness in solution disappeared. 3 g of MPTES modified FACs were added to the solution which was placed in water bath with a temperature of 25 °C. After being stirred for 1 h, the FAC particles were rinsed three times with DI water. The activated FACs was denoted as Ag^+ -FAC. In another activation method with tartrate, 3 g of MPTES modified FACs were added to the above silver ammonia solution. After being stirred for 1 h at 25 °C, 2 g of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ was added to the solution and stirred for 1 h, followed by being washed three times with DI water. The activated FACs were denoted as Ag-FAC.

2.3. Electroless Cu plating

3 g of NaOH, 9 g of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ and 12 mL of HCHO were dissolved in 150 mL of DI water containing 3 g of activated FACs, followed by agitation for 10 min. 3.6 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 150 mL of DI water, and the solution was slowly added into the FACs solution and stirred for 3 h at 60 °C. Then the Cu-coated FACs were washed with DI water and dried in a vacuum oven for 3 h at 80 °C. The resultant Cu-coated Ag^+ -FAC and Ag-FAC were denoted as Cu-FAC and CuAg-FAC, respectively.

2.4. Characterization

Surface morphology was observed with a S-3400N II (Hitachi, Japan) scanning electron spectroscopy (SEM) while EDS analysis (EX-250, Horiba, Japan) was used to investigate the chemical constituents. The crystal phases were identified by an XRD-6000 X-ray diffractometer (Shimadzu, Japan) using $\text{Cu K}\alpha$ radiation. The X-ray photoelectron spectra (XPS) were measured on an ESCALAB 250 spectrometer (Thermo, USA) with an Al K X-ray source (1486.6 eV). Shirley background subtraction and properly curve-fitted peaks were applied in the XPS spectra peak fitting procedure. All binding energies were referred to C1s neutral carbon peak at 284.6 eV.

2.5. Batch experiments

In a typical experiment, 0.1 g of the synthesized metal coated FACs were added into a conical flask containing 100 mL of 0.1 g/L Orange IV and 0.5 g/L NaBH_4 solution. The mixture was agitated using a magnetic stirrer at room temperature. At specific time intervals, about 1 mL of liquid sample was withdrawn from the reaction flask and diluted with 4 mL of DI water, and the solution was immediately measured to obtain the ultraviolet-visible (UV-

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