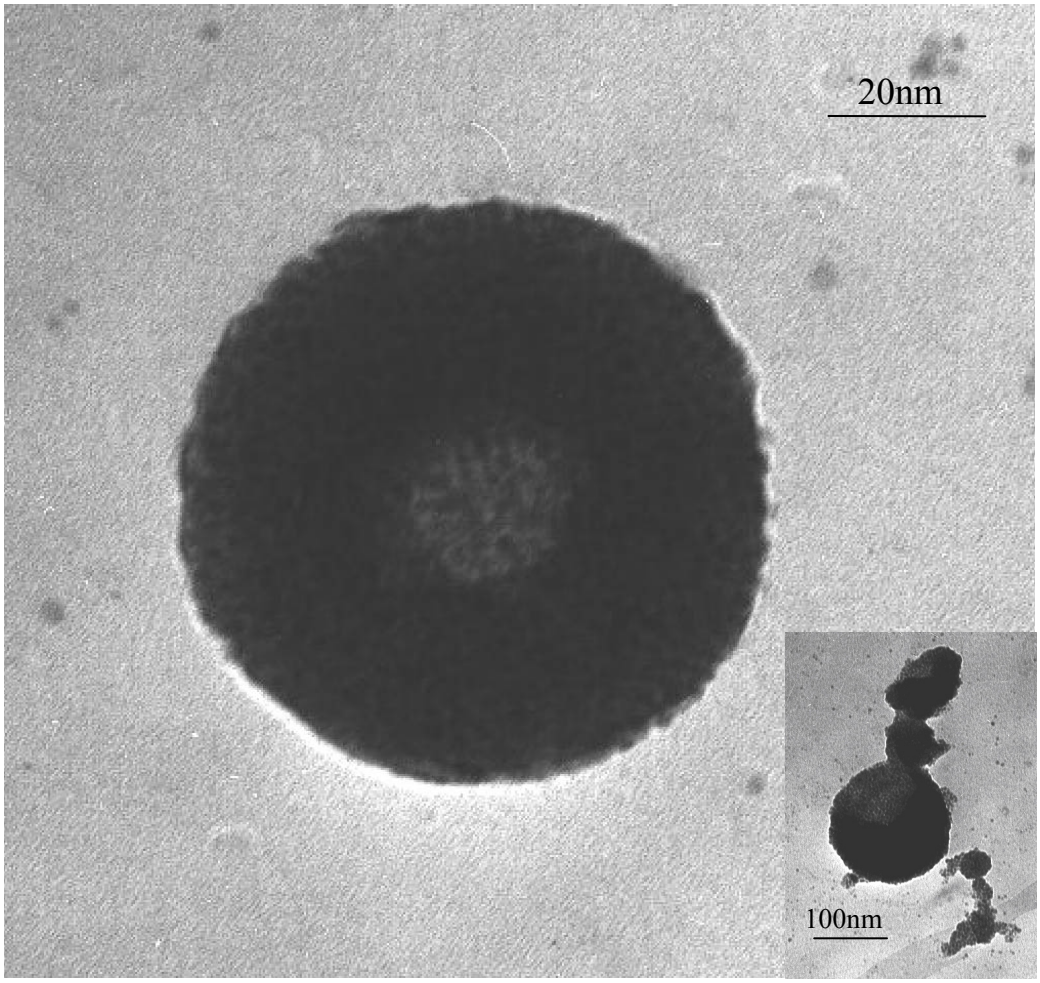


Figure S1 TEM images of the hollow spheres formed when the 2nm nanocrystals are precipitated from cyclohexane with methanol/water.

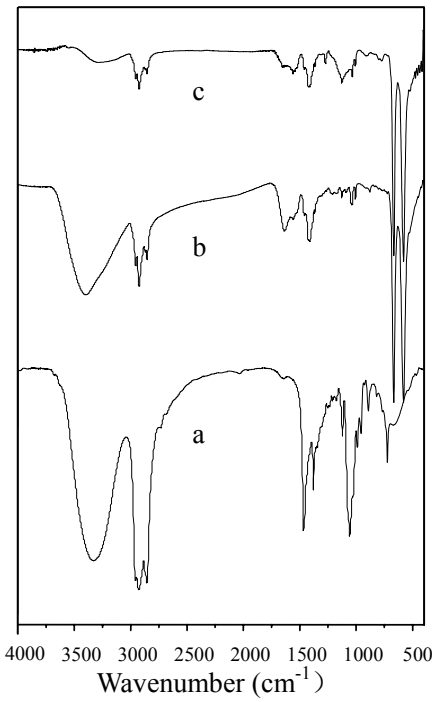


Figure S2 IR spectra of (a) *n*-octanol, (b) the 2nm nanocrystals and (c) the 2nm nanocrystals subjected to a heat-treatment at 260℃ for 5min. In order to assign the weight loss at *ca.*300℃ in the TG curves of the nanocrystals, the IR spectra (c) is record after the as-prepared 2nm nanocrystals are heated at 260℃ for 5min. Compared with those in the IR spectra of the 2nm nanocrystals (b), the relative intensity of the absorptions at *ca.*1550cm^{-1}, 1415cm^{-1} and 1115cm^{-1} become stronger, while the absorptions at *ca.*3400cm^{-1}, 2900cm^{-1} and 1630cm^{-1} are consumedly weakened due to the elimination of the chemically absorbed *n*-octanol and water molecules. The absorptions at *ca.*1550cm^{-1}, 1415cm^{-1} are characteristics of the asymmetry and symmetry stretching vibrations of carboxylate group, -COO^{-}, ν_{as}(OCO) and ν_{s}(OCO), respectively[16], and the absorption at 1115cm^{-1} is typical for the asymmetry stretching mode of SO_4^{2-} anions.

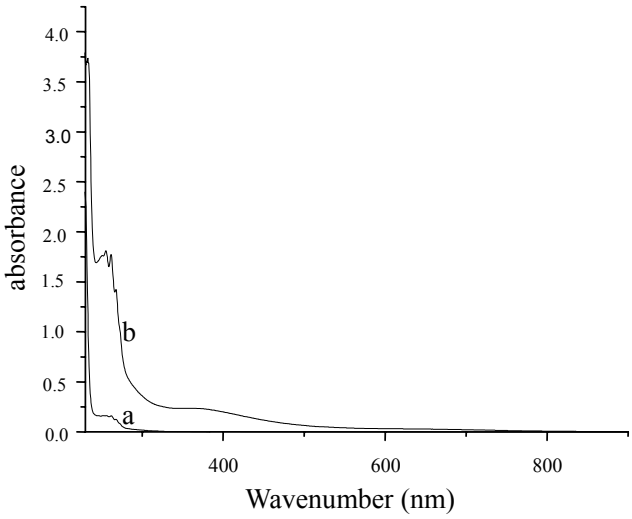


Figure S3 UV-vis. spectra of SDBS (a) and supernatant (b)

The absorptions at *ca.*255nm in a and b is attributed to the $\pi \rightarrow \pi^*$ electron transition in the aromatic ring of SDBS molecules. The characteristic absorption at *ca.*300nm for $\pi \rightarrow \pi^*$ electronic transition of NO_3^- does not exist.

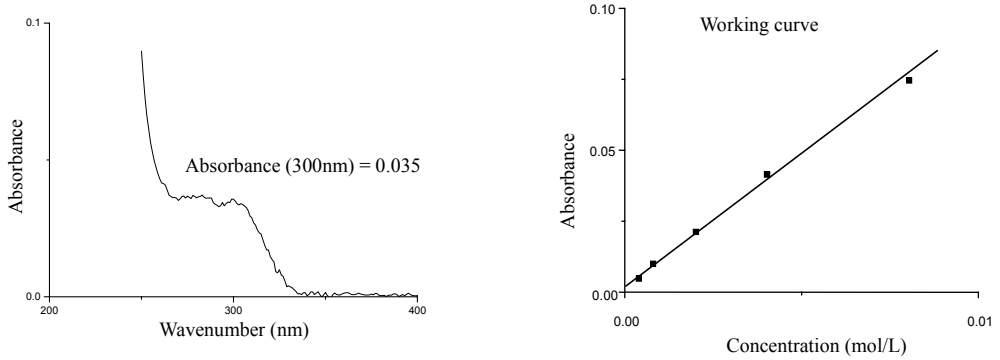
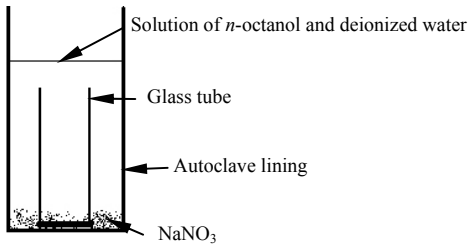


Figure S4 UV-vis. spectra of the dissolved sodium nitrate

An experiment is conducted to quantificationally measure the solubility of $NaNO_3$ in the reaction system, and the detailed experiment was depicted as follows: 250.0uL deionized water was dissolved into 22mL *n*-octanol, the solution and 6.88mmol $NaNO_3$ (0.5840g equal to the mass of the formed $NaNO_3$ in the typical experiment) were put into a 25mL autoclave, and then a 5ml one-end-open glass tube was carefully placed with its open end upwards in the autoclave, ensuring that the open end was below liquid level and no $NaNO_3$ entered the glass tube during manipulation (see Fig.1). After heat-treatment at 180℃ for 1.5hrs the glass tube was taken out, the liquid and salt particles sticking in the outside surface of the glass tube wall were eliminated by washing the outside surface with deionized water. When the outside surface of the glass tube wall was dried, the glass tube containing 5mL *n*-octanol and a little $NaNO_3$ was put into a conical flask, and then 50.00mL deionized water was added. The sodium nitrate in the glass tube was entirely dissolved into aqueous phase by ultrasonic agitation, the solution was transferred into a 100mL separating funnel, and the lower aqueous solution was separated when the funnel was standing for a certain period of time. The lower aqueous phase was used as sample for UV-vis absorption spectra measure, deionized water saturated with *n*-octanol was the blank. The peak at 300nm attributed to $\pi \rightarrow \pi^*$electronic transition of NO_3^- in UV-vis absorption spectra was used as the reference. Working curve was made by drawing the curve with the absorbance of 300nm peak as ordinate and $NaNO_3$ concentrations in water as abscissa. Thus the solubility of $NaNO_3$ was found from the working curve.



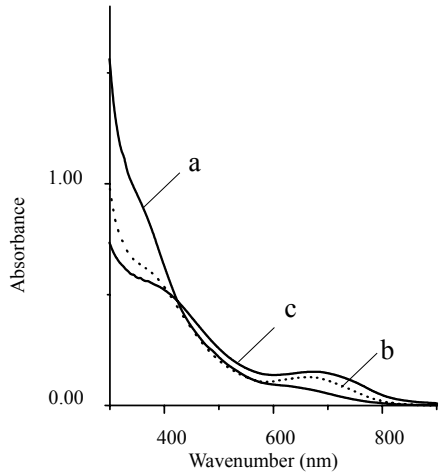


Figure S5 UV-vis. absorption spectra of the reaction liquid obtained after different high-temperature reaction time. The curve evolution from a (160℃ 20min.) to b (160℃ 80min.) indicates the formation of Co_3O_4 monomers; the red shift from b to c demonstrates the growth of the Co_3O_4.

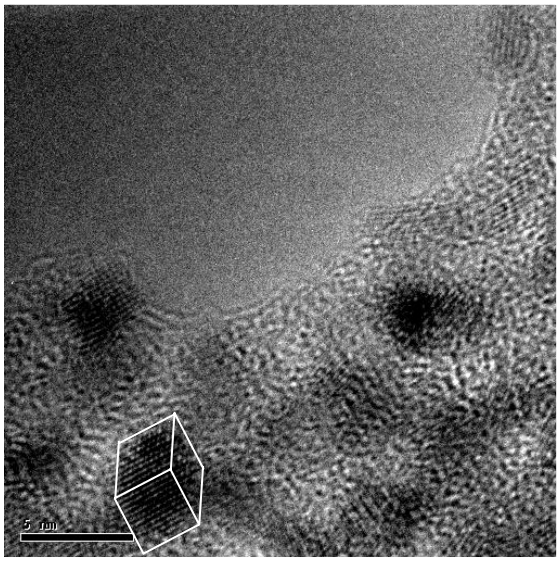


Figure S6 HRTEM images of the 2nm nanocrystals, among these nanocrystals, a few unperfect 2.5nm nanocubes can be detected.