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Facile synthesis of α-MnO_2 nanorod/graphene nanocomposite paper electrodes using a 3D precursor for supercapacitors and sensing platform to detect 4-nitrophenol

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ABSTRACT

Manganese dioxide (α-MnO_2)/reduced graphene oxide (RGO) nanocomposite paper was synthesized using a 3D precursor manganese benzoate dihydrazinate for supercapacitor and sensor applications. The new 3D precursor and residue-free synthesis are the advantages of this method. Transmission electron microscopy showed that MnO_2 nanorods with a mean diameter of <10 nm were decorated densely over the RGO surface. Owing to the paper's freestanding structure, the composite was used directly as a binder-free electrode in the electrochemical experiments. The composite exhibited a higher capacitance of 360 F g^{-1} at a current density of 2.5 A g^{-1} as well as a long cycle life with 7.0% capacitance loss after 10,000 cycles. The specific capacitance reached 228 F g^{-1} at a current density of 25 A g^{-1}. In addition, the developed electrochemical sensor showed a linear relationship with the 4-nitrophenol (4-NP) concentration from 1 to 100 μM with a detection limit of 0.017 μM. The sensor was used to determine the level of 4-NP in tap water and river water samples with good recovery, highlighting the sensor's feasibility for industrial applications. Overall, this composite paper is a promising electrode material for flexible supercapacitors and sensors.

1. Introduction

Recently, there has been increasing attention in exploring energy storage devices to meet the requirements for future reliable energy storage systems. Supercapacitors/ultracapacitors are among the most promising energy storage devices and have attracted extensive interest owing to their high power density, best reversibility, light weight, and small size [1]. Supercapacitors bridge the gap between conventional capacitors and batteries by contributing high power and energy densities. Supercapacitors can be classified into two types based on the charge storage mechanism: electric double layer capacitor (EDLC) and pseudo-capacitor. In EDLC, the energy is stored due to the adsorption of both anions and cations at the electrode/electrolyte interface, while for pseudocapacitor, they energy is stored through faradic reactions [2]. Pseudocapacitive materials, such as transition metal oxides (MnO_2, RuO_2, SnO_2, and NiO) and conjugated polymers (polypyrrole, polyaniline, and polythiophene) [3–6], have higher specific capacitances than carbon materials (EDLC). On the other hand, the performance of these metal oxides is limited by their poor electrochemical stability, less electrolyte accessibility, low rate capability, and low conductivity [7]. To address these disadvantages, the combination of metal oxides with high surface area carbon materials, such as activated carbon, xerogels, carbon nanotubes, and mesoporous carbon, is an ideal solution. This is because the energy storage mechanism depends on the surface area of the active materials.

Recently, 2D graphene has been considered a promising nanomaterial for charge storage applications owing to its high surface area, high charge mobility, and outstanding electrical conductivity [8–10]. Nevertheless, the agglomeration of graphene adversely affects its electrochemical performance. To date, various kinds of transition metal oxides have been synthesized and used as energy storage materials due to their outstanding properties. In particular, manganese dioxide (MnO_2) is a promising material for pseudocapacitors on account of its high specific capacitance (1370 F g^{-1}), high energy density, and low cost [11–13].

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Considering the exceptional properties of MnO_2 and graphene, a combination of MnO_2 nanorods with graphene might result in enhanced electrochemical performance.

Over the past few years, substantial research effort has been carried out on the synthesis of graphene/MnO_2 nanostructures for supercapacitors using a range of techniques. Yan et al. [14] prepared graphene-MnO_2 composites using a microwave irradiation for supercapacitor electrodes. For supercapacitors, Li et al. [15] fabricated graphene/MnO_2 composite flexible paper via the vacuum filtration of a graphene oxide (GO)/MnO_2 dispersion followed by thermal reduction. The authors [16] also synthesized reduced graphene/MnO_2 composites via hydrothermal method for supercapacitors. Lee et al. [17] fabricated MnO_2/graphene composite electrodes by the electrodeposition of MnO_2 onto a gold plate followed by the transfer of graphene synthesized by CVD. The multilayer MnO_2/graphene composite was used for supercapacitor applications. Sawangphruk et al. [18] fabricated MnO_2/reduced graphene oxide (RGO)/carbon fiber paper composites using a spray-coating technique for supercapacitor applications. Zhai et al. [19] prepared a large areal mass loading composite via the electrodeposition of MnO_2 on porous graphene gel/Ni foam for supercapacitors. Jafta et al. [20] developed an aqueous asymmetric electrochemical capacitor based on a MnO_2/graphene composite that had been synthesized via hydrothermal reaction using sodium dodecyl sulfate as a surfactant. He et al. [21] synthesized a freestanding 3D graphene/MnO_2 composite by the electrodeposition of MnO_2 on flexible graphene for supercapacitors. Zhang et al. [22] prepared a graphene/MnO_2 composite by a microwave sintering method for supercapacitors. Wu et al. [23] fabricated a 3D MnO_2/graphene hydrogel via *in situ* self-assembly for asymmetric supercapacitors. Although several papers have been published based on the fabrication of MnO_2/graphene nanocomposites for energy storage applications, there are few reports on the fabrication of composites with attractive morphologies [24–26]. Nanocomposites with different architectures are undoubtedly promising materials for high performance supercapacitors. In the above reported works, $KMnO_4$ [14,15,18,22–24], $KMnO_4 + K_2SO_4$ [16], $Mn(CH_3COO)_2$ [17], $Mn(NO_3)_2 + NaNO_3$ [21], $Mn(NO_3)_2$ [25], and $KMnO_4 + MnSO_4$ [26], were used as precursors for the decoration MnO_2 on the graphene surface.

In this study, a flexible, freestanding binder-free α-MnO_2 nanorod/RGO nanocomposite was fabricated using a 3D coordination complex as a precursor for supercapacitor and electrochemical detection of 4-nitropheneol (4-NP). The composite exhibited high specific capacitance and excellent cyclic stability. The composite also showed good sensitivity and a low detection limit toward the determination of 4-NP.

2. Experimental

2.1. Materials

Manganese (II) nitrate hexahydrate ($Mn(NO_3)_2{\cdot}4H_2O$), benzoic acid (C_6H_5COOH), hydrazine (N_2H_4), graphite, and 4-NP were purchased from Sigma-Aldrich. All other reagents were of analytical grade and used as received

2.2. Fabrication of MnO_2/RGO nanocomposite paper

GO was prepared using the Hummers' method with some modifications [27]. The precursor, manganese benzoate dihydrazinate, was prepared by adding 0.02 mol of hydrazinium benzoate solution drop-wise into a solution containing 0.01 mol of $Mn(NO_3)_2{\cdot}4H_2O$ with stirring for 30 min. The volume of the mixture was reduced to one-third and filtered. Finally, the product was washed with alcohol and dried in an oven at 50 °C for 12 h. In a typical experiment for the synthesis of MnO_2/RGO nanocomposite, 40 mg of GO was dispersed in 70 mL of ethanol for 60 min under sonication. The precursor complex (200 mg) was then added to the above dispersion and sonicated for another 60 min. The dispersion was transferred to an autoclave and the reaction was carried out at 350 °C for 5 h. The resulting composite mixture was vacuum filtered using a filter membrane and washed with ethanol and distilled water. The flexible freestanding film was then peeled off after drying the filter membrane at 50 °C for 1 h. Pure RGO paper was also prepared in a similar manner.

2.3. Electrochemical analysis

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry (CP) were performed using a VERSA STAT workstation with a composite paper working electrode, calomel reference electrode, and platinum wire counter electrode in a 0.5 M Na_2SO_4 solution. The masses of the exposed RGO and MnO_2/RGO composite paper electrodes with an area 1 cm × 1 cm were calculated to be 0.010 g and 0.015 g, respectively.

Electrochemical sensing analyses were performed using a CHI 660C instrument. A 0.1 M phosphate buffer solution (PBS) was used as an electrolyte, and the MnO_2/RGO composite was used as a working electrode. A platinum wire was employed as a counter electrode and all the potentials were measured versus a saturated calomel electrode (SCE).

2.4. Characterization

Morphological and selected-area electron diffraction (SAED) images were obtained by high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). The surface properties were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K–Alpha) using Al Kα radiation. Raman spectroscopy was performed on a Raman microscope (UniRAM, UniNanoTech., Korea). The crystallinity of the sample was examined by X-ray diffraction (XRD, X'Pert PRO MRD, Philips) using Cu Kα radiation. The Brunauer–Emmett–Teller (BET) surface area and mean pore diameter were obtained from the N_2 adsorption/desorption isotherm using a BELSORP max (Japan) apparatus at 77 K. The sample was degassed and dried under a vacuum at 200 °C for 5 h prior to the measurement.

3. Results and discussion

3.1. Mechanism

The MnO_2/RGO nanocomposite was synthesized from GO and a 3D coordination complex precursor, manganese benzoate dihydrazinate [$Mn(C_6H_5COO)_2(N_2H_4)_2$], which was prepared according to the following reactions:

$$Mn(NO_3)_2{\cdot}4H_2O + 2C_6H_5COON_2H_5 \rightarrow Mn(C_6H_5COO)_2(N_2H_4)_2 + 2HNO_3 + 4H_2O \quad (1)$$

$$Mn(C_6H_5COO)_2(N_2H_4)_2 + 15\ 1/2O_2 \rightarrow MnO_2 + 2N_2H_4 + 14CO_2 + 5H_2O \quad (2)$$

At a lower temperature, deposition of the precursor onto the RGO surface occurred. When the temperature reached 350 °C, both the thermal reduction of GO and the thermal decomposition of the precursor occurred simultaneously. The precursor decomposed completely, losing N_2H_4, CO_2, and H_2O. The complex was stable in air and insoluble in water. The importance of using such a complex is the distribution of metal ions in a 3D coordination sphere so that