Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for:

Reversible Formation of Hybrid Nanostructures via an Organic Linkage

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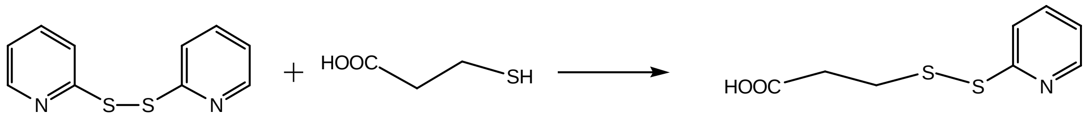
Generals

Reagents and solvents were obtained from commercial sources and used as received unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker DRX500 spectrometer at ambient temperature with residual deuterated solvent peaks as internal references. ESI mass spectra were obtained on a Finnigan LCQTM instrument. TEM was conducted on a JEOL JEM-100S instrument. SEM was conducted on a LEO 1530VP instrument. ζ potential was measured on a Brookhaven BI9000AT system.

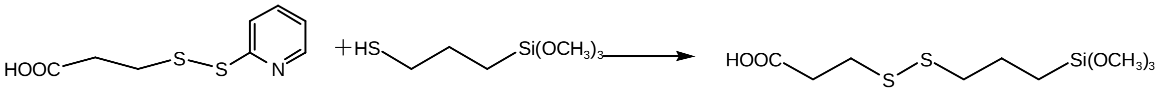
Synthesis of 2-[3-(trimethoxysilyl)-propyldisulfanyl]-propionic acid (2)[1]

2, 2'-dipyridyl disulfide (3.75 g, 17 mmol) was dissolved in 30 mL ethanol and a 5 mL ethanol solution of meraptoppropionic acid (2.1g, 20 mmol) was added dropwise. After 24 h of stirring at room temperature, the crude yellow oil product was isolated by rotary evaporation. The product was purified via alumina column chromatography by performing a two-step elution (eluent: first, CH_2Cl_2:CH_3CH_2OH = 3:2, v/v; then, CH_2Cl_2:CH_3CH_2OH:CH_3COOH = 30:20:2, v/v). The obtained final product 2-carboxyethyl-2-pyridyl-disulfide (**1**, 1.45 g, 6.8 mmol) corresponds to 40% yield. ^{1}H NMR (500MHz; $CDCl_3$): δ 2.83 (t, 2H, CH_2), 3.10 (t, 2H, CH_2), 7.20 (t, 1H, ArH), 7.66 (t, 1H, ArH), 7.72 (t, 1H, ArH), 8.51 (d, 1H, ArH); ESI MS (*m/z*): 216.1 [$M+H^+$], 238.1 [$M+Na^+$].



1

To make molecule **2**, the experiments were conducted under an argon atmosphere using Schlenk techniques. Tetrahydrofuran (THF) was vacuum transferred from sodium/benzophenone ketyl prior to use. Compound **1** (1.51 g, 7 mmol) was dissolved in 30 mL THF and transferred to a Schlenk flask, into which (3-mercaptopropyl)-trimethoxy silane (1.1 g, 5.6 mmol) was injected. The solution was stirred for 12 h. After flash evaporation of the solvent, the yellow product was purified by silica column chromatography using a mixed solvent (ethyl acetate:hexane = 1:2, v/v) as eluent. The purified product (0.8 g) was isolated with a 48% yield. ^{1}H NMR (500MHz; $CDCl_3$), δ 0.77 (t, 2H, CH_2), 1.83 (t, 2H, CH_2), 2.72 (t, 2H, CH_2), 2.82 (t, 2H, CH_2), 2.92 (t, 2H, CH_2), 3.60 (s, 9H, OCH_3); ESI MS (*m/z*): 300.7 [$M+H^+$], 321.9 [$M+Na^+$].



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Synthesis of SiO_2 NPs[2]

Monodisperse SiO_2 NPs (~400 nm) were prepared based on Stöber method. A solution consisting of 100 mL absolute ethanol and 44 mL ammonia (28-30%) was added to a three-necked, 250 mL round-bottom flask; then, 50 mL absolute ethanol solution of tetraethyl orthosilicate (0.9 mol) was added to the above mixture dropwise under vigorous stirring. The reaction was allowed to proceed for 12 h at room temperature.

Synthesis of Fe_3O_4 NPs[3]

Fe_3O_4 NPs (~18 nm) were prepared by chemical precipitation method as follows: deionized water (200 mL) was placed in a 500 mL four-necked round-bottom flask equipped with a condenser, a argon gas inlet, and a mechanical stirrer. Then, $FeCl_3{\cdot}6H_2O$ (2.76g) and $FeCl_2{\cdot}4H_2O$ (0.99g) in 2:1 molar ratio were added into the flask. The mixture was stirred under argon atmosphere for 30 min, followed by the addition of 1.5 M NH_4OH aqueous solution until the pH of the reaction mixture reached 8. Then the reaction was allowed to run for 2 h. Finally, the resulting magnetic NPs were separated by magnetic field and purified by dialysis.

Synthesis of Au NPs[4]

An aqueous solution (50 mL) of $HAuCl_4$ (0.01%, wt%) was heated to reflux and 0.5 mL aqueous solution of trisodium critrate (1%, wt%) was added quickly. After approximately 70 s the color changed into a brilliantly red. The mixture was allowed to reflux for an additional 5 min. The result solution was Au NPs (~25 nm).

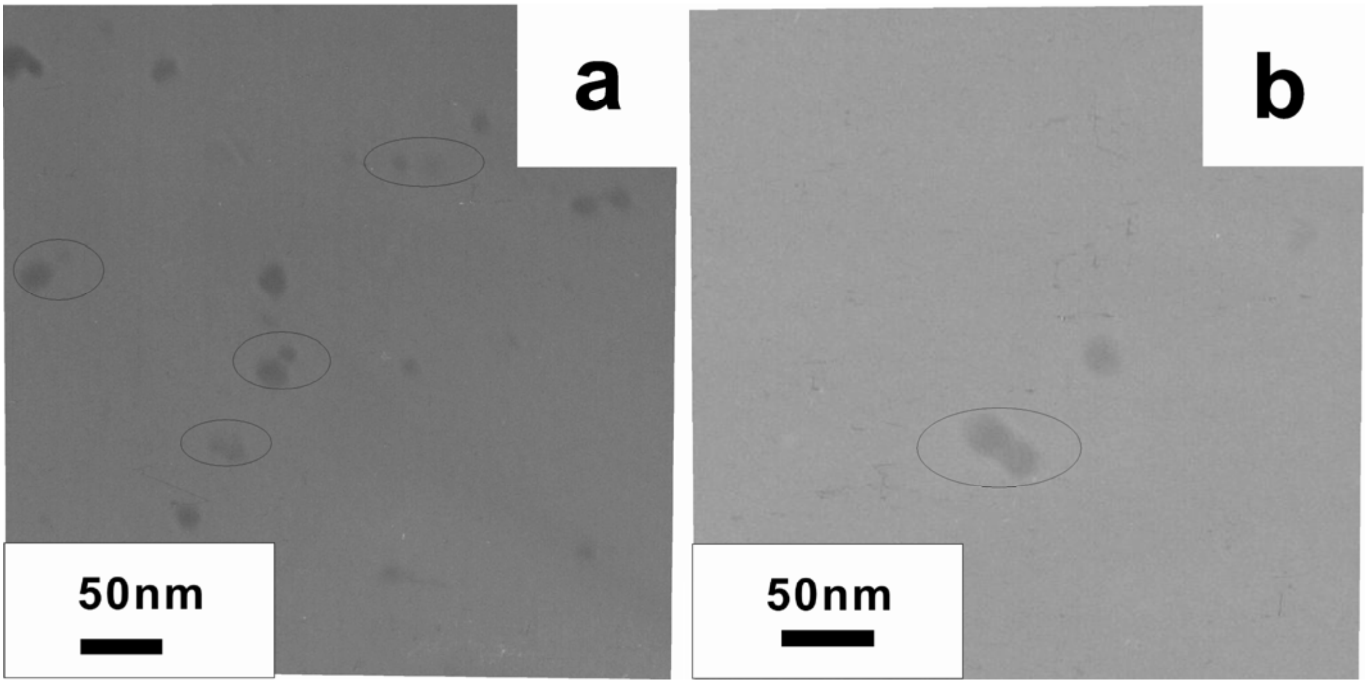

Fig.ESI1 TEM images of the possible Fe_3O_4 NP dimers.

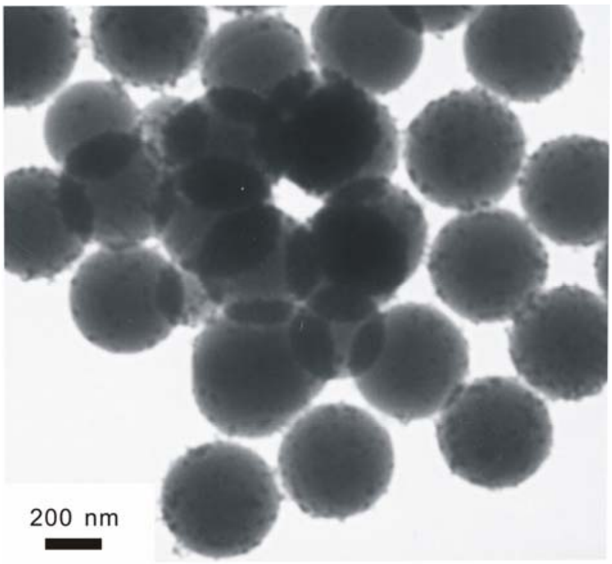

Fig.ESI2 TEM image of SiO_2-Fe_3O_4 hybrid nanostructures after butyric acid treatment.

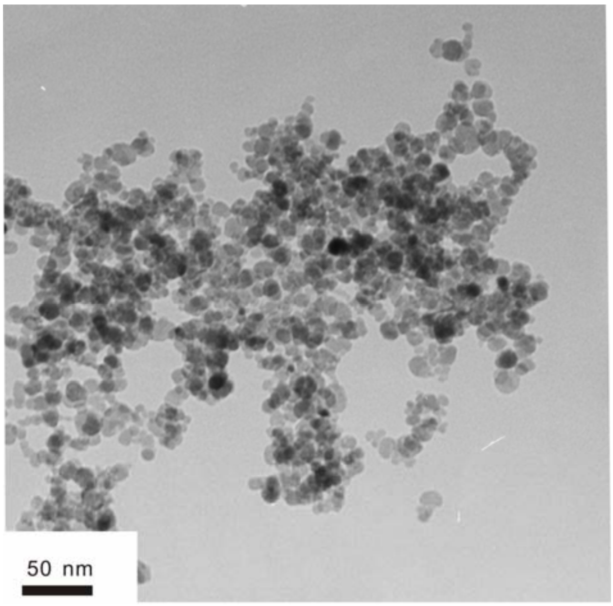

Fig.ESI3 TEM image of as-prepared Fe_3O_4 NPs.

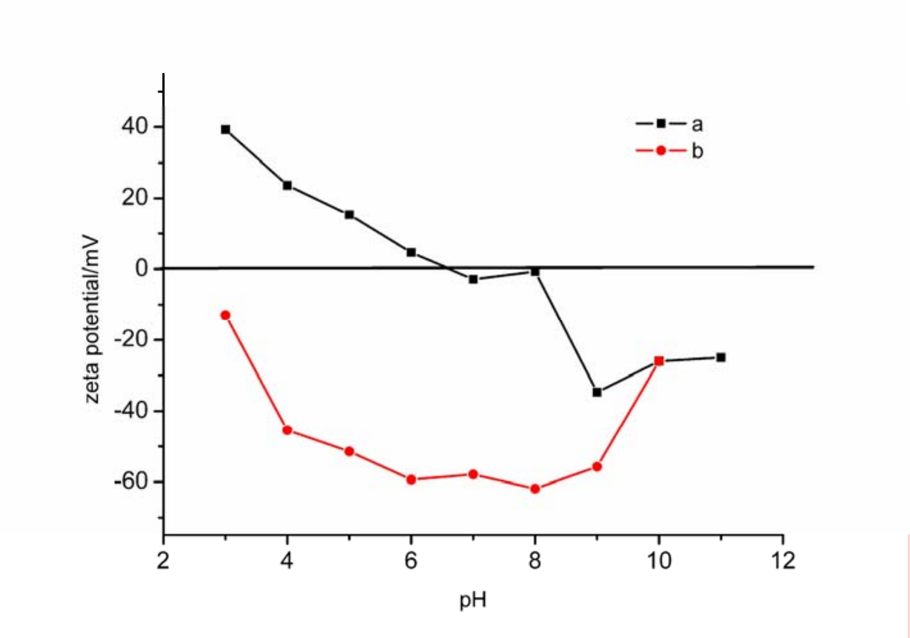

Fig.ESI4 ζ potential of (a) Fe_3O_4 and (b) SiO_2 NPs at different pH values.

Notes and references

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