

Novel Magnetic Separable Nano-Carriers For Chemical Catalysis & Bio-Catalysis

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ABSTRACT

Separation of homogeneous catalyst species from product mixture in liquid phase has been a major problem in industry. Thus, the facilitated separation of nanosize magnetic body carrying catalytically active species is of a tremendous interest. The major advantage is that the magnetic nano-catalysts display an excellent mass transfer coefficient (high surface area to volume ratio) comparable to soluble species but can still be easily separated from liquid using magnetic interaction with an external applied inhomogeneous magnetic field. However, their stability in reactive environment remains to be the key issue. Here, we show that S-capping species can isolate and protect the nano-size FePt magnetic core from environment. The functionalized surfaces can also offer anchoring sites for immobilization of catalytically active species (nano-metal particulates, homogeneous catalysts and enzymes). With such small magnetic catalyst bodies, the merits of homogeneous and heterogeneous catalysis can then be combined.

Keywords: magnetic separation, nanocatalyst, sulfur capping reagent, surface passivation, FePt

1 INTRODUCTION

Magnetic separation involves (i) tagging or labeling of desired biological/chemical entity on nanosize magnetic particle for recognition of complementary species in solution, and (ii) separation of the resulting solid entities via a fluid-based magnetic separation followed by regeneration of the species from the particle [1-3]. This technique has now been widely adopted in protein purification, immunoassays [4], pre-processing in polymerase chain reactions [5] and pre-concentration of biological entities [2]. Recently, applications of the magnetic separation to catalysis and bio-catalysis areas in order to regenerate expensive catalyst species [6] or enzymes [7,8] from reaction mixture have been particularly denoted. Referring to these particular applications, two main problems arise. First, an undesirable catalysis could also be introduced if reactive surface of the magnetic core is exposed to substrate molecules. Secondly, many

magnetic materials with a strong magnetization such as those of magnetic alloys are chemically susceptible for attacks (such as oxidation, hydrolysis) during use and thus deemed unsuitable for this purpose. Availability of reported chemical methods to modify surface properties and to add coating onto colloid nano-magnetic particles in solution is limited since the particles tend to agglomerate very easily during subsequent treatment(s).

In this paper, we show that the surface of new synthesized FePt magnetic nanoparticle can be capped or passivated by two different types of sulfur species, namely cystamine and 3-mercaptopropyl-trimethoxysilane (MTPS). The former surface capped species could offer surface tethered amine end groups and the latter could give a porous silica overlayer with surface -OH for catalyst (enzyme) immobilization.

2 EXPERIMENTAL

2.1 Synthesis

Monodispersed FePt magnetic nanoparticle is synthesized using modified polyol process [9], followed by sulfur capping of the alloy surface as follows: Analytical Graded Pt(acac)₂ (0.1972 g, 0.5 mmol.), FeCl₂·4H₂O (0.0994 g, 0.5mmol.), 1,2-hexadecanediol (0.52 g, 2.0 mmol.) and octyl ether (30 mL) were added into a flask under N₂ atmosphere. The mixture was heated up to 95 °C for 10 min. Then, oleic acid (0.16 mL, 0.5 mmol.) and oleyl amine (0.17 mL, 0.5 mmol.) were added upon before the mixture was continuously heated up to 200 °C. After that LiBEt₃H (1 M THF solution, 2.5 mL) was slowly added to the mixture *via* a syringe. The mixture was then heated to reflux at 263 °C for 3 hours (formation of black FePt colloid was observed) before it was cooled to room temperature. 50 mL ethanol was added into the black colloid to induce precipitation. The black precipitate was separated by centrifugation (1,200 rpm, 2 hours) and ethanol washed for at least 3 times (reached 81.93% theoretical yields of FePt) prior to their re-dispersion using 30 mL mixture of hexane and ethanol (1 : 1 v/v).

Synthesis of cystamine-stabilized FePt: Excess cystamine dihydrochloride (0.52 g, 0.0023 mol.) was added into the mixture with stirring. The system was continuously stirred

for overnight to allow the cystamine replace the oleic acid and oleyl amine adsorbed on the nano-magnet surface (no precipitation). The magnetic nanoparticles were then separated from the mixture by an external magnet ($BH_{max} = 38\text{MGOe}$). The supernatant was discarded. The precipitates were washed by both ethanol and the buffer solution three times to remove the excess cystamine and other organic species.

Synthesis of MPTS-stabilized FePt: Excess (3-mercaptopropyl)-trimethoxysilane (MPTS) (0.25 mL, 1.15 mmol.) was allowed to add into the hexane/ethanol FePt colloids slowly. The mixture was stirred overnight to allow the MPTS to displace the oleic acid and oleyl amine stabilizers on the FePt surface in order to produce MPTS modified FePt nanoparticle. It is particularly noted that the surface modified magnetic particles, similar to the above case, still remained in solution as a colloid. A black precipitate was then separated from solution by using an external magnetic field. It was found that the precipitate can be re-dispersed in 20 mL ethanol in a 250 mL round beaker under stirring.

Synthesis of S-capped FePt in silica: The ethanol solution containing MPTS-stabilized FePt was then hydrolyzed and condensed with added silica precursors to form S-capped FePt in silica. These were carried out by first adding 3 mL of sodium silicate solution (1.5 wt%) into the ethanol mixture. After that, another 200 mL ethanol was added before 0.2 mL TEOS (98%) was allowed to add into the mixture. Finally 1.0 mL ammonia solution (35 w/w% in water) was added gradually. The mixture was aged for 3 days with stirring where hydrolysis & condensation of the terminal surface attached silicon hydroxyl species (the hydrolytic product of MPTS) with added silica precursors (silicate and TEOS) to form silica overlayer. To ensure no precipitation during the synthesis we found that the procedure of adding ammonia solution was absolutely essential. It is believed each composite nanoparticles will carry the same but opposite charge on its surface (SiO^-) in alkaline solution hence avoiding them from aggregation. Notice that a black precipitate could only be collected from solution by centrifugation at 1,200 rpm for 2 hours. After washing the collected precipitate with ethanol and acetone, the final solid product was separated using the external magnetic field under nitrogen.

2.2 Characterization

Figure 1 shows a typical XRD pattern of for sulfur capped iron platinum alloy nanoparticle (1:1) in silica. Identical spectra were obtained over cystamine-stabilized FePt and MPTS-stabilized FePt samples (but no amorphous silica peak). The two strong peaks observed correspond to the d_{111} and d_{200} diffractions of a fcc iron-platinum alloy quoted in the International Centre For Diffraction Data, JCPDS-290718. From the pattern below, it also shows a very broad diffraction peak at lower angles corresponding to the non-

crystalline amorphous silica. Using Debye-Scherrer equation (with taking into account of instrumental broadening) to apply onto (111) plane for each samples, the average diameter of FePt nanoparticle in each samples was calculated to be 3.11 ± 0.5 nm.

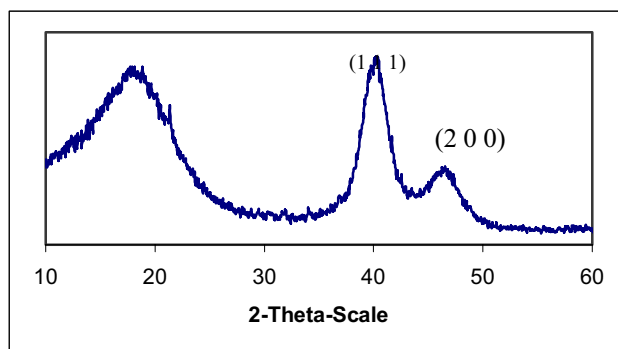


Figure 1: A X-ray diffraction spectrum of S capped iron platinum magnetic nanoparticle (1:1) in silica

Figure 2 shows a typical vibration saturation magnetization (VSM) of the silica encapsulated particles in a solid form (similar VSM responses were found over cystamine-stabilized FePt and MPTS-stabilized FePt samples). These materials exhibit a high saturation magnetization at > 1000 Oersted and thus can undergo magnetic induced precipitation upon exposure to external magnetic field (i.e. 38MGOe). One key challenge in developing material for magnetic separation is that any long range inter-particle magnetic interactions in the absence of magnetic field should be avoided. Otherwise, magnetic particles may not necessarily return to colloidal dispersed state upon removal of the field. It is noted that a long-range chemical ordered FePt alloy nanoparticles forming $L1_0$ phase has been reported when the sample is heat activated [9,15]. In contrast, all our data show extremely low coercivity and remanence values with no hysteresis (chemical disordered structure). Thus, these observations clearly suggest that all our coated magnetic nanoparticles (cystamine, MPTS and silica) synthesized at this low temperature will behave as little magnets in solution with respect to a strong external magnetic field leading to reversible precipitation (exhibit superparamagnetic behavior) as desired.

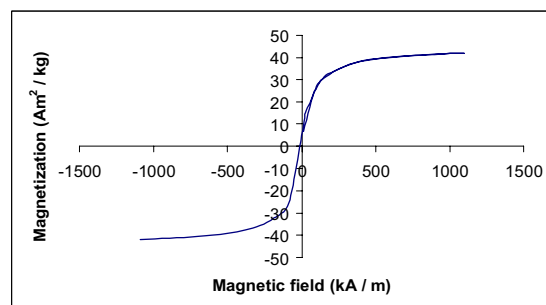


Figure 2: A VSM plot of S-capped FePt nanoparticle in silica (metal precursor molar ratio of Fe: Pt = 1 : 1).

Figure 3 shows the FT-IR spectra of FePt nanoparticles (from polyol) before and after addition of *cystamine*. The appearance of weak bands at 2605 cm^{-1} and 2523 cm^{-1} after cystamine addition corresponds to the S-H stretching. It can also be seen that the bands at 2994 cm^{-1} and 1458 cm^{-1} corresponding to C-H stretching and bending modes become stronger after the sulfur species immobilization. The band around 1429 cm^{-1} corresponds to the C-N stretching and the band at 1544 cm^{-1} corresponds to the N-H bend. The broad weak band at the region between 700 cm^{-1} and 600 cm^{-1} corresponds to the N-H out-of-plane bend. All of these new bands arisen clearly suggest that the immobilization of cystamine onto the nanoparticle is evident.

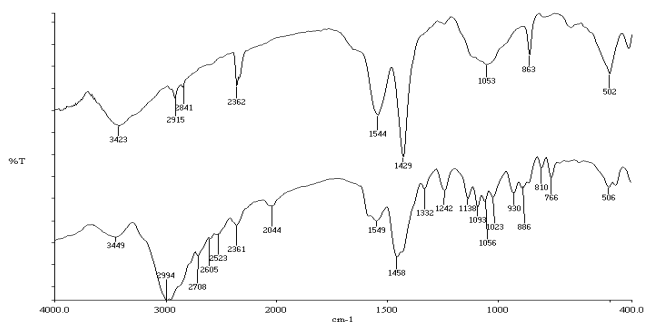


Figure 3. FTIR spectra of FePt nanoparticles before (upper curve) and after cystamine addition

Figure 4 shows the sulfur-stabilized FePt nanoparticles before (MPTS) and after the formation silica. Although no identification of Pt-S or Fe-S bonds is evident because of their weak absorptions at low wave-numbers, the C-Si [$\sim 800\text{ cm}^{-1}$] and Si-O [$\sim 1100\text{ cm}^{-1}$] linkages are clearly visible. For the MPTS-stabilized FePt nanoparticle a weak but distinctive peak at 1019 cm^{-1} indicative of the Si-O-C stretching is clearly evident. After hydrolysis/condensation the characteristic broad Si-O-Si asymmetric stretching ($\sim 1117\text{ cm}^{-1}$) together with a large shoulder of Si-O(H) stretching band ($\sim 980\text{ cm}^{-1}$) are present suggesting the formation of the immobilization of *MPTS* onto the surface followed by hydrolysis and condensation to form the silica over-layer as described in the Synthesis section.

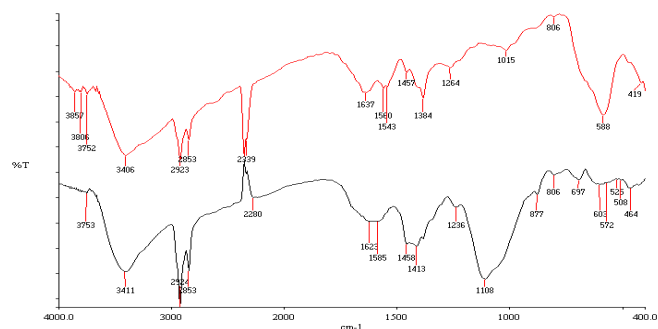


Figure 4: FTIR spectra of MPTS capped FePt nanoparticle before (---) and after (----) hydrolysis & condensation to

Figure 5 shows the elemental mapping of isolated nanoparticle of *S-capped FePt in silica* by Energy Dispersive X-rays (EDX) randomly selected from the sample. After taking the correction of response factor for each element into account, the atomic ratios of the particle were found to be Fe : Pt : Si : O : S = 12.43 : 12.79 : 24.90 : 42.99 : 7.01 with a maximum standard deviation of ± 1.01 from these data. (excluding carbon analysis because the use of carbon filmed holder). Taking the particle size of 3.1 nm (XRD) into consideration the estimated dispersion of the metal cluster (surface atoms/total atoms) is of about 0.284. This matches excellently with the obtained sulfur to metal ratio of 0.278. This value implies that the sulfur atoms (excess MPTS was used) are indeed covering the entire surface metal sites on alloy particle by forming strong M-S linkages [10]. In addition, simple experiments of mixing the all the three S-treated FePt nanoparticles (*cystamine-stabilized FePt*, *MPTS-stabilized FePt* and *S-capped FePt in silica*) with hydrazine (64 wt%, Sigma) clearly demonstrated its total inactivity towards hydrogen formation whereas the freshly polyol prepared FePt nanoparticles liberated hydrogen from this reagent at room temperature (also the S-capped materials showed no hydrogen chemisorption value). Thus, the passivation of the exposed active metal surface *via* capping with these sulfur species is clearly established. It is interesting to find that the Si/S ratio of the particle indeed exceeded unity (3.55) with respect to the MPTS molecule. Together with the reduction of oxygen content approaching O/Si = 2, the data undoubtedly support the fact that the terminal methoxyl groups of the capped MPTS had indeed undergone hydrolysis and condensation with the added silica precursors, giving the thin silica over-layer. The BET specific surface area and pore volume measurements of the S-capped FePt nanoparticle in silica in its solid condensed form using N_2 physisorption technique were carried out. The high surface area ($223\text{ m}^2\text{ g}^{-1}$), highly porous nature (mean pore size of 0.8 nm) and high pore volume (0.89 ml g^{-1} approaching to silica-gel value of $1.0\text{ m}^2\text{ g}^{-1}$) of the sample agree with the formation of porous silica overlayer on these magnetic particles.

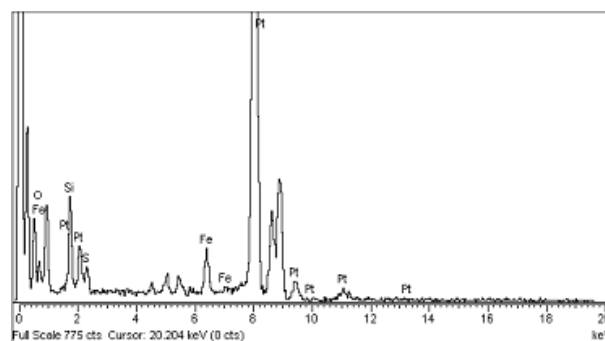


Figure 5: EDX spectrum of the sulfur capped FePt nanoparticle in silica (Fe : Pt = 1 : 1).

As a result, we show in this paper that the presence of S species on the three samples passivate the exposure of metal surfaces (forming a strong M-S). In the case of cystamine capped FePt the terminal group on surface is $-NH_2$ and in the cases of MPTS and silica coated FePt the surfaces are covered Si-OH. Many well developed methodologies on making uses of these surface active groups to carry catalyst or enzyme species have been reported. In addition, the high porosity of the silica overlayer in the case of S-capped FePt in silica allows immobilization as well as physical storage of chemical or biological species in its pores as a magnetic recoverable nano-vehicle [6,7,14].

3 CONCLUSION

To conclude, magnetic recoverable nano-catalysts require stable magnetic nanoparticle to carry chemical or biological catalytically active species and the particles should reversibly be precipitated from and to solution upon application or removal of external magnetic field. The described simple synthetic methodologies of using sulfur compounds can incorporate both magnetic and chemical storage functions into a single nano-magnetic nanoparticle, which could extend the application of strong but reactive magnetic alloys such as FePt, FePd, FeCoPt, FePt-Ag for magnetic separation in catalysis. It is also believed that the ability to assemble functional magnetic porous nano-carriers from bottom-up construction approach through nano-chemistry synthesis as presently demonstrated may enable exploitation of these materials for other exciting applications such as magnetic switch, magnetic drug delivery, optical magnet and magnetic recording, etc..

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