

Short Communication

Synthesis of SiO₂/C Nanocomposites and Their Electrochemical Properties

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SiO₂/C nanocomposites have been prepared by coating with aniline onto the surface of SiO₂ nanospheres via a diazotization reaction and carbonizing treatment. The XRD pattern and High-resolution transmission electron microscope (HRTEM) show that the amorphous SiO₂ nanoparticles are coated with carbon. The carbon content of SiO₂/C nanocomposites is confirmed to be 34.19% by elementary analysis. Electrochemical measurements show that the SiO₂/C composites have a good electrochemical performance; they exhibit a discharge capacity of 1200 mAh g⁻¹ on the second cycle, and 714.4 mAh g⁻¹ on the 20th cycle under a current density of 100 mA g⁻¹.

Keywords: SiO₂/C, Nanocomposites, Anode materials, Electrochemical properties

1. INTRODUCTION

Lithium-ion batteries (LIBs) with high energy density and long cycling lives regard as the most promising battery system, especially for hybrid vehicles. At present, graphite-based materials are widely used in commercial LIBs, however the limited capacity of 372 mA h g⁻¹ is obviously prevent the further development[1]. It still needs to find new anode materials with higher capacity than that of graphite-based materials.

Recently, SiO₂ materials have been considered as one promising materials due to its low discharge potentials[2], abundant on Earth and low cost. In the past decades, SiO₂ is considered to be electrochemically inactive for lithium storage, it does not react with Li due to its stability as an oxide. While it exhibits Li reactivity in nano-sized, amorphous states, coating with carbon and so on[3-6]. For example, Chang et al[7] prepared amorphous SiO₂ by using commercially SiO₂ (Quartz,) powder as

precursor, it showed a reversible capacity of 800 mA h g^{-1} and good cycling stability under a current density of 100 mA g^{-1} . Up to now, there are many reports on the preparation of nano-sized SiO_2 to achieve good electrochemical performance[8,9]. In addition, carbon coating is an effective way for most SiO_x materials to improve their electrochemical performance[10-13], while the reports about synthesis of SiO_2/C nanocomposites are relatively less[14].

Herein, we synthesized SiO_2/C nanocomposites by coating with aniline onto the surface of SiO_2 nanospheres via a diazotization reaction and carbonizing treatment. The as prepared SiO_2/C nanocomposites are amorphous, and the SiO_2 particles are coated with carbon. Electrochemical measurements show that the SiO_2/C composites have a good electrochemical performance.

2. EXPERIMENTAL

2.1 Synthesis precursor of SiO_2 nanospheres

The SiO_2 nanospheres were synthesized according to the well known Stöber method [15]. 158 mL absolute ethanol, 7.8 mL ammonia, and 2.8 mL distilled water were introduced in a 250 mL round-bottom flask and heated to $50 \text{ }^\circ\text{C}$ under stirring, then 5.8 mL tetraethyl orthosilicate (TEOS) was added into the solution and stirred at $50 \text{ }^\circ\text{C}$ for 24 h; SiO_2 spheres were obtained by drying the white solution at $70 \text{ }^\circ\text{C}$ for 24 h.

2.2 Synthesis of SiO_2/C nanocomposites

SiO_2/C nanocomposites were synthesized by coating with aniline onto the surface of SiO_2 nanospheres via a diazotization reaction[16], followed by carbonization under Ar atmosphere. Firstly, 0.1 g pphenylenediamine was dissolved in 10 mL of distilled water (contained 1.2 mL of concentrated hydrochloric acid) under continuous stirring. 0.05 g of SiO_2 (as-prepared) was then added. Subsequently, 2 ml of a 1.0 M NaNO_2 solution was added into the above mixture. After this, the mixture was kept continuously stirring for 12 h. The above reaction was carried out in an ice-water bath. The resulting solution were treated by filtration and washed with ethanol and distilled water for several times, and dried at $80 \text{ }^\circ\text{C}$ under vacuum for 12 h. Finally, the SiO_2/C nanocomposites were obtained by carbonizing in a furnace at $400 \text{ }^\circ\text{C}$ 4 h and $600 \text{ }^\circ\text{C}$ 1 h under Ar atmosphere.

2.3 Materials characterization

X-ray powder diffraction (XRD) patterns of the products were recorded on a Philips X'pert X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54182 \text{ \AA}$). Fourier transfer infrared (FTIR) spectras were measured using an IFS-85 (Bruker) spectrometer. The microstructure was observed with a field-emitting scanning electron microscope (SEM, JEOL-JSM-6700F), and a high-resolution transmission electron microscope (HRTEM, JEOL-2010) with an accelerating voltage of 200 kV. Elemental analyses were carried out on a vario EL-III elemental analyzer (Germany).

Charge/discharge tests were carried out using CR 2016 coin-type cells. The active material, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80: 10: 10 were mixed homogeneously with N-methyl-pyrrolidone, the obtained slurry was pasted on Cu foil and dried at 110 °C for 12 h in vacuum. The electrode sheet typically had an active material of 1-2 mg cm⁻². The coin cell was assembled in an argon-filled glove box (Mikrouna, Super 1220/750/900, China) and was consist of SiO₂/C nanocomposites, Celgard 2400 (separator), and lithium foil. 1 mol L⁻¹ solution of LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 volume ratio) was used as the electrolyte. Galvanostatic charge/discharge measurements were performed in a potential range of 0.01-0.6 V at room temperature on a LAND-CT2001A instrument, and the final capacities were calculated based on weight of the Li₂MnSiO₄.

3. RESULTS AND DISCUSSION

Fig. 1a shows the XRD pattern of SiO₂ nanospheres and SiO₂/C nanocomposites. Two samples have similar XRD pattern. The broadened and weak peaks indicate that the SiO₂ nanospheres and SiO₂/C nanocomposites are completely amorphous[7][17]. At the same time, no obvious carbon related diffraction peaks can be detected, and the carbon content of SiO₂/C materials is confirmed to be 34.19% by elementary analysis. This means that the carbon is also amorphous. The structure of SiO₂ nanospheres and SiO₂/C nanocomposites is further investigated by FT-IR spectroscopy (Fig. 1b). Two samples also have similar spectrum. The typical bands of SiO₂ are clearly presented, which are 461 cm⁻¹, 800 cm⁻¹, 1081 cm⁻¹, respectively. Those modes can be attributed to the symmetric stretching and asymmetric stretching of the intertetrahedral oxygen atoms in the SiO₂ structure[10][18].

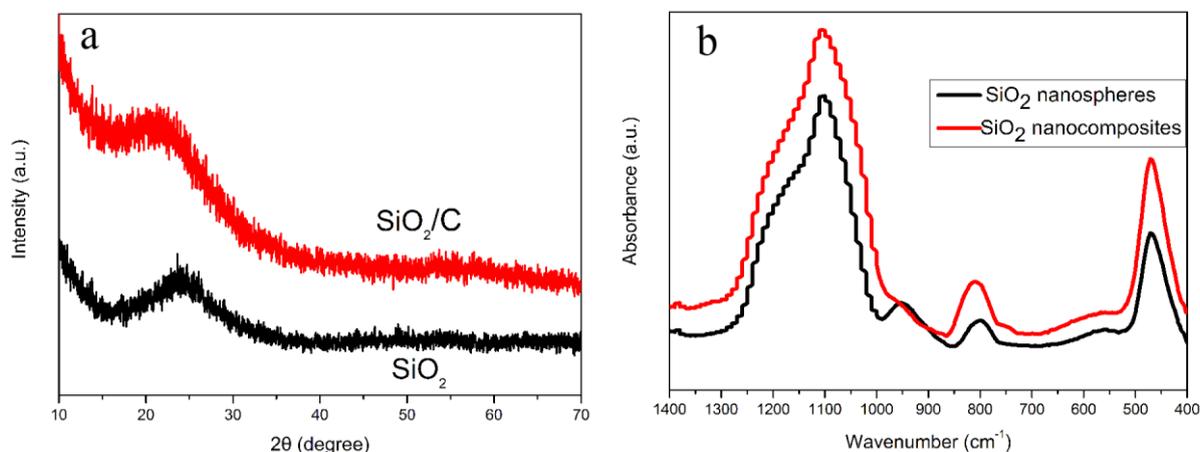


Figure 1. (a) XRD pattern of SiO₂ nanospheres and SiO₂/C nanocomposites, (b) FT-IR spectrum of the two samples.

Figure 2 shows SEM and TEM images of SiO₂ nanospheres and SiO₂/C nanocomposites. The monodisperse SiO₂ precursor exhibits spherical morphology with an average diameter of 50 nm (Fig

.2a). After diazotization reaction and carbonization, the as prepared SiO_2/C nanocomposites are agglomerated (Fig. 2b), SiO_2 particles and carbon are gathered together. And many pores can be seen from the sample. The TEM image (Fig. 2c) shows that the SiO_2/C nanocomposites have uniform morphology and an average size of 50 nm. The TEM image also clearly reveals the SiO_2 nanoparticles are coated by carbon and connected together. No ordered lattice fringes are observed in the HRTEM image of the SiO_2/C nanocomposites (Fig. 2d), which means that the as prepared composites are amorphous. This result is consisted with the XRD result. From this we can see that the SiO_2/C composites are successful prepare via a diazotization reaction and carbonization.

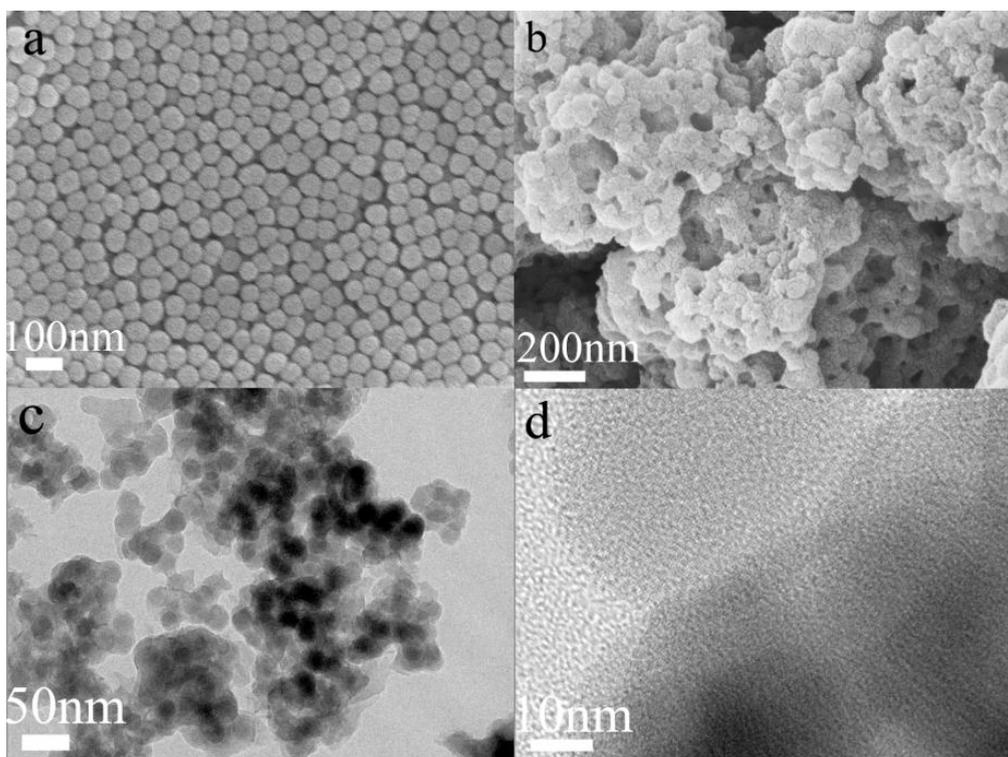


Figure 2. (a) SEM image of SiO_2 nanospheres, (b) SEM image of SiO_2/C nanocomposites, (c, d) TEM and HRTEM images of SiO_2/C nanocomposites.

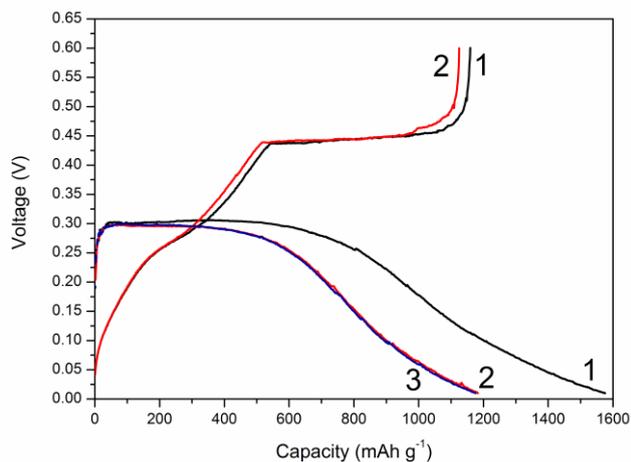


Figure 3. Charge and discharge curves of SiO_2/C nanocomposites under a current density of 100 mA g^{-1}

The as-prepared products were assembled into coin cells to test their electrochemical performances, the Galvanostatic charge-discharge measurements were carried out at 100 mA g^{-1} . Fig. 3 shows the charge–discharge curves of SiO_2/C nanocomposites at room temperature. The charge and discharge voltage plateau is around 0.35V . The composites exhibit an initial discharge capacity of 1575 mA h g^{-1} and charge capacity of 1235 mA h g^{-1} . The obvious decrease of the charge capacity compared to the discharge capacity during the initial cycle was attributed to the formation of an irreversible Li silicate (Li_4SiO_4) and some of the Li remained in the conducting agent (formation of solid electrolyte interphase) [7][10]. The discharge capacity decreases to 1200 mAh g^{-1} and 1183 mAh g^{-1} for the 2nd and 3th cycles, the composites exhibit good reversible capacity

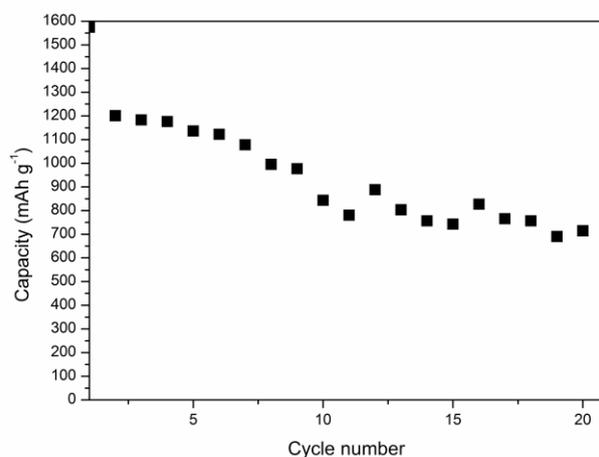


Figure 4. Cycling performance of SiO_2/C materials under a current density of 100 mA g^{-1}

Fig. 4 shows the discharge capacities and cyclic performances of SiO_2/C nanocomposites. The second discharge capacity is 1200 mAh g^{-1} . After 20 cycles, it remain keep a high discharge capacity

of 714.4 mAh g⁻¹. It is obvious that the SiO₂/C composites exhibit good electrical properties. Compared with the recently works, our composites shows higher specific capacity. For example, Chang et al. [7] reported about milled SiO₂, which exhibited a reversible capacity of 800 mA h g⁻¹. As for the composites, Dai et al.[10] successful prepared amorphous Si/SiO_x/SiO₂ nanocomposites, while the composites only show a stable cycling capacity of 600 mAh g⁻¹.

The good electrochemical performance of the SiO₂/C nanocomposites could be attributed to the to the nano-sized particles and the amorphous structure of SiO₂/C composites. The carbon and nano-sized SiO₂ ensure the fast and continuous transportation of electrons in the electrode, which is favorable for electrons moving unimpeded over nanoparticles to attain a good electrical properties, resulting in an increase in the utilization of the active materials[14]. In addition, the amorphous structure of the composites could prevent pulverization of particles during Li⁺ insertion[10].

4. CONCLUSIONS

In summary, SiO₂/C nanocomposites SiO₂/C nanocomposites have been prepared by coating with aniline onto the surface of SiO₂ nanospheres via a diazotization reaction and carbonizing treatment. The SiO₂/C nanocomposites are amorphous, and the SiO₂ particles are coated with carbon. Electrochemical measurements show that the SiO₂/C composites have a good electrochemical performance. The carbon and nano-sized SiO₂ is favorable for improving their electrical properties.

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