Synthesis of highly magnetic gold-coated zero-valent iron core-iron oxide shell nanoparticles with superparamagnetic behaviour

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Experimental:

Chemicals: iron pentacarbonyl (99.99%), 1-octadecene (1-ODE, 90%), oleylamine (98%), oleic acid (90%) sodium hydride (60 % dispersion in mineral oil), anhydrous *N,N*-dimethylformamide (DMF, 99.8%), 1-iodooctadecane (1-IOD, 95%), 2,4-pentanedione (PD, 99%), Igepal CO-520, ammonium hydroxide (30%), tetraethyl orthosilicate (TEOS, 98%), 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS, 80%), gold(III) chloride trihydrate (99.9%), tetramethylammonium hydroxide in methanol solution (25% (wt/vol) TMAOH in methanol solution), hydroxylamine hydrochloride (NH2OH.HCl), sodium citrate dihydrate, sodium borohydride were purchased from Sigma-Aldrich. Acetone, toluene, cyclohexane, methanol, nitric acid (69%), hydrochloric acid (32%) were purchased from Chem-Supply Australia. With the exception of oleylamine, all chemicals were used as received. Oleylamine was distilled under reduced pressure before reaction. Glassware was cleaned with freshly prepared *aqua regia* (HCl: HNO_3 in a 3:1 ratio by volume) followed by rinsing with Milli-Q water.

Synthesis of zero-valent iron core-iron oxide nanoparticles: magnetic nanoparticles were synthesized with a slightly modified thermal decomposition method reported in the literature.[1]

To ensure all reagents were air-free, all liquids were degassed under vacuum and argon before use. The chemicals and glassware were first transferred to a glovebox. A sum of 20 mg of 3-octadecyl-2,4-pentanedione (OD-PD)[1] and 5 mL of 1-ODE was added to a 25 mL two neck round bottom flask and vortexed to dissolve. The flask was sealed with a stopper and a closed condenser to ensure no air or moisture could go inside. To a 25 mL vial were added 48 mg of OD-PD, 1.47 mL of iron pentacarbonyl and 9 mL of the 1-ODE and vortexed to dissolve. The solution was transferred to a 20 mL syringe tube and sealed. The two necks round bottom flask and 20 mL syringe were carefully transferred to a laboratory fume hood. The flask was connected to a Schlenk line and opened to Ar gas flow. The syringe was loaded onto a syringe pump. The flask was heated *via* a hot plate to 220 ˚C while under a continuous flow of Ar. After reaching 220 ˚C the solution inside the syringe was added dropwise into the flask with a rate of 0.03 mL/min. Once the syringe was emptied the reaction was heated at 220 ˚C for another hour and then cooled down to room temperature. The two neck flask was carefully transferred to the glovebox. To change the ligand on the surface of the nanoparticles 500 µL of the sample was mixed with 2 mL of 1-ODE and 60 µL of oleylamine and transferred to a 25 mL round bottom flask while making sure the flask was totally sealed and then transferring the solution to a fume hood and heating to 70 ˚C and kept at 70 ˚C for one hour while stirring (under Ar atmosphere). The particles were cooled down to room temperature and transferred back to the glovebox. The particles were magnetically separated and transferred to a new round bottom flask. A total of 2 mL of 1-ODE and 1 mL of oleic acid were added to a new flask. The flask was sealed and then transferred to a fume hood heated to 70 ˚C while stirring and left for one hour (under Ar atmosphere). The nanoparticles were transferred to 5 mL centrifuge tubes and 2 mL of a solution 10:1 toluene to oleylamine and 1 mL of ethanol was added to the solution. The particles were centrifuged at 13500 rcf for 12 min and the supernatant was removed (repeated two more times). The particles were dispersed in 500µL of toluene (the concentration of nanoparticles was adjusted to 2.75 nM according to ICP).

Addition of a silica shell on the surface of the nanoparticles: a well-known microemulsion method was used to form the silica layer on the surface of the oleic acid capped zero-valent iron core-iron oxide shell nanoparticles.[2] An aliquot of 12 mL of cyclohexane was added to a 40 mL vial followed by addition of 770 µL of Igepal CO-520. The solution was vortex for 5 min to dissolve Igepal completely. Then 100 µL of the zero-valent iron core-iron oxide shell nanoparticles in toluene was added to the solution and shake with hand. Then an aliquot of 60 µL of the ammonium hydroxide was added. The solution was shaken by hand for few seconds and subsequently, 30 µL of TEOS was added and the vial was shaken for few more seconds. The vial then was left inside a fume hood for two days. A 7 µL of the AEAPTMS was added to the vial and the vial was shaken for 2 h at 200 rpm. 4 mL of the 50 mM TMAOH in methanol solution was added to the microemulsion system and the dark brown layer was carefully transferred to a new vial. To clean the particles 8 mL of acetone was added to the solution and the solution was transferred to centrifuge tubes. Particles were centrifuged at 1600 rcf for 15 min and the supernatant was carefully removed. To each centrifuge tube was added 4 mL of acetone and nanoparticles were centrifuged at 1600 rcf for 15 min again. The supernatant was removed and particles were dispersed in DMSO. To make sure that the free silica nanoparticles are removed, magnetic separation was done twice and final silica-coated zero-valent iron core-iron oxide shell nanoparticles were dispersed in 500 µL of DMSO (concentration of the particles was adjusted to 400 nM).

Gold seeding and gold shell growth: To form the gold nanoshell a seed-mediated method with modification was used.[3,4] The seeded nanoparticles were prepared by adding a solution of 1.7 mg gold chloride in 20 mL MilliQ water to a 40 mL beaker cooled to 4 ^{o}C with ice and mechanically stirred 500 rpm. To the solution, 110 uL particle solution was injected, followed by 150 µL sodium citrate solution (44 g mL^{-1} in MilliQ water). The solution was stirred for 2 minutes. Then, 1 mL sodium borohydride solution (.38 g mL^{-1} in MilliQ water) was injected and left to react for 6 min. The resulting seeded particles were purified by magnetic separation and washing with MilliQ water before redispersing in 2 mL MilliQ water.

In the second growth step, 0.367 mg gold chloride in 3.5 mL MilliQ water was stirred in a 20 mL vial for 6 h. To this vial, 3.6 mL sodium citrate solution (2.5 mg mL^{-1} in MilliQ water) was added and mixed by gentle shaking. The seeded particle solution was added to the reaction mixture and shaken for 1-2 minutes. Then, 39 µL hydroxylamine hydrochloride solution (2779 g mL^{-1} in MilliQ water) was added to the reaction mixsure and shaken for 10 s to combine. The vial was wrapped in aluminium foil and held at 4 ^{o}C without stirring for 24 h. The resulting gold-coated zero-valent iron core-iron oxide shell particles were purified by magnetic separation and redispersed in MilliQ water.

Characterization:

A CM200 transmission electron microscope was used to acquire the TEM images at an accelerating voltage of 200 kV. Nanoparticles were drop-casted onto a carbon-coated grid followed by air drying. An FEI Nova NanoSEM 450 was used to acquire the SEM images at an accelerating voltage of 4-25 kV. TEM and SEM images were characterized by ImageJ software. Cary 60 single-beam UV-Vis spectrophotometer was used to acquire the UV-Vis spectra of the gold-coated zero-valent iron core-iron oxide shell nanoparticles at room temperature. Zetasizer Nano ZS (Malvern Panalytical) was used to measure the hydrodynamic size and zeta potential of the nanoparticles. Colloidal stability of gold-coated iron core-iron oxide shell nanoparticles was investigated for the changes in the hydrodynamic size of the particles and PDI over time. To investigate the magnetic stability of the nanoparticles, cycles of collection and redispersion of particles via magnet and sonication (5 min) were repeated 25 times after each cycle, the hydrodynamic diameter was measured. The magnetic property was investigated by SQUID magnetometry with an external magnetic field ranging from 60,000 Oe (6 T) to -60,000 Oe (-6 T) at 300 K. X-ray diffraction (XRD) was performed on an Empyrean 2 (Malvern Panalytical) X-ray diffractometer with Co Kα (1.79 Å) radiation with all samples analyzed from 30° to 90° (2θ). nanoparticles concentration was measured with Nanoparticle tracking analysis (NanoSight NS300, Malvern Panalytical). A dark-field microscope (Olympus BX51) was used to acquire dark field images. Gold-coated zero-valent iron core-iron oxide shell was immobilized onto APTES modified glass coverslips and left for 10 min. Glass coverslips were then rinsed with Milli-Q water and then dried under a stream of nitrogen. The coverslip was mounted on the aluminium holder and imaged in an Olympus BX51 dark-field microscope. A 100 W halogen lamp was used as the excitation source and was focused through a dark-filed condenser with NA>0.8. the scattered light was collected by an objective of 100 x magnification and imaged using a Canon 100D CMOS camera (22.3 mm x 14.9 mm sensor size, 4.3 µm x 4.3 µm pixel size).

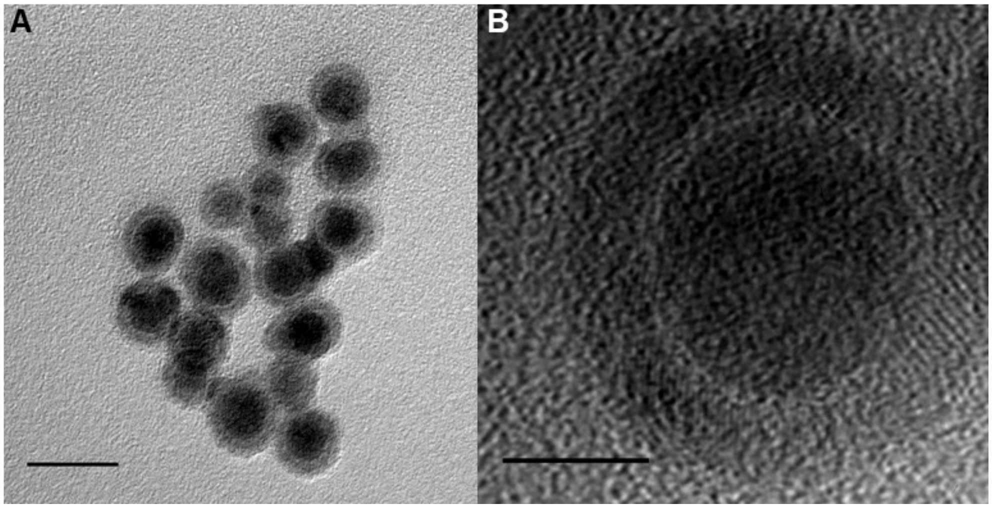

Figure S1. A and B) TEM images of the zero-valent iron core-iron oxide shell magnetic nanoparticles. Scale bars A) 20 nm and B) 5 nm.

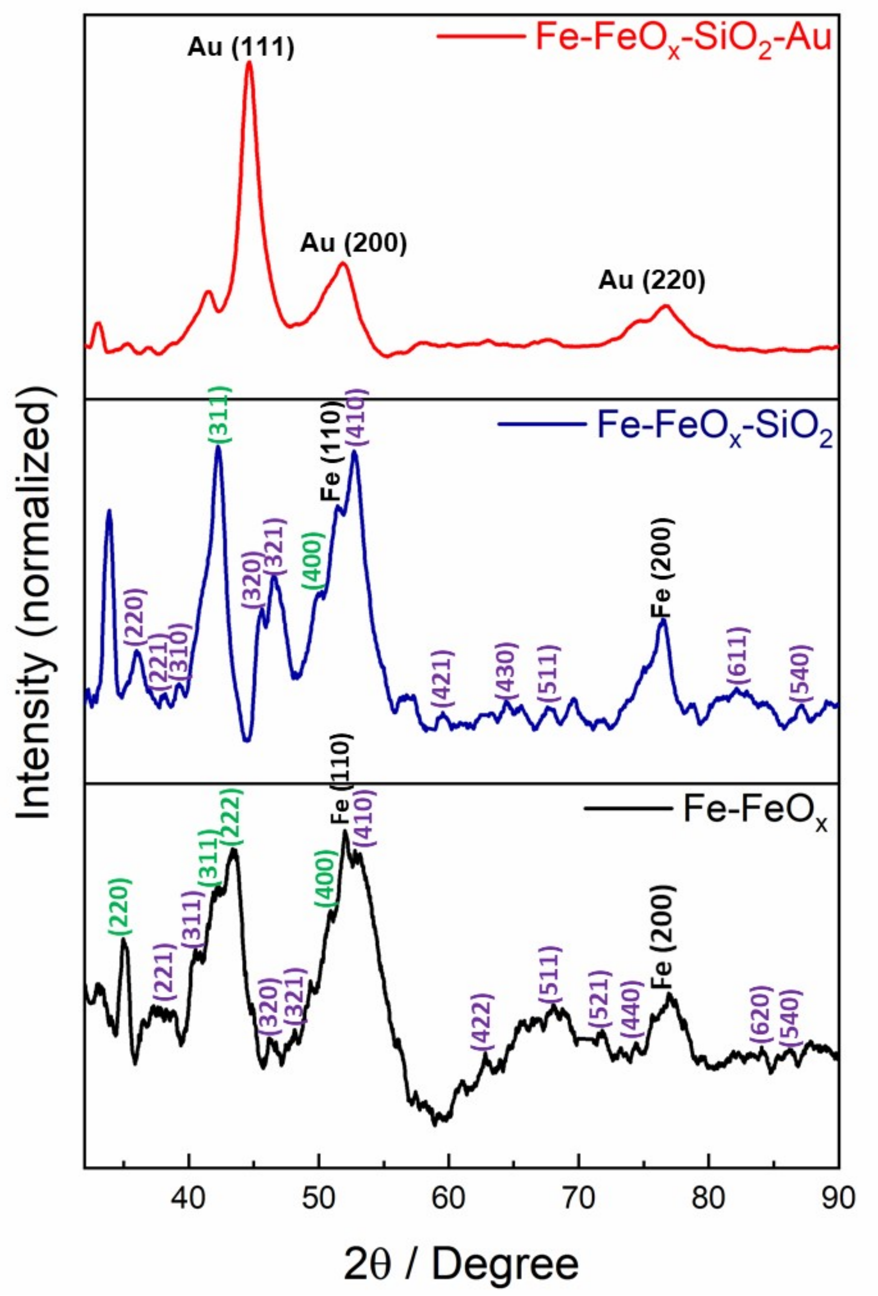

Figure S2. X-ray diffraction (XRD) spectra of zero-valent iron core – iron oxide shell magnetic nanoparticles (black), silica-coated zero-valent iron core – iron oxide shell magnetic nanoparticles (blue) and gold-coated zero-valent iron core – iron oxide shell magnetic nanoparticles (red). Magnetite and maghemite peaks are indexed in green and purple respectively.

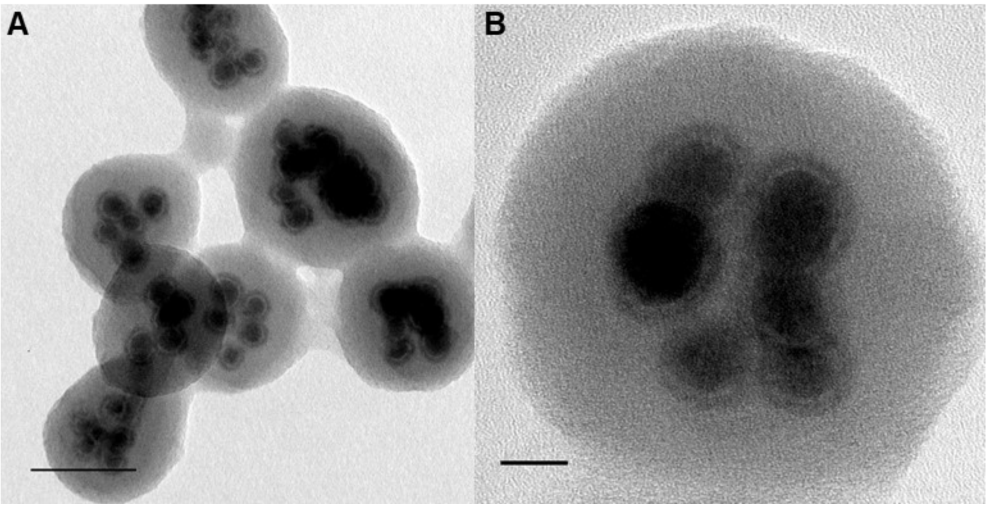

Figure S3. A and B) TEM images of the silica-coated zero-valent iron core-iron oxide shell magnetic nanoparticles. Scale bars A) 50 nm and B) 10 nm.

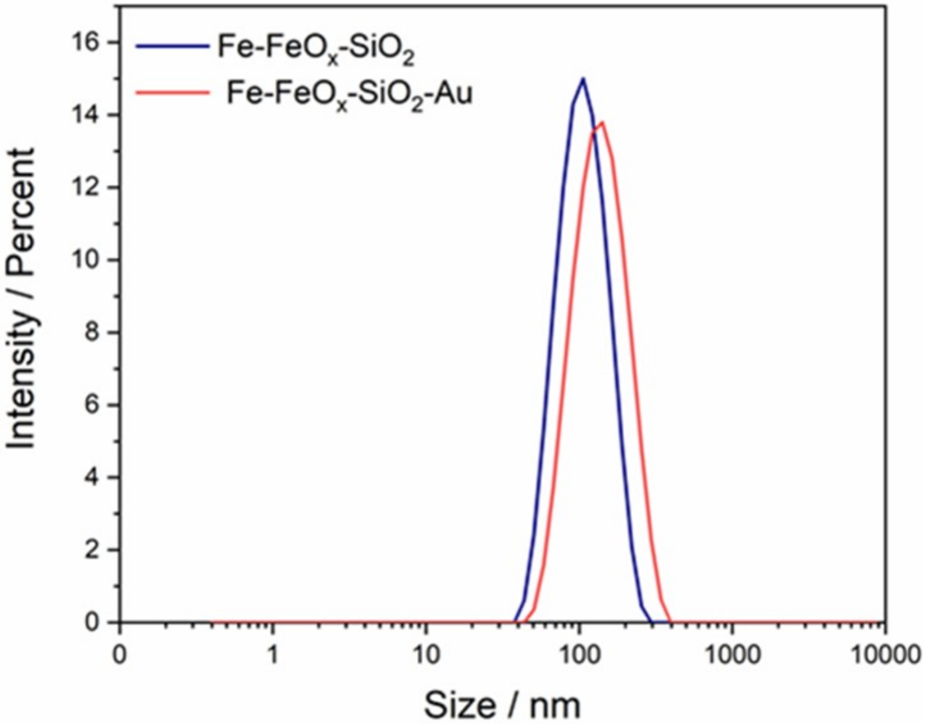

Figure S4. Dynamic light scattering (DLS) measurements of silica-coated zero-valent iron core – iron oxide shell magnetic nanoparticles in Milli-Q water (hydrodynamic size=100 nm; PDI=0.217) (blue) and Gold-coated zero-valent iron core – iron oxide shell magnetic nanoparticles in Milli-Q water (hydrodynamic size=120nm; PDI=0.213) (red).

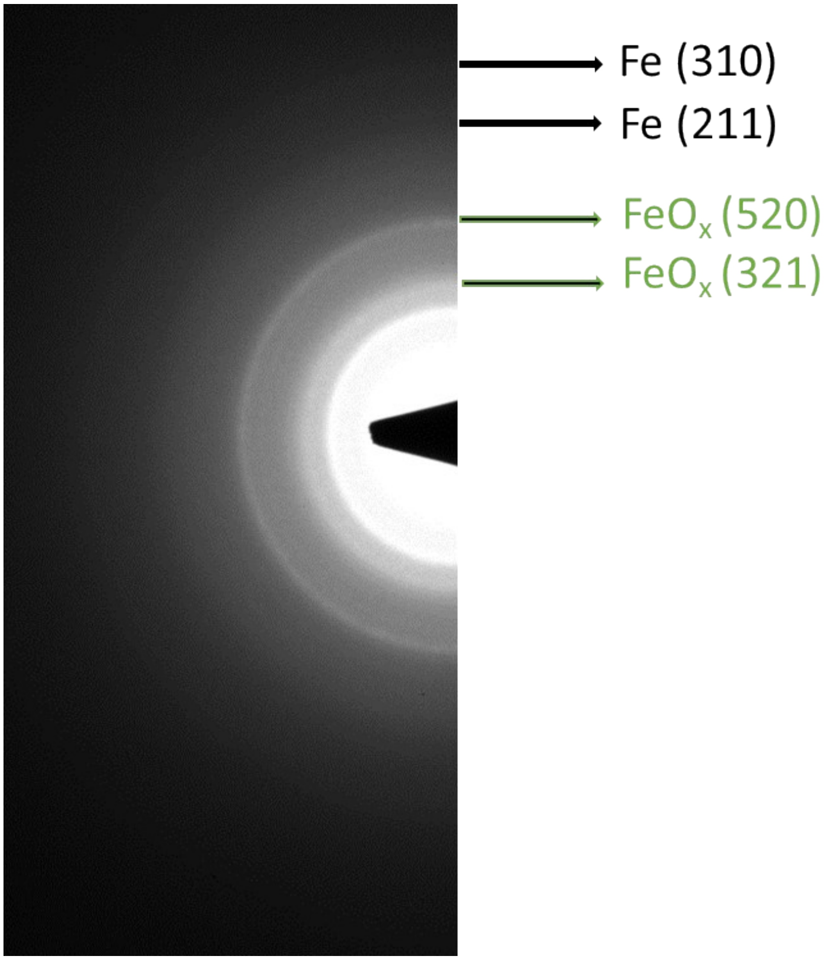

Figure S5. Selected area electron diffraction patterns for the silica-coated zero-valent iron core – iron oxide shell magnetic nanoparticles rings are indexed to body centered cubic iron (black labels) and spinel-type iron oxide (magnetite or maghemite, green labels).

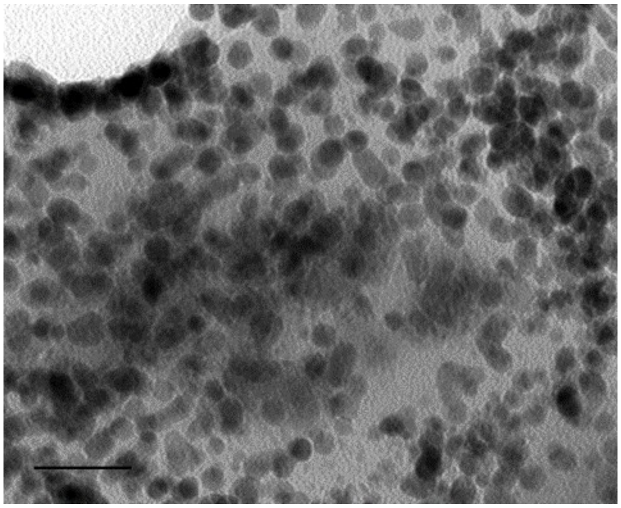

Figure S6. TEM image of the surface of the silica-coated zero-valent iron core-iron oxide shell magnetic nanoparticles seeded with ultra-small gold nanoparticles (≤4 nm). Scale bar 20 nm.

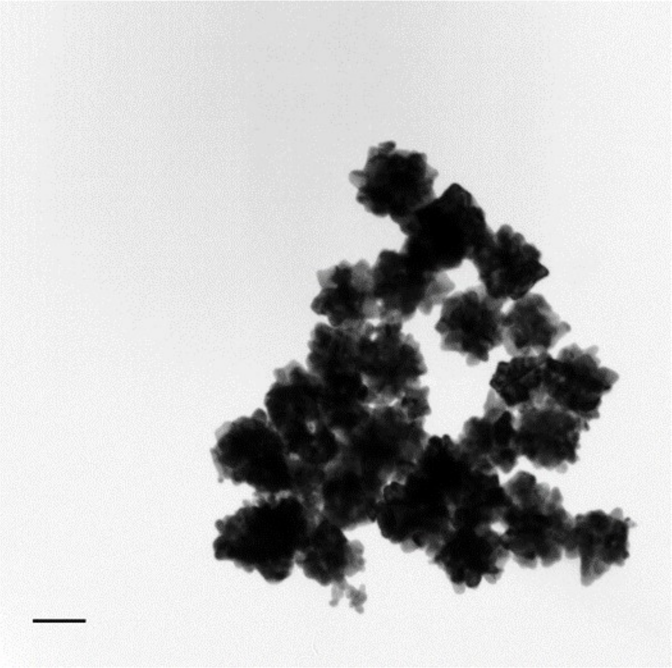

Figure S7. TEM image of the gold-coated zero-valent iron core-iron oxide shell magnetic nanoparticles. Scale bar 100 nm.

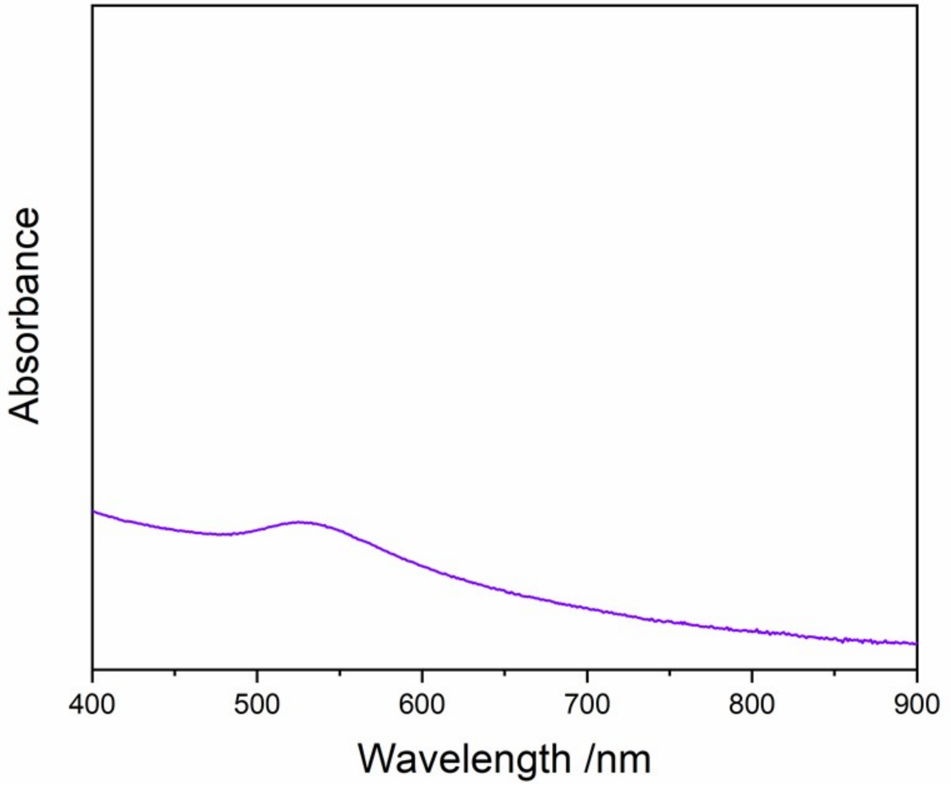

Figure S8. UV-Vis spectrum of gold-seeded silica-coated zero-valent iron core – iron oxide shell magnetic nanoparticle.

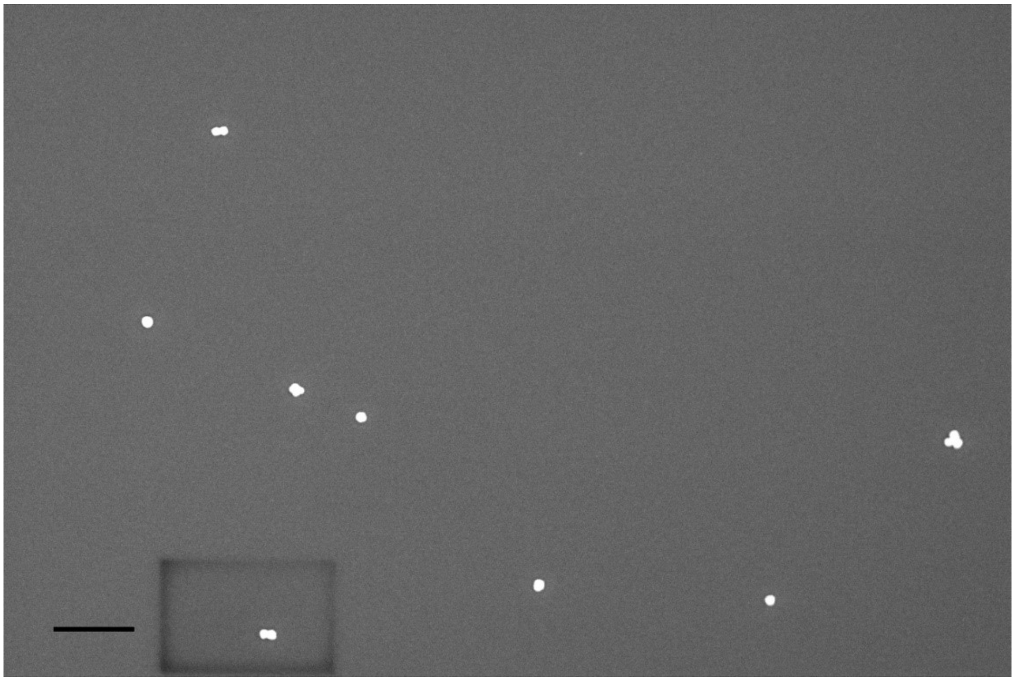

Figure S9. SEM image of the gold-coated zero-valent iron core-iron oxide shell magnetic nanoparticles. scale bar 1 µm.

References:

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