

Supporting Information

Iron Nanoparticles in Capsules: Derived from Mesoporous Silica-Protected Prussian Blue Microcubes as Efficient Selenium Removal

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1. Experimental section

1.1 Materials

Potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$), polyvinylpyrrolidone (PVP), hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium chloride (CTAC), ammonia aqueous solution (28 wt.%), sodium selenite (Na_2SeO_3) and triethanolamine (TEA) were purchased from Sigma-Aldrich (UK). Deionized water was used to prepare all solutions used in this study.

1.2 Methods

1.2.1 Synthesis of Prussian blue microcubes

Prussian blue microcubes with an edge length of 450 nm were prepared according to the previous report with a minor modification by Zhang et al.¹ Briefly, 22.8 g of PVP and 0.66 g of $K_4Fe(CN)_6 \cdot 3H_2O$ were dissolved in a 200 mL of aqueous solution containing 0.1 M of HCl under magnetic stirring. After stirring for 60 min, a clear solution was obtained and placed into an electric oven under 80 °C for 24 h. The obtained blue product was collected by centrifugation and washed several times with distilled water and absolute ethanol. Finally dried the products in a vacuum oven at 60 °C overnight.

1.2.2 Synthesis of PB@mSiO₂ core-shell micro-boxes

The dendritic mesoporous silica with thickness of 20 nm was coated on the surface of the PB microcubes through an oil-water biphasic stratification approach.² For a typical preparation procedure, a mixture solution containing 0.25 g of PB microcubes, 60 mL of H₂O, 6 g CTAC and 0.18 mL of TEA were added into a 100-mL round bottom flask and stirred for 1 h at 60 °C. Then 20 mL of TEOS (20 v/v % in cyclohexane) was gently dropped. The reaction was maintained at 60 °C for 12 h in an oil bath with reflux under magnetic stirring (70 rpm). The products were collected after removal of the upper oil layer, then centrifuged and washed with ethanol and water for several cycles.

1.2.3 Preparation of Fe/C@mSiO₂ core-shell capsules

The core-shell Fe/C@mSiO₂ capsule was obtained by calcination and reduction of the PB@mSiO₂ powder at 400-600 °C for 3 h under H₂ atmosphere. A series of products calcined at different temperatures are named as Fe/C@mSiO₂-400, Fe/C@mSiO₂-500 and Fe/C@mSiO₂-600 according to the calcination temperature of 400, 500 and 600 °C, respectively.

1.2.4 Heavy metal extraction from water

Batch experiments were conducted in a series of 50 mL three-neck flask, with 40-200 mg/L Fe/C@mSiO₂ capsule added to 35 mL of 5-135 mg/L Se (IV) solution. Each reactor had three ports, one for a mechanical stirrer, one for high-purity nitrogen (N₂, >99.9%) gas purging and the last one for adding and retrieving solutions. To eliminate dissolved oxygen, the Se (IV) solution was purged with high-purity N₂ for 30 min before the addition of Fe/C@mSiO₂ capsule. The initial pH was adjusted to 7.0. After 3 hours, the mixed solution was separated by centrifuging and magnetic separation. The supernatant was analyzed by using an inductively coupled plasma spectrometer (ICP) to detect the ionic metal contents of heavy metals and iron, and the slurry was dried in

air for material characterization. The comparison experiments between nZVI particles and Fe/C@mSiO₂ capsule for Se (IV) removal at the same environment were conducted at the Se (IV) concentration of 35 mg/L, with a contact time of 3 h.

1.3 Characterizations

The morphologies and dispersity of the samples were observed by scanning electron microscopy (Hitachi S-4800, Japan). The TEM images were taken using a JEM-2100F transmission electron microscope (JEOL, Japan). The phase of the samples was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan) equipped with CuK α radiation. Thermal gravimetric analysis (TGA) was carried out on a Q5000IR TG-DTA instrument with a heating rate of 10 °C min⁻¹ under air atmosphere. Nitrogen adsorption-desorption isotherms were tested at 77 K with a Micromeritics Tristar 3020 analyzer. The samples were degassed under vacuum at 180 °C for at least 6 h before measurements. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The pore volumes and pore size distributions were obtained by using the Barrett-Joyner-Halenda (BJH) model from the adsorption branches of isotherms. The total pore volumes (V) were evaluated according to the adsorbed amount at a relative pressure P/P₀ of 0.995. Raman spectra were performed on Via-Reflex via Raman spectroscopy.

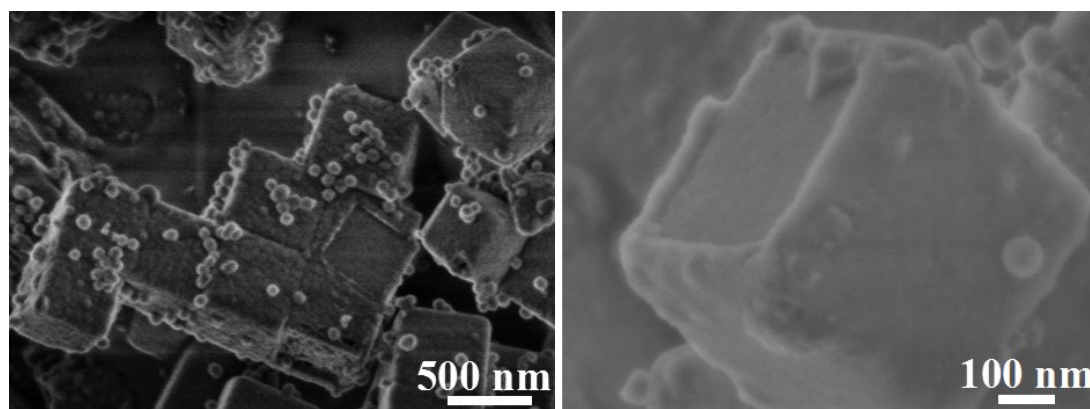


Fig. S1 SEM images of PB@mSiO₂ core-shell structured micro-boxes, prepared by oil-water biphasic stratification approach.

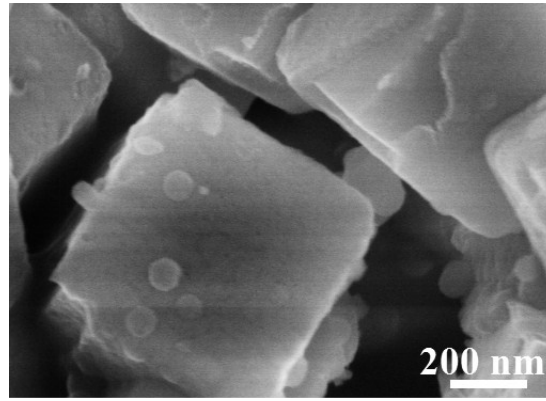


Fig. S2 SEM image of Fe/C@mSiO₂ core-shell structured capsules with radially oriented mesopores, calcined at 500 °C for 3 h under H₂ atmosphere.

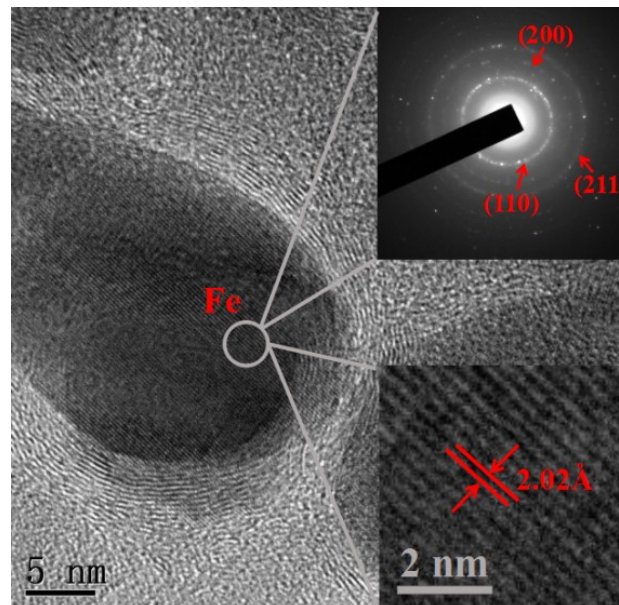


Fig. S3 High-resolution TEM images with the corresponding SAED pattern (inset) for Fe/C@mSiO₂ core-shell structured capsules.

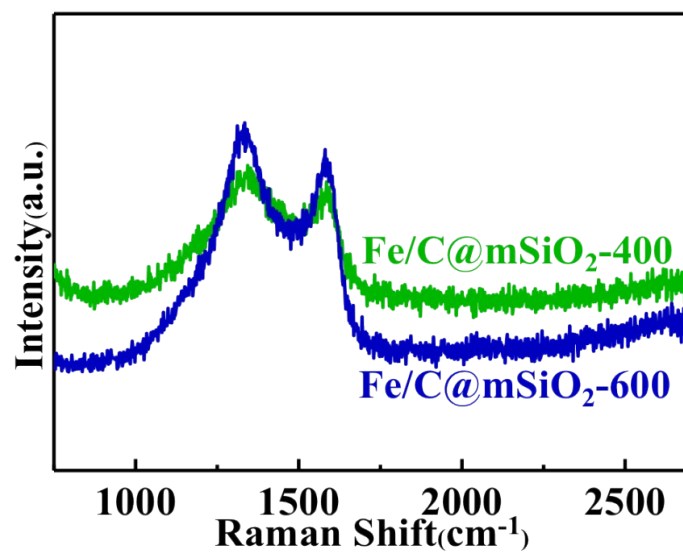


Fig. S4 Raman spectra of Fe/C@mSiO₂-400 and Fe/C@mSiO₂-600 samples.

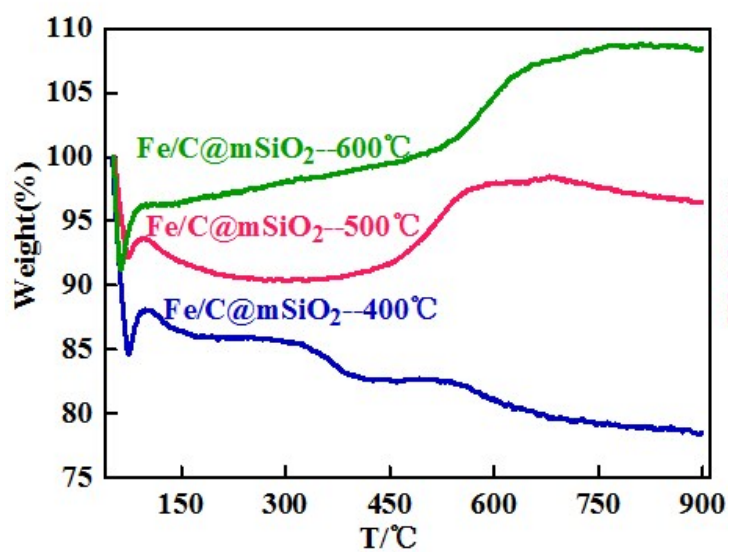


Fig. S5 TGA plots of Fe/C@mSiO₂-400, Fe/C@mSiO₂-500 and Fe/C@mSiO₂-600 samples.

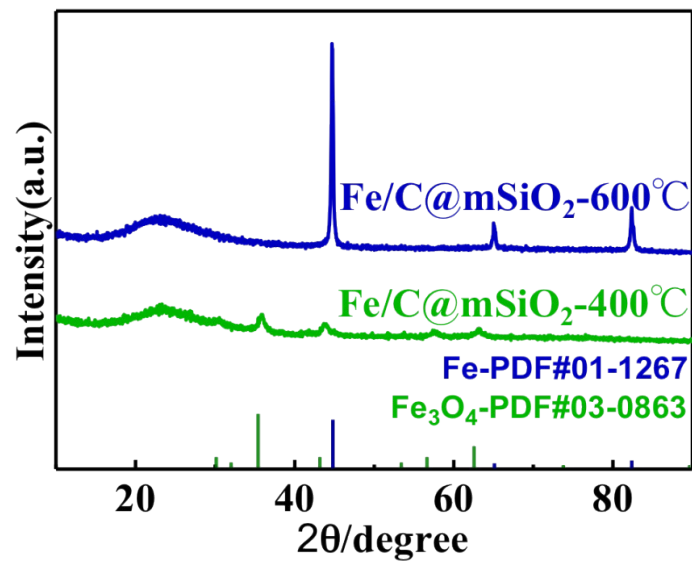


Fig. S6 XRD patterns of Fe/C@mSiO₂-400 and Fe/C@mSiO₂-600 samples, which are reduced at 400 and 600 °C for 3 h under H₂ atmosphere.

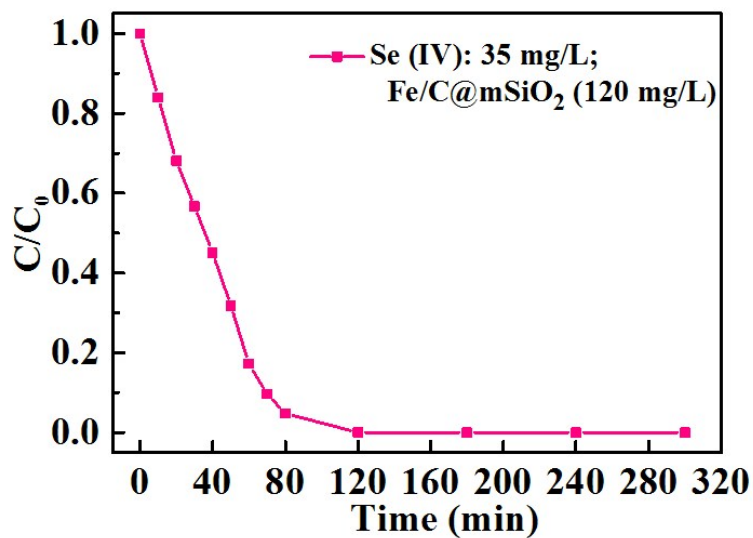


Fig. S7 The kinetic of Se (IV) removal with the Fe/C@mSiO₂ core-shell structured capsules.

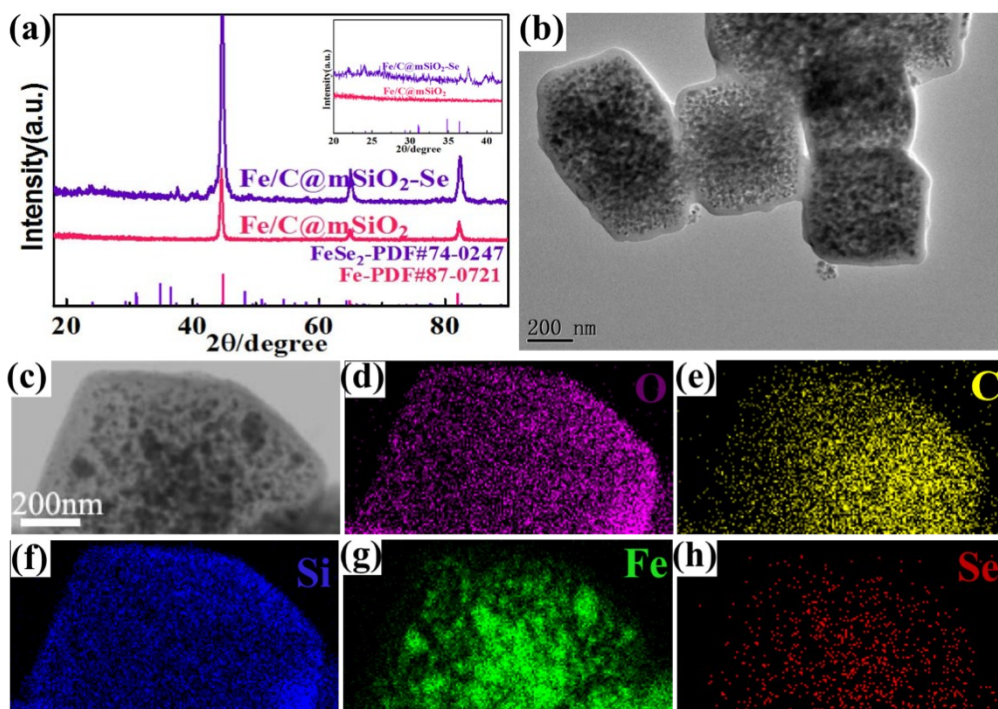


Fig. S8 (a) XRD patterns and (b) TEM of Fe/C@mSiO₂-Se capsules after removal of Se; (c) STEM, and (d-h) EDX elemental mapping of Fe/C@mSiO₂-Se for Si, O, Fe, C and Se.

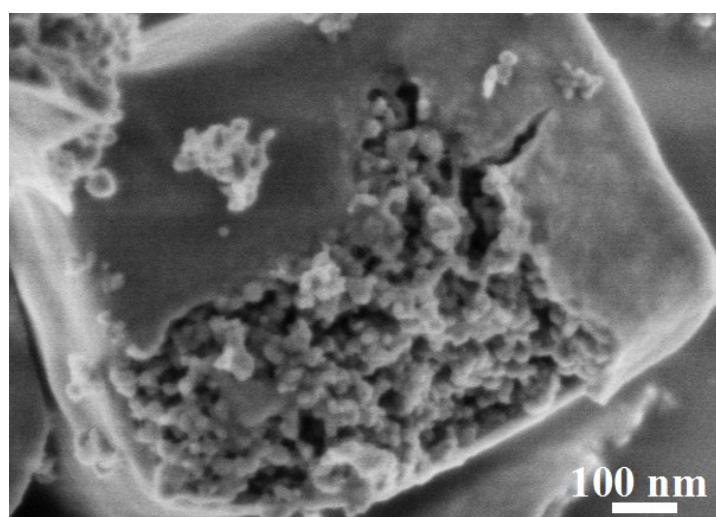


Fig. S9 SEM image of Fe/C@mSiO₂-Se after removing Se from low concentration aqueous solution. It can be found that the Se with uniformly small nanoparticles are capped in the Fe/C@mSiO₂ core-shell structures from a broken capsule.

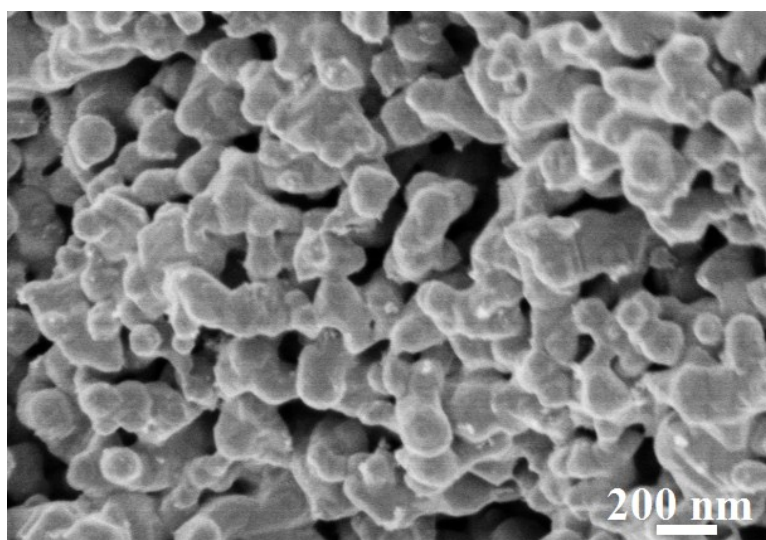


Fig. S10 SEM image of compared nanoscale zero-valent iron (nZVI) particles. It can be observed that the nZVI particles are seriously aggregated.

Table S1 Summary of different samples for the removal of Se(IV).

Sample	Carrier	Synthesis method	Dosage of sample	Actual content of Fe ⁰	Initial concentration of Se(IV)	Removal rate of Se(IV)	Ref
nZVI	none	chemical reduction	500 mg/L	500 mg/L	100 mg/L	99% for 3h	[3]
magnetic graphene oxide (MGO)	graphene oxide	Hummers method	1 g/L	1 g/L	300 mg/L	80% for 24h	[4]
dendrimer functionalized graphene oxide	graphene oxide	poly(amid-oamine)functionalized graphene oxide	200 mg/L	200 mg/L	80 mg/L	37.5% for 24h	[5]
thin-film composite nanofiltration membranes	nanofiltration membranes	co-polymer P(MPC-co-AEMA) modified membranes	/	/	350 mg/L	98.2%	[6]
nanoparticles sol (NanoFe)	none	sol-gel method	120 mg/L	120 mg/L	12 mg/L	95% for 3h	[7]
Fe/C@mSiO₂	C-mSiO ₂	spatially confined reduction	120 mg/L	40 mg/L	35 mg/L	99.9% for 3h	This work

Reference

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