Dopamine-assisted one-pot synthesis of zinc ferrite-embedded porous carbon nanospheres for ultrafast and stable lithium ion batteries

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Experimental Section

Materials

Zinc chloride (≥98.0%), iron (II) chloride tetrahydrate (98.0%), 3, 4-dihydroxyphenethylamine hydrochloride (98%), tris(hydroxymethyl)aminomethane (Tris, 99%) were purchased from Aldrich-Sigma. All chemicals were analytical grade used as received without further purification.

Synthesis of ZnFe$_2$O$_4$@CPDA nanospheres

In a typical process, the dopamine hydrochloride was firstly dissolved in a mixture of water and ethanol (volume ratio of 5:1) with the concentration of 0.8 mg/mL based on volume of water. Then, 0.4 mM (based on water amount) of zinc chloride and 0.8 mM of iron (II) chloride tetrahydrate (keep Zn/Fe mole ratio of 1:2) were added into the above solution with mild stirring. Subsequently, the pH of the solution was adjusted to 8.5 using Tris buffer. The solution was mild stirred for three days at room temperature for the polymerization of dopamine. After that, the product was centrifuged and washed with deionized water for five times and then dried. Finally, the sample was calcined at 600 °C at a heating rate of 2°C min$^{-1}$ for 2h under Ar atmosphere to obtain ZnFe$_2$O$_4$@CPDA nanospheres. The sample discussed
in this work was prepared with ZnCl₂ concentration of 0.4 mM without otherwise specified. Polydopamine derived carbon (C-PDA) nanospheres were prepared under the same reaction conditions except in the absence of metal cations.

**Characterization**

The UV absorbance spectra were measured using a Shimadzu 2501PC UV-Vis Spectrometer. Fourier transform infrared spectroscopic (FTIR) measurements were performed using a Perkin-Elmer Instruments Spectrum GX FTIR spectrometer. X-ray diffraction (XRD) patterns were acquired using a D8 Discover GADDs (Bruker AXS, Germany) powder diffractometer. Scanning electron microscopic (SEM) images and elemental mapping were obtained on a JEOL-7600F field emission scanning electron microscope equipped with an energy dispersive X-ray (EDX) detector. Thermogravimetric analyses (TGA) were performed on a TGA Q500 under air atmosphere. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) experiments were performed on a JEOL 2100 transmission electron microscopy at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) test was determined via a Micromeritics Tristar II-3020 nitrogen adsorption apparatus. Pore size distribution plot was obtained by the Barrett-Joyner-Halenda (BJH) method.

The electrochemical performances were evaluated with a standard CR2032 coin cell with lithium metal as counter electrode, Celgard 2600 as the separator, and a solution of 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 by volume) as electrolyte. The working electrode was composed of 80 wt.% active materials, 10 wt.% Super P, and 10 wt.% polyvinylidene fluoride. The cells were assembled in an argon-filled glove box and tested in the voltage range of 0.005 and 3.0 V (vs. Li⁺/Li) with a Neware-CT3008 battery test system (Neware Technology Limited, Shenzhen, China). For rate performance testing, the coin cells were aged at 0.1 A/g before cycled at different current densities. The contribution of ZnFe₂O₄ nanoparticles to the overall performance can be identified by the following simple equation:

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C_{ZnFe_2O_4@CPDA nanospheres} = C_{ZnFe_2O_4 nanoparticles} \times 28\% + C_{C-PDA nanospheres} \times 72\%
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Fig. S1 Photographic images of colour changes for the initial reactants and their mixtures.

Fig. S2 UV-Vis absorbance spectra of the initial reactants and their mixtures.

Fig. S3 FT-IR spectra for (a) dopamine, (b) ZnCl$_2$ and (c) mixture solution of dopamine and ZnCl$_2$. 
Fig. S4 (a) A SEM image of the Zn/Fe@PDA nanospheres synthesized with 0.4 mM ZnCl₂ and (b) corresponding EDX mapping.

Fig. S5 TGA curve of the ZnFe₂O₄@CPDA nanospheres synthesized with 0.4 mM ZnCl₂.

Fig. S6 (a) SEM images of ZnFe₂O₄@CPDA nanospheres synthesized with 0.4 mM ZnCl₂ and (b) the corresponding statistical distribution of the sphere diameters.
Fig. S7 SEM images of ZnFe$_2$O$_4$@CPDA nanospheres synthesized with different concentrations of ZnCl$_2$: (a, b) 0.2 mM and (c, d) 0.6 mM. (e, f) are the corresponding statistical distribution of the sphere diameters.

Fig. S8 TEM images of ZnFe$_2$O$_4$@CPDA nanospheres synthesized with different concentrations of ZnCl$_2$: (a, b) 0.2 mM and (c, d) 0.6 mM.