A silver-nanoparticle-catalyzed graphite composite for electrochemical energy storage

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HIGHLIGHTS

- A new composite containing silver nanoparticles and graphite is developed.
- Ag NPs enhance the electrochemical performance for energy storage.
- There was a six-fold improvement in specific capacitance.
- Li^+ enabled from double-layer to pseudocapacitive behavior.

ARTICLE INFO

ABSTRACT

A new composite containing silver nanoparticles and graphite is developed in order to improve electrochemical energy storage. The nanocomposite uses silver (Ag) nanoparticles as a catalyst to enhance the electrochemical performance. Results indicate that the graphite composite decorated with Ag shows up to a six-fold improvement in specific capacitance. Electron/charge transfer is enhanced through a shift from double-layer to pseudocapacitive behavior, mediated by Li^+ intercalation. Decoration with Ag nanoparticles allows for improvements in electrochemical impedance response, ease of electronic/ionic charging, and overall energy storage capability. This research provides a promising alternative solution for the next generation of safe and cost-effective lithium-ion devices.

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1. Introduction

Electrochemical energy storage devices are in demand for portable electronics, smart grid, electric vehicles, and energy recovery systems [1–8]. Lithium ion batteries (LIB) and supercapacitors (SC) are two typical mediums of storage. In device fabrication, significant efforts have been devoted to explore better candidate materials as anodes. Carbon-based materials [9,10], silicon [11–13], sulfur and sulfides [14–18], metal oxides [19,20], and metal carbides [21–23] are such representative materials. The performance in energy storage depends on the morphology and structure of the building blocks of these materials. In order to increase energy capacity, power density, and durability, nanoparticles (NPs) [24–26], nanowires [27–29], nanotubes [30,31], hollow nanostructures [32], core–shell nanostructures [33,34], and ordered mesoporous systems [35] have been utilized for active material. However, integration of the high energy capacity of a LIB with the high power density of a SC remains challenging in a single electrochemical energy storage device [36–39]. In principal, the electrochemical storage is based on the reactions of electrolyte-soluble charged species with the surface of the electrode. If such chemical reactions could be accelerated, a storage device should display an enhanced rate of electrochemical work. A suitable catalyst that is able to mediate the electrochemical reactions is needed to obtain the desirable large energy capacity and high power density. To date, noble metal nanoparticles have been widely studied as efficient catalysts. Those metals include silver (Ag) [40],

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gold (Au) [41], platinum (Pt) [42], palladium (Pd) [43], ruthenium (Ru) [44], rhodium (Rh) [45], rhenium (Re) [46], osmium (Os) [47], and iridium (Ir) [48], among others. We propose an alternative approach in making nanocomposite electrodes, using such noble metals.

This research aims at designing catalytic electrochemical reactions for conventionally-used graphite electrodes. A facile route based on decomposition of an Ag precursor is adopted to prepare the desired graphite-Ag NP composite. Preliminary electrochemical investigations are performed to reveal its capability in improving energy storage. This novel catalytic composite would enable further innovations to meet growing demands for high-power/high-energy systems.

2. Experimental

2.1. Materials

A commercial graphite powder (~325 mesh, 99.8%) purchased from Alfa Aesar was used in this research. Other chemicals were purchased from Sigma–Aldrich: silver acetate (CH_3COOAg, 99%), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, 1.1% in H_2O), dimethyl sulfoxide (DMSO, 99.5%), ethanol, and lithium sulfate (Li_2SO_4, 98.5%).

2.2. Loading Ag NP onto graphite

A wetting-thermal decomposition method was used to load Ag NPs onto graphite [40]. The 120 mg graphite powder was dispersed in 10 ml saturated solution of CH_3COOAg under ultrasonication. The graphite-dispersed CH_3COOAg solution was transferred into a ceramic boat and dried in air overnight. With protection under an argon atmosphere, the dried powder was thermally treated at 350 °C for 4 h. The graphite-Ag NP composite product was then collected for further characterization. As a reference sample, pure graphite powder was heat treated under the same conditions.

2.3. Drop casting of electrode

Conductive polymer, PEDOT:PSS, was used as a binder during the electrode fabrication. The 9 ml 1.1% PEDOT:PSS solution, 450 μl DMSO solution, and 6.25 ml ethanol were added to 99.75 ml de-ionized water. The mixed PEDOT:PSS solution was stirred for 12 h before use. Active material (10 mg pure graphite or graphite-Ag NP composite) was dispersed in 1 ml of as-prepared polymer solution via 2 h of ultrasonication. The electrodes for measurements of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were prepared by drop casting the active materials onto copper (Cu) foils. Using a vacuum oven, the drop-casted Cu foils were finally baked at 80 °C for 30 min after drying at 60 °C for 2 h. The thickness of the casted electrode was ~200 μm, and the typical material loading on the electrode was ~50 mg cm^{-2}.

2.4. Characterization

A field emission scanning electron microscope (FESEM, FEI QUANTA 600) was used to image the samples. The energy dispersive X-ray spectrum (EDS) was recorded using an instrument connected with the FESEM. The X-ray diffraction (XRD) patterns of the graphite before and after the Ag NP loading were collected using a Bruker, D8 advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) operating at 40 kV, 50 mA. The 2θ ranging from 10° to 80° was scanned at a rate of 0.02° s^{-1}.

Using a Gamry Reference 600™ potentiostat, CV and EIS experiments were carried out in a 0.5 M Li_2SO_4 electrolyte with a

three-electrode system. The as-fabricated electrode, a standard saturated calomel electrode (SCE, Hg/Hg_2Cl_2), and a platinum filament served as the working electrode, reference electrode, and counter electrode, respectively. CV profiles were recorded at different scanning rates from 5 mV s^{-1} to 75 mV s^{-1}. During the EIS measurement, a sinusoidal signal (10 mV of oscillation amplitude) was applied to the working electrode at a frequency ranging from 100 kHz to 0.1 Hz. The step width was selected to be 10 s per decade.

3. Results and discussion

3.1. Structural and compositional characterization

During the wetting-thermal decomposition, CH_3COOAg was *in-situ* decomposed into Ag NPs on the graphite surface following reactions (1) and (2):

$$2\ CH_3COOAg \rightarrow 2Ag + 2CO_2 + C_2H_6 \tag{1}$$

$$2\ CH_3COOAg \rightarrow 2Ag + 1/2O_2 + C_4H_6O_3 \tag{2}$$
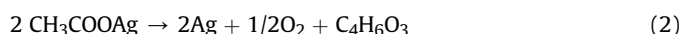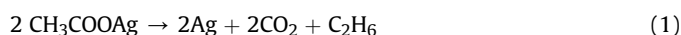
The presence and structure of Ag NPs in the composite graphite samples was confirmed with SEM imaging, EDS spectrum, and XRD analysis. Fig. 1(a) shows an SEM image of the graphite sample before the Ag NPs were loaded. Fig. 1(b) shows the corresponding SEM image of the graphite-Ag NP composite. The size of Ag NPs produced, visible in Fig. 1(b), is estimated to be between the tens of nanometers to ~100 nm. The elemental analysis performed with EDS, shown in Fig. 1(c), further proves the presence of Ag in the composite. The Pt detected was from sample preparation for the SEM imaging and was not present in the electrochemical experiments. Fig. 2 shows the XRD patterns of the graphite sample before (bottom in black) and after (top in red) the decoration of Ag NPs. The bottom black XRD pattern shows the crystal structure of the reference sample to be characteristic of hexagonal graphite (JCPDS
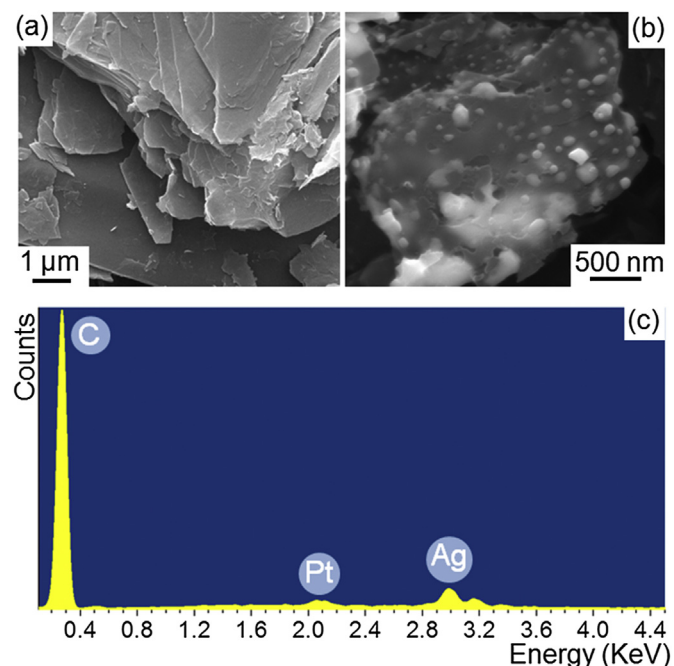

Fig. 1. (a) SEM image of the reference graphite. (b) SEM image of the graphite-Ag NP composite. (c) EDS spectrum of the graphite-Ag NP composite.