

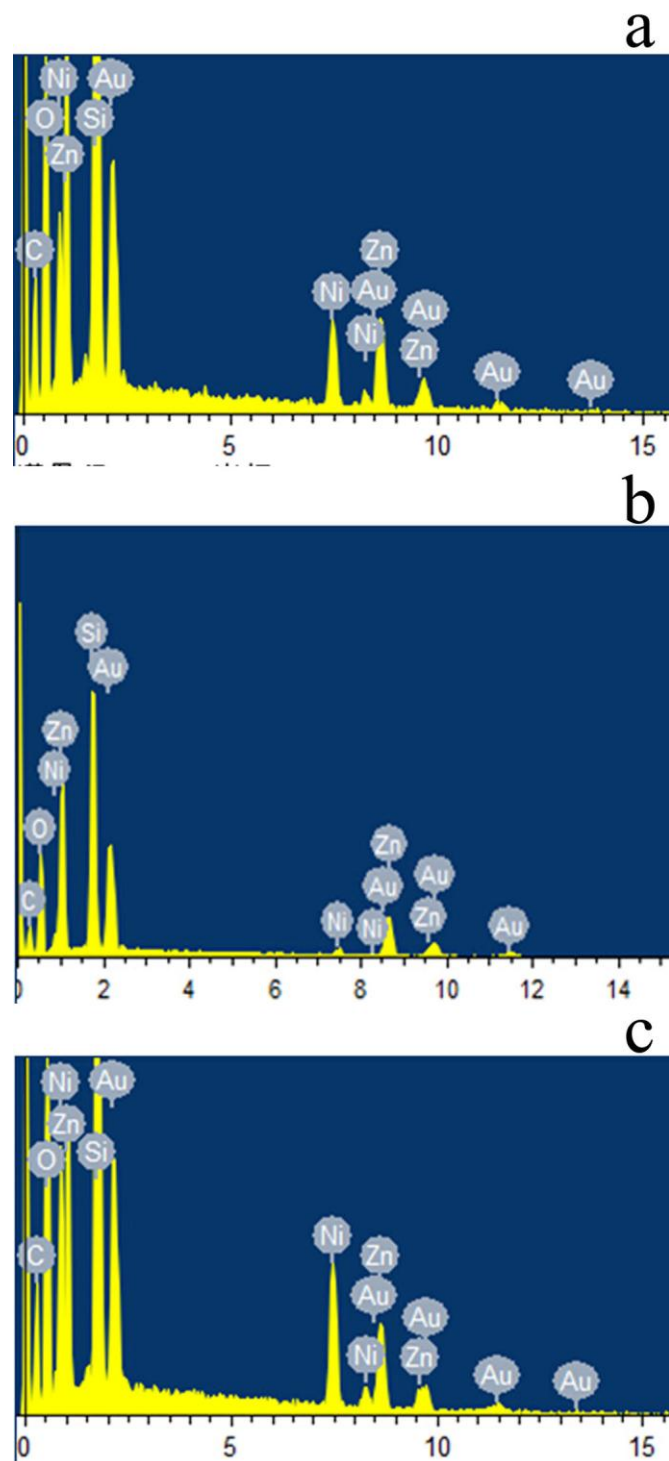
Supplementary Information

Facile fabrication of various zinc-nickel citrate microspheres and their transformation to ZnO-NiO hybrid microspheres with excellent lithium storage properties

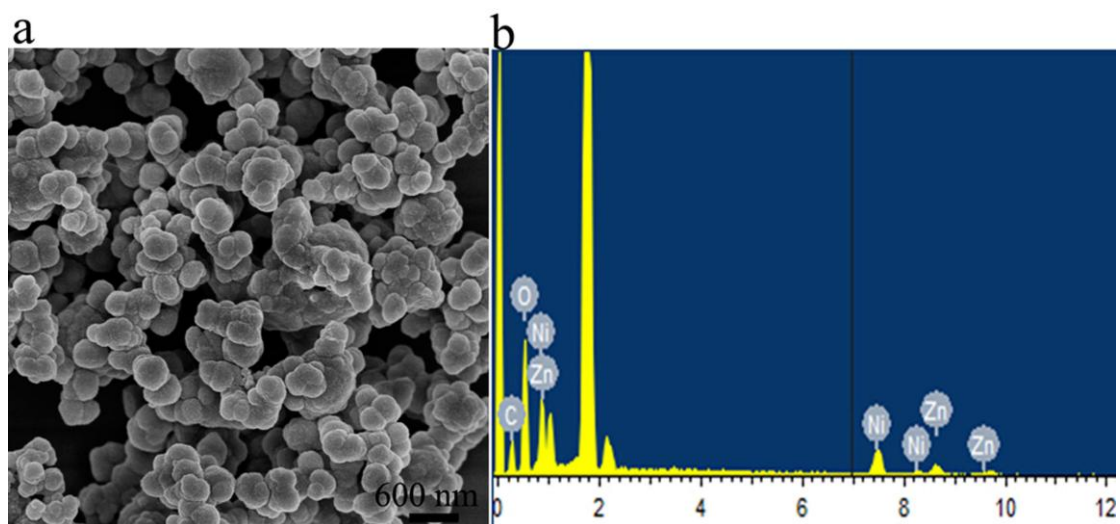
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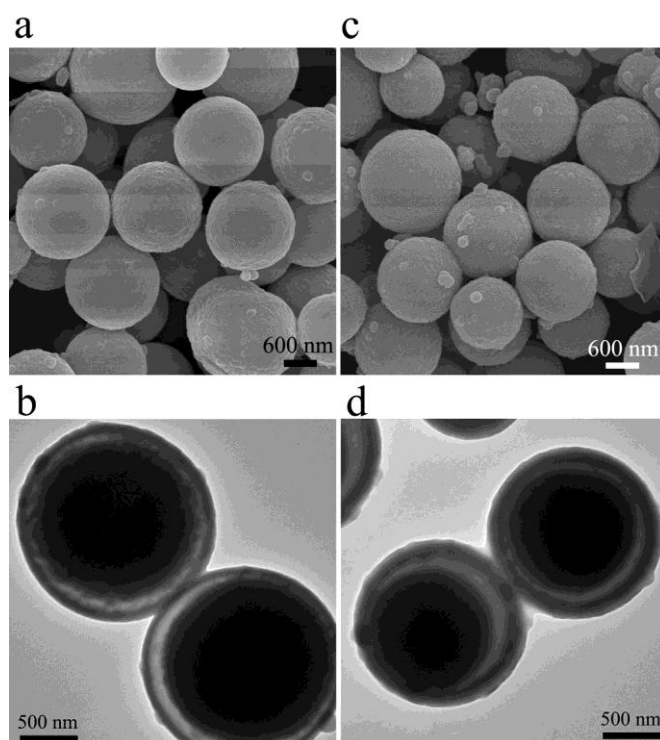
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Supplementary Figure S1-EDS spectra of zinc-nickel citrate yolk-shell (a), solid (b) and hollow (c) microspheres. The Si and Au signals come from substrates and the coated conductive Au layer for SEM observation, respectively.



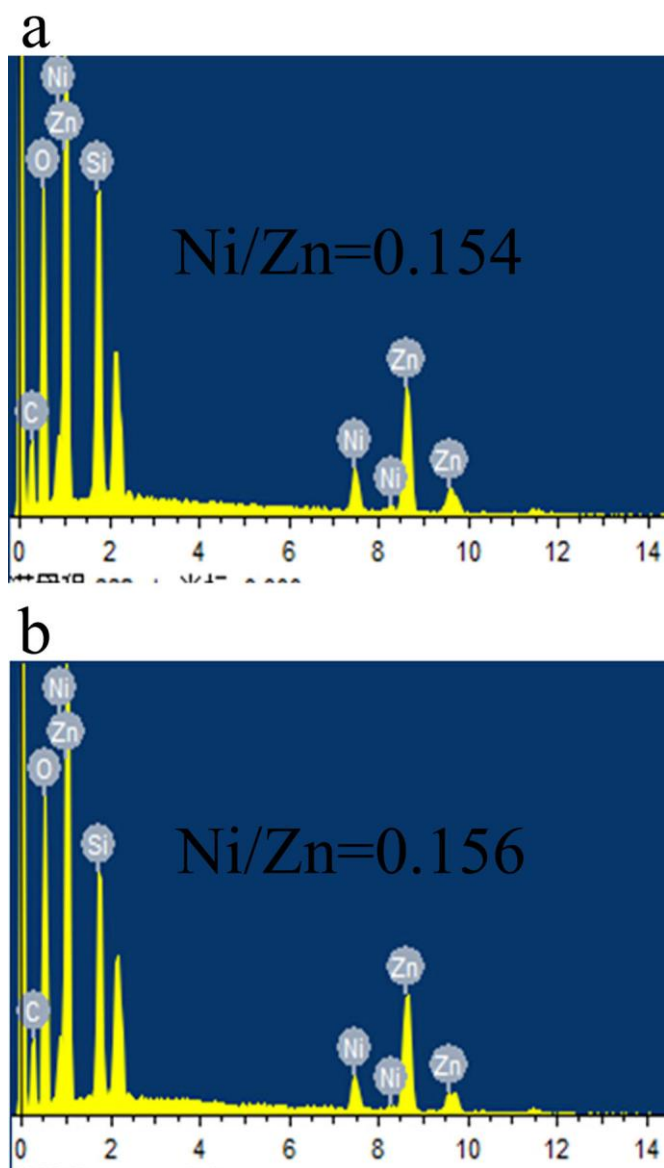
Supplementary Figure S2-The SEM image (a) and EDS spectrum (b) of zinc-nickel citrate obtained from 0.3 M of nickel nitrate solution for 1 h.



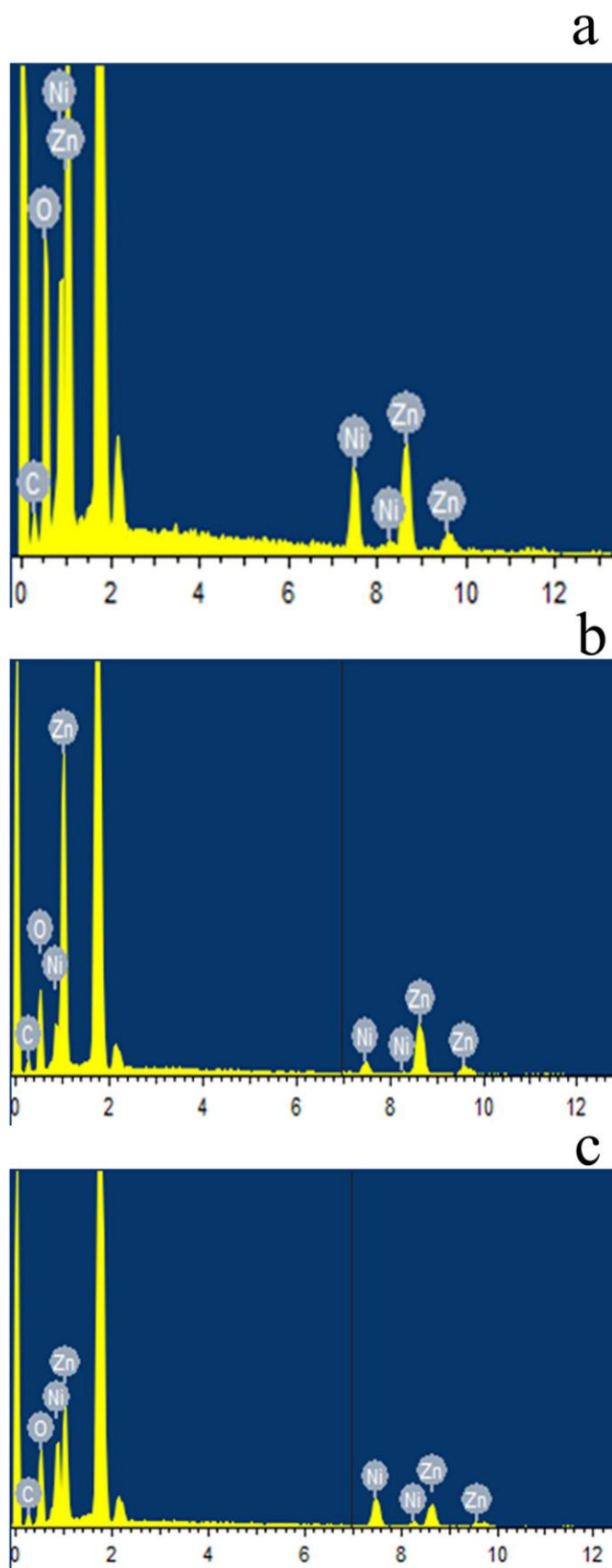
Supplementary Figure S3-The SEM and TEM images of zinc-nickel citrate microspheres synthesized at 0.1 M of nickel nitrate solution for 2 h (a-b) and 8 h (c-d).

Meanwhile, the effect of aging time was also tested. Zinc citrate solid microspheres were aged at 0.1 M of nickel nitrate solution for 2 and 8 h. As revealed in Fig. S3a-b, zinc-nickel citrate yolk-shell microspheres can be harvested when the aging time increases to 2 h. However, the void space between the core and the shell (Fig. S3b)

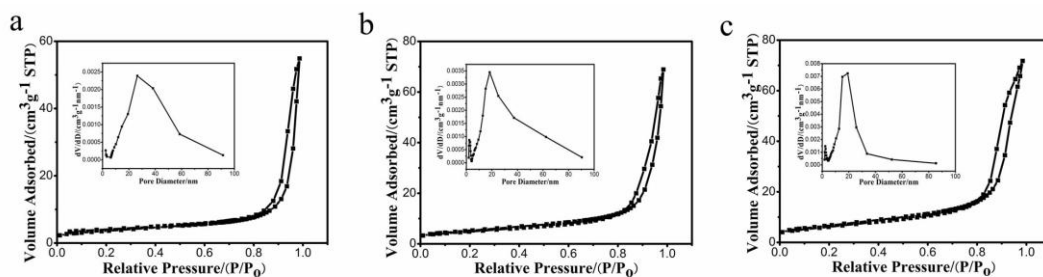
are still very small, similar to solid microspheres acquired for 1 h (Fig. 1f). Further increasing the aging time to 8 h, the morphology and the composition of the obtained zinc-nickel citrate do not change obviously (Fig. S3c-d and Fig. S4). According to the above observations, one can conclude that the aging time do not have a decisive effect on the morphology and composition of the obtained zinc-nickel citrate.



Supplementary Figure S4-EDS spectra of zinc-nickel citrate microspheres obtained at 0.1 M of nickel nitrate solution for 2 h (a) and 4 h (b).

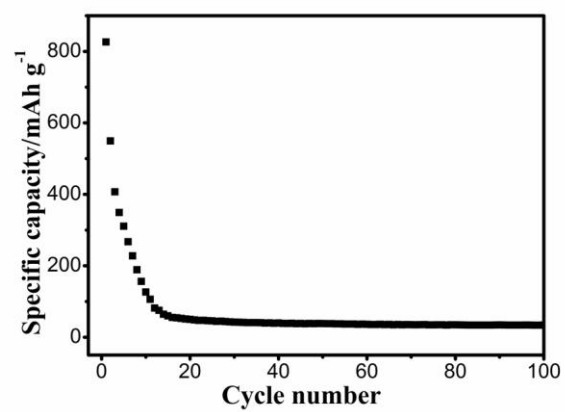


Supplementary Figure S5-EDS spectra of ZnO-NiO yolk-shell (a), solid (b) and hollow (c) hybrid microspheres.



Supplementary Figure S6-N₂ adsorption-desorption isotherms and the corresponding pore size distributions of ZnO-NiO solid (a), yolk-shell (b) and hollow (c) hybrid microspheres.

N₂ adsorption-desorption measurements were carried out to measure the specific surface areas and pore diameter distributions of the obtained ZnO-NiO hybrids and the corresponding results are shown in Supplementary Fig. S6. All three samples show the similar IV isotherm profiles, indicating the presence of mesopores in the hybrid microspheres. The specific surface areas of ZnO-NiO solid, yolk-shell and hollow hybrid microspheres are 12.8, 18.7 and 24.1 m² g⁻¹, respectively. ZnO-NiO hollow hybrid microspheres possess the largest surface area, followed by yolk-shell and solid counterparts. The pore sizes in ZnO-NiO solid, yolk-shell and hollow hybrid microspheres are mainly centered at 26.4, 18.3 and 18.9 nm on the basis of the Barrett-Joyner-Halenda method (the insets in Supplementary Fig. S6). The presence of mesopores in electrode materials is conducive to the diffusion of electrolyte within the electrode and can effectively accommodate the volume variation during the repetitive lithium intercalation/deintercalation process, resulting in the improvement of lithium storage properties.



Supplementary Figure S7-The discharge capacities of ZnO solid microspheres at 100 mA g⁻¹ in 0.01-3 V.