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Synthesis of graphene–carbon sphere hybrid aerogel with silver nanoparticles and its catalytic and adsorption applications

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HIGHLIGHTS

- We present a facile synthetic method for a graphene-based hybrid aerogel.
- The hybrid aerogel exhibits catalytic activity for the reduction of 4-nitrophenol.
- The hybrid aerogel effectively adsorbs Cr(VI), U(VI) and methylene blue.

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ABSTRACT

In this study, we report the fabrication of a graphene–carbon sphere hybridaerogel decorated with silver nanoparticles (G/AgCS). Graphene oxide (GO) and carbon spheres doped with silver nanoparticles (AgCS) were prepared separately. G/AgCS hydrogel was then synthesized by induced reduction and gelation of a mixture of GO and AgCS in an oil bath. The G/AgCS aerogel was obtained by freeze drying the hydrogel. The synthesized G/AgCS aerogel was characterized using field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman and infra-red spectroscopy. The G/AgCS showed promising efficacy for the catalytic reduction of 4-nitrophenol in the presence of $NaBH_4$. The catalytic activity did not significantly decrease during more than 10 cycles of the catalytic reaction. The adsorption capability of chromium(VI), uranium(VI), and methylene blue on the G/AgCS aerogel was also evaluated using a Langmuir isotherm model in comparison to commercial activated carbons.

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1. Introduction

Carbon has a greater number of known allotropes than other substances. The three best known carbon allotropes are amorphous carbon, graphite, and diamond. The synthesis of new allotropes of elemental carbon, including graphene, carbon nanotubes (CNT), and fullerene, gives rise to a new era of advanced materials with enormous scientific and technological impacts [1]. Graphene and its composites have attracted considerable interest around the world due to its exceptional physical and chemical properties and flexible structure [2–6]. A number of studies have revealed the potential applications of graphene based composites in the fields of energy storage, sensing, electrocatalysis, environmental remediation, and many others. Recently, graphene- and graphene oxide (GO)-based hydrogels and aerogels have attracted attention in the material chemistry field due to their macroscopic and multifunctional properties [7–9]. The additive-free syntheses of graphene hydrogels were studied via hydrothermal and ultrasonication methods [7,10,9]. The addition of polymers, macromolecules, small organic compounds, divalent cations, and noble metals, and the change in the physical condition, such as pH and temperature, were also reported for the preparation of graphene-based hydrogels [11–17]. The oxygen functionality on the GO surface makes it more useful for the growth of new composites.

One of the major applications of carbon-based materials is water purification. Activated carbon (AC) and its derivatives, including powdered activated carbon (PAC) and granular activated carbon (GAC), were mainly used as conventional AC implementations for water purification [18]. The efficacy of nanostructured carbon materials, viz. CNT [19], carbon nanofiber (CNF) [20],

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fullerene [21], carbon sphere (CS) [22], and graphene [23,24] have been exploited as high capacity adsorbents for water purification. Various types of chemical and biological contaminants exist in natural water; carbon derived materials usually exhibit an adsorption capacity for some contaminants but are not efficient for others. A broad-spectrum adsorbent is desirable for environmental remediation processes.

A hierarchical nanostructure that consists of various types of carbon with different structural dimensions and/or porous structures, such as graphene, CNT, CS, and chitosan may greatly improve the adsorptive and catalytic performance of a candidate material through an advanced synergistic effect. Guo et al. have synthesized nanostructures composed of graphene and CS, and have found an excellent application in supercapacitors, providing proof that assemblies of various carbon types into hierarchical structures can give better alternatives to science and society [25]. Recently, a few reports were published on the combination of different carbon based 3D macroscopic structures, such as graphene–CNTs aerogels, [26,27] and chitosan–graphene hydrogels [28] as new materials for the degradation of water contaminants including organic dyes and heavy metals. Graphene-based hydro- and aerogels incorporated with iron oxide nanoparticles also have been demonstrated for the contaminant removal [8]. These composite materials exhibit superior capacity for the adsorption of organic and inorganic compounds than the single material graphene. In addition, the metal doping on these hydro- and aerogels [29] can impart additional catalytic activity to the material. In spite of several previous studies on the graphene-based hydro- and aerogels, the synthesis of graphene-based carbon–carbon composite with metal doping and its catalytic and adsorption applications were rarely reported.

Herein, we report a novel self-assembly approach to prepare a hierarchical nanostructured aerogel, composed of zero-dimensional (0-D) CS decorated with silver nanoparticles (AgCS) and two-dimensional (2-D) GO sheets using induced reduction and gelation with cysteine. The hierarchical nanostructure composed of graphene and CS may improve the adsorption efficacy of the carbon material (compared to the single graphene-based material), and the metallic silver can catalyze the reductive degradation of nitroaromatic compounds. The synthesized graphene/AgCS (G/AgCS) were tested for the catalytic reduction of 4-nitrophenol, and the adsorption amelioration of methylene blue (MB) dye, Cr(VI), and U(VI) has been explored.

2. Materials and methods

2.1. Reagents

Graphite flakes (100 mesh size), concentrated sulfuric acid, sodium nitrate, potassium permanganate, hydrogen peroxide, silver nitrate, L-cysteine, sodium borohydride, 4-nitrophenol (4-NP), potassium di-chromate, and MB were obtained from Sigma–Aldrich Co. Dextrose, PAC, and GAC were purchased from Daejung Chemical Co. All the chemicals were used as received without further purification. All solutions were prepared using 18 MΩ Milli-Q water from a Millipore system.

2.2. GO synthesis

GO was synthesized from graphite flakes using a modified Hummer's method [30]. Briefly, 3 g of natural graphite was placed in a 1 L flask. Seventy milliliters of concentrated H_2SO_4 was added to the flask, followed by the addition of 1.5 g of $NaNO_3$. Next, 9 g of $KMnO_4$ was slowly added with constant stirring in an ice bath with the temperature maintained below 4 °C for 30 min. The mixture was then stirred for 24 h for complete oxidation. Then, 150 ml of water was added to the above mixture, followed by the addition of 300 ml of water. Finally, 18 ml of H_2O_2 solution was added and the solution changed color from brown to yellow, indicating a high oxidation level of graphite to graphite oxide. The graphite oxide was washed three times via simple centrifugation and decantation of the supernatant with 1 M HCl solution, and was then washed with deionized water. This viscous solution was diluted with water and ultrasonicated for 1 h to make a GO suspension.

2.3. Synthesis of AgCS

To date, many authors have used the hydrothermal method for CS synthesis. Most authors have used > 85–100% filling carbohydrate solution for the synthesis of CS using hydrothermal synthesis [31–34]. Recently, Li et al. used ~66% glucose solution for the synthesis of CS by hydrothermal method [35]. We used a 50% filling dextrose solution for the synthesis of CS. To synthesize CS, we placed 100 ml of a 0.35 M dextrose solution in a 200-ml Teflon cup, then maintained the vessel at 175 °C for 5 h and allowed the solution to cool naturally to room temperature. The CS was collected after being washed with three cycles of centrifugation at 15000 rpm for 20 min, redispersed in water/alcohol/water, and dried in air.

Freshly prepared CS was well dispersed in 10 ml of water to prepare a 0.3% wt suspension, and $AgNO_3$ was added slowly to make a 1 M silver ion solution. The solution was vigorously shaken for 15 min and stirred overnight (200 rpm) at room temperature to make a homogenous mixture. This mixture was then centrifuged at 3000 rpm for 15 min to remove any remaining silver ions in the solution, and the silver nanoparticle (AgNPs)-decorated CS (AgCS) was washed three times with water and alcohol. The resulting filtrate was redispersed in 10 ml of water and ultrasonicated for 1 h to make a homogenous solution.

2.4. Synthesis of G/AgCS hybrid hydrogel and aerogel

Eight milliliters of GO dispersion (~3 mg/ml) was mixed with 10 ml of AgCS solution. After 1 h of ultrasonication, a suitable amount of cysteine was added and mixed well to chemically reduce and gelate the 2D GO sheets into a 3D graphene hybrid hydrogel. Then, this mixture was left undisturbed in an oil bath at 80 °C for 9 h. Finally, the 3D structure was removed and washed with ultrapure water. This black monolith was freeze-dried to convert it into an aerogel for further catalytic and adsorption applications. For the synthesis of graphene and graphene/CS (G/CS) hydrogel, 10 ml of water and 10 ml of CS solution were added in 10 ml of AgCS solution, keeping all the other conditions constant.

2.5. Characterizations

Electron microscope images were recorded using a Hitachi Cold field emission scanning electron microscope (FE-SEM) at 10 kV. Transmission electron microscope (TEM) images were collected using a JEOL high-resolution transmission electron microscope with an acceleration voltage of 200 kV. Raman scattering was performed on a WITec Micro-Raman system using a 532 nm Helium Neon laser source. Diffraction data were acquired on a Rigaku High Power X-ray diffractometer (XRD). Powder diffraction data were recorded for 2θ angles between 5° and 80° with a scanning speed of 0.05°/s. The various functional groups present in the hybrid aerogels were measured using a Nicolet 6700 infra-red (IR) spectrometer over the spectral range of 4000–400 cm^{-1}. The silver content in G/AgCS was calculated by acidifying the material and measuring the concentration of released silver ion on an atomic absorption spectrophotometer (AAS, AAnalyst 700, Perkin Elmer Co). The surface area and the pore size of PAC and G/AgCS were analyzed by a Micromeritics Gemini V system.

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