Graphene Oxide as a Novel Nanoplatform for Direct Hybridization of Graphene-SnO$_2$

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Graphene oxide (GO) has been of particular interest because it provides unique properties due to its high surface area, chemical functionality and ease of mass production. GO is produced by chemical exfoliation of graphite and is decorated with oxygen-containing groups such as phenol hydroxyl, epoxide groups and ionizable carboxylic acid groups. Due to the presence of those functional groups, GO can be utilized as a novel platform for hybrid nanocomposites in chemical synthetic approaches. In this work, GO-SnO$_2$ nanocomposites have been prepared through the spontaneous formation of molecular hybrids. When SnO$_2$ precursor solution and GO suspension were simply mixed, Sn$^{2+}$ was spontaneously formed into SnO$_2$ nanoparticles upon the deoxygenation of GO. Through further chemical reduction by adding hydrazine, reduced GO-SnO$_2$ hybrid was finally created. Our investigation for the electrocapacitive properties of hybrid electrode showed the enhanced performance (389 F/g), compared with rGO-only electrode (241 F/g). Our approach offers a scalable, robust synthetic route to prepare graphene-based nanocomposites for supercapacitor electrode via spontaneous hybridization.

Key Words : Graphene oxide, SnO$_2$, Supercapacitors, Hybrid, Nanocomposites

Introduction

Graphene oxide (GO) is commonly made by reacting graphite powders with strong oxidation agents and acids.\textsuperscript{12} During this process, graphene is oxidized and derivatized with oxygen containing functional groups, and consequently is readily exfoliated from graphite into single GO layer in water.\textsuperscript{3,4} However, the presence of functional groups including hydroxyl, epoxide, and carboxylic acid groups on a carbon sheet and amorphous carbon regions on basal plane causes this carbon sheet to be electronically insulating. Therefore, considerable works have been focused on recovering the poor electrical properties of GO through the development of efficient reducing strategies or the exclusion of harsh oxidation steps for realizing the highly motivated properties of pristine graphite.\textsuperscript{5-7} Despite those disadvantageous properties, however, GO has attracted increasing research interest owing to its unique properties including large surface area, high water solubility, facile processibility, and easy large-scale production.\textsuperscript{8-11} In particular, the functional groups of GO may play an important role in facilitating molecular organization into functional hybrid nanocomposites.\textsuperscript{12}

A variety of metal oxides, such as MnO$_x$, RuO$_x$, and CuO$_x$, with pseudo-capacitive properties have been used to form nanocomposites with graphene and have been utilized in supercapacitors because of the improved capability to store more charges than carbon-only electrodes.\textsuperscript{13-16} Up to date, the preparation methods including hydrothermal synthesis or a polyol process have been successfully achieved to create nanocomposites.\textsuperscript{17-20} However, the development of a scalable, robust synthetic process is still required to achieve the practical utilization of graphene into high performance supercapacitors.

In this work, we introduce a straightforward preparation approach to prepare a hybrid of graphene and SnO$_2$ via the directed hybridization. SnO$_2$ has attracted much attention as an excellent electrode material for supercapacitors and secondary Li-ion batteries due to its interesting properties of high theoretical capacity, good electroconductivity and low cost.\textsuperscript{21,22} GO was first prepared through chemical exfoliation of graphite and was mixed with a SnO$_2$ precursor solution. During solution mixing, the reduction of GO and the conversion of SnO$_2$ nanoparticles from Sn$^{2+}$ occur simultaneously. After further reduction of GO by adding hydrazine and thermal annealing, nanocomposites (rGO-SnO$_2$) were created. Hybrid materials showed the increased supercapacitance values and the more stable electrochemical performance over a wide range of voltage scan rates, compared with the rGO-only electrode.

Experimental

Materials. Graphite powders were purchased from Bay carbon (SP-1). Other chemicals, including hydrazine, hydrochloric acid, sulfuric acid, hydro peroxide, and tin acetate (Sn(CH$_3$COO)$_2$), were purchased from Sigma-Aldrich. All chemicals were used as received without additional purification.

Synthesis of GO. GO was prepared using a modified Hummers method from graphite powder as reported elsewhere.\textsuperscript{10-12} An aqueous GO dispersion was extensively washed and filtered with 1 M HCl and then was dialyzed with a dialysis membrane (Spectra Dialysis Membrane, MWCO: 6-
Synthesis of Graphene-SnO$_2$ Nanocomposites. Tin acetate (Sn(CH$_3$COO)$_2$) was dissolved in a 1:10 DI/MeOH mixture at 20 mg/mL. Then, 3 mL of the SnO$_2$ precursor solution was added dropwise into 40 mL of the GO solution (3.2 mg/mL) under vigorous stirring at room temperature. To measure sheet resistivity of hybrid, the nanocomposites film of 10 μm thickness was prepared with a vacuum filtration kit using a hydrophilic PTFE membrane (Millipore, pore size: 450 nm). For further reduction of composites, 30 μL of hydrazine (Sigma-Aldrich, 64%) was added into a GO-SnO$_2$ solution and mechanically stirred at 70 °C for 2 h. The finally obtained rGO-SnO$_2$ nanocomposites were annealed at 400 °C for 2 h under air.

Characterization. The morphologies of the nanocomposites were characterized with a scanning electron microscopy (JEOL JSM-6701F) and a transmission electron microscopy (JEOL JEM-2100F). TEM samples were prepared by dispersing a small amount of the nanocomposite powder in MeOH with sonication and then applying a few drops of the dispersion onto a lacey-carbon TEM grid (Ted Pella, Inc.). Thermogravimetric analysis (TGA) was performed on SDT Q600 (TA Instruments) in the temperature range between 25 and 800 °C at a heating rate of 10 °C/min under air atmosphere. X-ray diffraction (XRD) was carried out using Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Scientific Theta probe with monochromatic Al Kα radiation. Sheet resistivity of hybrid films was measured with Advanced Instrument Technology (CMT-Series).

Electrochemical Measurements. The electrochemical behavior of rGO and rGO-SnO$_2$ was characterized by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements using a Bio-Logic (SP-200) in 1 M H$_2$SO$_4$ electrolyte. The working electrode was prepared by dropping 10 μL of active material solution (5.0 mg/mL) in NMP onto the glassy carbon electrodes. Prior to experiments, the electrolyte was purged with pure N$_2$ gas for 30 min to remove dissolved oxygen. Experiments were carried out in a three-electrode glass cell at room temperature. Platinum foil was used as a counter electrode and an Ag/AgCl electrode as the reference electrode.

Results and Discussion

As shown in Figure 1(a), the GO solution was brown in color, and there was no precipitation. To prepare a GO-SnO$_2$ hybrid, a tin acetate (Sn(CH$_3$COO)$_2$) precursor solution was added dropwise under vigorous mechanical mixing. As soon as the tin acetate solution was added, the GO solution became viscous, as shown in images of Figure 1(b) and (c). When the concentration of GO was higher than 4.0 mg/mL or the precursor solution of 20 mg/mL was added more than 3.0 mL, the complex easily formed a gel. This change in the fluidity of the mixture solution is due to the formation of the molecular networks between carbon sheets and SnO$_2$ nanoparticles, as often exhibited in the percolated solution of hydro-organo-gels.\cite{23-25}

In this work, the concentration of GO and tin acetate solution was kept consistently under the gel-forming critical concentration to avoid heterogeneous mixing. In addition, the color of GO suspension changed to dark brown, which further indicates the deoxygenation of GO. Compared with insulating GO paper, thin films of GO-SnO$_2$ hybrid showed a much lower sheet resistivity of 8.2 × 10$^4$ Ω/sq. due to the reduction effect of GO and the presence of the electroconductive SnO$_2$ nanoparticles on GO sheet. The further reduction of GO was carried out by loading a small amount of hydrazine solution, and the reduced GO (rGO)-SnO$_2$ hybrid composites were annealed to enhance the crystallinity of SnO$_2$ nanoparticles at 400 °C. The weight ratio of SnO$_2$ nanoparticles in the hybrid was verified with TGA (Figure 1(d)). A significant weight loss between 400 and 700 °C is attributed to the decomposition of the carbon sheets.\cite{26} Based on the TGA result, it is confirmed that the hybrid contains SnO$_2$ nanoparticles of approximately 6.8 wt %.

The morphology of the rGO-SnO$_2$ hybrid was characterized by field emission scanning electron microscopy (FE-SEM) before and after annealing, as shown in Figure 1(e) and (f), respectively. We note that, though the surface of hybrid composites is quite roughened and crumpled before annealing (Figure 1(e)), the rough surface wasn’t entirely flattened and the nanocomposites didn’t agglomerate even after high temperature annealing (Figure 1(f)).
The crystalline structure of the annealed SnO$_2$ nanoparticles and their spatial distribution over carbon sheets were examined with the high-resolution transmission electron microscopy (HR-TEM). Figure 2(a) shows the isolated single layer of rGO-SnO$_2$ hybrid. The rGO was uniformly coated with SnO$_2$ nanoparticles and this nanocomposite was not densely aggregated. As shown in the higher magnification image (Figure 2(c)) of the indicated region with a white arrow in (a), the size of SnO$_2$ particles was 3-5 nm in diameter and evenly dispersed throughout the rGO sheet. It should be noted that the structure of well-distributed nanoparticles over rGO sheets improves electron transfer, resulting in enhanced electrochemical properties. Figure 2(b) shows the selected area electron diffraction (SAED) pattern of the rGO-SnO$_2$ hybrid; this result is consistent with a typical electron diffraction pattern for cassiterite SnO$_2$ (Figure 2(d)). As shown in Figure 2(c), the crystal lattice fringes were observed over the entire sample, demonstrating the high crystallinity of SnO$_2$ nanoparticles. As indicated in the inset image of Figure 2(c), the crystal lattice spacing of 3.35 Å is distinct. This corresponds to the (110) lattice plane of a cassiterite SnO$_2$ crystal.

Figure 2(d) presents the powder X-ray diffraction (XRD) patterns of rGO-SnO$_2$ nanocomposites with six well-resolved diffraction peaks. Those peaks are typical diffraction peaks from the (110), (101), (200), (211), (112) and (301) crystalline lattice planes of the cassiterite of SnO$_2$ phase (JCPDS No. 41-1445). The peaks of the sample annealed at 400 °C for 2 h were greatly enhanced.

The crystalline morphology of the hybrid. (a) TEM image of isolated rGO-SnO$_2$ nanocomposites. (b) A selected area electron diffraction (SAED) pattern of hybrid (a). (c) A magnified HRTEM image corresponding to the pointed region with a white arrow in (a). The inset image of (c) shows the crystal lattice fringes of highly crystalline SnO$_2$ nanoparticles. The crystalline lattice spacing is 3.35 Å corresponding to the (110) lattice plane of a cassiterite SnO$_2$ crystal. (d) X-ray diffraction of rGO-SnO$_2$ nanocomposites. XRD pattern of hybrid has six well-resolved peaks assigned as the diffraction peaks of cassiterite of SnO$_2$ phase (JCPDS No. 41-1445). The peaks of the sample annealed at 400 °C for 2 h were greatly enhanced.

The crystallite size of 3.3 nm was calculated using the Scherrer equation:

$$L = \frac{0.9 \lambda}{B(2 \theta) \cos(\theta)}$$

where $L$ is the crystallite size and $B(2 \theta)$ is the line width. The value is completely consistent with the results of TEM characterization. The intensity of the crystalline SnO$_2$ peaks increased after thermal annealing. The most intense peak of rGO (at around 2$\theta$ = 16.9°) indicates much larger interlayer spacing (0.41 nm), compared with the pristine graphite (0.34 nm).

Figure 3(a) and (b) show the full range XPS spectra of GO and rGO-SnO$_2$ hybrid, respectively. As presented in Figure 3(b), the Sn 3p, 3d, 4s, 4p, and 4d peaks appear due to the presence of SnO$_2$ nanoparticles, and the peak of C 1s is attributed to rGO. In the high-resolution Sn 3d XPS spectrum in Figure 3(c), peaks of Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ are at 487.3 and 495.7 eV, with an 8.4 eV peak-to-peak separation, which indicates the formation of SnO$_2$ nanoparticles on graphene. The C 1s XPS spectra of the GO and hybrid nanocomposites are shown in Figure 3(d)-(f). The bands at 285-289 eV corresponding to the oxygenated functional groups were definitively shown in Figure 3(d).

Compared with GO, the C 1s XPS spectrum of the GO-SnO$_2$ nanocomposites (Figure 3(e)) shows a significant
increase in the intensity of C-C at 284.7 eV and the much smaller amount of oxygen-containing functionalities, indicating a successful deoxygencation. It implies that the GO plays a key role for hybridization as an oxygen-provider to form SnO$_2$ nanoparticles. In addition, as confirmed in Figure 2(a) and (c), the even distribution of SnO$_2$ on graphene sheet indicates the presence of abundant oxygen-containing defect sites throughout the basal plane and edges of GO.$^{31}$ Adding hydrazine in a GO-SnO$_2$ composite suspension resulted in suppressed oxygen-related peaks, indicating the further reduction of GO (Figure 3(f)). However, at the end of the reduction, these peaks did not completely disappear. This is due to the screening effect of SnO$_2$ nanoparticles attached to carbon sheets for an access of hydrazine to some partially negative epoxy and hydroxyl groups.$^{29}$ Note that the XPS characterization results indeed indicate that simple mixing of a GO and SnO$_2$ precursor solution not only leads to the reduction of GO to rGO, but also simultaneously results in the formation of SnO$_2$ nanoparticles. Based on our observation, the possible reaction mechanism$^{10}$ is proposed as follows:

$$\text{Sn(CH}_3\text{COO)}_2 + \text{GO} + \text{H}_2\text{O} \rightarrow \text{SnO}_2 + \text{rGO} + 2\text{CH}_3\text{COOH}.$$ 

Owing to the effect of strong pseudocapacitive character of SnO$_2$ and the highly electro-conductive rGO support, hybrids are expected to be an excellent electrode material for supercapacitors. The performance of supercapacitor electrodes was analyzed using cyclic voltammetry (CV) and gavanostatic charge-discharge at room temperature. Typical three-electrode configuration was employed in 1 M H$_2$SO$_4$ electrolyte. Figure 4(a) and (b) show the CVs of the rGO and rGO-SnO$_2$ electrodes, scanned at various scan rates in a potential range of 0 to 1.0 V. The voltammograms of the rGO and rGO-SnO$_2$ exhibit a nearly rectangular shape, indicating a good capacitive behavior in the electrochemical supercapacitors.$^{31}$ The higher capacitive current and redox peaks are observed in the CV for the rGO-SnO$_2$, which are attributed to the efficient electric double layer capacitor performance of the carbon support and pseudocapacitive properties from redox reactions on tin oxide. The specific capacitances of electrode can be calculated according to the following equation:

$$C = (\int I dV)/(v \cdot m \cdot V)$$  \hspace{1cm} (2)

Where $I$ is the response current (A), $V$ is the potential (V), $v$ is the potential scan rate (mV/s), and $m$ is the mass of the electroactive materials in the electrodes (g). The specific capacitance values of rGO and rGO-SnO$_2$ electrodes at 50 mV/s are 241 and 389 F/g, respectively. Specific capacitance values of rGO and rGO-SnO$_2$ at various scan rates are compared in Figure 4(c). The rGO-SnO$_2$ electrode shows the enhanced capacitance performance for various scan rates. The rGO-SnO$_2$ composites exhibit high specific capacitance values from 477 to 362 F/g as the scan rate increases from 5 to 100 mV/s and maintain 75.9% of its specific capacitance at a high rate. The capacitance retention of 52.9% from 411 to 218 F/g at the rates from 5 to 100 mV/s of the rGO electrode is shown in Figure 4(d). These results are due to the enhanced electrolyte accessibility, facilitated charge propagation along the hybrid electrode and the high electrochemical stability for the redox transition of electrodes at higher scan rates.

Figure 4(e) shows the galvanostatic charge-discharge curves of rGO and rGO-SnO$_2$ electrodes at a current density of 5 A/g in a potential rage between 0 and 1.0 V. The galvanostatic curve of the hybrid is similar to that of rGO, which is linear and symmetrical, and shows no obvious $iR$ drop, indicating low inter-resistance and instant $I$-$V$ response of the hybrid.$^{32}$ Also, from the charge-discharge curves, the specific capacitance values were calculated according to the following equation:

$$C = I/(m(\Delta V/\Delta t))$$  \hspace{1cm} (3)

Where $I$ is the constant current during discharge (A), and $\Delta V/\Delta t$ is the slope of the discharge curve (V/s). The specific capacitance of rGO and rGO-SnO$_2$ nanocomposites at 5 A/g was about 190 and 362 F/g, respectively. To further investigate the cyclability of rGO and the rGO-SnO$_2$ hybrid, the galvanostatic charge-discharge was performed for 500 cycles at 5 A/g (Figure 4(f)). During first 100 cycles the specific capacitance of rGO and rGO-SnO$_2$ increased about 2.6 and 2.4%, respectively. Such an increase in capacitance can be ascribed to an activation process, in which the active
materials become fully utilized in the electrochemical reaction. After the entire activation, rGO and rGO-SnO2 sustained the constant specific capacitance values, indicating the excellent cycle stability and high reversibility.

Conclusion

In summary, we have demonstrated the preparation of rGO-SnO2 hybrid materials through a straightforward hybridization method. By simple mixing of GO and a SnO2 precursor solution, a hybrid complex of GO-SnO2 was achieved. In this hybrid process, the oxygen functional groups in GO played a key role in conversion of Sn2+ into SnO2 nanoparticles. Furthermore, hybrids of rGO and SnO2 produced via a facile solution-processing route showed enhanced electrochemical properties. Owing to the synergistic effects from carbon and metal oxide components, these hybrids demonstrate remarkable performance as supercapacitor electrodes. Therefore, this work has shown that GO is an excellent nanoplatform for hybrid nanocomposites for electrode applications. Our hybrid strategy not only provides a high throughput and scalable synthetic route, but also illustrates the effectiveness of oxygen functionalized graphene sheet (GO) for the synthesis of functional nanomaterials.

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References

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