

Controllable synthesis of carbon coated SiO_x particles through a simultaneous reaction between hydrolysis-condensation of tetramethyl orthosilicate and polymerization of 3-aminophenol

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1. Introduction

Core-shell particles have recently received considerable attention as highly functional materials for energy and environmental applications due to their unique and fascinating properties.¹ Although many methods have been developed for the preparation of core-shell particles, the precise design and control of their structure still remains a great challenge.

In this work, we report a fundamental modification of the synthetic process by utilizing tetramethyl orthosilicate (TMOS) as a silica precursor rather than the conventionally used tetraethyl orthosilicate (TEOS). We propose a strategy to synthesize carbon coated SiO_x (SiO_x@C) core-shell particles via a sol-gel method. The fabrication process using the simultaneous hydrolysis-condensation of TMOS and polymerization of 3-aminophenol and formaldehyde in the presence of ammonia as a basic catalyst and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant in the mixed solution of water and methanol, generating 3-aminophenol/formaldehyde (APF) resin coated SiO₂ (SiO₂@APF resin) core-shell particles. It can be converted into carbon through a simple carbonization process to obtain the SiO_x@C particles. Results from this study provide new insight into the design of core-shell particles by using TMOS as an effective silica precursor for the first time with well-controlled reaction rate and spherical morphology. These core-shell particles will give a great potential interest because the constituent materials have complementary properties: the carbon shell has high electrical conductivity, whereas the silica core is easily functionalized. To demonstrate the benefits of core-shell structure in energy storage, the performance of SiO_x@C as an anode material for lithium-ion batteries (LIBs) is evaluated.

2. Experimental Method

In a typical procedure synthesis of SiO_x@C particles, an aqueous solution was prepared by stirring 3-aminophenol, ammonia solution, and ultrapure water at room temperature until a clear solution was obtained. CTAB dissolved in methanol

was added to the solution and the mixture was stirred for 15 min. TMOS and formaldehyde were simultaneously added to the solution. The mixture was subjected to microwave irradiation with the temperature set at 40°C. After 15 min, the temperature was elevated to 70°C and kept constant for 75 min. The obtained particles were separated from the solution by centrifugation and washed several times with ultrapure water and ethanol to remove the remaining impurities. After drying, the particles were carbonized by heat treatment in a nitrogen atmosphere (1.0 L min⁻¹) for 3 h at 1200°C.

3. Results and Discussion

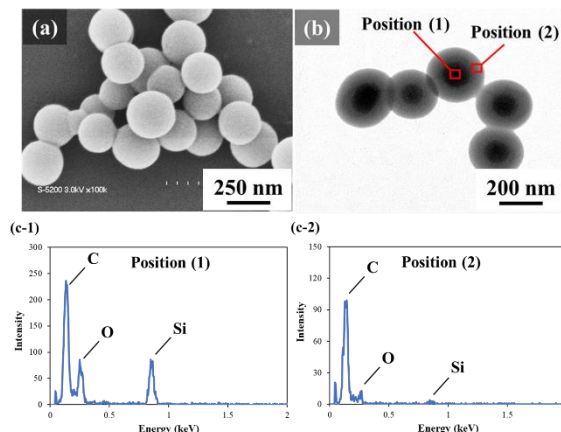


Fig. 1. (a) SEM, (b) TEM, and (c) EDX images of SiO₂@APF resin particles.

The core-shell particles with highly uniform spherical morphology were successfully formed as shown in the SEM and TEM results (Fig. 1(a) and 1(b)). The TEM image in Fig. 1(b) implied that the coating of APF resin was well-distributed outside as the shell and most part of SiO₂ particles act as the core were inserted. A clear contrast gap can be distinguished between the core and the shell, which further demonstrated the core-shell structure. In addition, EDX analysis was further confirmed the elemental distribution of carbon, silicon, and oxygen in this sample. As seen in Fig. 1(c-1) and 1(c-2), the contents of silicon and oxygen elements inside the obtained particles were higher than those outside.

The SiO₂@APF resin particles can be readily converted into carbon through a simple

carbonization process in a nitrogen atmosphere at 1200°C to obtain the SiO_x@C particles, which maintained their structural integrity and spherical morphology, as can be observed in the SEM and TEM images in Fig. 2(a). For a better understanding of the characteristics of SiO_x@C particles, different characterizations were carried out as shown in Fig. 2(b-g). The TGA result (Fig. 2(b)) demonstrated that the SiO_x content in the SiO_x@C particles was approximately 33.3 wt%. The XPS results (Fig. 2(c-e)) indicated that there were different chemical states of Si in SiO_x, which was probably caused by the carbothermal reduction occurring between silica and carbon during the heating process. As shown in the Raman spectroscopy (Fig. 2(f)), two obvious characteristic peaks corresponding to the D band (1362 cm⁻¹) and G band (1589 cm⁻¹) were clearly observed, indicating that the successful transformation of APF shell into a conductive carbon layer through the high temperature treatment. The nitrogen adsorption-desorption isotherms of SiO_x@C particles (Fig. 2(g)) showed a high BET specific surface area of 139 m²g⁻¹ and the total pore volume of 0.11 cm³g⁻¹.

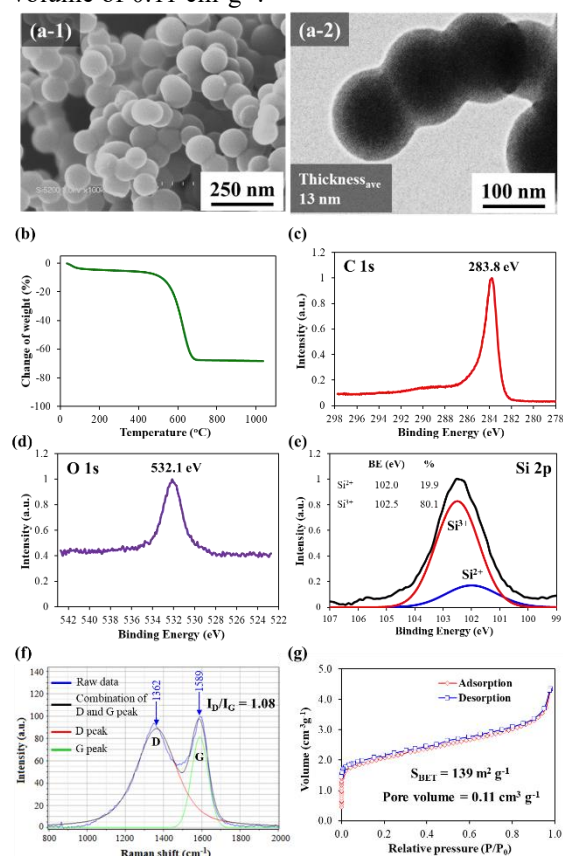


Fig. 2. (a) SEM and TEM images; (b) TGA curve; (c), (d) and (e) XPS spectra of C 1s, O 1s and Si 2p, respectively; (f) Raman spectrum; and (g) Nitrogen adsorption-desorption isotherms of SiO_x@C particles.

The electrochemical activity of SiO_x@C particles in lithium storage was investigated as the anode

material for LIBs (Fig. 3). The obtained SiO_x@C particles delivered a reversible capacity of 509.2 mAh g⁻¹ at 100 mA g⁻¹ and the capacity retention was approximately 80% after 100 cycles. The significantly improved electrochemical performance in comparison with that reported in our previous paper² can be explained by the structure of material. The SiO_x@C particles with core-shell structure guarantee an optimum contact with the carbon matrix and the round shape of carbon shell is highly resilient toward stress. These will contribute to improving the conductivity of SiO_x and exerting the function of carbon.

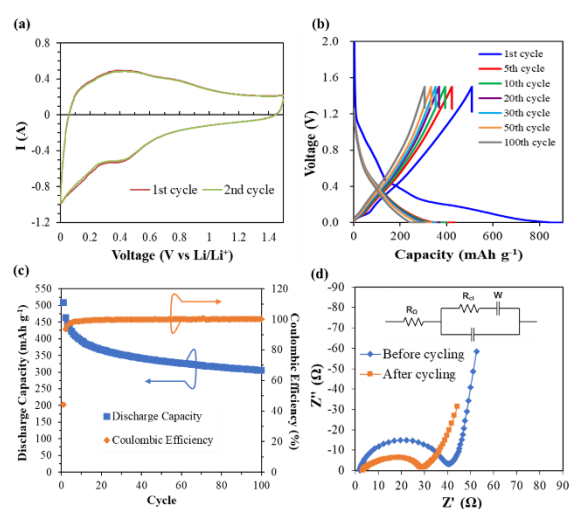


Fig. 3. (a) Cyclic voltammogram, (b) Galvanostatic charge-discharge profile, (c) Cyclic performance, and (d) Nyquist plots of SiO_x@C particles.

4. Conclusion

In summary, we have successfully synthesized SiO_x@C core-shell particles via a sol-gel method followed by carbonization process, using TMOS instead of the traditionally used TEOS. The core-shell particles can be obtained with structural integrity and spherical morphology, which makes TMOS as an excellent silica precursor and renders this approach attractive for future applications. The electrochemical performance of SiO_x@C particles was significantly better than those achieved in our previously reported studies owing to the morphology and structure of material. These results suggest that the use of TMOS and our developed synthetic strategy will open up new opportunities for the development of functional SiO_x@C particles with core-shell structure for diverse applications.

5. References

1. T. Ogi et al., *Adv. Powder Technol.* **2014**, *25*(1), 3–17.
2. T. Izawa et al., *Mater. Res. Bull.* **2019**, *112*, 16–21.