SUPPORTING INFORMATION:

POLYOXOMETALATE-STABILIZED, WATER DISPERSIBLE Fe_2Pt MAGNETIC NANOPARTICLES

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The potassium salt of the α-undeca-silico-tungstate, $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$, was prepared according to the procedure described in ref. (1). The purity was ascertained by cyclic voltammetry and infrared spectroscopy. Other reagents and solvents were purchased from Sigma-Aldrich and used as received. Elemental analysis was performed by inductively-coupled-plasma optical-emission-spectroscopy (ICP-OES) on solutions prepared by treating the nanoparticles in a nitric acid/hydrogen peroxide mixture of ratio 3:1 mixture (for the W analysis) or in a hydrochloric acid/nitric acid mixture of ratio 3:1 (for the Fe and Pt analysis) and diluted with water to a known volume. IR spectra were recorded as KBr pellets in transmission mode on a Bruker Vertex 70 spectrometer. Cyclic voltammetry was performed using a BioLogic SP-150 potentiometer. A saturated solution of the product was prepared in acetonitrile and tetrabutylammonium perchlorate (0.1 M) was used as electrolyte. The working electrode was a glassy carbon disk, the reference electrode a silver wire in silver nitrate solution (3 M in acetonitrile) and the counter electrode a platinum wire. The scanning speed was 100 mVs^{-1}.

Synthesis of $TMHDA_{7.3}K_{0.2}H_{0.5}[SiW_{11}O_{39}]\cdot 19H2O$ (denoted TMHDA-{SiW_{11}})

To a 10:1 water:ethanol solution of trimethylhexadecylammonium bromide (TMHDA-Br) (0.47 g, 1.35 mmol in 200 mL water and 20 mL ethanol), $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 13H_2O$ (1.0 g, 0.31 mmol) was slowly added under vigorous stirring. The pH of the solution was kept at pH 6 throughout the whole procedure by adding 1 M HCl solution dropwise. A white precipitate formed immediately. The suspension was further stirred for 15 min, the solid was then filtrated and dried under vacuum at 50 °C for 1 h. (1.0 g. 0.2 mmol, 65% based on $K_8[SiW_{11}O_{39}]\cdot 13H_2O$, 100% based on TMHDA-Br). IR (KBr), ν/cm^{-1}: 520m, 536m, 735s, 791s, 891vs, 946s, 991m, 1468m, 1642w, 2851s, 2921s, 3038w. CV (vs. Ag^+ 3M/Ag) in MeCN: –1.75 V ($2e^-$), –1.95 V ($2e^-$). Elemental analysis, found: C 32.8, H 7.70, K 0.12, N 2.05, Si 0.56, W 40.3%; calculated for $C_{138.7}H_{345.1}K_{0.2}N_{7.3}O_{77}SiW_{11}$: C 32.7, H 6.8, K 0.15, N 2.0, Si 0.56, W 39.6%.

Synthesis of $SiW_{11}Fe$-Fe_2Pt core-shell particles

The synthesis of bi-metallic core shell nanoparticles is based on the polyol-reaction used extensively in colloid chemistry (2). The reaction was adjusted towards a *one-pot* synthesis of Fe_2Pt core-shell nanoparticles using iron(II) acetylacetonate and platinum(II) actetylacetonate salts for chemical reduction as reported by K. E. Elkins et al. (3). TMHDA-{SiW_{11}} (1.0 g, 0.2 mmol), oleic acid (160 µL, 0.5 mmol) and oleyl amine (170 µL, 0.5 mmol) were stirred under argon overnight in dioctyl ether (16 mL). Oleic acid (0.84 mL, 2.7 mmol), oleyl amine (0.83 mL, 2.6 mmol), iron(II) acetylacetonate (254 mg, 1.0 mmol), platinum(II) actetylacetonate (197 mg, 0.5 mmol) and 1,2-hexadecane-diol (387.7 mg, 1.5 mmol) were added under constant stirring. The suspension was, under argon, heated at a rate of 5 °C/min to 280 °C and left at this temperature to react for 2 h before cooling down to room temperature. The black suspension was opened in air, washed with *n*-hexane and precipitated by ethanol. The solid was then collected by centrifugation. This procedure was repeated until the supernatant was clear and the compound was stored at room temperature dispersed in *n*-hexane. In order to remove the organic components of the shell the hexane dispersion of the core-shell nanoparticles was introduced into the cartridge of a Soxhlet apparatus and washed for 16 hours with heptane. Subsequently the black nanoparticle powder was collected and stored in heptane.

Element ratios from elemental analysis: W/Pt 1.3±0.2, Fe/Pt 2.1±0.2. IR (KBr), ν/cm^{-1}: 532m, 720sh, 793vs, 883m, 918vs, 971s, 1012m, 1125w, 1191w, 1377w, 1457m, 1558m, 1643w, 2851s, 2922vs, 3042w, 3135w.

The control sample was synthesized analogously as described above without the TMHDA-{SiW_{11}} compound and overnight stirring.

Element ratios from elemental analysis: Fe/Pt 3.1±0.3. IR (KBr), ν/cm^{-1}: 618w, 664w, 723w, 819w, 894w, 970w, 1082w, 1190w, 1378m, 1462s, 1593m, 1715w, 2852m, 2868w, 2924s, 2957m.

HR-STEM and EDX analysis

The HR-STEM analysis of the {SiW_{11}Fe}-Fe_2Pt nanoparticles and the non-coated Fe_3Pt sample was performed on commercially available non-porous silicon grids of 5 nm thickness in an aberration-corrected FEI Titan 80-300 STEM at an electron acceleration voltage of 300 kV in the scanning mode. The energy dispersive X-ray analysis (EDX) data were collected from an ensemble of approximately 20 particles in an FEI Technai G2 F20 transmission electron microscope. An average integration time of 20 minutes was necessary to obtain a spectrum as shown in Fig. 2 (c). The TEM samples were prepared by pipetting 1-2 μL of nanoparticle suspension onto non-porous Si membranes of a thickness of 5 nm.

SAXS measurements

The small angle X-ray scattering experiments were carried out in liquid suspension using *n*-hexane as solvent filled into borosilicate glass capillary tubes of 1 mm diameter on a NanoStar (Bruker AXS). The $I(q)$ scattering curves for {SiW_{11}Fe}-Fe_2Pt nanoparticles and the non-coated Fe_3Pt sample were calibrated absolutely using a secondary standard after radially averaging over the time-normalized data. All data were corrected for detector sensitivity, background scattering and dark current noise. A rotating anode source operated at 40 kV and 40 mA, with collimation and monochromatization to the Cu Kα line of wavelength 1.54 Å was used. The maximal resolution of approximately 0.006 Å^{-1} was determined by the size of the primary beamstop (diameter 2 mm) positioned at a distance of 1.05 m from the sample. A VANTEC 2000 xenon-filled detector with a 2048 x 2048 wire grid was used to record the 2-dimensional patterns of scattered intensity. Transmissions of the samples were determined from absorbance measurements using a glassy carbon sample placed in the optical path in-between sample and detector. The scattering vector ranges from 0.006 Å^{-1} to 0.30 Å^{-1}.

Magnetic measurements

The magnetization of the core-shell and non-coated Fe_3Pt nanoparticle samples was obtained by filling a liquid suspension of nanoparticles of Fe_3Pt and $\{SiW_{11}Fe\}$-Fe_2Pt separately into glass ampules of 3 mm diameter and 20 mm length. After evaporating the hexane solvent at 50 °C further suspension was added. We repeated this procedure until 5 mg of nanoparticles were gathered and finally sealed the glass ampules. The measurements of magnetization were carried out in a Quantum Design Physical Properties Measurement System at temperatures down to 2 K and in magnetic fields up to 9 Tesla using an extraction technique. The contributions of the sample holder and the glass ampule were determined separately and carefully subtracted.

Ligand Exchange and Amide Coupling Reaction

The Fe-rich core of the {SiW$_{11}$Fe}-Fe$_2$Pt nanoparticles and the demand for sterically accessible carboxylic groups for a subsequent amide coupling reaction to amino acids such phenylalanine proposes a ligand exchange procedure using mercapto undecanoate. This compound replaces the oleyl amine, oleic acid ligands and chemisorbed {SiW$_{11}$Fe} shell of the core shell nanoparticles. The ligand exchange was carried out as described in H. G. Bagaria et al. (4). A volume of 1 mL of concentrated and purified {SiW$_{11}$Fe}-Fe$_2$Pt nanoparticle suspension was mixed with a solution of 2.5 g mercapto undecanoate in 5 mL cyclohexanone in a centrifuge tube and left for 60 min for the particles to precipitate. After centrifugation for 5 min at 3500 rpm the supernatant was discarded and the nanoparticles were redispersed in 10 mL cyclohexanone. Another cycle of centrifugation and discarding the supernatant followed and then the excess mercapto undecanoate was removed by adding 10 mL of ethanol. The suspension was again centrifuged for 5 min at 3500 rpm, the supernatant removed and the nanoparticles redispersed in 10 ml acetone. Finally, the suspension was centrifuged for 5 min at 3500 rpm once more and after discarding the supernatant the nanoparticles were redispersed in 2.25 mL of deionized water and 0.25 mL of 1 N NaOH. The preparation of the phenylalanine coupled particles was achieved following standard solution phase peptide coupling reaction conditions. A 1.2 mL aqueous suspension of mercapto undecanoate ligand exchanged core-shell nanoparticles in an Eppendorf snap-top vial was centrifuged at 3000 rpm for 3 minutes and then the supernatant solvent was removed *via* pipette. The solids were then re-suspended in ~1.2 mL dimethylformamide (DMF) and sonicated for 2 minutes. The centrifugation-dissolution-sonication step was then repeated once more.

To the particles suspended in DMF was added H-Phe-OMe·HCl salt (107 mg, 0.50 mmol), *N,N'*-diisopropylcarbodiimide (315 mg, 2.50 mmol) and *N,N*-diisopropylethylamine (323 mg, 2.50 mmol) sequentially. The mixture was then agitated with a mechanical shaker overnight in an Eppendorf snap-top vial. Subsequently the reaction mixture was centrifuged at 3000 rpm for 3 minutes and then the supernatant solvent was removed using a pipette. The solids were then re-suspended in ~1.2 mL distilled water and sonicated for 2 minutes. The centrifugation-dissolution-sonication step was then repeated once more to remove any excess amino acid and coupling by-products.

UV-visible Spectrometry

All samples were measured in aqueous suspension at room temperature using a Perkin Elmer Lambda 20 UV-visible spectrometer over the range of 200-700 nm in 10 mm quartz cuvettes. Though no direct method of determining the concentration of the particles was available, in an attempt to maintain similar concentrations for measurements, 15 μL of each sample was taken from the suspension after the sonication step and diluted with 985 μL of distilled water and then measured.

References

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