# Supporting Information for New Journal of chemistry

# Facile synthesis of chitosan assisted multifunctional magnetic

# Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CS@pyropheophorbide-a fluorescence nanoparticles

# for photodynamic therapy

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## 1. Experimental

## **Chemicals and Reagents**

All the chemicals reagents were used without further purification. All the solvents were distilled and purified by standard procedures. The pure water was obtained from a Milli-Q synthesis system (Millipore, Billerica, MA. USA). Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 98%), Sodium oleate, Oleic acid, Tetraethyloxylsilicate (TEOS), Hexadecyl trimethyl ammonium bromide (CTAB, 99%), Dimethyl sulfoxide (DMSO) and 3-(4,5-dimethylthiazol-2-yl)-2,5-dipheny-ltetrazolium bromide (MTT) were purchased from Sigma-Aldrich. 1-octadecene, glutaryl dichloride, N-Hydroxysuccinimide (NHS), Sodium azide (SA), D-Mannitol (DM), 1-(3-Dimethyl aminopropyl)-3-ethylcarbodiimide (EDC) and Chitosan were purchased from Alfa Aesar Chemical Company. Ethanol, n-hexane, Chloroform, Triethanolamine, Methanol, Dichloromethane, N,N-Dimethylformamide (DMF), Sodium hydroxide (NaOH), were analytical reagent. Dulbecco's modified eagle medium (DMEM), penicillin, fetal bovine serum (FBS), and streptomycin were purchased from Beijing Dingguo Biotechnology Co. Phosphate buffered saline (PBS) purchased from Invitrogen (10010) was used as a balanced salt solution in cell culture. PBS used in other experiments was prepared by mixing stock solutions of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

## Synthesis of magnetic Fe<sub>3</sub>O<sub>4</sub> NPs

FeCl<sub>3</sub> (2.7 g,10 mmol) and sodium oleate (9.13 g,30 mmol) were dissolved in a mixture solvent (20 mL ethanol, 15 mL water, 35 mL hexane). The mixed solution was stirred at 70°C for 4 h. The upper organic layer which contained the iron-oleate complex was separated in a separation funnel and washed with 10 mL distilled waters.<sup>50</sup>After evaporating off the organic solvent. The resulting mixture was dissolved in 50 g of octadecene (198.4 mmol) and oleic acid (1.425 g, 4.685 mmol). The reaction mixture was heated to 320°C within 100 min (3.3°C/min), and kept this temperature for 30 min. After cooling to room temperature, added 125 mL of anhydrous ethanol to precipitate the nanocrystals. In high-speed centrifugation condition (13000r/min), Fe<sub>3</sub>O<sub>4</sub> NPs were separated and dispersed in chloroform for further use.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs

Fe<sub>3</sub>O<sub>4</sub> (25 mg) were dispersed in 45 mL of chloroform, ultrasonically for 1 h, then pouring into the solution which contained 80 mL of hexadecyl trimethyl ammonium bromide water solutions (CTAB, 0.11 mmol/mL). The resulting solution was stirred vigorously on a water bath for 30 min at 32 °C. The resulting mixture was heated up to 60 °C to evaporate the chloroform. Subsequently, NaOH aqueous solution (0.1 M) was added to adjust the pH between 8-9. Then added 20% TEOS ethanol solution (550  $\mu$ L) to it, stirred the reaction mixture vigorously for 24 h at 60 °C. After the reaction, then added 100 mL of ethyl alcohol to dissolve CTAB and precipitate the nanoparticles, stirred vigorously for 15 min. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs were collected by centrifugation (13000r/min) and washed several times with 500 mL of ethyl alcohol, then dried in vacuum for further use.

## 2. Results and discussion



Figure S1. N<sub>2</sub> adsorption-desorption isotherm of  $Fe_3O_4@SiO_2$  core-shell nanoparticles.



Figure S2. FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b), CS (c), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CS (d), PPA (e), and MFCSPPA (f), respectively.



Figure S3. TGA of MFCSPPA (a) and Fe $_3O_4@SiO_2@CS$  (b) was performed in the range of 25 $\sim800$  °C.