Electronic Supplementary Material (ESI) for RSC Advances.

Facile Route to magnetic mesoporous core–shell structured silicas Containing Covalently Bound Cyclodextrins for removal of doxycycline antibiotic from water

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1. Preparation of Fe_3O_4@SiO_2@mSiO_2microspheres

1.1. Synthesis of Fe_3O_4 microspheres

The Typically, 1.08g of $FeCl_3 \cdot 6H_2O$ was dissolved in 20mL of ethylene glycol under magnetic stirring. A clear yellow solution was obtained after stirring 30min at 40°C. Then, 1.8g of sodium trihydrate was added to this solution and being stirred for another 1h. Afterward, 0.25g of trisodium citrate was added. After forming a homogeneous dispersion, the mixture was transferred into a Teflon-lined stainless-steel and heated at 200°C for 10h. The black magnetic particles were collected with help of a magnet filed, followed by washing with a recycle of ethanol of deionized water six times. The product was then dried under vacuum at 60°C.

1.2. Synthesis of Fe_3O_4@SiO_2 microspheres

The coating layer of $SiO_2$was prepared through a modified Stöber method. In a typical process, as-prepared Fe_3O_4 particles (0.1 g) were dispersed in a mixture of ethanol (40mL), 10mL of deionized water, concentrated ammonia aqueous solution (28 wt%, 1.2mL), 0.35mL of TEOS was added and ultrasonication 15min, 15min, 30min, 45min, respectively. The products were collected and washed with deionized water and ethanol and then dried vacuum at 60°C.

1.3. Synthesis of Fe_3O_4@SiO_2@mSiO_2 microspheres

Briefly, 0.6g CTAB was dissolved in deionized water (24mL) by vigorous mechanical stirring to obtain a clear solution. Then, 0.2g TEA and 36mL of deionized water mixed solution was added and continue vigorous mechanical stirring for 30min.

0.2g Fe_3O_4@SiO_2microspheres was added and treated ultrasonication for 30min. Afterwards, 2mL of TEOS and 18mL of cyclohexane added. The mixture was under ultrasonication for 30min and then mechanically stirred at 60°C for 12h. The products were collected and washed with deionized water and ethanol and then dried vacuum at 60°C. Finally, the product was calcined at 550°C for 6h.

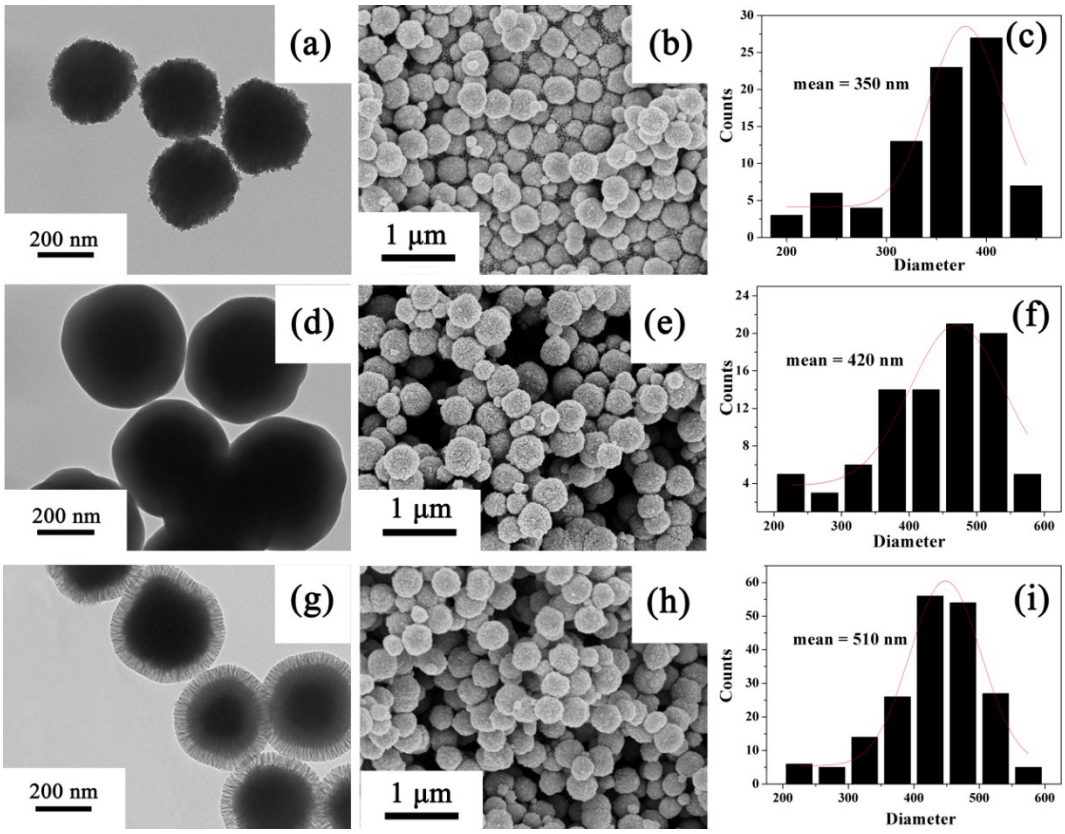

Fig. S1.TEM images of Fe_3O_4 (a), Fe_3O_4@SiO_2 (d) and Fe_3O_4@SiO_2@mSiO_2 (g) microspheres, SEM images of Fe_3O_4 (b), Fe_3O_4@SiO_2(e) and Fe_3O_4@SiO_2@mSiO_2 (h) microspheres. Size distribution histogram of Fe_3O_4 (c), Fe_3O_4@SiO_2 (f)and Fe_3O_4@SiO_2@mSiO_2 (i) microspheres calculated from SEM images.

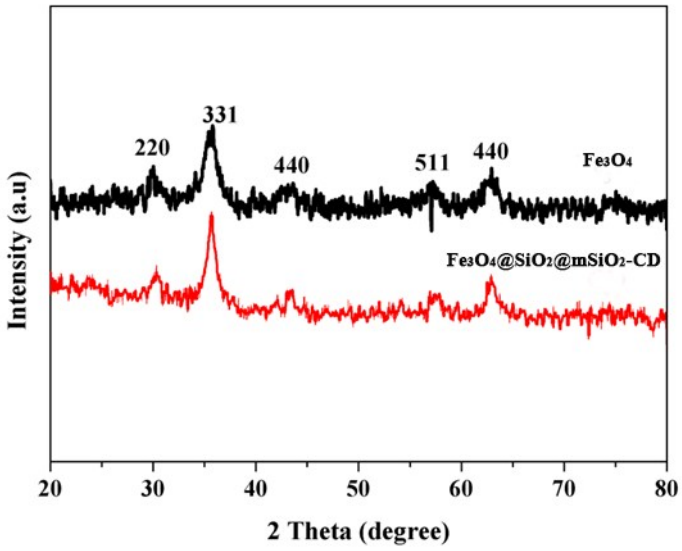

Fig. S2. XRD patterns of the Fe_3O_4 and the Fe_3O_4@SiO_2@mSiO_2-CD microspheres.

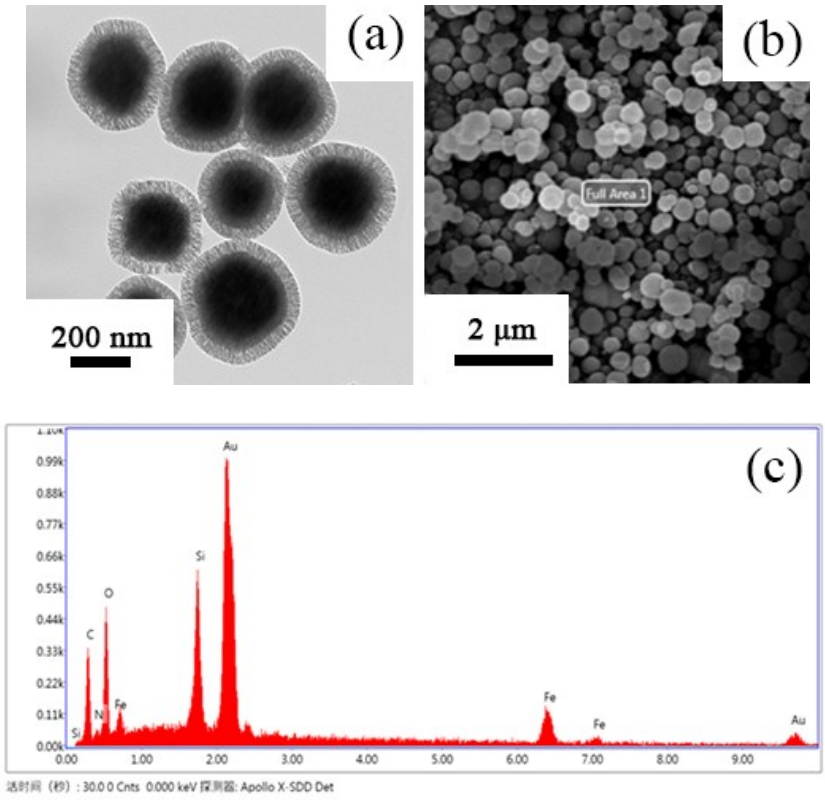

Fig. S3. TEM of images of Fe_3O_4@SiO_2@mSiO_2-CD (a), SEM images of Fe_3O_4@SiO_2@mSiO_2-CD and Fe_3O_4@SiO_2@mSiO_2-CD energy dispersive spectrometer (EDX) from SEM images.

Eqs.S1. The pseudo-first order kinetic model: $ln(q_e - q_t) = lnq_e - k_1 t$

The pseudo-second order equation: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

Where, q_e and q_t, mg g^{-1}, are equilibrium adsorption capacity and adsorption capacity at time t, respectively; k_1 (min^{-1}), k_2 (g $mg^{-1}h^{-1}$) are the pseudo-first-second order kinetic rate constant, respectively.

Eqs.S2. The Langmuir, Freundlich and D-R isotherm models are shown below:

Langmuir models: $q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$

Freundlich models: $q_e = K_F C_e^{1/n}$

Dubinin-Radushkevich models: $\ln q_e = \ln q_m - \beta\varepsilon^2$

$\varepsilon = RT\ln(1 + {}^{1}/_{C_e})$

$E = (2\beta)^{-{}^{1}/_{2}}$

Where Q_{max} is the maximum adsorption capacity (mg g^{-1}), n is a dimensionless number related to surface heterogeneity, K_F is Freundlich affinity coefficient ($mg^{1-n}L^n g^{-1}$) and K_L is the Langmuir fitting parameter (L mg^{-1}), β is a constant related to sorption energy; ε is Polanyi sorption potential, related to the sorption energy E required to move one molecule of solute from infinity to the surface of adsorbents. R is the ideals gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

Eqs.S3. The thermodynamic parameters, such as the Gibbs free energy (ΔG^0), the enthalpy (ΔH^0), the entropy(ΔS^0) were calculated using the following equations:

$\Delta G = -RT\ln K_c$

$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$

Where Kc is the distribution coefficient, which is the radio of the amount of DOX adsorbed on solid to the residual concentration of DOX in solution at equilibrium.