Supporting information for *Chemical Communications*

Dense covalent attachment of magnetic iron oxide nanoparticles onto silica particles using a diazonium salt chemistry approach.

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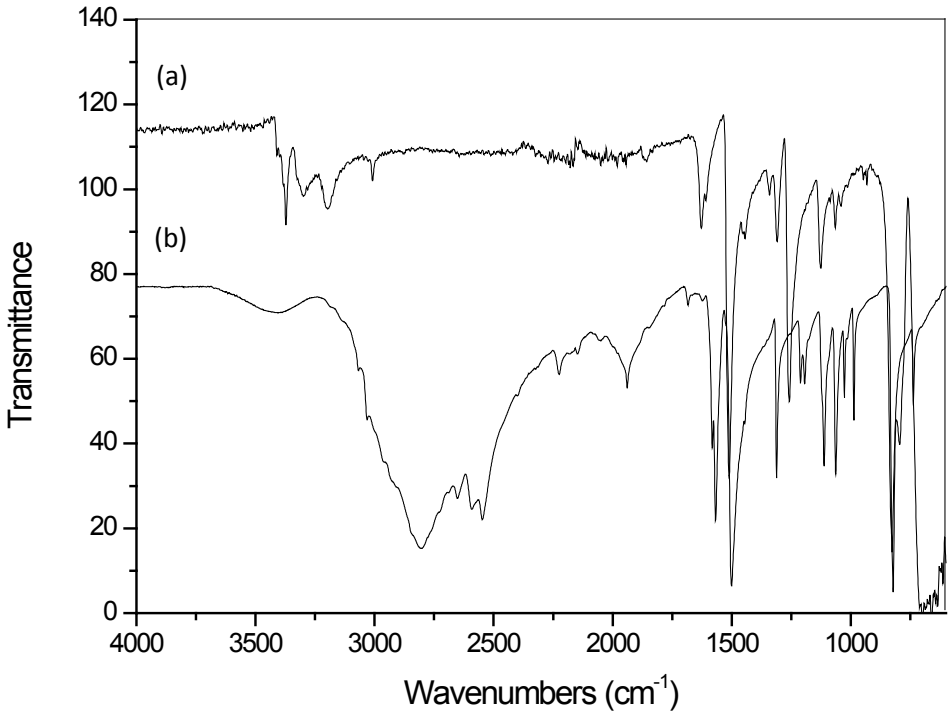
I. Synthesis

Materials. We used ammonium hydroxide solution, 25% (Sigma-Aldrich), absolute ethanol (Honeywell), deionized water, tetraethoxysilane (TEOS, GPR Rectapure, VWR Prolabo) for the silica particles synthesis.

Phenylenediamine (Sigma), tetrafluoroboric acid (ACROS), terbutylnitrite (Aldrich) were used for synthesis of 4-aminophenyldiazonium tetrafluoroborate.

$FeCl_3.6H_2O$, $FeSO_4.7H_2O$, NaOH (Aldrich) were used for the synthesis of iron oxide (magnetite) nanoparticles.

Synthesis of 4-aminophenyldiazonium tetrafluoroborate (BF_4^-, $^+N_2$-C_6H_4-NH_2): To 3.71 g (34 mmol) of phenylenediamine, cooled at 0°C in an ice bath, was added dropwise 10 ml of tetrafluoroboric acid (HBF_4) under continuous vigorous stirring. 2.35 g (17 mmol) of terbutylnitrite was added and the reaction was left to proceed for 10 min. The powder was dried and stored at -5°C.



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ig. S1. ATR-IR spectra of the paraphenylenediamine (a) and (b) the free diazonium salt BF_4^-, $^+N_2$-C_6H_4-NH_2.

Synthesis of iron oxide nanoparticles (magnetite). Iron oxide nanoparticles were synthesized as follows: in a typical reaction, 2.9 mmol of $FeCl_3$ and 1.2 mmol of $FeSO_4$ were dissolved in 5 mL of deionized water. The solution was purged with nitrogen, and the inert atmosphere was maintained for the duration of the synthesis. Then 3 mL of NaOH (c = 1 M) were rapidly added under vigorous stirring. The color of the solution changed immediately from yellow to dark, indicating the formation of Fe_3O_4 nanoparticles. The particles were washed several times with water.

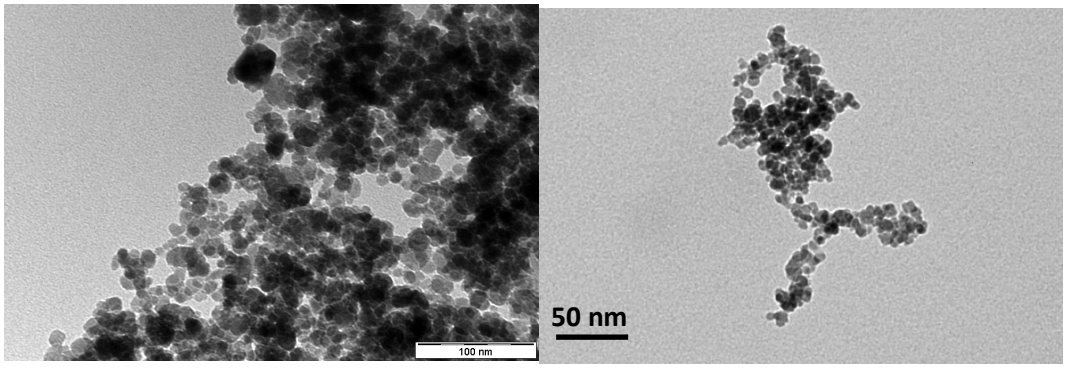

Figure S2. Transmission electron micrograph of the synthesized Fe_3O_4 nanoparticles. The particles are roughly spherical with a typical size (diameter) of about 10-15 nm.

II. Characterizations

ATR-IR. Attenuated total reflectance infrared (ATR-IR) spectra were measured thanks to a Bruker Vertex spectrometer over the range of 400 – 5000 cm^{-1} with a 4 cm^{-1} spectral resolution. Before measurements the samples were dried at 60°C overnight.

TEM. Transmission electron microscopy (TEM-CM100, Philips) operating at 80 keV was used to determine the size and morphology of the synthesized particles. Samples for TEM were prepared by drying one droplet of 0.5 vol % of particles onto a carbon-coated (300 mesh) grid.

SEM. Scanning electron microscopy (SEM) observations were performed with a FEI XL30 Sirion operating at 15 kV. The samples were deposited on the sample holder, dried and gold-coated prior to examination.

EDX. X-ray energy dispersion spectroscopy of the core silica@magnetic shell hybrid material was conducted with an EDAX GENESIS analyzer installed on SEM.