Supplementary data

A facile enantioseparation for amino acids enantiomers using β-cyclodextrins functionalized Fe_3O_4 nanospheres

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Materials and methods

Chemicals

Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ferric trichloride ($FeCl_3$), hydrochloride (HCl), sodium hydroxide (NaOH), β-cyclodextrin, ethanol, all D- and L- amino acids enantiomers were obtained from Beijing Chemical Reagent Ltd and used without further purification. Milli-Q water (18.2 MΩ·cm) was used in all the cases. The cationic azo-surfactant: 4-methyl-4'(trimethylaminopropoxy) azobenzene bromide (AzoTAB) was synthesized in analogy to the previous procedures and the molecular structure was shown in Scheme 1.

Synthesis of β-CD modified Fe_3O_4 nanoparticles

The magnetite nanoparticles were synthesized in analogy to the previous simple one-pot synthesis procedures. Briefly, $FeSO_4 \cdot 7H_2O$ (2.78g) and $FeCl_3$ (3.25g) were dissolved in 25 ml of HCl aqueous solution (1.0 mol/L) with vigorous stirring and under N_2. After 30 min of vigorous stirring, 250 ml of 4.0 mol/L sodium hydroxide solution (including 12.8 g β-CD) was dropwise added. The reaction was allowed to proceed for 1.5h to produce a water-based suspension with constant and vigorous stirring under a nitrogen flow (40 ml/min) at room temperature. Finally the suspension was filtered using a sintered disc. The obtained β-CD modified Fe_3O_4 nanoparticles were washed 3 times with ethanol and deionized water, separately and then were dried at 60 ^oC under vacuum for 4 h.

Characterization.

X-ray powder diffraction (XRD) patterns of the samples were performed at room temperature on an MAC Science M18X X-ray diffractometer using Cu Ka line (λ=0.154 nm). The tube current and voltage were 30mA and 40 kV, respectively. Transmission electron microscopy (TEM) measurements were performed on a JEOL-2000 microscope operated at 200 kV. All samples subjected to TEM characterization were ultrasonically dispersed in alcohol and drop-cast onto copper grid. Fourier transform infrared (FT-IR) spectra were recorded on a MAGNA 750

FTIR spectrometer by use of KBr pellets. ^{1}H NMR spectra were recorded on Bruker 400MHz NMR spectrometer (Bruker, Switzerland) with sample solution in D_2O. The ultraviolet-visible (UV-vis) spectra were measured using a SHIMADZU UV-2550 PC spectrophotometer. After the magnetically separation process, the residual amino acids concentration was determined by colorimetry in the principle of color reaction between amino acids and ninhydrin. Optical activity measurements were taken with a WZZ-1 polarimeter at room temperature with a cell-path length of 10 cm.

Morphology and structural characterization of β-CD functionalized Fe_3O_4 nanoparticles.

The morphology and structure of the prepared Fe_3O_4 nanoparticles modified with, and without β-CD, have been characterized by TEM and XRD analysis. As shown in Fig.1a, Fe_3O_4 nanoparticles showed rather uniform size and shapes with average particle sizes of about 25 nm. Although a certain degree of aggregation can be observed, the morphology and boundaries of most nanoparticles were clear. After modification with β-CD, the boundaries of Fe_3O_4 nanoparticles became very vague, and the contrast value decreased significantly which indicated the coating of β-CD (as shown in Fig 1 b). The β-CD functionalized Fe_3O_4 nanoparticles showed excellent magnetically controllable aggregation behavior by placing a magnet near the vessels containing the aqueous dispersion of the nanoparticles (as shown in Fig 1c), which allow them for further application in magnetic separation. The crystalline structures of Fe_3O_4 and β-CD functionalized Fe_3O_4 nanoparticles were further determined by powder XRD patterns (as shown in Figure S2). Above Fe_3O_4 nanoparticles displayed several relatively strong reflection peaks in the 2θ region of 20-70^o, which matched well with JCPDS card (19-0629). No other iron oxide or hydroxide phase was observed, which indicated the success preparation of Fe_3O_4 nanoparticles. By use of Debye-Scherrer equation for the full width at half-maximum of the (311) reflection peak, the average particle sizes were calculated to be about 25 nm, consistent with the TEM results. After β-CD modification, no obvious change could be observed, which indicated that the crystalline structures of Fe_3O_4 would be maintained during the coating of β-CD. There were characteristic absorption bands at around 632 and 453 cm^{-1}, corresponds to the Fe–O bond of Fe_3O_4. After β-CD modification, the broad characteristic absorption band in the range of 1200~900 cm^{-1} for β-CD and a little shift of the characteristic absorption bands for Fe_3O_4 could be observed in the FTIR analysis for the as-synthesized β-CD modified Fe_3O_4 nanoparticles (as shown in Fig. S3), which confirmed the successful preparation of β-CD modified Fe_3O_4 nanoparticles.

Measurment of the absorption coefficients P

To verify enantioseparation capacity of β-CD modified Fe_3O_4 nanoparticles for amino acids isomers, 100 mg β-CD modified Fe_3O_4 nanoparticles were respectively added into 25 ml of a racemic mixture solution of amino acids isomers (alanine, tryptophane and tyrosine with the mol ratio of L-:D- = 1:1). As the reference samples, a 25 ml racemic mixture of amino acids isomers without adding β-cyclodextrin modified Fe_3O_4 nanoparticles was prepared. After the magnetically separation process,

the residual amino acids left in solution after chiral capture by the nanoparticles, was determined using colorimetry by exploiting the color reaction between amino acids and ninhydrin. In this experiment, the absorption time was kept constant (2h) during the whole magnetic separation process. And the absorption coefficients was defined as

$$P=\frac{\Delta CV}{M} \quad (1)$$

where ΔC was the change in concentration of amino acids isomers in concentration, V was the solution volume (25 mL) and M was the mass of the β-CD modified Fe_3O_4 nanoparticles. The value of P for L- and D-alanine (0.01 $molL^{-1}$), L- and D-tryptophane (0.01 mol L^{-1}), L-and D- tyrosine (0.005 mol L^{-1}) were measured to be 3.1×10^{-3} mol g^{-1}, 2.1×10^{-3} mol g^{-1}, 3.0×10^{-3} mol g^{-1}, 1.9×10^{-3} mol g^{-1}, 2.5×10^{-3} mol g^{-1}, and 2.6×10^{-3} mol g^{-1}, respectively.

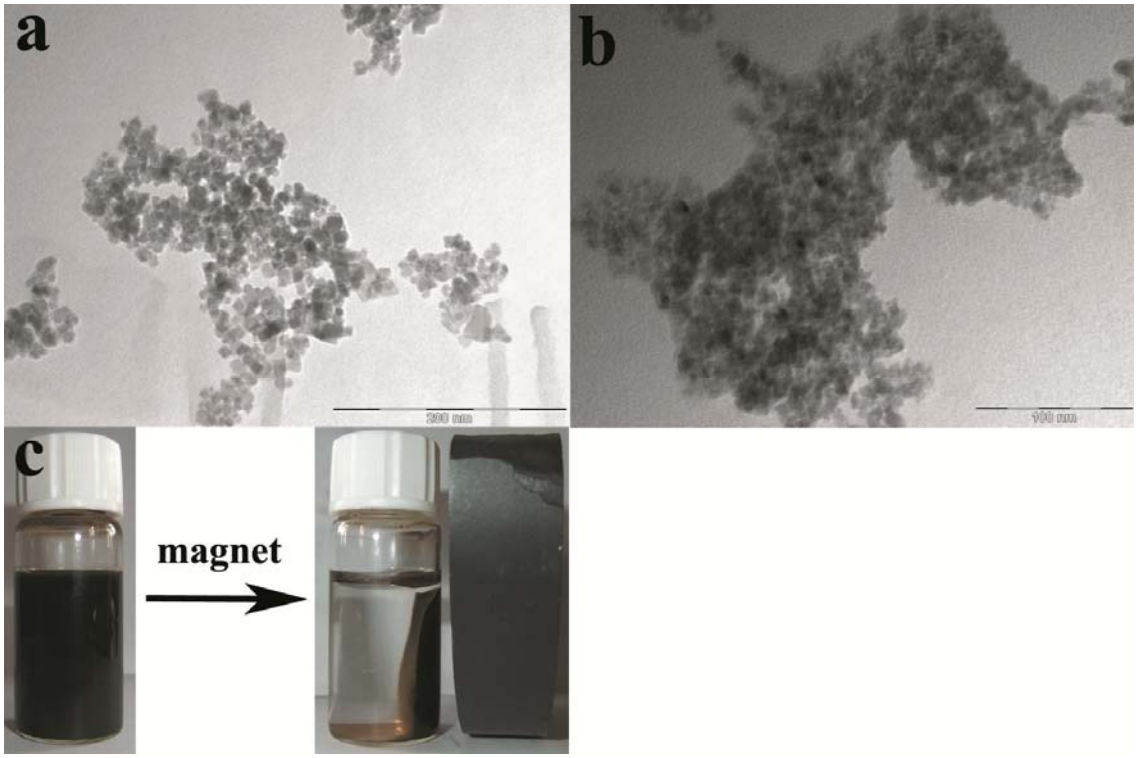

Figure S1. TEM images of (a) Fe_3O_4 nanoparticles and (b) β-CD modified Fe_3O_4 nanoparticles. (c) The separation process of β-CD modified Fe_3O_4 nanoparticles from suspension under an external magnetic field.

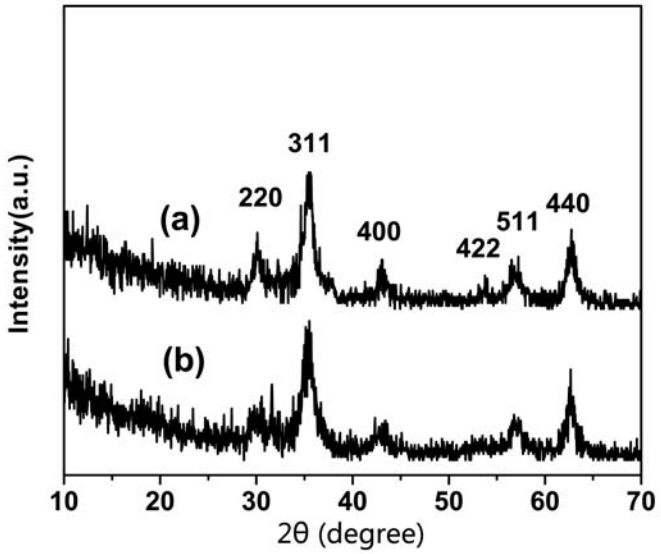

Fig S2. The XRD Spectra for (a) magnetic Fe_3O_4 nanoparticles and (b) β-CD modified Fe_3O_4 nanoparticles.

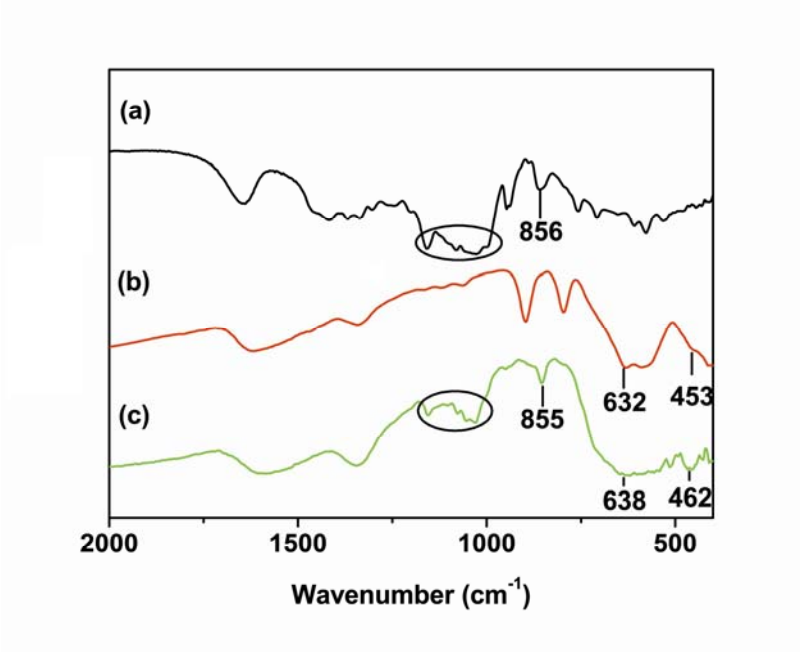

Fig S3. The FTIR Spectra for (a, black line) pure β-CD, (b, red line) magnetic Fe_3O_4 nanoparticles and (c, green line) β-CD modified Fe_3O_4 nanoparticles.

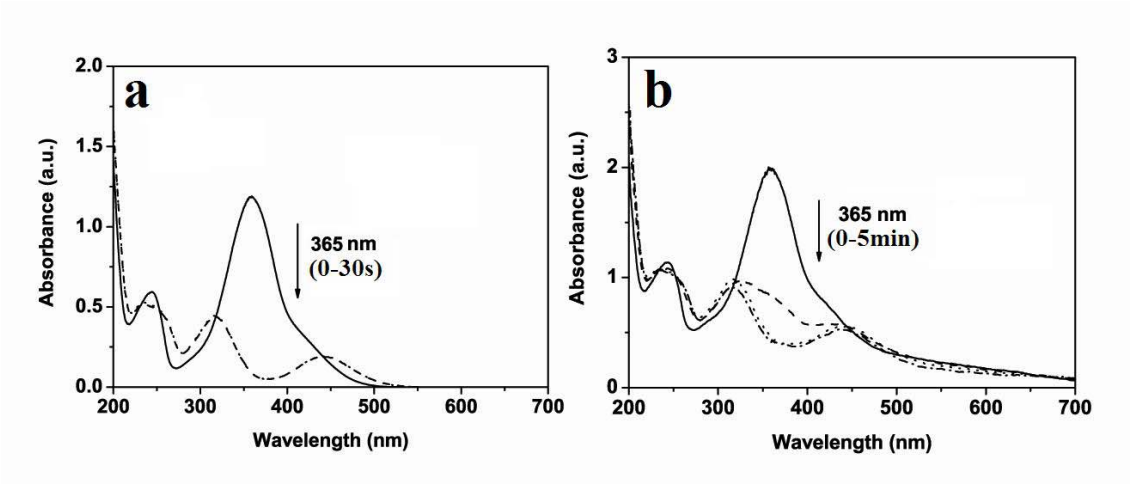

Fig S4. UV–vis absorption spectra of (a) pure AzoTAB solutions and (b) AzoTAB interacted with β-CD modified Fe_3O_4 nanoparticles solution under 365 nm UV light irradiation.

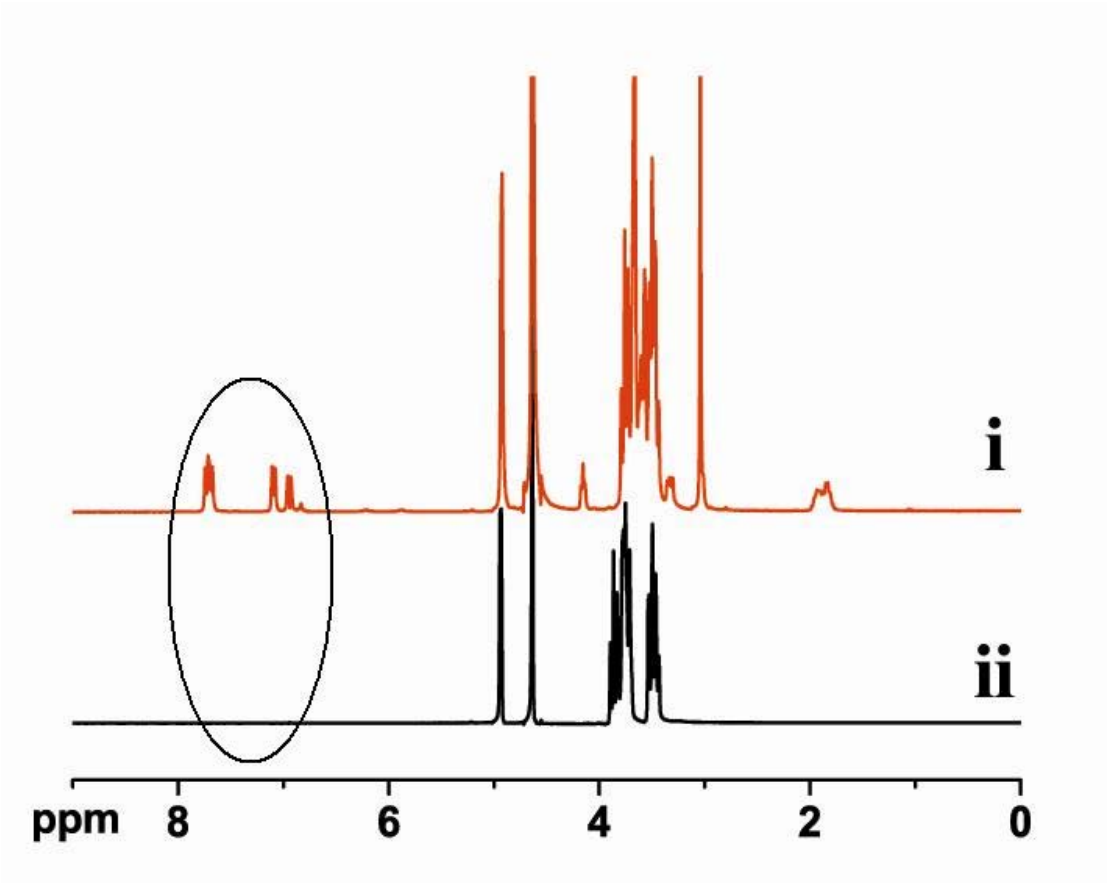

Fig S5. H^1NMR of the β-CD modified Fe_3O_4 nanoparticles (interacted with AzoTAB) (a) before and (b) after 10 min irradiation of UV (365 nm).