Cavity Engineering of Amorphous Zeolitic Imidazolate Framework Colloids and Their Core-Shell Architectures

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Methods

$ZnCl_2$, imidazole, benzimidazole, 5-chlorobenzimidazole, triethylamine, and tannic acid, were acquired from Sigma-Aldrich. All reagents were procured from commercial suppliers and employed without further purification.

Synthesis of amorphous ZIF-7 sphere. The synthesis procedure is based on our previous work. Solution A was prepared by separately dissolving 6 mg of $ZnCl_2$ and 6 mg of benzimidazole in 5 mL of ethanol, followed by thorough mixing. Solution B was obtained by dissolving 1 mL of triethylamine in 11 mL of ethanol. Both solutions were combined in a sealed beaker. The reaction mixture was stirred continuously at room temperature for 3 h. The product was then collected by centrifugation, washed three times with ethanol, and dried at room temperature.

Synthesis of amorphous Zn-5-chlorobenzimidazole sphere. The synthesis was performed according to our previous method with minor modifications. Briefly, 3 mg of $ZnCl_2$ was dissolved in 5 mL of ethanol to form solution A. 15 mg of 5-chlorobenzimidazole was dissolved in another 5 mL of ethanol to form solution B. The two solutions were then combined and mixed thoroughly. The above mixture was combined with a triethylamine solution (3 mL of triethylamine in 9 mL of ethanol) in a sealed beaker. The reaction mixture was stirred for 4 h and then separated by centrifugation.

Synthesis of PB@Zn-5-chlorobenzimidazole. The preparation of the core-shell structures was based on the synthesis steps established for the Zn-5-chlorobenzimidazole sphere. Solution A was formed by mixing 3 mg of $ZnCl_2$ and 0.5 mg of Prussian Blue (PB) nanocubes.15 mg of 5-chlorobenzimidazole was dissolved in another 5 mL of ethanol to form solution B. The two solutions were then combined and mixed thoroughly. The above mixture was combined with a triethylamine solution in a sealed beaker. The reaction mixture was stirred for 4 h. Subsequently, the resulting core-shell nanoparticles were collected via centrifugation and washed three times with ethanol.

Synthesis of amorphous Zn-imidazole sphere. The synthesis was based on our previous method. $Zn(NO_3)_2\ 6H_2O$ (15 mg) and imidazole (4 mg) were first dissolved in 10 mL of absolute ethanol to produce a transparent mother solution, which was kept in an open 40 mL vial. In a separate uncapped vial, 0.5 mL of triethylamine (TEA) was dissolved in 11.5 mL of ethanol. The two vials were then enclosed together within a sealed 500 mL beaker under ambient conditions. During the reaction, the mother solution was continuously stirred under mild conditions. Vapor-phase TEA gradually migrated from its solution into the mother solution. After 6 hours, the resulting amorphous ZIF-zni microspheres were isolated and subjected to three washing cycles with pure ethanol.

Synthesis micron-sized Si@Zn-imidazole. The core-shell architectures were prepared via a method derived from the synthesis of Zn-imidazole spheres. $Zn(NO_3)_2\ 6H_2O$ (15 mg) and imidazole (4 mg) were first dissolved in 10 mL of absolute ethanol to produce a transparent mother solution, which was kept in an open 40 mL vial, followed by the addition of 1 mg of Si seeds. In a separate uncapped vial, 0.5 mL of triethylamine (TEA) was dissolved in 11.5 mL of ethanol. The two vials were then enclosed together within a sealed 500 mL beaker under ambient conditions. The rection solution was continuously stirred under mild conditions for 6h. The resulting amorphous micron-sized Si@Zn-imidazole core-shell architectures were collected via centrifugation and washed three times with ethanol.

Synthesis of hollow ZIF spheres. Disperse 10 mg of ZIF nanospheres in 1 mL of water using ultrasonication to obtain a uniform suspension. Subsequently, introduce 0.3 mL of tannic acid aqueous solution (40 g/L) into the suspension. After ultrasonic treatment for 5 minutes, separate the resulting hollow ZIF structures by centrifugation, then purify the product by washing three times with ethanol.

Synthesis of yolk-shell architectures. First, disperse 20 mg of core-shell nanoparticle in 1 mL of water by ultrasonication to obtain a uniform suspension. Then, add 0.3 mL of an aqueous tannic acid solution (40 g/L) and continue sonicating the mixture for 5 minutes. Separate the resulting yolk-shell architecture by centrifugation, and then purify them by washing three times with ethanol.

Characterization

The powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 diffractometer with Cu Kα1 radiation (wavelength of 1.5406 Å). Microstructures of the hollow samples were captured using transmission electron microscopes (FEI Talos F200S). FT-IR spectra were detected by using a Nicolet iS5 FTIR Spectrometer from Thermo Scientific. The nanostructure of the synthesized samples was characterized using a LEO 1530 field-emission scanning electron

microscope.

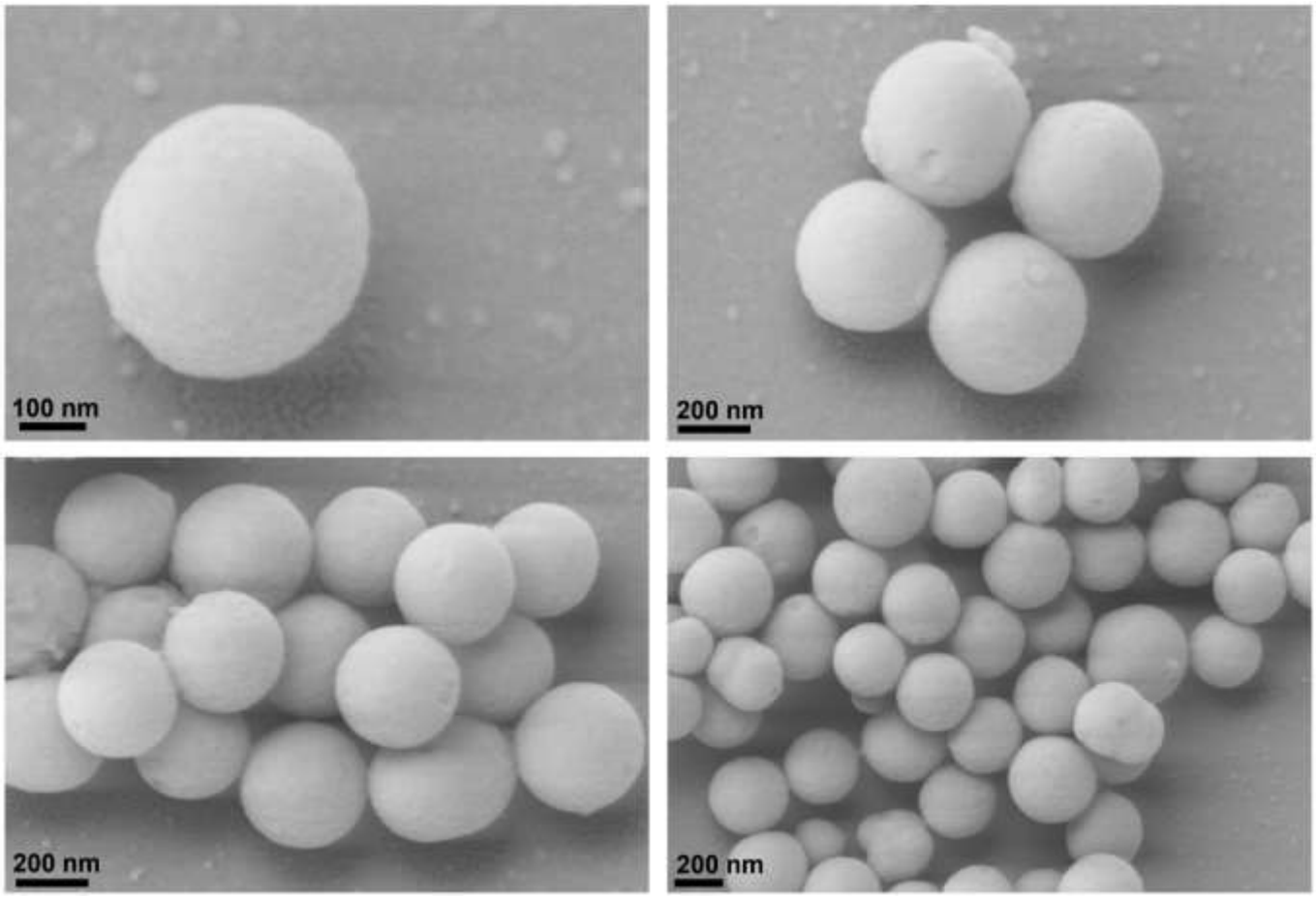

Figure S1. SEM images of amorphous ZIF-7 spheres with different magnifications.

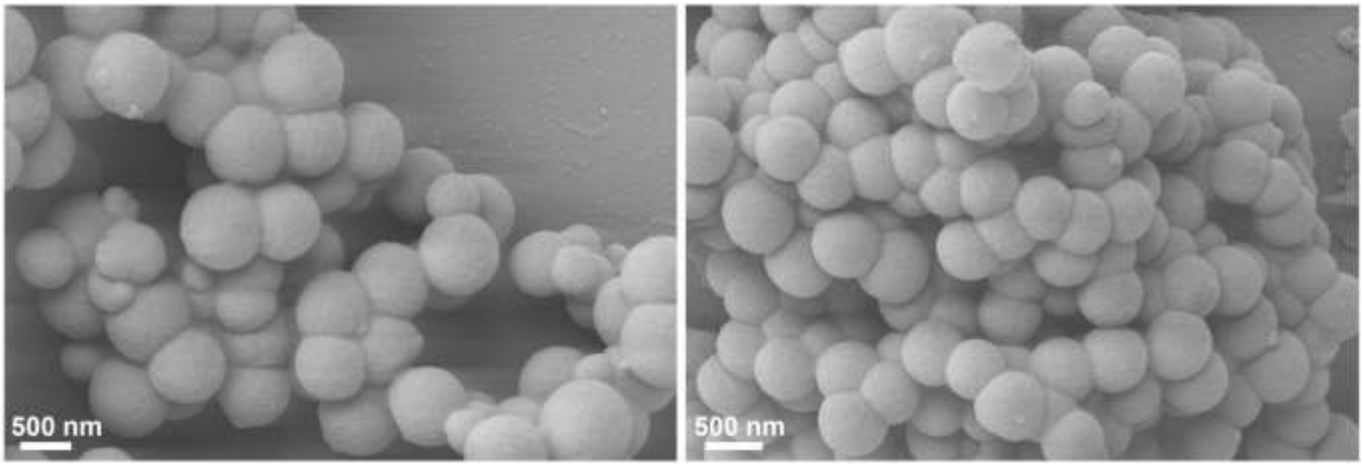

Figure S2. SEM images of hollow amorphous ZIF-7 spheres.

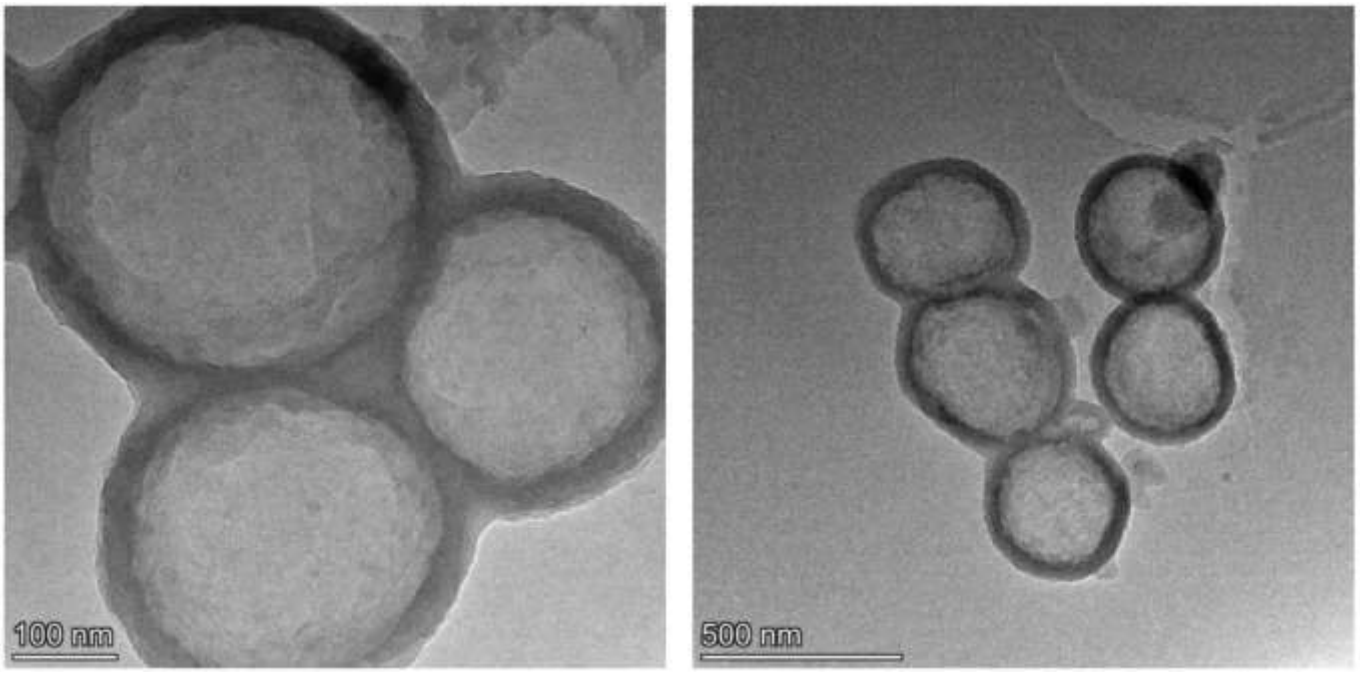

Figure S3. TEM images of hollow amorphous ZIF-7 spheres.

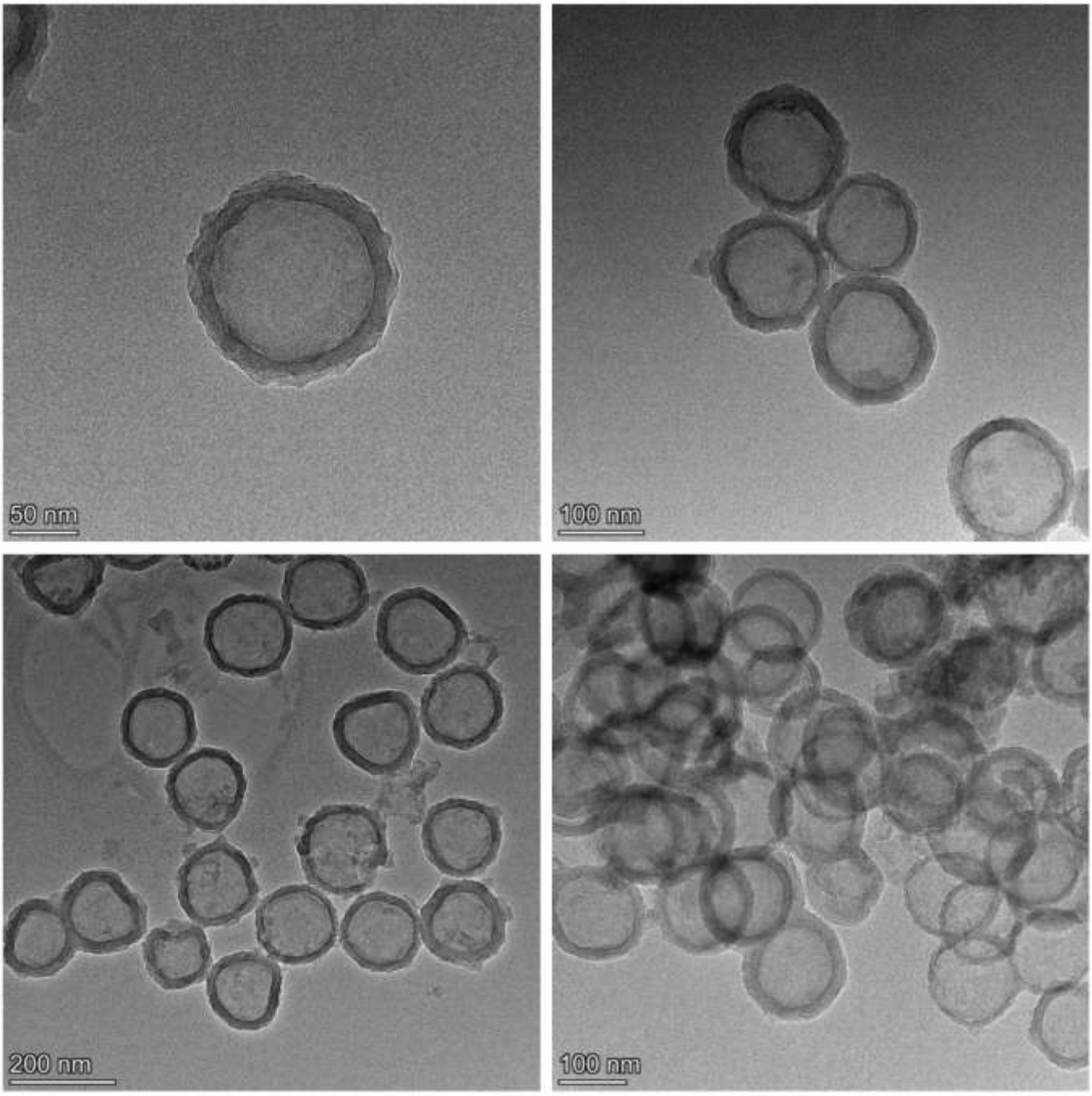

Figure S4. TEM images of hollow amorphous Zn-imidazole spheres with different magnifications.

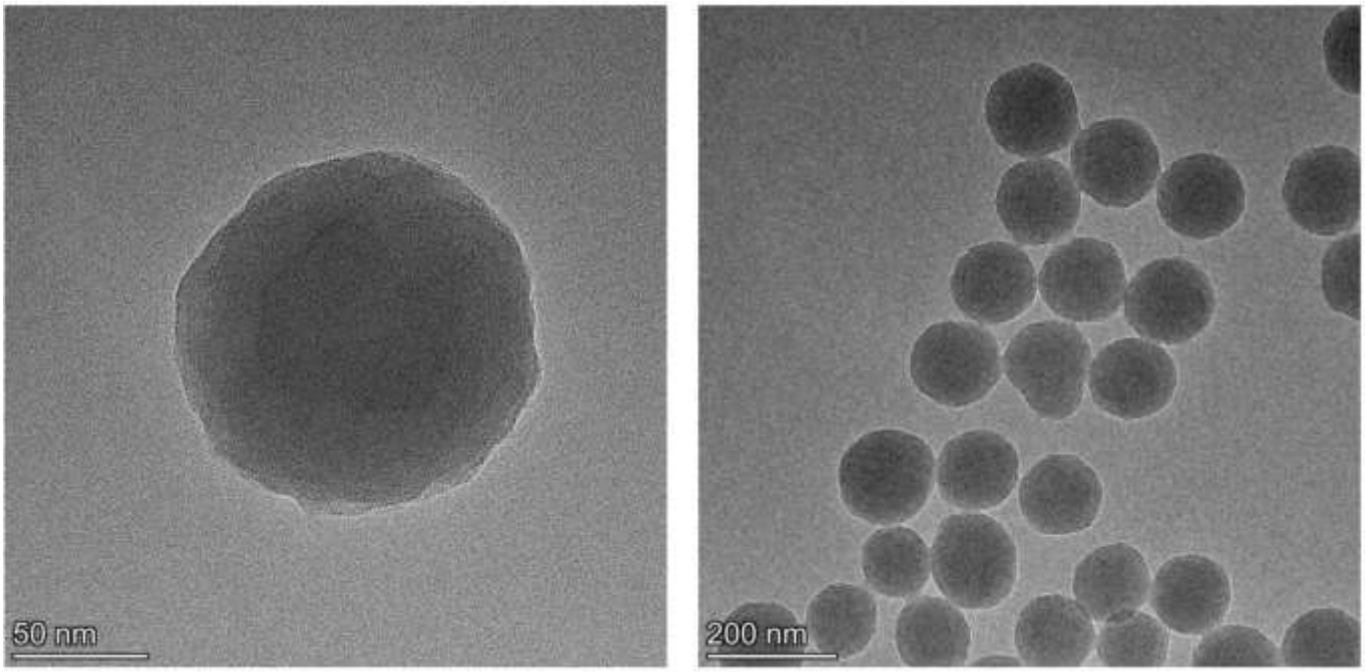

Figure S5. TEM images of amorphous Zn-5-chlorobenzimidazole spheres.

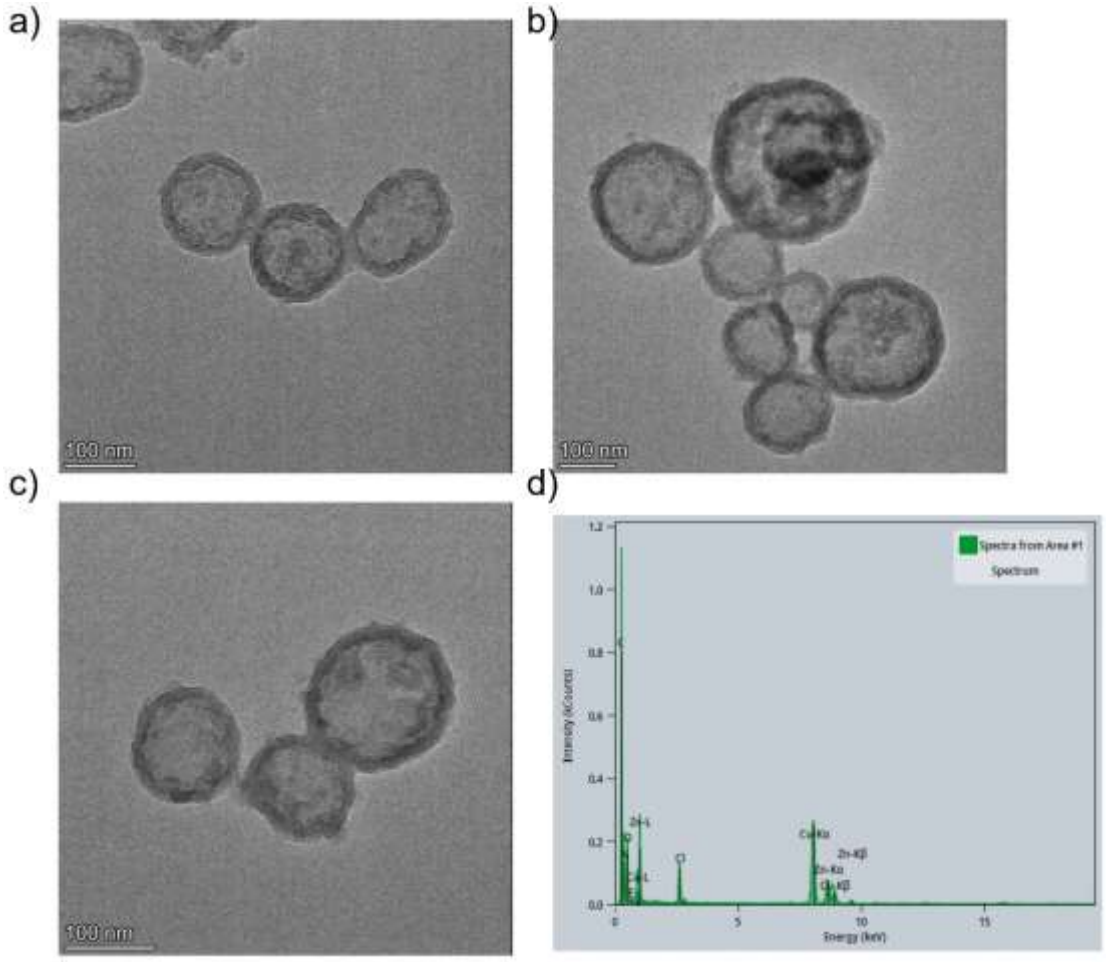

Figure S6. (a-c) TEM images of hollow amorphous Zn-5-chlorobenzimidazole spheres. (d) The representative energy dispersive X-ray (EDX) spectrum of hollow amorphous Zn-5-chlorobenzimidazole spheres.

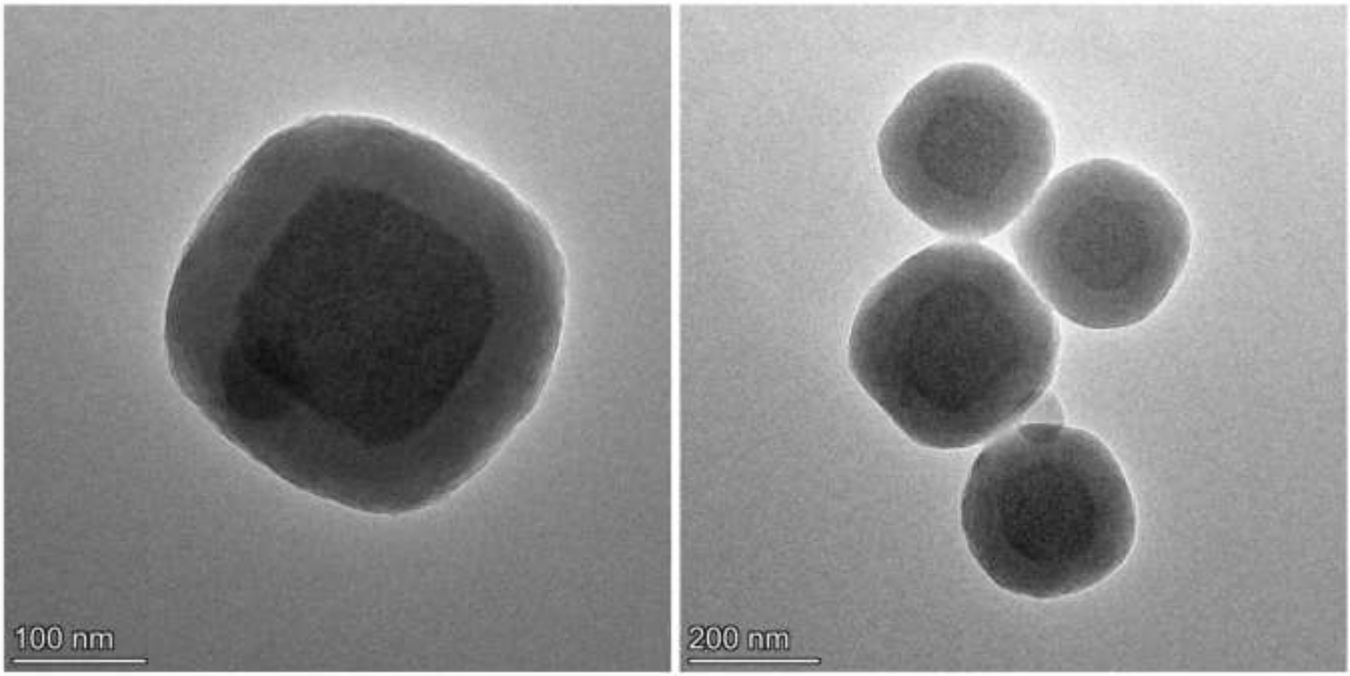

Figure S7. TEM image of PB@ Zn-5-chlorobenzimidazole core-shell nanoparticles.

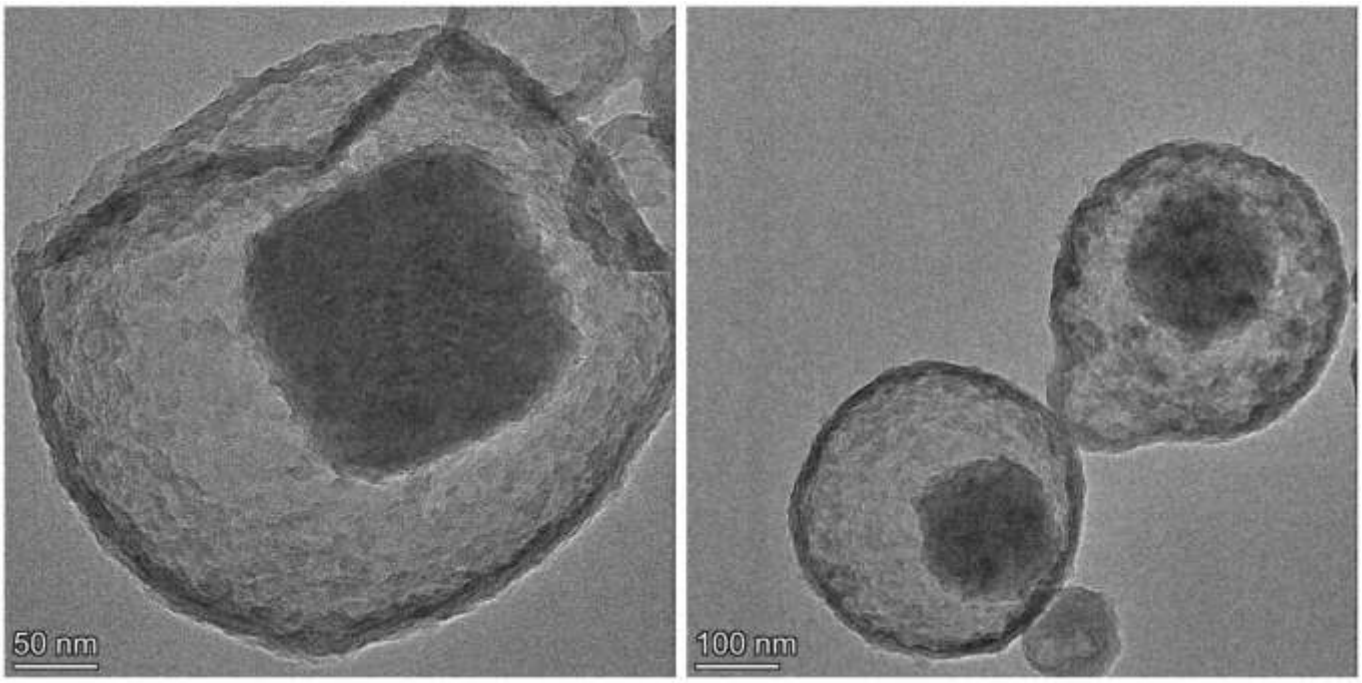

Figure S8. TEM image of PB@Void@ Zn-5-chlorobenzimidazole yolk-shell nanoparticles.

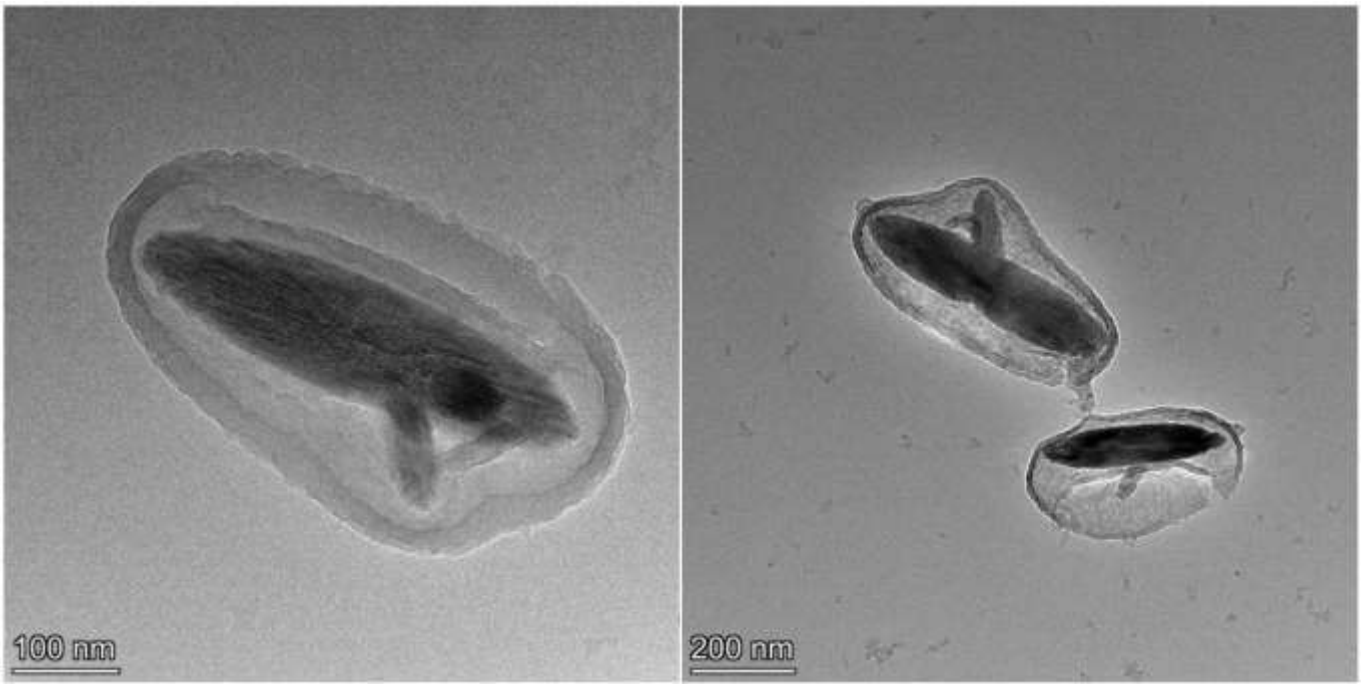

Figure S9. TEM image of β-FeOOH@Void@Zn-imidazole yolk-shell nanoparticles.

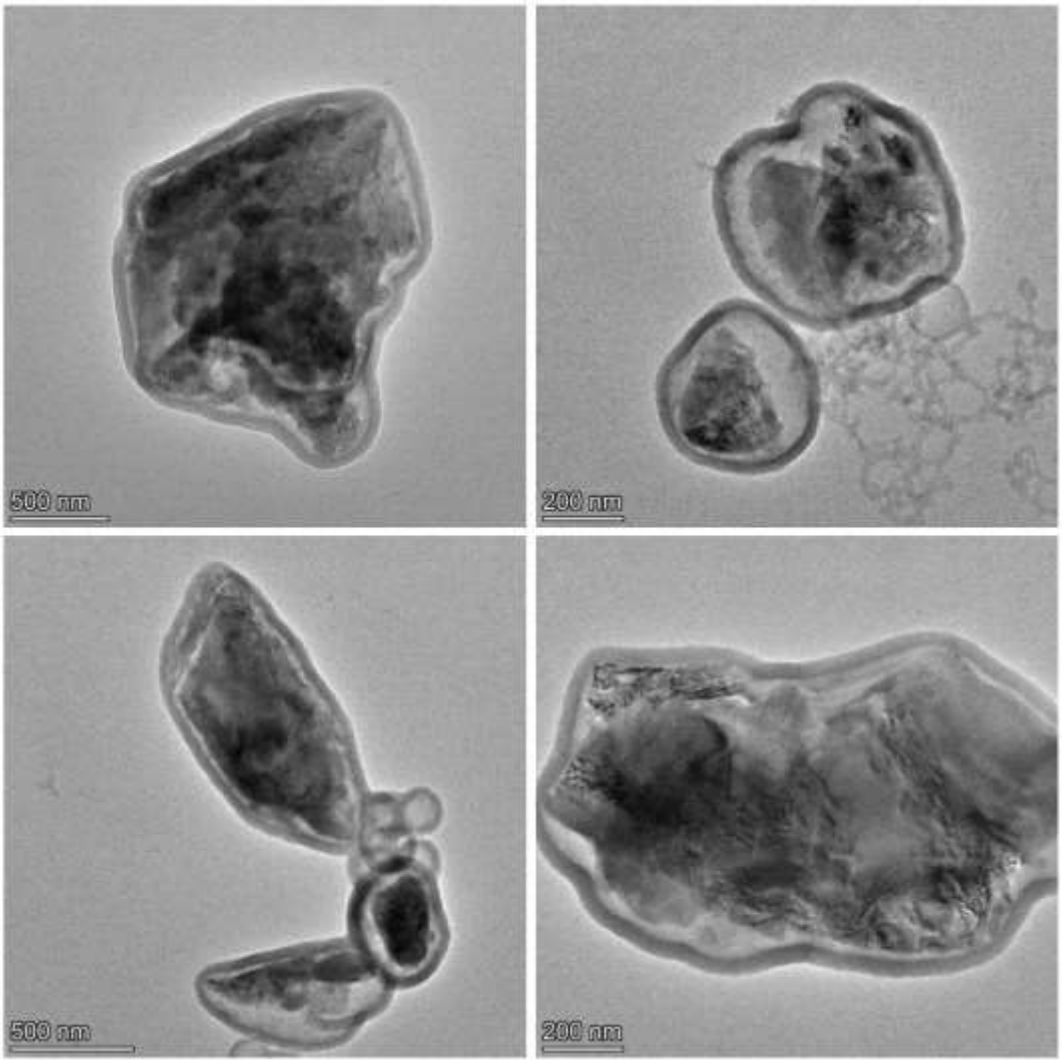

Figure S10. TEM image of Si@Void@ Zn-imidazole yolk-shell nanoparticles.

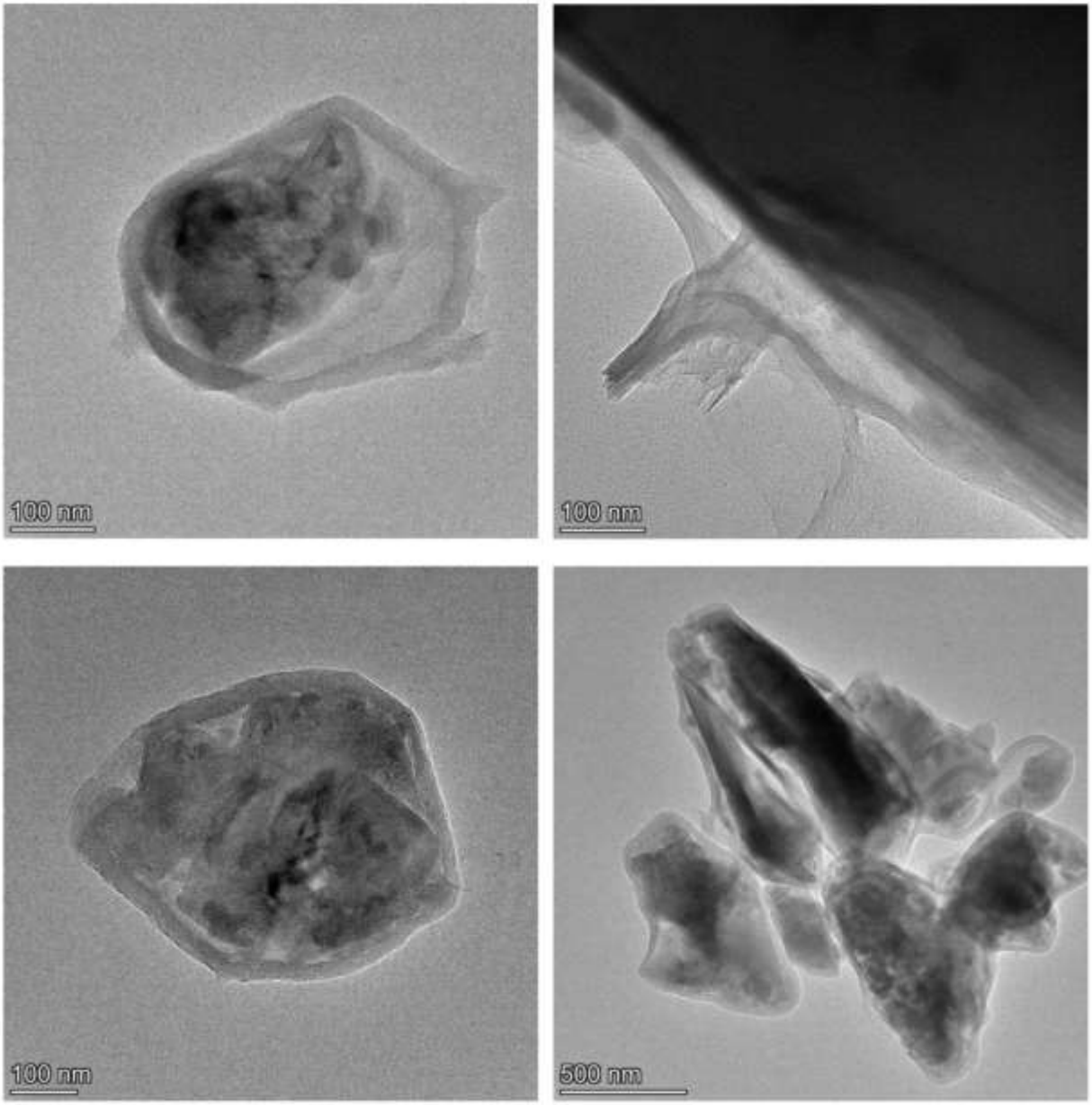

Figure S11. TEM images of Si@Void@Porous carbon yolk-shell nanoparticles.