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Facile PSS-assisted Synthesis of SnO_2/Single-walled Carbon Nanohorn Composites for Supercapacitors

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In this study, we proposed an effective and rational method for *in situ* decoration of tin dioxide (SnO_2) nanoparticles on single-walled carbon nanohorns (SWNHs) by using poly (sodium 4-styrenesulfonate) (PSS) as dispersing agent and stabilizer. The morphology and nanostructure of SnO_2/SWNH composites were tested by TEM, XRD and XPS in detail. The results indicated that uniform dispersion of SnO_2 nanoparticles with mean size about 5nm on the SWNHs. The nanocomposites as electrode materials for high-performance supercapacitors were tested by cyclicvoltammetry (CV) and galvanostatic charge-discharge (GCD). Experimental results exhibited a high specific capacitance of 180.69 F/g at 1 A/g in 1 M Na_2SO_4 electrolyte. The SnO_2/SWNH composites showed good cycling stability, which the retention rate of the specific capacitance was 80.72% after 1200 times of charge and discharge cycles.

Keywords: Supercapacitor; SnO_2; SWNH; PSS-assisted synthesis

1. INTRODUCTION

At present, energy problems have become an important issue, and attracted worldwide attention in our society [1]. Supercapacitors are one of energy-storage devices which possess higher energy density than that of conventional dielectric capacitors, and they have higher power density than common batteries) [2]. In addition, they have high cycling ability, light weight and green environmental protection, which make them promising energy storage devices in the future. [3, 4] Ion adsorption (electric double layer capacitor, EDLC) and rapid, reversible reaction induced current (pseudocapacitor) are two stored energy ways of supercapacitor [5]. According to the properties and characteristics of electrode materials, these two mechanisms can act simultaneously. Composites of transition metal oxides/carbon materials or electrically conducting polymers/carbon materials are

reported to have more outstanding capacitive performance than that of their individual counterparts [6].

SnO_2 is considered to be one of an excellent material for stored energy due to its high specific capacity up to 720 F/g, nontoxicity, low cost, good safety and other advantages. [7-9] However, SnO_2 has a lower conductivity and poor cycling stability, thereby limiting its development in electrochemical field. Some experimental results have indicated that hybridizing SnO_2 with carbon materials is an effective method to improve electrochemical activities and properties of SnO_2. [10, 11]

Single-walled carbon nanohorn (SWNH) is cone-shaped single-layered graphitic aggregation with a typical diameter of 50-100 nm, and cost-effectively produced by laser ablation of pure graphite rod with high purity and high yield. [12] SWNH has caused a great deal of attention due to its scientific significance and various applications, such as: sensors [13], supercapacitors [14, 15], drug delivery system [16], catalyst supports [17], clean-energy technologies [18] and so on.

Herein, we prepared SnO_2/SWNH composites through PSS-assisted chemical reactive process and high temperature annealing method. The nanosized SnO_2 particles were uniformly distributed on the SWNHs, The as-obtained composites exhibit high electrochemical performance for supercapacitor.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

SWNHs are provided by Nanjing XFNano Technology Co., Ltd. (China) and activated according to literature [19] prior to use. Other reagents (analytical grade) were obtained from Aladdin reagent Co., Ltd. (China) and used without further treatment. The solutions were prepared with ultrapure water (>18MΩ).

2.2. Synthesis of SnO_2/SWNH composites

A 100mg purified SWNHs were dispersed in 100 mL of ethylene glycol by sonication in a round bottom flask under stirring at 50 °C for 6 hr. Then, 50 mL aqueous solution of $SnCl_2 \cdot H_2O$ (0.5 mg) was added into the above solution. After stirring for 1hr, 2mL of 30% H_2O_2 were stepwise added into the mixed solution, and the solution was refluxed at 190 °C for 6 hr. Subsequently, the black solid products were collected by filtration, washed with deionized water and ethanol several times, and dried in vacuum at 60 °C. Finally, the product was annealed at 500 °C for 3 hours under a nitrogen atmosphere.

2.3. Material Characterization

The product morphology was obtained through a JEM-2010 transmission electron microscope (TEM) operated at 200 kV. The microstructure of the samples was examined by X-ray diffraction

(XRD), Shimadzu, X-6000, Cu Kα radiation (λ= 0.1542 nm)). The mean crystalline size of SnO_2 powders could be calculated through the XRD patterns according to Scherrer's formula. X-ray photoelectron spectroscopy (XPS) measurement was carried out by using a Thermo Fisher X-ray photoelectron spectrometer.

2.4. *SnO_2/SWNHs electrode preparation*

For the SnO_2-based composite supercapacitor tests, It was conducted with electrochemical workstation (CHI 660E, Shanghai) employing a three-electrode system, which was composed of a saturated calomel electrode (SCE) and platinum wire were used as the reference and counter electrode, respectively. The working electrode was prepared by mixing 80wt% SnO_2/SWNH composites, 10wt% PTFE and 10wt% carbon black, which was pressed on the clean nickel foam (1 ×2cm^2) and dried at 80 ◦C in a vacuum oven for 12 h. SWNH electrode were prepared by similar method. Cyclic voltammetry (CV) with the voltage between 0 and 0.8 V and galvanostatic charging/discharging (GCD) tests at varied current densities were employed to investigate the electrochemical performance of the working electrode.

3. RESULTS AND DISCUSSION

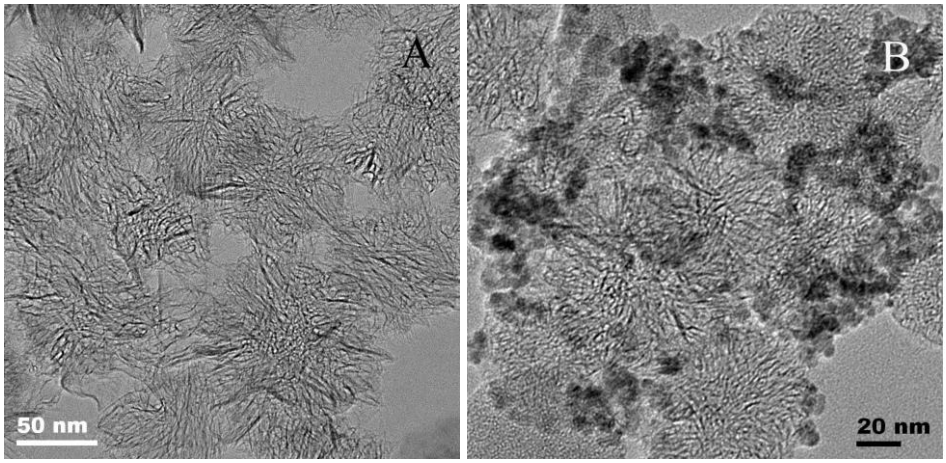


Figure 1. TEM images of (A) SWNHs and (B) SnO_2/SWNH composites

TEM images of the dahlia flower-like SWNH aggregates are shown in Figure 1A, and their average diameter is about 100 nm. The synthesis of SWNHs without metal catalysts means that the effects of metal impurities can be eliminated.） Moreover, the rough external surface, thermal stability and excellent electrical conductivity made SWNHs be used as electrochemical catalyst supports. It can be clearly seen from Figure 1B that SnO_2 nanoparticles are uniformly dispersed on the surface of SWNH, and SWNH still maintain their own unique structural features after SnO_2 doping, which provides the necessary conditions for the free movement of carrier electrons in SWNH.

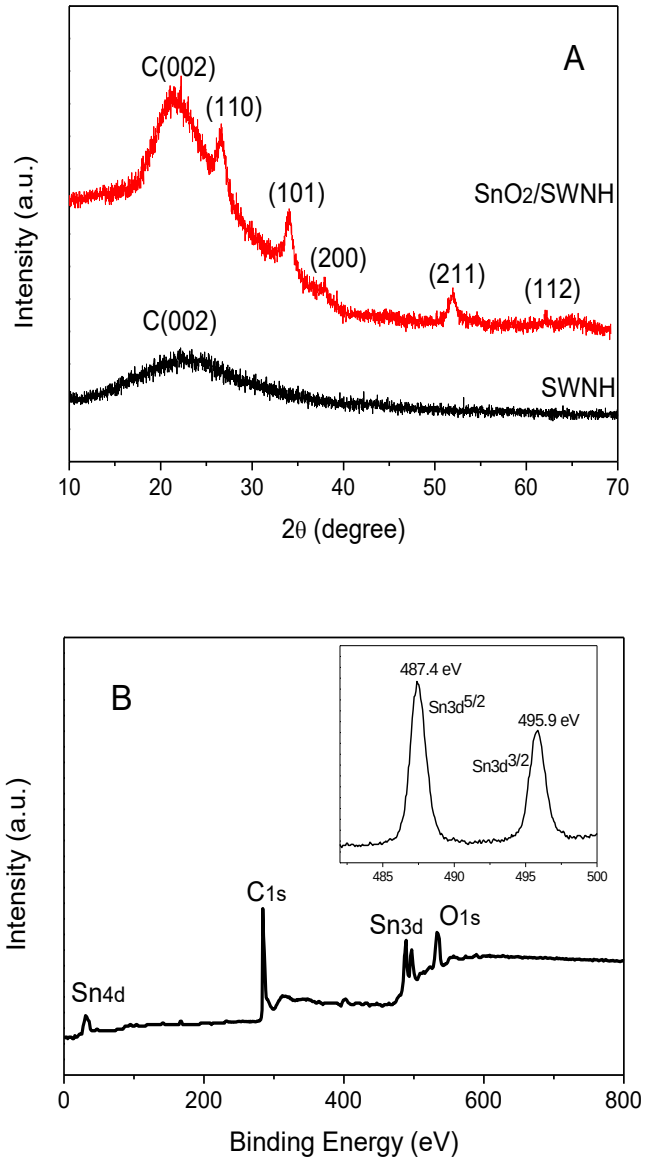


Figure 2. (A) X-ray diffraction (XRD) patterns of the pristine SWNHs and SnO_2/SWNH composites, (B) XPS spectrum of the SnO_2/SWNH and high-resolution XPS spectrum of Sn3d.

XRD measurements were employed usually to estimate the crystal phase and the microstructure of the products. The XRD patterns of the pristine SWNHs and SnO_2/SWNH composites are indicated in Figure 2A. A strong and broad diffraction peak at around 23° is due to the (002) plane of graphite from the SWNHs. The other characteristic diffraction peaks of SnO_2/SWNH appearing at 27.5°, 34.6°, 38°, 52.5°and 63.5° could be readily indexed as (110), (101), (200), (211) and (112) , respectively. Moreover, there is no peak of impurities detected, suggesting that almost all of the tin element is converted into the SnO_2 structures after solvothermal reduction and thermal treatment at 500 ^oC. This indicates that SnO_2 particles have been loaded onto the surface of SWNHs. Figure 2B shows the XPS spectrum of SnO_2/SWNH composites.

To further determine the existing forms of elements and compositions of SnO_2/SWNH nanocomposite, XPS test is carried out and the survey scan spectrum (Figure 2B) from XPS analysis indicates clearly the sample contained Sn, C, O elements, which further proves that there are no other impurities in the sample. The inset of Figure 2B shows Sn 3d spectrum of the composite. The two prominent peaks are at around 487.4 eV and 495.9 eV corresponding to Sn $3d^{5/2}$ and Sn $3d^{3/2}$, respectively [20]. Furthermore, The 8.5 eV peak-to-peak separation is in consistent with the standard spectrum of SnO_2 [21], which confirmed the formation of SnO_2 perfectly.

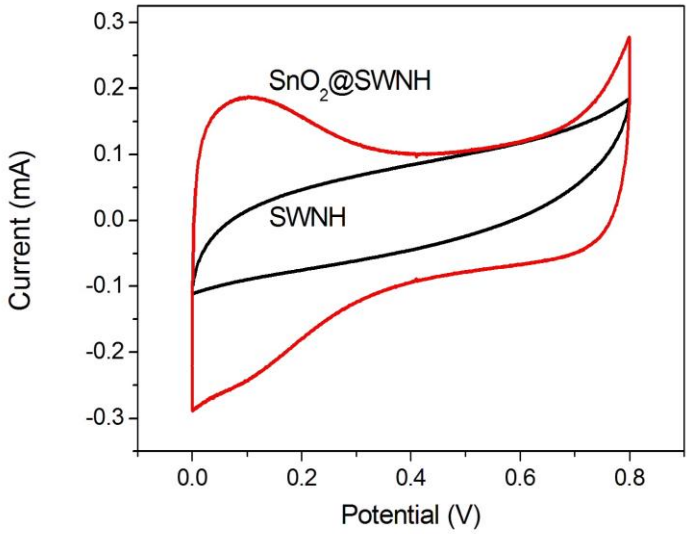
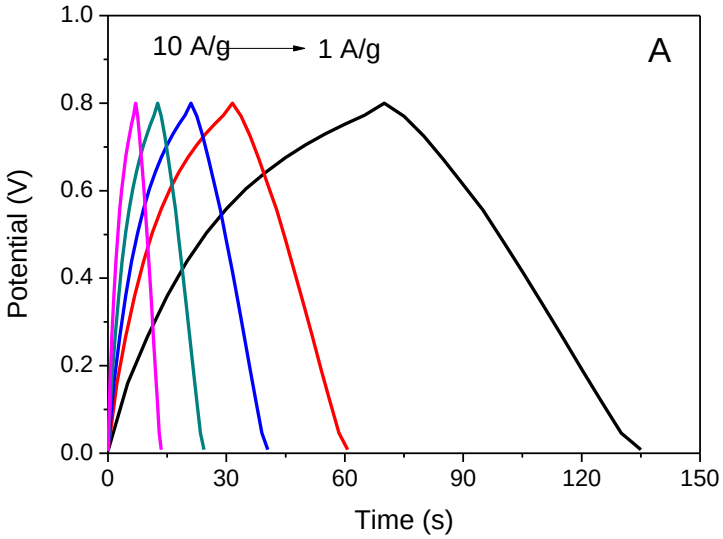


Figure 3. Cyclic voltammograms (CVs) for the second cycle of the SWNH and SnO_2/SWNH composite electrodes at 20mV/s.



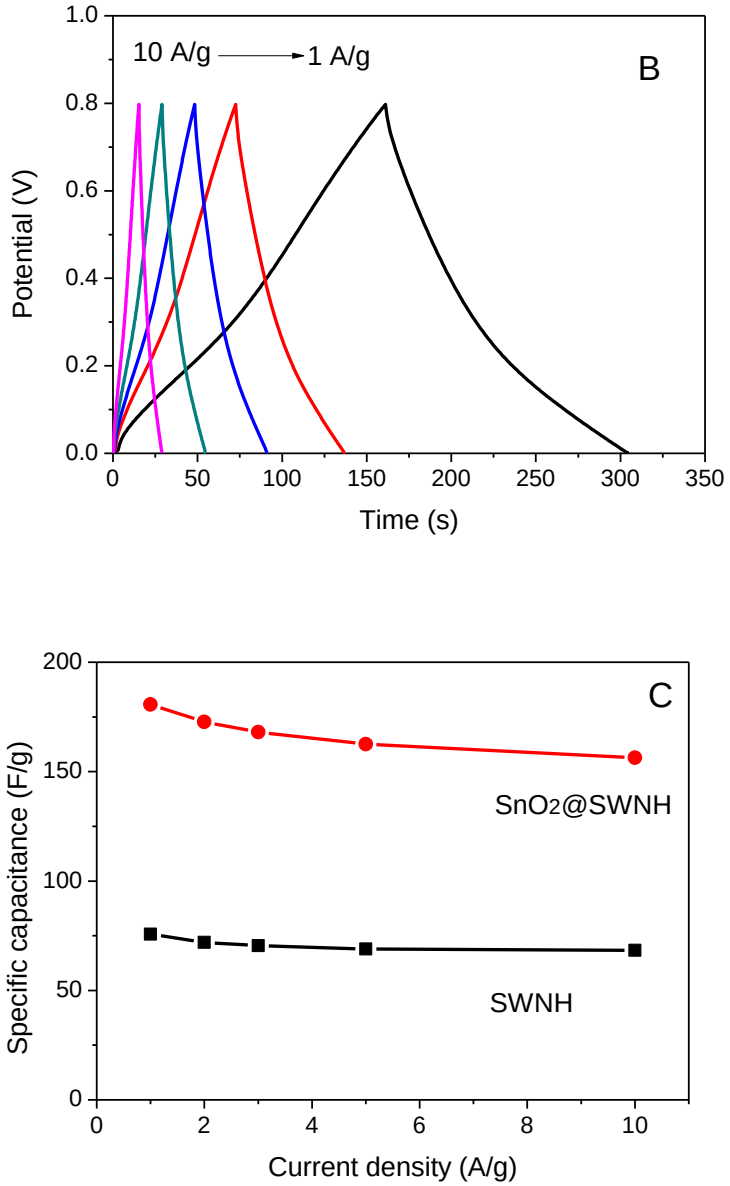


Figure 4. (A), (B) Galvanostatic charging/discharging (GCD) curves of SWNHs and SnO_2/SWNH composites at different current densities, respectively. (C) Variation of the specific capacitance with different current density for SnO_2/SWNH composites.

Cyclic voltammetry (CV) is an ideal tool for the study of the capacitive properties of electrode materials. Figure 3 shows the typical CVs of SWNH and SnO_2/SWNH composites in 1.0 mol/L Na_2SO_4 electrolyte. The scanning speed was 20mV/s and the potential range from 0 to 0.8V. The pure SWNH and SnO_2/SWNH electrode materials exhibit a near-rectangular cyclic voltammetry curve, respectively. In general, the specific capacitance of electrode materials is proportional to the area of CV. The area of closed CV loop of SnO_2/SWNH is much larger than that of SWNH, which indicates SnO_2/SWNH is an ideal supercapacitor material.

GCD technique is reliable approach to measure the electrochemical performance of active electrode materials. The Figure 4A and 4B show the GCD curves of SWNHs and SnO_2/SWNH composites at different current densities (1, 2, 3, 5, 10A/g), respectively. Obviously, **t**he shape of the

triangle remains unchanged, suggesting good charge/discharge capacitive performance and good conductivity of as-prepared electrode materials. However, with the increase of current densities, specific capacitance (*Cs*) decreases gradually. The higher *Cs* at low current density is due to the enough transfer time for ions between the electrolyte and the working electrode. The Cs of SWNHs and SnO_2/SWNH composites were calculated according to $Cs = I \times \Delta t/(\Delta V \times m)$ from the discharge curves, where I is the constant discharge current, Δt is the discharge time, and ΔV is the potential drop during discharge. At the current density of 1 A/g, the gravimetric Cs is 180.69 F/g for SnO_2/SWNH composites and 75.75 F/g for SWNHs, which indicates pseudocapacitance of SnO_2 nanoparticles play a key role in improving Cs values of the electrode materials.

Figure 4C shows the variation in Cs as a function of current density. It can be observed that the Cs values decreases with an increase current density from 1 A/g to 10 A/g. It is also seen that the Cs values of SnO_2/SWNH composites is much higher than that of pristine SWNHs at the same current density. The high capacitance characteristics are due to the introduction of highly dispersible SnO_2 nanoparticles on the surface of conductive SWNH materials.

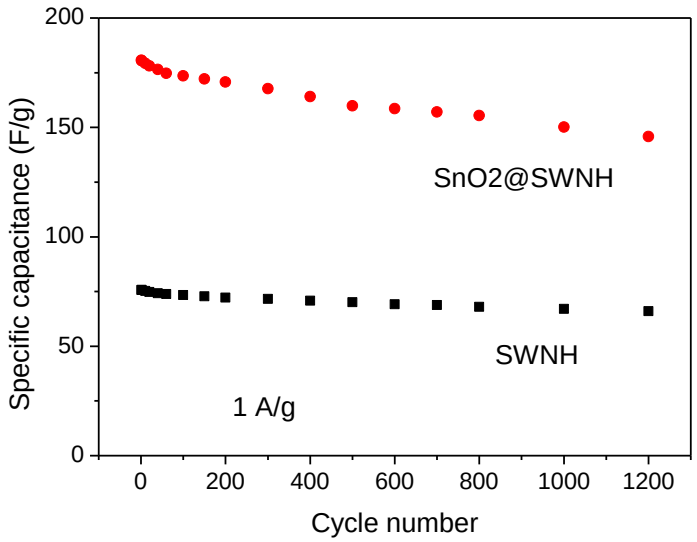


Figure 5. Cycle performance of SWNHs and SnO_2/SWNH composites at 1 A/g

The cycle stability performances are of great importance for supercapacitor applications. The cycling measurement of SWNHs and SnO_2/SWNH composites electrode was carried out at 1 A/g for 1200 cycles as shown in Figure 5. In the first cycle, the Cs is 180.69 F/g for SnO_2/SWNH composites and 75.75 F/g for SWNHs. After 1200 cycles, the retention of the Cs of SWNHs and SnO_2/SWNH composites is 87.15% and 80.72%, respectively. This stable cycle performance indicates that both the electrode materials have got highly durable and very high degree of reversibility in mild aqueous electrolytes.

A comparison was made with the current material as shown in Table 1. The SnO_2/SWNH composites in this paper have good electrochemical activity and could be used for supercapacitor

applications. The excellent capacitance of our work may be attributed to high dispersed SnO_2 particles with mean size about 5nm on the SWNHs.

Table 1. Comparison of other SnO_2-based composites modified electrodes for Cs

Electrode Materials	Cs (F/g)	Electrolyte	References
SnO_2/MWCNTs	133.00	1M Na_2SO_4	[22]
SnO_2/VC	112.14	1M Na_2SO_4	[22]
SnO_2/SWCNTs	320	1M Na_2SO_4	[23]
SnO_2/CNT	188.42	2M KCl	[24]
SnO_2/Graphene	99.7	1M H_2SO_4	[25]
SnO_2/Carbon	25.8	1M KOH	[26]
SnO_2/GSP	429	1M H_2SO_4	[27]
SnO_2/Polyaniline	305.3	1M H_2SO_4	[28]
SnO_2/SWNHs	180.69	1M Na_2SO_4	This work

ABBREVIATIONS:
MWCNTs: Multiwalled carbon nanotubes, VC: Vulcan carbon, SWCNTs: Single walled carbon nanotubes, CNT: carbon nanotube, SnO_2/GSP: SnO_2-decorated graphene/polyaniline (GSP) nanocomposite

4. CONCLUSION

In summary, SnO_2/SWNH composites were synthesized successfully via PSS -assisted by ethylene glycol solvothermal process. The as-obtained composites exhibit an excellent electrochemical performance for supercapacitor, because of the high-dispersed SnO_2 nanoparticles anchored on the surface of SWNHs. The electrochemical experimental results suggest that the as-obtained SnO_2/SWNH composites exhibit a high specific capacitance of 180.69 F/g and Cs retention retains up to 80.72% after 1200 cycles at 1 A/g. This work demonstrates that the high-dispersed SnO_2 nanoparticles on SWNH can be used efficiently as electrode material for supercapacitor applications.

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