

Hierarchical Mn₂O₃ Microspheres In-Situ Coated with Carbon for Supercapacitors with Highly Enhanced Performances

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1. The Dynamic Structure Evolution of Precursor Microspheres

In order to investigate the formation of MnCO₃ precursor microspheres in the reactions, dynamic evolution (Figure S1) of the microsphere structures was performed by conducting the reaction from 1 to 24 hours. It was found that sphere-like particles of $1.35 \pm 0.36 \mu\text{m}$ in diameter together with a lot of small nanoparticles (Figure S1a) were generated after reacting for 1 hour. MnCO₃ nanoparticles, which nucleate rapidly in the reaction, act as seeds to grow sphere-like particles with rough surfaces. After reacting for 2 hours, however, microspheres of $1.95 \pm 0.47 \mu\text{m}$ (Figure S1b) were produced in the reaction on a large scale, and the smaller nanoparticles completely disappeared in the system. The microspheres further grown into bigger in diameter of $2.05 \pm 0.37 \mu\text{m}$ (Figure S1c) and $3.96 \pm 0.55 \mu\text{m}$ (Figure S1d) after prolonging the reaction time to 6 and 12 hours, respectively. The bigger microspheres also possess smoother surfaces in consuming of smaller nanoparticles. The Ostwald ripening mechanism can be applied to explain the disappearances of smaller nanoparticles with higher energy and the growth of microspheres with bigger size and smoother surfaces. The uniformity of the microspheres can be improved dramatically after performing the reaction for 12 hours. However, the microspheres with smaller diameters and rougher surfaces were again produced after further conducting the reactions for 18 and 24 hours as shown in Figure S1e-f, respectively.

The precursor microspheres with different diameters as shown in Figure S2 can be also produced on a large scale by performing reaction at 120, 140, 180 and 200 °C, respectively. It is convenient for us to control the sizes of MnCO₃ microspheres by simply adjusting the reaction time and temperature.

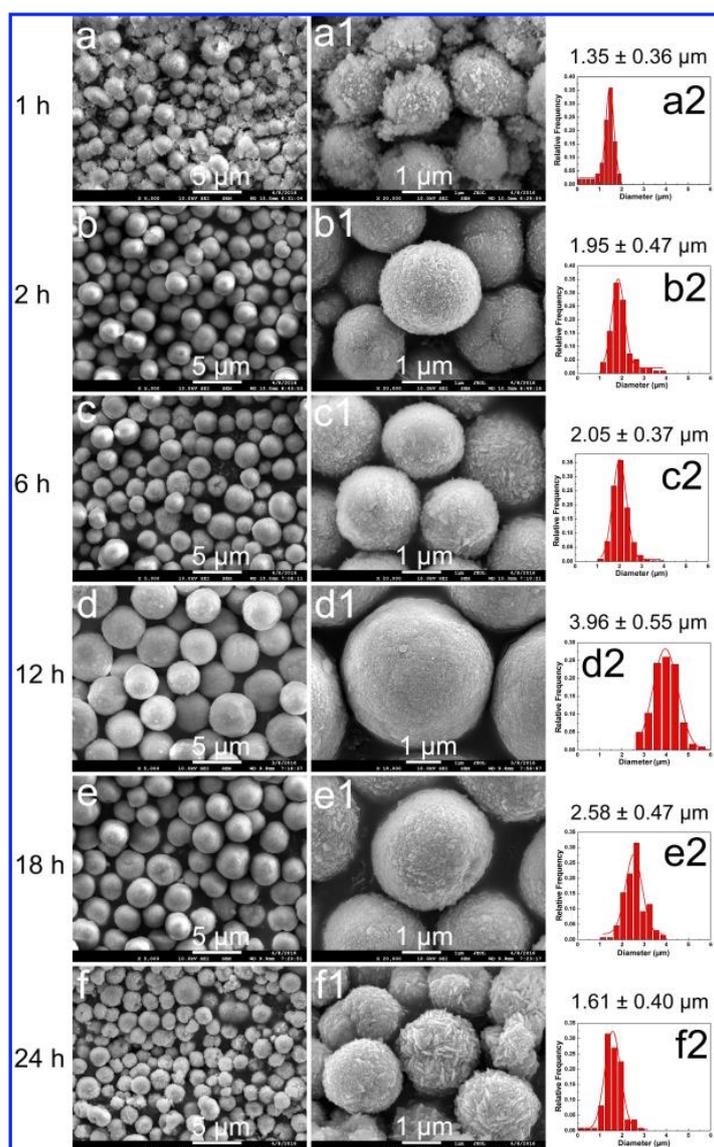


Figure S1. (a–f) Low and (a1–f1) high magnification FESEM images and (a2–f2) size distributions of MnCO_3 microspheres synthesized at 160 °C for 1, 2, 6, 12, 18 and 24 h, respectively.

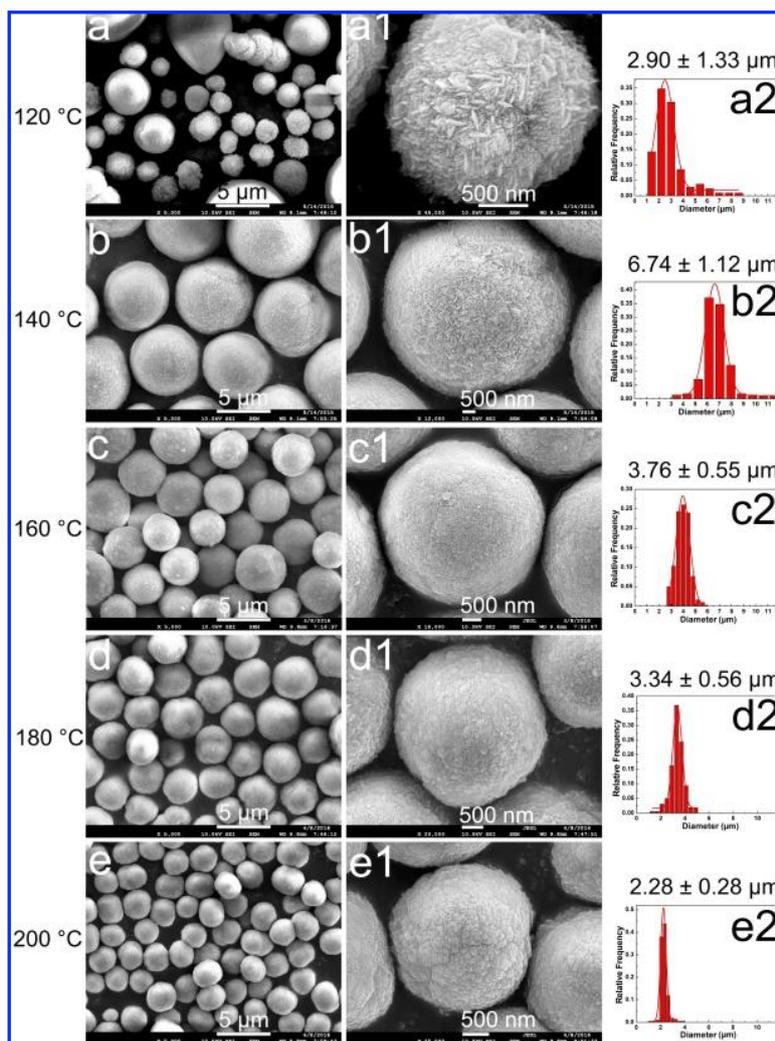


Figure S2. (a–f) Low, (a1–f1) high magnification FESEM images and (a2–f2) size distribution of MnCO_3 microspheres synthesized at 120, 140, 160, 180 and 200 °C, respectively.

2. Xps Spectra of Precursor Microspheres before and after Annealed At 500 °C

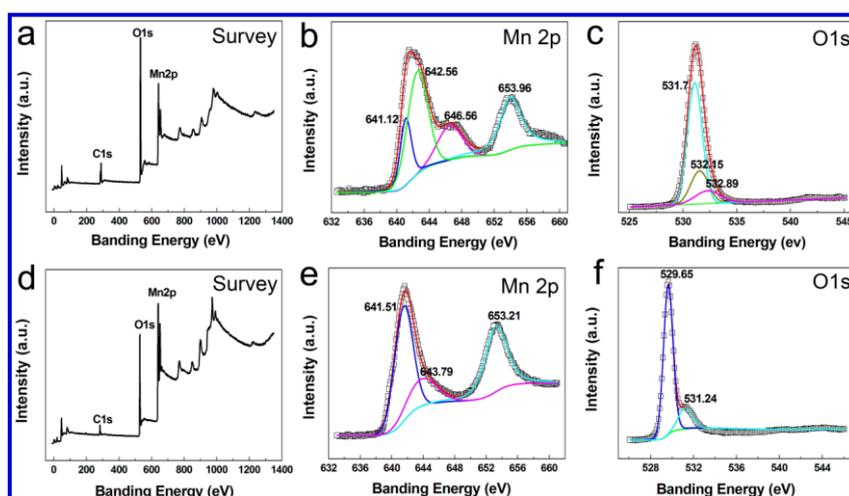


Figure S3. XPS spectra of MnCO_3 precursor and $\text{GC@Mn}_2\text{O}_3$ microspheres Surveys of (a) MnCO_3 and (d) $\text{GC@Mn}_2\text{O}_3$ microspheres, Mn-2p core-level XPS spectra of (b) MnCO_3 and (e) $\text{GC@Mn}_2\text{O}_3$, and O-1s core-level XPS spectra of (c) MnCO_3 and (f) $\text{GC@Mn}_2\text{O}_3$.

3. Electrochemical Properties of Active Carbon (Ac)

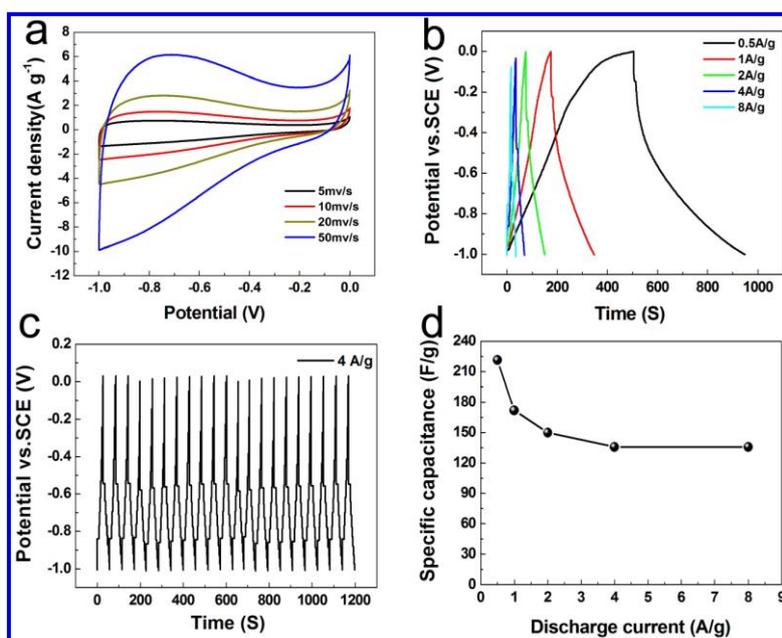


Figure S4. Electrochemical properties of electrodes made with active carbon. (a) CV curves at different scan rates, (b) galvanostatic charge/discharge curves at different current densities, (c) cycle stability at current density of 4 A g⁻¹, and specific capacitances at different current densities.

4. Electrochemical Properties of Materials After Annealed at 400 °C

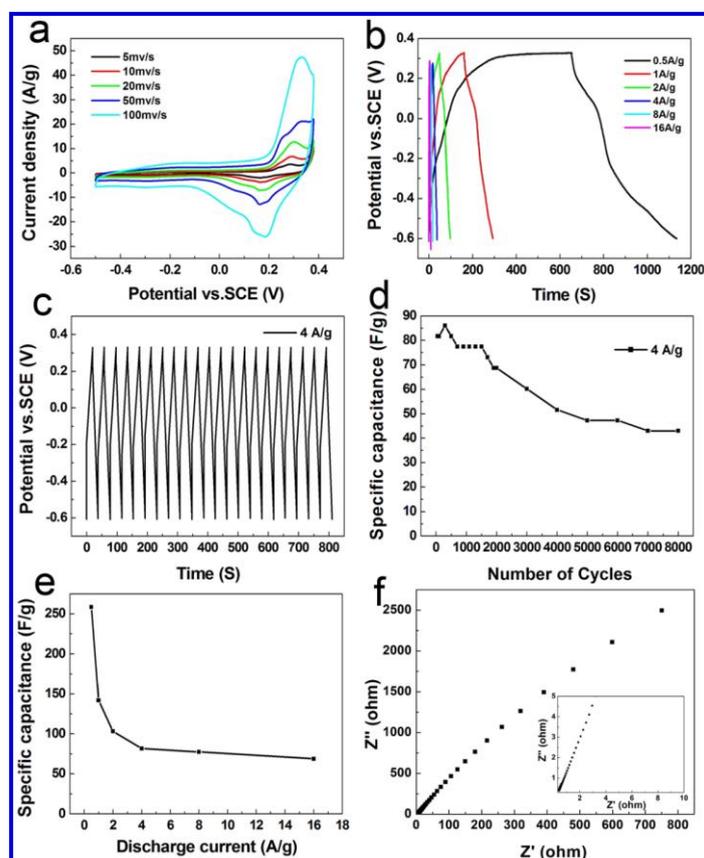


Figure S5. Electrochemical properties of electrodes made with monodispersed microspheres after annealed at 400 °C. (a) CV curves at different scan rates, (b) galvanostatic charge/discharge curves at

different current densities, (c,d) cycle stability at current density of 4 A g⁻¹, (e) specific capacitances at different current densities and (f) EIS spectrum.

5. Electrochemical Properties of Materials After Annealed At 600 °C

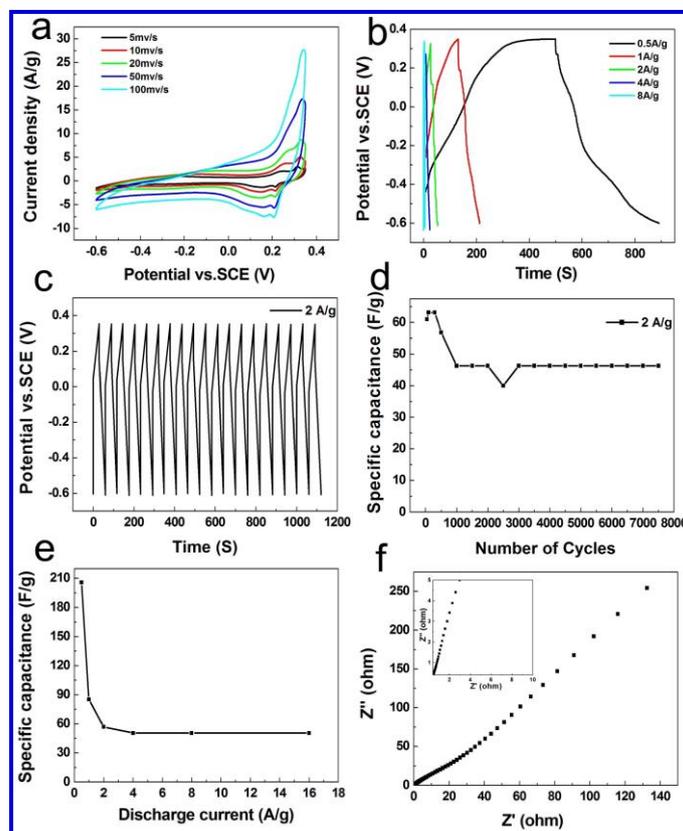


Figure S6. The electrochemical properties of electrodes made with monodispersed microspheres after annealed at 600 °C. (a) CV curves at different scan rates, (b) galvanostatic charge/discharge curves at different current densities, (c,d) cycle stability at current density of 2 A g⁻¹, (e) specific capacitances at different current densities and (f) EIS spectrum.