

Short Communication

## Synthesis of SiO<sub>2</sub>/C Nanocomposites and Their Electrochemical Properties

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SiO<sub>2</sub>/C nanocomposites have been prepared by coating with aniline onto the surface of SiO<sub>2</sub> nanospheres via a diazotization reaction and carbonizing treatment. The XRD pattern and High-resolution transmission electron microscope (HRTEM) show that the amorphous SiO<sub>2</sub> nanoparticles are coated with carbon. The carbon content of SiO<sub>2</sub>/C nanocomposites is confirmed to be 34.19% by elementary analysis. Electrochemical measurements show that the SiO<sub>2</sub>/C composites have a good electrochemical performance; they exhibit a discharge capacity of 1200 mAh g<sup>-1</sup> on the second cycle, and 714.4 mAh g<sup>-1</sup> on the 20th cycle under a current density of 100 mA g<sup>-1</sup>.

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**Keywords:** SiO<sub>2</sub>/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<sup>-1</sup> 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, SiO<sub>2</sub> 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, SiO<sub>2</sub> 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 SiO<sub>2</sub> by using commercially SiO<sub>2</sub> (Quartz,) powder as

precursor, it showed a reversible capacity of  $800 \text{ mA h g}^{-1}$  and good cycling stability under a current density of  $100 \text{ mA g}^{-1}$ . Up to now, there are many reports on the preparation of nano-sized  $\text{SiO}_2$  to achieve good electrochemical performance[8,9]. In addition, carbon coating is an effective way for most  $\text{SiO}_x$  materials to improve their electrochemical performance[10-13], while the reports about synthesis of  $\text{SiO}_2/\text{C}$  nanocomposites are relatively less[14].

Herein, we synthesized  $\text{SiO}_2/\text{C}$  nanocomposites by coating with aniline onto the surface of  $\text{SiO}_2$  nanospheres via a diazotization reaction and carbonizing treatment. The as prepared  $\text{SiO}_2/\text{C}$  nanocomposites are amorphous, and the  $\text{SiO}_2$  particles are coated with carbon. Electrochemical measurements show that the  $\text{SiO}_2/\text{C}$  composites have a good electrochemical performance.

## 2. EXPERIMENTAL

### 2.1 Synthesis precursor of $\text{SiO}_2$ nanospheres

The  $\text{SiO}_2$  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;  $\text{SiO}_2$  spheres were obtained by drying the white solution at  $70 \text{ }^\circ\text{C}$  for 24 h.

### 2.2 Synthesis of $\text{SiO}_2/\text{C}$ nanocomposites

$\text{SiO}_2/\text{C}$  nanocomposites were synthesized by coating with aniline onto the surface of  $\text{SiO}_2$  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  $\text{SiO}_2$  (as-prepared) was then added. Subsequently, 2 ml of a 1.0 M  $\text{NaNO}_2$  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  $\text{SiO}_2/\text{C}$  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.

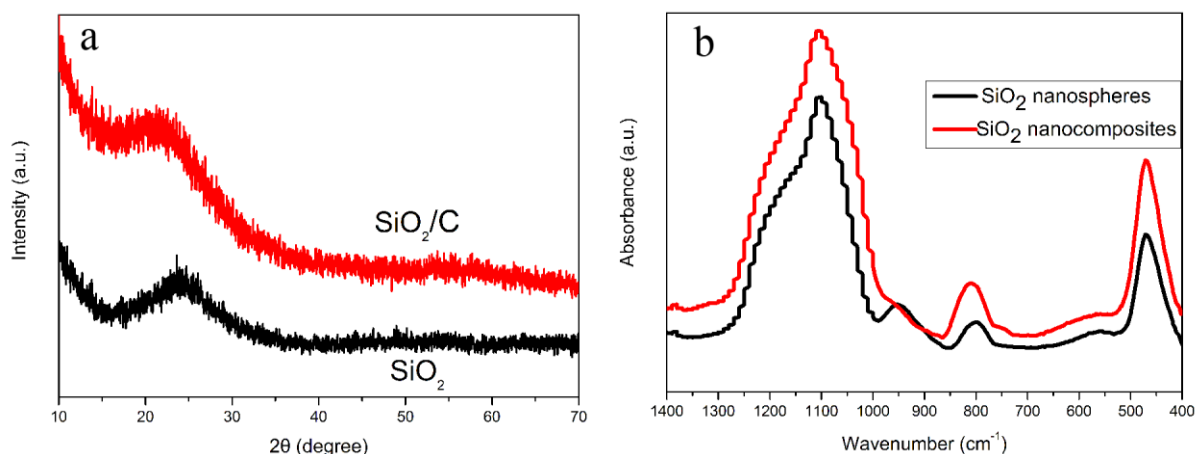
### 2.3 Materials characterization

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<sup>-2</sup>. The coin cell was assembled in an argon-filled glove box (Mikrouna, Super 1220/750/900, China) and was consist of SiO<sub>2</sub>/C nanocomposites, Celgard 2400 (separator), and lithium foil. 1 mol L<sup>-1</sup> solution of LiPF<sub>6</sub> 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 Li<sub>2</sub>MnSiO<sub>4</sub>.

### 3. RESULTS AND DISCUSSION

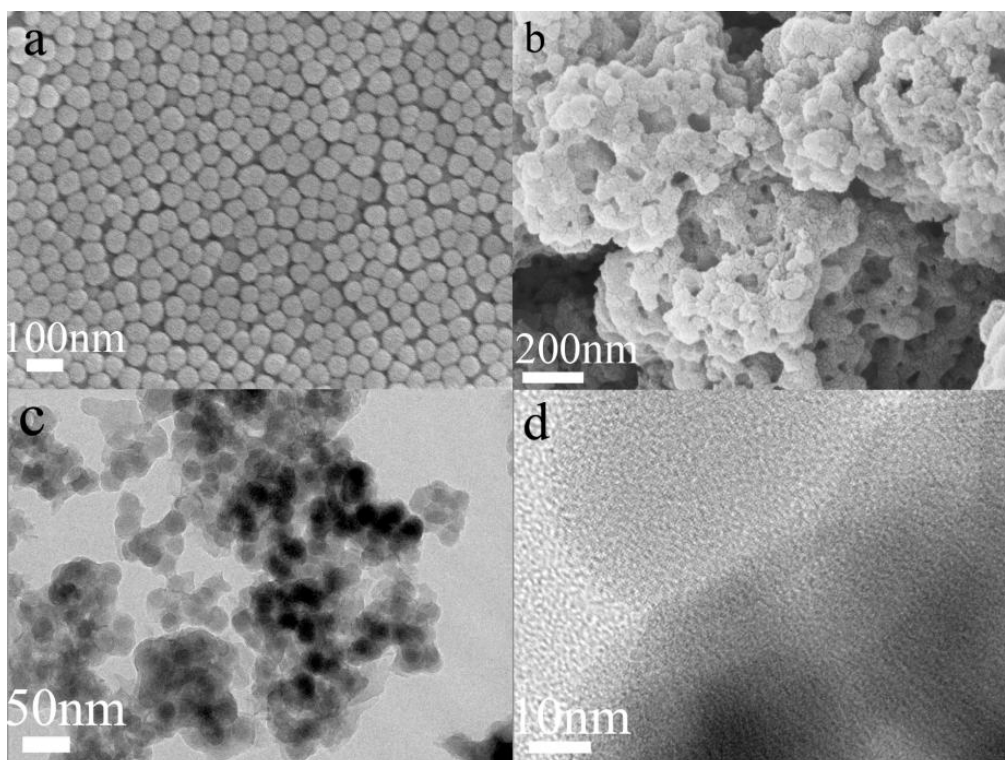
Fig. 1a shows the XRD pattern of SiO<sub>2</sub> nanospheres and SiO<sub>2</sub>/C nanocomposites. Two samples have similar XRD pattern. The broadened and weak peaks indicate that the SiO<sub>2</sub> nanospheres and SiO<sub>2</sub>/C nanocomposites are completely amorphous[7][17]. At the same time, no obvious carbon related diffraction peaks can be detected, and the carbon content of SiO<sub>2</sub>/C materials is confirmed to be 34.19% by elementary analysis. This means that the carbon is also amorphous. The structure of SiO<sub>2</sub> nanospheres and SiO<sub>2</sub>/C nanocomposites is further investigated by FT-IR spectroscopy (Fig. 1b). Two samples also have similar spectrum. The typical bands of SiO<sub>2</sub> are clearly presented, which are 461 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, 1081 cm<sup>-1</sup>, respectively. Those modes can be attributed to the symmetric stretching and asymmetric stretching of the intertetrahedral oxygen atoms in the SiO<sub>2</sub> structure[10][18].



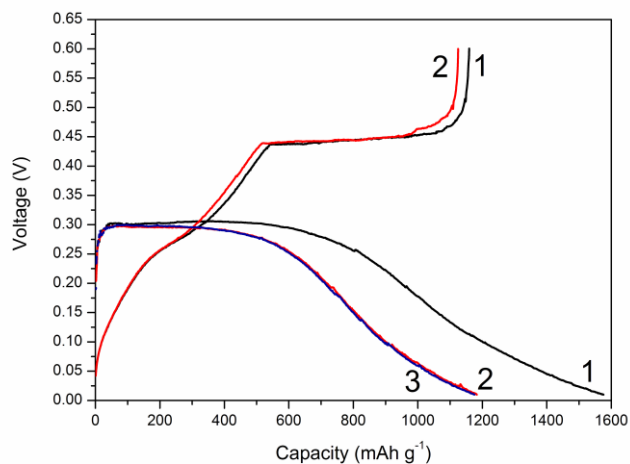
**Figure 1.** (a) XRD pattern of SiO<sub>2</sub> nanospheres and SiO<sub>2</sub>/C nanocomposites, (b) FT-IR spectrum of the two samples.

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

.2a). After diazotization reaction and carbonization, the as prepared  $\text{SiO}_2/\text{C}$  nanocomposites are agglomerated (Fig. 2b),  $\text{SiO}_2$  particles and carbon are gathered together. And many pores can be seen from the sample. The TEM image (Fig. 2c) shows that the  $\text{SiO}_2/\text{C}$  nanocomposites have uniform morphology and an average size of 50 nm. The TEM image also clearly reveals the  $\text{SiO}_2$  nanoparticles are coated by carbon and connected together. No ordered lattice fringes are observed in the HRTEM image of the  $\text{SiO}_2/\text{C}$  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  $\text{SiO}_2/\text{C}$  composites are successful prepare via a diazotization reaction and carbonization.

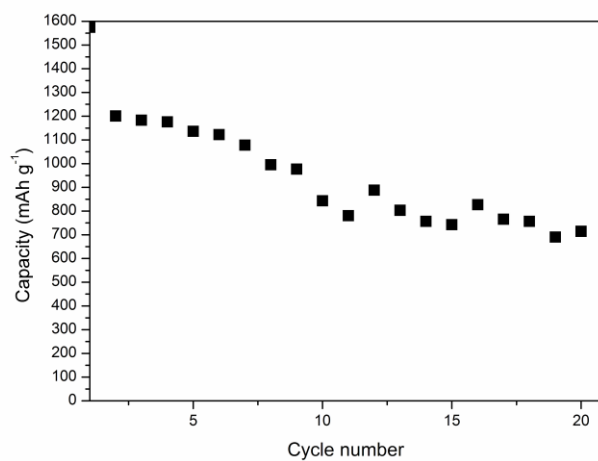


**Figure 2.** (a) SEM image of  $\text{SiO}_2$  nanospheres, (b) SEM image of  $\text{SiO}_2/\text{C}$  nanocomposites, (c, d) TEM and HRTEM images of  $\text{SiO}_2/\text{C}$  nanocomposites.



**Figure 3.** Charge and discharge curves of  $\text{SiO}_2/\text{C}$  nanocomposites under a current density of  $100 \text{ mA g}^{-1}$

The as-prepared products were assembled into coin cells to test their electrochemical performances, the Galvanostatic charge-discharge measurements were carried out at  $100 \text{ mA g}^{-1}$ . Fig. 3 shows the charge-discharge curves of  $\text{SiO}_2/\text{C}$  nanocomposites at room temperature. The charge and discharge voltage plateau is around  $0.35\text{V}$ . The composites exhibit an initial discharge capacity of  $1575 \text{ mA h g}^{-1}$  and charge capacity of  $1235 \text{ mA h g}^{-1}$ . 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 ( $\text{Li}_4\text{SiO}_4$ ) and some of the Li remained in the conducting agent (formation of solid electrolyte interphase) [7][10]. The discharge capacity decreases to  $1200 \text{ mAh g}^{-1}$  and  $1183 \text{ mAh g}^{-1}$  for the 2nd and 3th cycles, the composites exhibit good reversible capacity



**Figure 4.** Cycling performance of  $\text{SiO}_2/\text{C}$  materials under a current density of  $100 \text{ mA g}^{-1}$

Fig. 4 shows the discharge capacities and cyclic performances of  $\text{SiO}_2/\text{C}$  nanocomposites. The second discharge capacity is  $1200 \text{ mAh g}^{-1}$ . After 20 cycles, it remain keep a high discharge capacity

of 714.4 mAh g<sup>-1</sup>. It is obvious that the SiO<sub>2</sub>/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 SiO<sub>2</sub>, which exhibited a reversible capacity of 800 mA h g<sup>-1</sup>. As for the composites, Dai et al.[10] successful prepared amorphous Si/SiO<sub>x</sub>/SiO<sub>2</sub> nanocomposites, while the composites only show a stable cycling capacity of 600 mAh g<sup>-1</sup>.

The good electrochemical performance of the SiO<sub>2</sub>/C nanocomposites could be attributed to the to the nano-sized particles and the amorphous structure of SiO<sub>2</sub>/C composites. The carbon and nano-sized SiO<sub>2</sub> 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<sup>+</sup> insertion[10].

#### 4. CONCLUSIONS

In summary, SiO<sub>2</sub>/C nanocomposites SiO<sub>2</sub>/C nanocomposites have been prepared by coating with aniline onto the surface of SiO<sub>2</sub> nanospheres via a diazotization reaction and carbonizing treatment. The SiO<sub>2</sub>/C nanocomposites are amorphous, and the SiO<sub>2</sub> particles are coated with carbon. Electrochemical measurements show that the SiO<sub>2</sub>/C composites have a good electrochemical performance. The carbon and nano-sized SiO<sub>2</sub> is favorable for improving their electrical properties.

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#### References

1. J. Dahn, T. Zheng, Y. Liu, J. Xue, *Science*, 270 (1995) 590.
2. M. Miyachi, H. Yamamoto, H. Kawai, T. Ohta, M. Shirakata; *J. Electrochem. Soc.*, 152 (2005) A2089.
3. B. Guo, J. Shu, Z. Wang, H. Yang, L. Shi, Y. Liu, L. Chen, *Electrochem. Commun.*, 10 (2008) 1876.
4. Q. Sun, B. Zhang, Z.-W. Fu, *Appl. Surf. Sci.*, 254 (2008) 3774.
5. D. Fu, B. Luan, S. Argue, M.N. Bureau, I.J. Davidson, *J. Power Sources*, 206 (2012) 325..
6. Y.-S. Lee, S.H. Ju, J.-H. Kim, S.S. Hwang, J.-M. Choi, Y.-K. Sun, H. Kim, B. Scrosati, D.-W. Kim, *Electrochem. Commun.*, 17 (2012) 18..
7. W.-S. Chang, C.-M. Park, J.-H. Kim, Y.-U. Kim, G. Jeong, H.-J. Sohn, *Energy Environ. Sci.*, 5 (2012) 6895.
8. Q. Sun, B. Zhang, Z.-W. Fu, *Appl. Surf. Sci.*, 254 (2008) 3774.
9. K.C. Leonard, W.E. Suyama, M.A. Anderson, *Electrochim. Acta*, 56 (2011) 10137.
10. F. Dai, R. Yi, M.L. Gordin, S. Chen, D. Wang, *RSC Adv.*, 2 (2012) 12710.

11. H. Nara, T. Yokoshima, T. Momma, T. Osaka, *Energy Environ. Sci.*, 5 (2012) 6500.
12. T. Morita, N. Takami; *J. Electrochem., Soc.*, 153 (2006), A425.
13. J.-H. Kim, H.-J. Sohn, H. Kim, G. Jeong, W. Choi, *J. Power Sources*, 170 (2007) 456.
14. T. Doi, M. Tagashira, Y. Iriyama, T. Abe, Z. Ogumi, *J. Appl. Electrochem.*, 42 (2012) 69.
15. S.-W. Zhang, S.-X. Zhou, Y.-M. Weng, L.-M. Wu, *Langmuir*, 21 (2005) 2124.
16. C. Du, M. Chen, L. Wang, G. Yin, *J. Mater. Chem.*, 21 (2011) 15692.
17. L. Ji, Z. Lin, A.J. Medford, X. Zhang, *Carbon*, 47 (2009) 3346-3354.
18. N. Primeau, C. Vautey, M. Langlet, *Thin Solid Films*, 310 (1997) 47-56.