Room-Temperature Synthesis of Colloidal SnO₂ Quantum Dot Solution and Ex-Situ Deposition on Carbon Nanotubes as Anode Materials for Lithium Ion Batteries

Xuan Lu,^a Hongkang Wang,^{a,*} Zhenyu Wang,^a Yizhe Jiang,^a Daxian Cao,^a Guang Yang^b

^a Center of Nanomaterials for Renewable Energy (CNRE), State Key Lab of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, China 710049

^b Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, China 710049

*Address correspondence to hongkang.wang@mail.xjtu.edu.cn

Abstract

Colloidal SnO₂ quantum dots (QDs) have been successfully prepared via a facile aqueous wet-chemical synthetic approach using tin dichloride as tin source and thiourea as accelerating and stabilizing agent under magnetic stirring at room temperature. The SnO₂ QDs with average size of ~3.5 nm are well-dispersed in the aqueous solution with high stability. A facile *ex-situ* deposition of SnO₂ QDs on carbon nano tubes (CNTs) is developed, allowing large loading amount of SnO₂ QDs on the CNTs with uniform distribution. When used as anode material for lithium ion

batteries, the as-prepared SnO₂-CNT nanocomposites exhibit superior lithium storage properties, delivering a stable discharge capacity of 845 mAh/g at 100 mA/g after 90 cycles. More importantly, the novel synthetic strategy is promising for the cost-effective and large-scale fabrication of SnO₂-CNT nanocomposites as high-performance anodes for electrochemical energy-storage.

Keywords: room-temperature synthesis, colloidal SnO₂ QDs, ex-situ deposition, SnO₂-CNT nanocomposite, lithium storage properties

Introduction

Rechargeable lithium ion batteries (LIBs) have attracted great attention owing to their unique merits such as high energy density, long lifespan and high operating voltage.[1, 2] As a promising anode material for LIBs, SnO₂ has been widely investigated in the last few decades, due to its higher theoretical specific storage capacity (~782 mAh/g) compared with that of commercial graphite (~372 mAh/g).[3, 4] The lithium storage mechanism for tin-based anode is based on the alloying-dealloying process: $\text{Sn} + \text{Li}^+ + \text{xe}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$).[5, 6] One Sn atom can accommodate maximum 4.4 Li atoms, which contributes the high lithium storage capacity but also results in the huge volume change (up to 300%) and thus resultant drastic pulverization problems.[7, 8] To solve this problem, various strategies have been developed to optimize the composition as well as the morphology of the SnO₂ materials, such as using 0D nanoparticles,[9, 10] 1D nanorods/nanowires,[11, 12] 2D nanosheets,[13, 14] and their high-level composite or hierarchical architectures.[15, 16] However, great improvement in applying tin-based anodes in practical applications has not yet been realized, which on one aspect was limited by the poor cycle performance and less-efficient fabrication strategies.

Recently, fabrication of ultra-small SnO₂ nanoparticles and their composite structures with carbon-based materials such as carbon nanotubes (CNTs) have

received considerable interest, which are promising on overcoming the severe pulverization problems of tin-based materials.[6, 17, 18] Currently, various *in-situ* methods have been reported to prepare the SnO₂-CNT nanocomposite, such as solvo/hydrothermal methods and chemical vapor deposition (CVD).[19-21] Jin *et al* prepared SnO₂ nanoparticles (~3 nm) on acid-treated CNTs by hydrothermal method at 150 °C, which delivered a discharge capacity of 420 mAh/g at 156 mA/g after 100 cycles.[6] Kim *et al* coated CNTs with SnO₂ nanoparticles via CVD, delivering a discharge capacity of 780 mAh/g at 1C after 100 cycles.[22] These techniques require complicated process, expensive equipment, or high temperature and inert atmosphere, which limit the practical and industrial application as electrode materials for LIBs. Alternatively, *in-situ* synthesis of SnO₂ on CNTs at room temperature has been developed via the hydrolysis and crystallization of SnCl₂ aqueous solution.[23-25] For example, Han *et al* reported the coating of SnO₂ (~4 nm) on single-walled carbon nanotubes (SWCNTs) by sonicating and stirring the precursor solution containing SnCl₂-HCl-SWCNTs.[24] Ke *et al* demonstrated the coating of SnO₂ on multi-walled carbon nanotubes (MWCNTs) through hydrolyzing SnCl₂ merely in pure water at room temperature.[25]

Different from the above-mentioned *in situ* methods, we develop a facile method to prepare well-dispersive colloidal SnO₂ QD solution, which allows for the efficient *ex-situ* deposition on CNTs. The colloidal SnO₂ QD solution is prepared by hydrolysis of tin dichloride with the presence of thiourea as accelerating and stabilizing agent under magnetic stirring at room temperature. Subsequently, directly immersing CNTs into the SnO₂ QD solution allows the easy deposition of SnO₂ nanoparticles on the CNTs with uniform distribution, and the relative ratio can be readily controlled by tuning the introduction amount of each component. When used as anode materials, the as-prepared SnO₂-CNT nanocomposites showed excellent electrochemical properties. More importantly, the current synthetic strategy is facile to handle and the yield can be easily scaled up, which can be applied to other supporting substrates.

Experimental Section

Materials Synthesis. All chemicals including tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Aldrich) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, Aldrich) were used as received without further treatment.

Synthesis of acid-treated CNTs. Pristine CNTs were produced by chemical vapor deposition (CVD) using Co/Fe- Al_2O_3 as catalysts, ethylene as carbon source, which were then heated in air at 773 K for 1 h and washed with 5 wt% HF solution for 24 h to remove amorphous carbon and residual metal catalysts. The acid-treated CNTs were obtained by dispersing the pristine CNTs in a mixture of concentrated sulfuric acid and ammonium peroxydisulfate at room temperature under magnetic stirring for 48 h.

Wet-chemical synthesis of SnO_2 QD solution. In a typical synthesis, 0.9 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.3 g thiourea ($\text{CH}_4\text{N}_2\text{S}$) were added in 30 mL distilled water under magnetic stirring at room temperature, forming a milky suspension. After successive stirring for 24h, a yellow and clear aqueous solution containing SnO_2 QDs was obtained.

Ex-situ deposition of SnO_2 QDs on CNTs. In a typical synthesis, 20 mg acid-treated CNTs were dispersed in 25 mL deionized water under ultrasonic irradiation for 1 h, then 5 mL as-prepared SnO_2 QD solution was added under magnetic stirring, during which the SnO_2 QDs were *ex-situ* deposited on CNTs. Finally, a black precipitate composed of SnO_2 -CNTs was collected by centrifugation, washed with water and ethanol thoroughly, and then dried in a vacuum oven at 60°C overnight.

Materials Characterization. The morphologies of the products were characterized using transmission electron microscopy (TEM, JEOL JEM-2100). Powder X-ray diffraction (XRD) patterns of the products were recorded on a Bruker D2 PHASER X-ray diffractometer using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) with an operating voltage of 30 kV and a current of 10 mA. The Raman spectra were recorded with a Renishaw Raman RE01 scope using a 514 nm excitation argon laser. Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO thermal analysis TGA/DSC system.

Electrochemical Measurements. Electrochemical measurements were performed using CR2025 coin-type cells assembled in an Ar-filled glove box with H₂O and O₂ content less than 1.0 ppm. The working electrodes were fabricated by casting a paste composed of active material, acetylene black (AB) and polyacrylic acid (PAA, MW=100000, Aldrich) with a weight ratio of 8:1:1 on copper foil. Then, the electrodes were dried in a vacuum oven at 120 °C overnight. Lithium foil was used as the counter electrode and a Celgard 2400 microporous membrane was used as separator. An electrolyte containing 1 M LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (1:1 in volume) was used. Galvanostatic discharge/charge tests of the cells were carried out on a battery test system (NEWARE BTS, Neware Technology Co., Ltd., China) in the range of 0.01-2.5 V (vs. Li/Li⁺) at room temperature (25°C). Cyclic voltammetry (CV) was carried out using electrochemical station (Autolab PGSTAT 302N) in the range of 0.01-2.5 V at a scan rate of 0.2 mV/s. The specific capacities were reported on the basis of the total mass of SnO₂ and SnO₂-CNT composite.

Results and discussion

Scheme 1 illustrates the facile wet-chemical synthesis of SnO₂ QD solution and subsequently *ex-situ* deposition on CNTs under magnetic stirring at room temperature. Firstly, a transparent yellow aqueous solution containing colloidal SnO₂ QDs was obtained via the hydrolysis, dehydration and oxidation of SnCl₂·2H₂O in distilled water with the presence of thiourea (CH₄N₂S) as accelerating and stabilizing agent. It has been reported that SnCl₂·2H₂O could self-evolved into ultra-small SnO₂ nanoparticles through the hydrolysis-oxidation process.[24, 26] However, such SnO₂ nanoparticles are prone to aggregate as precipitation. Usually, SnCl₂·2H₂O undergoes the hydrolysis, dehydration and oxidation processes, which can be described by following equations (1-3):

In the first step, a white precipitate of Sn(OH)Cl would be produced once the exposure of SnCl₂·2H₂O in distilled water due to its fast hydrolysis nature, which undergoes successive hydrolysis, dehydration and oxidation, finally forming SnO₂ nanoparticles. In our synthesis, thiourea acting as an important accelerating and stabilizing agent was introduced, which played an important role on the formation of the colloidal QD solution. In case of the absence of thiourea, it takes days for the milky suspension to convert into a transparent yellow SnO₂ solution, and such aqueous solution is not stable and prone to precipitate and change yellow color to white. However, after the introduction of thiourea in the precursor solution, the milky suspension converts into the transparent yellow SnO₂ solution within 24 h, which shows high stability and can be stored for months, indicating the extremely important role of thiourea on the aspects of reaction acceleration and product stabilization. As is well known, thiourea is a chemically interesting compound with three functional groups including amino (-NH₂), imino (-NH), and thiol (-SH), which results from tautomerism between thiourea and isothiurea especially in the acidic medium.[27-29] In the current reaction system, the HCl generated by hydrolysis and dehydration of SnCl₂ can be consumed by reaction with thiourea, greatly facilitating the ongoing of reactions (1-2) and finally the acceleration of formation of SnO₂ QDs. Besides, the thiol groups are prone to couple with metal ions (ex. Sn²⁺),[28] while the protonated amino groups (-NH₃⁺) with positive charge are surrounding the as-produced SnO₂ QDs, which would contribute to the extreme stability of the as-prepared SnO₂ QDs.

Scheme 1. Schematic illustration of the wet-chemical synthesis of colloidal SnO₂ QD solution and the ex-situ deposition of SnO₂ QDs on CNTs at room temperature.

Due to the small particle size and the stabilization of thiourea, the SnO₂ QDs in the aqueous solution are hard to be precipitated by centrifugation. However, when acid-treated CNTs with negatively charged carboxylate groups (–COO[–]) and also surface defects are introduced into the SnO₂ QD solution, the positively charged colloidal SnO₂ nanoparticles can be easily loaded on the surfaces of CNTs through electrostatic attraction.[17] The SnO₂-CNT composite can be easily collected by centrifugation, and the supernatant becomes clear and colorless, indicating the SnO₂ nanoparticles are captured by CNTs. More importantly, the current strategy allows the facile control on the ratio of CNTs and SnO₂.

Figure 1. (a) XRD patterns of the pure SnO₂ QDs and SnO₂-CNT nanocomposites. (b) Raman spectra of the pristine CNTs (red line) and SnO₂-CNT nanocomposites (black line).

Figure 1a shows the XRD patterns of SnO₂ QDs and SnO₂-CNT nanocomposites. The apparent peaks located at 26.6°, 33.8°, 37.9°, 51.8° can be correspondingly indexed to (110), (101), (200) and (211) reflections of the pure tetragonal phase of crystalline SnO₂ (JCPDS card no. 41-1445). Raman scattering, which indicates the vibrational modes of both crystalline and amorphous materials, could provide complementary structural information. Figure 1b displays two obvious peaks located at around 1578 and 1324 cm⁻¹, which can be assigned to the G-band and the D-band of typical carbonaceous materials, respectively. And the I_D/I_G intensity ratios for both pristine CNT and SnO₂-CNTs are almost the same (I_D/I_G ≈ 1.7). In addition, a prominent peak located at about 620 cm⁻¹ in SnO₂-CNTs appears, which can be attributed to the Raman active A_{1g} mode of rutile SnO₂ (space group D_{4h}) with tetragonal symmetry, relating to the expansion and contraction vibration mode of Sn-O bonds.[30]

The morphology of as-prepared SnO₂ QDs and SnO₂-CNT nanocomposites were investigated by transmission electron microscopy (TEM). Figure 2a shows the SnO₂ QDs with an average size of 3.5 nm were uniformly monodispersed on the TEM grid (Figure 2a), and the high-resolution TEM (HRTEM) image displays the crystal lattice fringes of 0.33 nm, which corresponds to the (110) planes of the rutile phase of SnO₂ (Figure 2b). In the SnO₂-CNT nanocomposites, the SnO₂ QDs are well-distributed on

the surfaces of acid-treated CNTs with high loading amount (Figure 2c-d), indicating the *ex-situ* deposition method is highly efficient.

Figure 2. TEM and HRTEM images of (a-b) pure SnO₂ QDs and (c-d) SnO₂-CNT nanocomposites. Inset of (a) shows the particle size distribution of SnO₂ QDs in the aqueous solution.

Figure 3. (a) Survey XPS spectrum of SnO₂-CNT nanocomposites. (b, c) High-resolution XPS spectra of Sn 3d (b) and C 1s (c).

To further reveal the chemical composition of SnO₂-CNT nanocomposites, X-ray photoelectron spectroscopy (XPS) analysis was performed, as shown in Figure 3.

Figure 3a displays the survey spectrum of SnO₂-CNTs, clearly showing the presence of C 1s, O 1s, and Sn 3d, Sn 3p, and Sn 4d, respectively. No peaks can be attributed to the N and S, indicating that thiourea acts as catalyst without participation of the chemical reactions. Figure 3b displays the typical high-resolution XPS spectra of Sn 3d, and two peaks located at 487.5 and 495.4 eV can be indexed to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively, which are in good agreement with the SnO₂ phase in the previous reports.[31, 32] Figure 3c displays the high-resolution XPS spectra of C 1s, where the major peak can be deconvoluted into three peaks at 284.5, 285.6, and 289.1 eV. The peak at 284.3 eV can be assigned to the sp²-hybridized carbon in the CNTs. The peaks at 285.6 and 289.1 eV can be attributed to the C-O and C=O oxygen-containing carbonaceous bands formed in the process of oxidizing acid treatment of CNTs.[33]

Figure 4. Electrochemical properties of SnO₂-CNT nanocomposites. (a) Cyclic voltammogram (CV) curves at a scan rate of 0.2 mV/s in the range of 0.01-2.5 V. (b) Galvanostatic charge-discharge profiles at a current density of 100 mA/g in the range of 0.01-2.5 V. (c, d) Comparison of (c) the cycle performance and (d) the rate

capability of the pure SnO₂ QDs and the SnO₂-CNTs at different current densities in the range of 0.01-2.5 V.

The electrochemical properties of the SnO₂ QDs and SnO₂-CNTs were investigated to demonstrate their potential application as anode materials in LIBs. Figure 4a shows the initial three CV cycles for SnO₂-CNTs, which show similar profiles. A less prominent peak located at round 0.75 V is observed in the first discharge process but disappeared in the subsequent cycles, which corresponds to the irreversible transformation of SnO₂ into metallic Sn ($\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow 2\text{Li}_2\text{O} + \text{Sn}$).[34] The broad cathodic peaks at below 0.5 V during discharge processes and the corresponding anodic peaks at around 0.6 V in the charge processes are clearly observed and can be assigned to Li-Sn alloying-dealloying processes ($\text{Sn} + \text{Li}^+ + \text{xe}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$), respectively.[30, 35, 36] Moreover, the similar CV profiles in the following scans suggest the highly reversible electrochemical reaction during the charge/discharge processes and consequently better cycling performance.[21] It's also observed that the anodic current increased in the following cycles, indicating the successive activation of electrode materials. In addition, one weak anodic peak located at around 1.26 V can be observed, which was attributed to the partially reversible re-oxidation of Sn.[37, 38] Figure 4b shows the galvanostatic discharge/charge profiles at cycle number ranging from 1st to 70th at a current density of 100 mA/g in the voltage range of 0.01-2.5 V. The discharge and charge capacities for the first cycle are 1841.6 and 1179.4 mAh/g, respectively, with a Coulombic efficiency of 64%. The large initial capacity loss is mainly attributed to the reduction of SnO₂ by Li metal, the formation of solid electrolyte interface (SEI) film and electrolyte decomposition.[39] The capacity gradually decreased in the following cycles until to 30th cycle and stabilized at around 845 mAh/g. Figure 4c compares the cycle performances of SnO₂ QDs and SnO₂-CNT nanocomposites at a current density of 100 mA/g in the range of 0.01-2.5 V. Obviously, the SnO₂-CNT electrode displayed a reversible capacity of ~845 after 90 cycles, which is much higher than that of pure SnO₂ (294.3 mAh/g at 100 mA/g after 40 cycles). The improved lithium storage

performance of SnO₂-CNT nanocomposites can be attributed to both the ultra-small size effect of SnO₂ nanoparticles and the buffering effect of conductive CNT matrixes, as the small SnO₂ nanoparticles can shorten the pathway length of the lithium ions and facilitate liquid electrolyte diffusion. The CNT matrix can accommodate the large volume change of SnO₂ due to its flexible tubular structure.[9, 10, 15, 20] Figure 4d compares the rate capabilities of pure SnO₂ QDs and SnO₂-CNT nanocomposite at various current rates from 100 to 1000 mA/g. The reversible capacities for SnO₂-CNT nanocomposites is 962.5, 850.6, 722.1 and 641 mAh/g after successively cycling at 100, 200, 500 and 1000 mA/g for 10 cycles, respectively. When recovering the current density to 100 mA/g, a capacity of 800.9 mAh/g was maintained, which are twice of that of pure SnO₂ electrode, indicating the better rate capability of the SnO₂-CNT composites.

As the relative content of SnO₂ and CNTs can greatly affect the lithium storage properties of the SnO₂-CNTs nanocomposites. As shown in Figure 5a, the loading amount of SnO₂ QDs in the SnO₂-CNTs can be readily controlled by varying the introduction amount of as-prepared SnO₂ QD solutions, in which the amount of CNTs remained constant (20 mg). When 1 mL SnO₂ QD solutions was introduced, the relative content of SnO₂ was ~45 wt.% in the SnO₂-CNTs, which further increased to ~75 wt.% and ~80 wt.% when increasing SnO₂ QD solution from 5 and 10 mL, indicating the saturation of loading amount. Interestingly, the discharge capacities increased with decreasing the introduction amount of SnO₂ QDs (Figure 5b), delivering discharge capacities of 645.8, 563.1 and 513.0 mAh/g for 1, 5 and 10 mL SnO₂ QD solutions, respectively. And the corresponding capacity retention rates are 61.3%, 57.2% and 59.1% after 100 cycles at a high current density of 500 mA/g, further indicating the good cycle and rate performance in the long term, even though they underwent fast capacity fading at the early cycle stage. This may result from the aggregation of SnO₂ QDs away from the CNTs, as revealed by the TEM image in Figure 6a. After 100 cycles at 500 mA/g, the electrode was disassembled, and amorphous nanoparticles were observed to attach on the CNT surface (Figure 6b),

indicating the robust hybrid structures, which contributed to the good cycle performance.

Figure 5. (a) TGA analysis (b) cycle performance of the SnO₂-CNTs with different introduction amount of SnO₂ QD solutions.

Figure 6. TEM and inset HRTEM images of the SnO₂-CNT nanocomposites (a) before and (b) after 100 cycles at 500 mA/g.

Conclusions

In summary, a colloidal SnO₂ QD solution with high stability and small average particle size of ~3.5 nm has been successfully prepared via a facile wet-chemical synthesis at room temperature, utilizing the regulated hydrolysis of tin dichloride with thiourea as controlling and stabilizing agent. Facile *ex-situ* deposition of SnO₂ QDs on CNTs was developed with uniform distribution and large loading amount. When examined as an anode for LIBs, the SnO₂-CNT nanocomposites displayed a higher reversible capacity of 845.4 mAh/g and better rate capability when compared with pure SnO₂ QDs. The improvement was attributed to the ultrafine size of SnO₂ QDs as well as their well-distribution on CNTs, which improved the ion diffusions and alleviated the volume changes. More importantly, the synthetic strategy developed in this work is cost-effective and can be easily scaled up for industrial applications, which may open up a way to the practical application of tin-based anodes and to rational design of new functional SnO₂-base nanocomposite materials.

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