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Post-infiltration of a multilayered carbon nanofilm with MnO_2 at low loadings for improved capacitive properties

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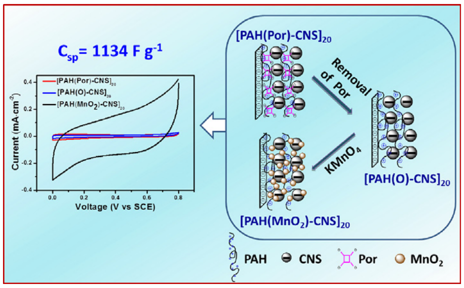
HIGHLIGHTS

- Carbon nanosphere/MnO_2 multilayers are fabricated by LBL-post-infiltrating approach.
- MnO_2 acted as a spacer to allow a decreased ion-diffusion length.
- The nanoscaled carbon/MnO_2 interfaces provide a more ideal utilization of MnO_2.
- A specific capacitance (based on MnO_2) of 1134 F g^{-1} is obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

A multilayered carbon nanosphere (CNS)/manganese oxide (MnO_2) nanofilm is fabricated by a newly developed layer-by-layer (LBL)–post-infiltration approach. The multilayered architecture effectively shortens the length over which ions diffuse, and the nanoscaled carbon/MnO_2 interface provides an interconnected pathway for electron conduction. MnO_2 acts not only as the redox center for charge storage, but also as the spacer between the LBL-assembled multilayers for more rapid electrolyte transport. A specific capacitance (based on MnO_2) of 1134.0 F g^{-1} is achieved at a loading of 5.22 μg cm^{-2} in a neutral electrolyte. This strategy provides a promising approach for fabricating high-power and high-energy electrochemical capacitors with precise control of electrode thickness on geometric device surfaces.

1. Introduction

Electrochemical supercapacitors are high-performance energy-storage devices that exhibit several beneficial characteristics, such as long cycle lifetimes and high power densities [1–3]. According to their charge-storage mechanism, electrochemical supercapacitors are classified into electrical double layer capacitors (which undergo non-faradaic electrode charge-storage processes) and pseudocapacitors (which undergo faradaic redox reactions of their electro-active materials during charging/discharging). Carbon materials (e.g., active carbon, carbon nanotubes, and graphene) are promising candidates for electrical double layer capacitors because of their excellent electrical properties and chemical stabilities [4–8]. However, carbon materials have poor volumetric capacitances (~100 F cm^{-3}) because of charge accumulation in the electrical double layers [9,10]. For pseudocapacitors, metal oxides (e.g., RuO_2, MnO_2, V_2O_5, TiO_2, NiO, Co_3O_4 and $CoMoO_4$) are often used as active

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materials [11–15]. Recently, Liu and coworkers have reported bismuth-based anion intercalation compounds can be used as the materials for supercapacitors [16]. These materials have high theoretical specific capacitances. For example, the theoretical specific capacitance of RuO_2 is from 1400 F g^{-1} to 2200 F g^{-1} [17], while that of MnO_2 is ~1370 F g^{-1} [1]. Nevertheless, due to their poor conductivities, metal oxide-based pseudocapacitors often have specific capacitance that is far below their theoretical limits. To overcome these challenges, asymmetric supercapacitors have been developed in which both metal oxides and carbon are used as active materials to design higher-performance electrolytes. Asymmetric supercapacitors can achieve superior conductivities and have significantly wider operating voltages, thereby improving energy density.

Another key factor limiting the electrochemical capacitance of asymmetric supercapacitors is the faradic process that the pseudocapacitor's materials undergo. This is observed only at very low scan rates because of the very slow rate of ion diffusion. One effective strategy to overcoming this challenge is to create thin films of the electrode materials or to use porous or layered materials to shorten the interlayer distance, thus reducing the charge-transfer resistance of the bulk materials [18,19]. Layer-by-layer (LBL) assembly is a simple and versatile technique to prepare multilayers. In general, LBL assembly consists of repeatedly immersing a solid substrate into two solutions to form layers by electrostatic adsorption, hydrogen bonding, or ligand coordination. Till now, LBL assembly has been widely used to create complementary and layer-stacked structures with highly tunable thicknesses on surfaces with various geometries [20–24]. Very recently, Shi and coworkers have demonstrated a promising strategy called "post-infiltration" that could be used to introduce cross-linking molecules into the multilayers prepared by Au/Fe_3O_4 and poly(allylamine hydrochloride) (PAH) to obtain a more stable composite architecture [22–24].

In this work, we develope a multilayered carbon nanosphere (CNS)/MnO_2 nanofilm using the LBL—post-infiltration approach. This approach consists of a three-step procedure that included (i) the LBL assembly of multilayers, (ii) the extraction of meso-tetra(4-carboxyphenyl)-porphine (Por), and (iii) the *in situ* redox reaction of CNS with post-infiltrated $KMnO_4$ to form MnO_2 in the multilayers. To the best of our knowledge, this is the first time that an LBL—post-infiltration method is employed to prepare an electrochemical supercapacitor. The specific capacitance of the resulting $[PAH(MnO_2)\text{-}CNS]_n$-based supercapacitor increases with increasing bilayer number. The nanoscaled carbon/MnO_2 interfaces provide an interconnected electron-conduction pathway. The $[PAH(Por)\text{-}CNS]_n$ hybrid is a multilayered nanofilm with an effectively shortened ion-diffusion length and exhibits significantly improved pseudocapacitor properties.

2. Experimental

2.1. Reagents and apparatus

PAH (M_w = 15000), Por and (3-mercaptopropyl)-trimethoxysilane (MPTS) were purchased from Sigma-Aldrich. Carboxylic group-functionalized CNSs were prepared by a previously reported method [25]. All reagents were of analytical grade. All aqueous solutions were prepared in deionized (DI) water. Surface morphologies were characterized using scanning electron microscopy (SEM Hitachi S4800, Japan) and atomic force microscopy (AFM, Dimension 3100, Veeco). X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer Physical Electronics 5600 spectrometer using Al Ka radiation at 13 kV, and the C 1s signal at 284.6 eV was used as a reference. A CHI660D electrochemical workstation (CH Instrument Co., China) was used to control electrochemical experiments at room temperature (25 °C). The mass of MnO_2 on the samples was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, Agilent 7500a, United States). For this, the $[PAH(MnO_2)\text{-}CNS]_{20}$ sample (1.25 cm × 1.52 cm × 0.10 cm) was first dissolved in concentrated 1.0 mL 37% HCl and 2.0 mL 30% H_2O_2 in a microwave digester. The solution was then diluted to 1.0×10^4 mL. The concentration of Mn^{2+} was concluded by the standard curve of Mn^{2+} (1.0 μg/L ~ 9.0 μg/L). The reported results are the average of three replicates. The weight of $[PAH(MnO_2)\text{-}CNS]_{20}$ was determined according to the difference of sample weight before and after assembling the multilayers (averaging the difference of 10 samples).

2.2. Surface treatment of substrates

Glassy carbon electrodes (GCEs) were polished to a mirror finish using alumina powder (particle size of ~50 μm) in a water slurry. A layer of hydroxyl and carboxyl groups were generated on the GCE by electrochemical oxidation in phosphate buffered saline (PBS, pH = 7.0) at a potential of +1.8 V (*vs.* saturated calomel electrode (SCE)) for 300 s. The GCE was then scanned from −0.8 V to +1.0 V (*vs.* SCE) for 50 cycles until a stable CV curve was obtained, as shown in Fig. S1. Quartz sheets and silicon wafers were treated according to Ref. [20]. Briefly, these substrates were first cleaned in piranha solution (H_2SO_4/H_2O_2, (v/v = 7:3)) for 1 h. After being thoroughly rinsed with DI water, the substrates were incubated in toluene containing MPTS (1×10^{-5} M) for 12 h to obtain a layer of mercapto groups on their surfaces. The substrates were then immersed in H_2O_2/acetic acid (v/v = 1:5) at 50 °C for 1 h to oxidize the mercapto groups, forming sulphonic groups.

2.3. Layer-by-layer assembly of multilayered thin films

A PAH(Por) (pH 6.0) aqueous solution containing 0.83 mg mL^{-1} Por and 5 mg L^{-1} PAH was prepared. The substrates were alternately immersed into the PAH(Por) solution and a suspension of CNSs (10 mg mL^{-1}) for 20 min to create single layers of [PAH(Por)-CNS]. Between each step, the substrates were thoroughly washed in DI water and dried in N_2. This LBL method was repeated to obtain the desired number of multilayers (n) to form $[PAH(Por)\text{-}CNS]_n$.

2.4. The removal of Por and insertion of MnO_2

Por was removed by immersing the $[PAH(Por)\text{-}CNS]_n$ multilayers in a NaOH (pH 12) solution for 15 min. The obtained multilayers ($[PAH(O)\text{-}CNS]_n$) were thoroughly washed by DI water and dried in N_2. Subsequently, the samples were dipped into a solution of $KMnO_4$ (5.0 mg mL^{-1}) to post-infiltrate $KMnO_4$ into the multilayers. The post-infiltrated samples are referred to as $[PAH(MnO_2)\text{-}CNS]_n$.

3. Results and discussion

3.1. Characterization of multilayers

Scheme 1 illustrates the steps used to prepare the $[PAH(MnO_2)\text{-}CNS]_n$ multilayers. $[PAH(Por)\text{-}CNS]_n$ multilayers were formed on the substrate (i.e., glassy carbon electrode (GCE), quartz, Si, etc.) in the first step using a traditional LBL-assembly method. Because plenty −COOH groups are present on their surfaces, the CNSs are negatively charged [25]. The PAH(Por) complex is positively charged at pH 6 [22]. Ultrathin $[PAH(Por)\text{-}CNS]_n$ layers were then created by the sequential adsorption of positively charged PAH(Por) and negatively charged CNS via electrostatic attraction. The time