

## PREPARATION AND CHARACTERIZATION OF PVA COATED MAGNETIC NANOPARTICLES\*

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**Abstract** Polyvinyl alcohol coated magnetic particles (PVA ferrofluids) have been synthesized by chemical co-precipitation of Fe(II)/Fe(III) salts in 1.5 mol/L  $\text{NH}_4\text{OH}$  solution at 70°C in the presence of PVA. The resultant colloidal particles have core-shell structures, in which the iron oxide crystallites form the cores and PVA chains form the shells. The hydrodynamic diameter of the colloidal particles is in the range of 108 to 155 nm, which increases with increasing PVA concentration from 5 wt% to 20 wt%. The size of the magnetic cores is ca. 5–10 nm, which is relatively independent of PVA concentration. Under transmission electron microscopic (TEM) examination, the magnetic cores exhibit somewhat irregular shapes varying from spherical, oval, to cubic. Magnetometry measurement revealed that the PVA coated magnetic particles are superparamagnetic. The saturation magnetization of 5 wt% and 20 wt% PVA ferrofluids at 300 K is 54 and 49 emu/g, respectively. All the PVA ferrofluids exhibited excellent colloidal stability in pure water and phosphate buffer saline (PBS, pH = 7.4). The ferrofluids can remain stable in above solutions for more than three months at 4°C.

**Keywords** Magnetic nanoparticles, Polyvinyl alcohol, Ferrofluids, Core-shell structure

### INTRODUCTION

Magnetic fluids or ferrofluids refer to the stable colloidal suspensions of magnetic particles in a carrier liquid<sup>[1]</sup>. Usually, the magnetic particles have core-shell structures in which the cores are made of magnetic crystallites and the shells are made of organic substances. For most ferrofluids, the size of magnetic cores is in the range of several nanometers to tens of nanometers, containing only a single magnetic domain. Owing to their extremely small size, the magnetic particles exhibit superparamagnetic behavior<sup>[2]</sup>. This means that the magnetic particles are magnetically responsive but remain nonmagnetic in the absence of the magnetic field. The colloidal magnetic particles can be readily dispersed in a liquid to form a ferrofluid<sup>[3]</sup>.

A variety of coatings such as self-assemblies, liposomes and polymers have been used to coat the magnetic nanocrystallites to prepare ferrofluids<sup>[4–6]</sup>. The functions of the coating layers are twofold: (1) to prevent inter-particle agglomeration by reducing the crystalline surface tension, and (2) to provide the particles with necessary functionality. In some cases, the coating layers can also protect the iron oxide from the attack of corrosive media such as acidic or alkaline conditions. By tailoring the coating layers, the ferrofluids can be manipulated to meet various kinds of applications in biological and medicinal areas such as immuno-magnetic cell separation, magnetic resonance imaging, hyperthermia and targeted drug delivery<sup>[7]</sup>.

Polymer coated magnetic particles are the most important ferrofluids in practical use<sup>[5, 8, 9]</sup>. Accordingly, various synthetic strategies have been developed for the fabrication of polymer ferrofluids<sup>[10]</sup>. Among these preparations, the co-precipitation method proposed by Molday *et al.*<sup>[5]</sup> is the simplest one. Using this method,

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colloidally stable ferrofluids can be obtained in one step. In the past two decades, such particles have been widely used in areas where high diffusion speed and small size are needed<sup>[11–13]</sup>. However, in these preparations, most of the coating materials were limited to natural polymers such as dextran and starch, and relatively little attention has been paid to synthetic polymers. In order to explore synthetic polymer ferrofluids, in this work we have used PVA as the coating material to prepare ferrofluids by the co-precipitation technique. The effect of polymer molecular weight and concentration on particle properties such as size, structure, and magnetic properties has been examined.

## EXPERIMENTAL

### *Preparation of PVA Coated Magnetic Particles*

The PVA coated magnetic particles were prepared by co-precipitation of ferric and ferrous chlorides in the presence of PVA. Unless specified otherwise, a PVA sample with an average molecular weight ( $M_w$ ) of 20 KD (98% hydrolyzed,  $M_w/M_n = 1.7$ ) was used. The molar ratio of Fe(II)/Fe(III) was kept at 0.5 to ensure the preferential formation of magnetite ( $\text{Fe}_3\text{O}_4$ )<sup>[2]</sup>. Typically, an appropriate amount of PVA was dissolved in 20 mL of deionized water to form 5 wt% to 20 wt% PVA solution. Then the weighed amount of ferric and ferrous chlorides was added to achieve concentrations of 54 mg/mL and 20 mg/mL, respectively. Under vigorous stirring, the PVA solution was added to 100 mL of 1.5 mol/L  $\text{NH}_4\text{OH}$  aqueous solution with temperature preset at  $\sim 70^\circ\text{C}$ . In this step, a dark brown solution was immediately generated. After heating the dispersion at  $70^\circ\text{C}$  for another 15 min, the solution was cooled down to room temperature and neutralized to  $\text{pH} = 7\sim 8$ . Aggregation was removed by three-cycle centrifugation at a speed of 10,000 rpm for 10 min each. The magnetic particles were separated from the unbound PVA and non-magnetic particles by a high gradient magnetic separator (HGMS). The purified magnetic particles were then re-dispersed in phosphate buffer saline (PBS,  $\text{pH} = 7.4$ ) to form the PVA ferrofluids.

### *Dynamic Light Scattering*

A Brookhaven light scattering spectrometer (Model BI9) with an emission laser wavelength  $\lambda = 514\text{ nm}$  was used to measure the hydrodynamic diameter of the colloidal magnetic particles. All the measurements were performed at an angle of  $\theta = 90^\circ$ . The data were processed with CONTIN program. Acrodisc  $0.45\text{ }\mu\text{m}$  filter was used for the clarification of the ferrofluid solutions.

### *Transmission Electron Microscopy*

Transmission electron microscopy (TEM) was performed on a JEOL 100CX instrument operating at an accelerating voltage of 60–100 kV. For the determination of iron oxide crystal size, a drop of the ferrofluid solution (ca. 1 mg/mL) was placed on a carbon-coated copper grid and dried under ambient conditions. Samples prepared in this way were directly used for TEM observation without further modification.

### *Magnetometry*

The magnetic properties of PVA ferrofluids were measured with superconducting quantum interference device (SQUID) magnetometer. The ferrofluid liquid was placed in a quartz cylinder holder and sealed. The measurement was carried out at a temperature of 300 K with an applied magnetic field of up to 10 kOe.

## RESULTS AND DISCUSSION

### *Synthesis of PVA Ferrofluids*

In alkaline solution, the ferric and ferrous ions were firstly hydrolyzed to hydrated iron oxides ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{FeO} \cdot \text{H}_2\text{O}$ ). Then the two hydrated iron oxides were combined to form  $\text{Fe}_3\text{O}_4$  crystallites. In the absence of polymers, the structure and size of the  $\text{Fe}_3\text{O}_4$  crystallites were mainly governed by temperature, pH and concentration of iron oxides. In the presence of PVA, the existent PVA chains will competitively be adsorbed onto the crystal surface to form colloidal particles. Therefore, PVA is an important factor affecting both the properties of  $\text{Fe}_3\text{O}_4$  crystallites as well as the colloidal particles. In order to minimize the adverse effect of

polymer chains, in an experiment a high precipitation temperature of 70 °C was used to facilitate the crystallization of  $\text{Fe}_3\text{O}_4$  and a relative low concentration of iron salts was used to reduce the formation of particle agglomerations<sup>[5, 6]</sup>.

Four PVA samples with average  $M_w$  of ~10 kD, ~20 kD, ~40 kD and ~80 kD have been examined for preparing PVA ferrofluids. It was found that the 20 kD PVA was the best to achieve colloiddally stable magnetic particles. In a broad concentration range of 5 wt%~20 wt%, stable colloidal magnetic particles have been produced with high yield (above 50%). For other PVA samples, stable colloidal particles were generated with much lower yield. Specifically, for 10 kD PVA, the ferrofluids were not stable after removing the extra PVA chains from the solution. For PVA with  $M_w > 40$  kD, the PVA/iron salts solutions were too viscous to form a good dispersion. The resultant colloidal particles were agglomerated with each other. After removing the agglomerations, only a small amount of colloidal particles will remain in suspension.

### Effect of PVA Concentration on Colloidal Particle Size and Structure

Figure 1 shows the effect of PVA concentration on the particle size of PVA ferrofluids formed at various polymer concentrations. As the PVA concentration increases from 5 wt% to 20 wt%, the particle size increases almost linearly from 108 to 155 nm. Each of the colloidal particle solutions shows mono-modal size distribution with relatively low polydispersity (variance less than 0.05). In terms of size and size distribution, the particles are similar to those used in bio-medicinal applications<sup>[7]</sup>. In comparison with dextran ferrofluids, the PVA ferrofluids showed differences in the following two respects: (1) the particle size of PVA ferrofluids increases with increasing of PVA concentration, while for dextran ferrofluids the colloidal particle size decreases slightly with increasing dextran concentration<sup>[11]</sup>, (2) the PVA ferrofluids were produced at low PVA concentration (below 20 wt%) while the dextran ferrofluids were generally obtained at high dextran concentration (above 50 wt%). The differences may be attributed to the adsorbing abilities of the two polymers. PVA chains can be more effectively adsorbed onto the surface of iron oxide crystals than dextran chains. The stronger adsorption of PVA chains will give rise to the particle size of PVA colloids at high concentrations.

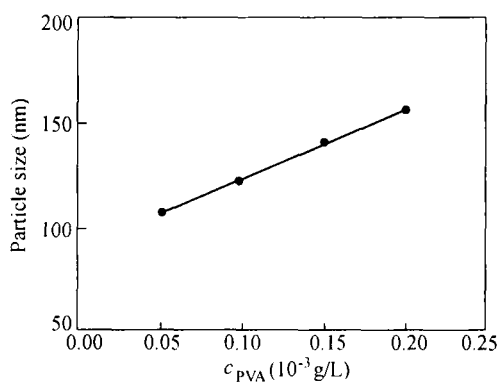


**Fig. 1** Effect of PVA concentration on particle size for PVA ferrofluids formed at various polymer concentrations from 5 wt% to 20 wt%

Figures 2(a) and (b) show the TEM images of PVA coated magnetic particles formed in 5 wt% and 20 wt% PVA solutions, respectively. The dark colour structures in the photograph are the iron oxide crystallites, and the light colour substance surrounded the iron oxides is PVA. The crystalline nature of iron oxides was confirmed by their dark field images, in which the iron oxides appeared as bright structures. Close inspection of Fig. 2 revealed that the iron oxide crystallites exhibit rather irregular shapes including spherical, oval, and cubic. Unlike the colloidal particles, the size of the iron oxide crystallites is nearly independent of the PVA concentration. In both pictures, the size of most iron oxide particles is in the range of 5 to 10 nm.

The core-shell structure of the colloidal particles can be more clearly seen from a few individual particles from 20% PVA ferrofluid. As shown in Fig. 3, the particles in the field of vision clearly show the core-shell

structures. All the iron oxide cores were surrounded by a layer of PVA polymers. The thickness of PVA layers is ca. 5–10 nm. This picture also shows that multi-core particles are formed in the co-precipitation. As shown by the two particles located in the central row, one has two cores and the other may have more than two cores. The same phenomenon has also been observed by Fahlvik *et al.*<sup>[9]</sup> and was considered to be a flaw of this preparation because it will increase the polydispersity of the colloidal particles. In this connection, it is interesting to note that the shrunken PVA shells have the similar contour shapes as their cores.

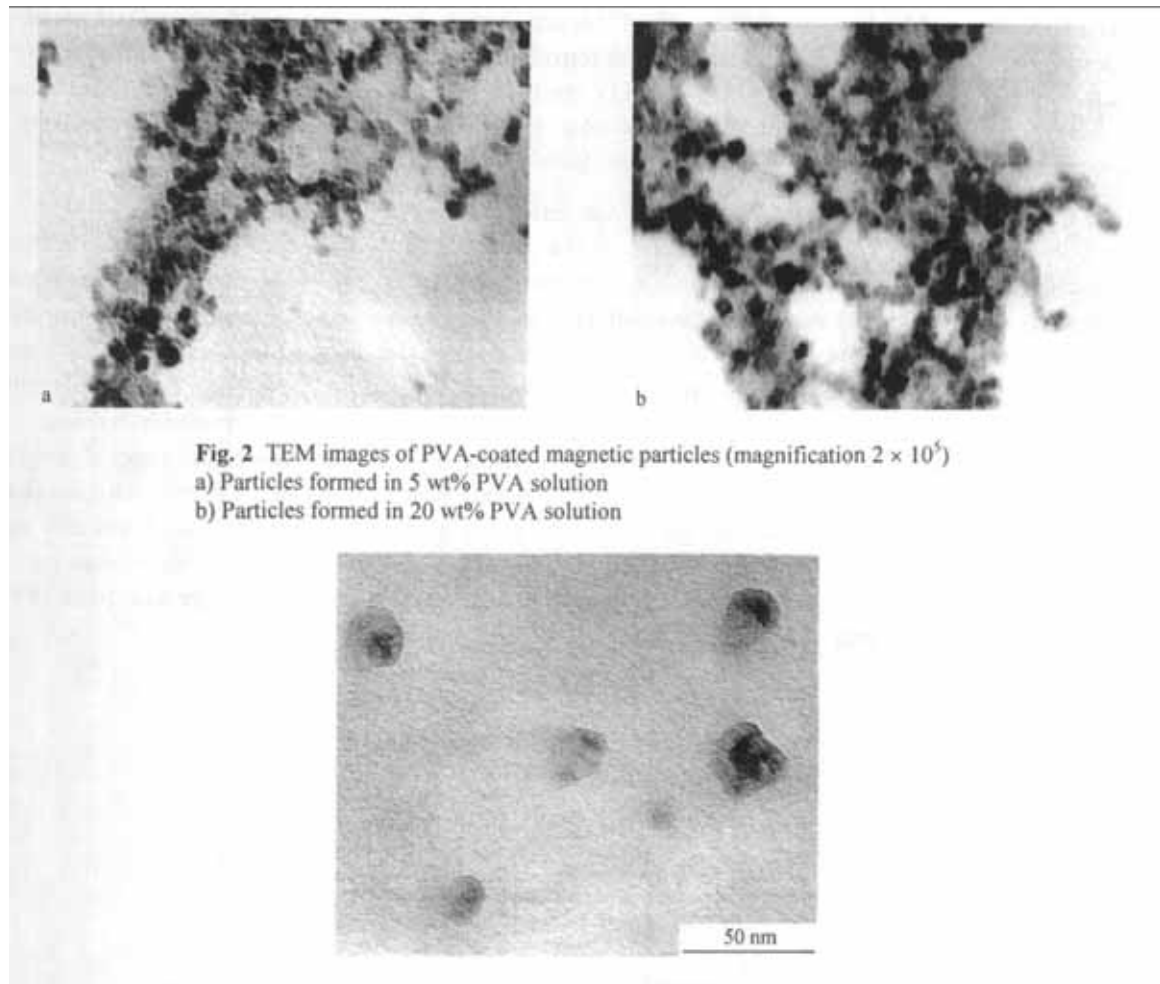


**Fig. 3** TEM images of PVA-coated magnetic particles formed in 20 wt% PVA solution

### **Magnetic Properties of PVA Ferrofluids**

Figure 4 shows the two magnetization curves of 5 wt% and 20 wt% PVA ferrofluids. Both of the magnetization curves exhibit no hysteresis and coercivity, indicating that at 300 K these two kinds of ferrofluids are superparamagnetic. The saturation magnetization ( $M_s$ ) of 5 wt% and 20 wt% PVA ferrofluids per gram iron oxide is 54 and 49 emu/g, respectively. The  $M_s$  values are not only substantially lower than that of bulk  $\text{Fe}_3\text{O}_4$  (90 emu/g), but also lower than that of the magnetic nanoparticles generated by free precipitation. The  $M_s$  of free precipitation particles sized 5–10 nm is in the range of 70–75 emu/g<sup>[2, 10]</sup>, which is ~20% less than that of bulk  $\text{Fe}_3\text{O}_4$  owing to the quantum size effect<sup>[14]</sup>. As evidenced by the irregular particle size of iron oxides, the adsorption of PVA may also hinder the crystallization of  $\text{Fe}_3\text{O}_4$ , which further decreases the  $M_s$  values. It should be mentioned that the  $M_s$  values of PVA coated magnetic particles are very similar to those formed within the micelles of dodecyl sulfate<sup>[15, 16]</sup>.

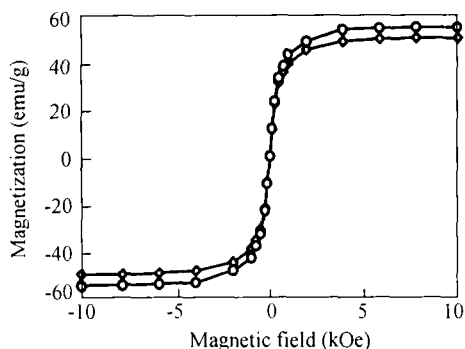


**Fig. 4** Magnetization curves of PVA ferrofluids formed in 5 wt% PVA solution (○) and in 20 wt% solution (◇)

## CONCLUSION

PVA coated magnetic particles have been prepared by the co-precipitation of Fe(II)/Fe(III) salts in the presence of PVA. By varying the concentration of PVA, colloidal magnetic particles with hydrodynamic diameters ranging from 100~150 nm have been synthesized. The PVA stabilized particles thus obtained have excellent colloidal stability. The ferrofluids are stable for more than three months at 4 °C. In addition, the colloidal magnetic particles exhibit superparamagnetic behavior. The saturation magnetization of 5 wt% and 20 wt% PVA ferrofluids is 54 and 49 emu/g, respectively, which is lower than the saturation magnetization of the bare iron oxides of the same particle size.

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