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Description	

Amine-terminated water-dispersible FePt nanoparticles

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Abstract

Chemically disordered face-centered cubic FePt nanoparticles (NPs) were synthesized via pyrolysis of iron(III)ethoxide and platinum(II)acetylacetonate. The surface ligands of these NPs were then exchanged from oleic acid to 2-aminoethanethiol (AET). The AET-capped FePt NPs were found to be well dispersed in water when $\text{pH} < 8$, and the zeta potential was more than +30 mV when $\text{pH} \leq 7$.

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Keywords: FePt nanoparticle; superparamagnetism; water-dispersible; 2-aminoethanethiol

Introduction

Chemically-disordered superparamagnetic FePt nanoparticles (NPs) are expected to perform well as high-performance nanomagnets for use in medicine [1-3], because they show high magnetocrystalline anisotropy energy and high saturation magnetization compared to superparamagnetic iron oxide NPs, which are the currently-used nanomagnets. To utilize the FePt NPs as nanomagnets in medicine, however, the FePt NPs should be dispersible in a physiological, aqueous medium, because chemically synthesized FePt NPs are usually capped with fatty acid, such as oleic acid, and are thus hydrophobic. In addition, the magnetic NPs sometimes need to be conjugated with biomolecules, e.g. DNA, proteins, or antibodies. The 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) coupling technique is one of the most popular methods in coupling NPs and biomolecules via the amino (NH_2) or carboxyl (COOH) groups existing on the NP surfaces. However, there have been few reports with respect to NH_2 - or COOH -terminated water-dispersible FePt NPs. Gu *et al.* have developed cystamine-capped FePt NPs [4], the surfaces of which are positively-charged in water owing to the NH_2 group exposed on the NP surfaces. In other cases, water-dispersible FePt NPs capped with trifluoroethylene-PEG-thiol ligands (NH_2 -terminated) [5] and mercaptoalkanoic acid (COOH -terminated) [6] have also been reported recently.

Wuister *et al.* have developed highly luminescent water-soluble CdTe quantum dots (QDs) via a

ligand exchange from trioctylphosphine/dodecylamine (TOP/DDA) to 2-aminoethanethiol (AET) [7]. Since the Cd-thiol bond is much stronger than the Cd-amine bond, AET replaced the TOP/DDA capping molecules of the CdTe QD immediately. The AET-capped CdTe QDs dispersed in water are stabilized by a positive surface charge, since the dissociated AET molecules have an NH_3^+ group [7]. This strategy is also applicable to FePt NPs, because the Pt-thiol bond is much stronger than the Pt-amine bond. Additionally, we recently found that FePt NPs capped with 1-octanethiol or 1-dodecanethiol show larger saturation magnetization than as-synthesized NPs capped with oleic acid owing to a thinning of the nonmagnetic shell [8]. The saturation magnetization of FePt NPs decreases owing to an increase in electron donation from the ligand to the Fe *d* bands. In general, thiols are known to form weaker bonds with iron oxides than carboxylic acids do, though thiols do strongly bind to Pt. Thus, a significant fraction of thiols is considered to adsorb on Pt sites on the surface of NPs. The ligands adsorbing on Pt sites would influence magnetic properties of NPs much less than the ligands binding to Fe sites. Hence, the alkanethiol-capped FePt has a thinner nonmagnetic shell than the FePt capped with other ligands. For this reason, we exchanged the surface ligands of chemically-synthesized FePt NPs from oleic acid to AET to obtain NH_2 -terminated water-dispersible FePt NPs, in this letter.

Experimental

Synthesis of FePt NPs

Superparamagnetic FePt NPs were synthesized using a previously reported method [9] with some modifications. Briefly, 1.0 g of iron(III)ethoxide [Fe(OEt)₃] (Alfa Aesar) was dissolved in 1 mL of ethanol. Then, 191 μL of ethanol solution of Fe(OEt)₃, 0.5 mmol of platinum(II)acetylacetonate [Pt(acac)₂] (Aldrich), 7.5 mmol of oleic acid (Aldrich), 10 mmol of oleylamine (Aldrich), and 17 mL of dioctylether (Aldrich) were placed in a 50-mL three-necked flask and the mixture was stirred for 5 min under an Ar atmosphere. Subsequently, the temperature was raised to 260°C under an Ar atmosphere. After 30 min of reaction at 260°C, FePt NPs were separated from the matrix by centrifugation. As-synthesized FePt NPs were characterized by transmission electron microscopy (TEM), X-ray diffractometry (XRD), energy dispersive X-ray (EDX) analysis, and Fourier-transform infrared (FT-IR) spectroscopy. The mean diameter and standard deviation of the size distribution were found to be 6.3 nm and 13%, respectively, from TEM images. XRD confirmed the crystal structure of FePt NPs was obtained in the chemically disordered face-centered cubic (fcc) phase. EDX and FT-IR analyses confirmed the average composition of as-synthesized NPs was Fe₃₅Pt₆₅ and the dominant surface ligand molecule was oleic acid.

Ligand exchange

Ligand exchange from oleic acid to AET was carried out following a method described in the literature [7] with some modifications (Scheme 1). As-synthesized FePt NPs were redispersed in 20 mL of hexane. Thirty mL of ethanol was added to the FePt/hexane dispersion; then, the mixture was

left at rest for 10 min at room temperature. After the rest, 33 mg of FePt NPs were separated from the matrix by centrifugation once again. Subsequently, 13.2 mL of chloroform was added to 33 mg of FePt NPs; then, 15.8 mL of methanol solution of AET (0.5M) was added to the FePt/chloroform dispersion. The mixture was vigorously stirred for 10 min; then, 15.8 mL of pure water was poured into the mixture while continuing agitation. After the injection of water, the mixture was stirred for another 5 min followed by 5 min rest. The oil- (transparent and colorless) and aqueous-phases (transparent and black) clearly separated. The black aqueous phase (upper phase) was separated and centrifuged. Clear and colorless supernatant was discarded and black precipitates were obtained. Subsequently, 50 mL of pure water was added to dissolve the precipitates; then, the dispersion was centrifuged. Clear and black supernatant was extracted and then filtered using a 0.2- μm syringe filter. Finally, the aqueous dispersion of AET-capped FePt NPs of 0.3mg/mL concentration was obtained.

Results and Discussion

Figure 1a is a photograph of an as-synthesized (oleic acid-capped) NP/hexane dispersion (upper phase) and pure water (lower phase). Figure 1b is a photograph of pure hexane (upper phase) and an AET-capped NP/water dispersion (lower phase). The AET-capped NPs in water resulted in a clear dispersion. Figures 2a and 2b show TEM images of oleic acid-capped and AET-capped FePt NPs, respectively. As shown in Fig. 2b, large aggregates were not observed in AET-capped FePt NPs, indicating that the AET-capped FePt NPs were well-dispersed in water. These results directly

indicate that the surface ligands were successfully exchanged from hydrophobic oleic acid to hydrophilic AET exposing the NH_2 group to the outside. This means the AET-capped FePt NPs in water are stabilized by a positive surface charge.

To confirm this hypothesis, zeta potential measurements were carried out for the AET-capped FePt NPs using a Malvern Zetasizer Nano ZS. The pH of the NP dispersions was adjusted using 0.1 M HCl and 0.05 M NaOH. Figure 3 is a plot of the zeta potential vs pH for the AET-capped FePt NPs. As expected, the zeta potential of the AET-capped FePt NPs was positive when $\text{pH} < 9$, indicating that the NH_2 group was exposed to the outside and transformed into an NH_3^+ group. An isoelectric point was found for $\text{pH} \sim 9.3$. The zeta potential was more than +30 mV, which is considered as the threshold value for electrostatic stabilization [10], when $\text{pH} \leq 7$. However, the zeta potential was lower than +30 mV when $9 > \text{pH} > 7$, suggesting the AET-capped FePt NPs are not stable in alkaline conditions. In fact, we observed precipitation of NPs within a couple of hours when $\text{pH} \approx 8$. When $\text{pH} > 9$, the dispersion was unstable and NPs rapidly precipitated within an hour.

Figure 4 shows the number-weighted size distributions of the AET-capped NPs in water obtained by dynamic light scattering measurements at different pH values. The inset in Fig. 4 shows the peak sizes plotted vs pH. As shown in Fig. 4, the aggregation of NPs hardly took place when $\text{pH} < 8$ within the experimental time scale of several hours. On the other hand, large NP aggregates were immediately formed when $\text{pH} > 9$. These results are consistent with the pH-dependence of the

zeta potential. The long-term dispersion stability of the AET-capped FePt NPs in water (pH~5) was investigated using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. The diluted NP dispersion was placed in a quartz cell with a screw cap to avoid evaporation of the solvent. Then, the change in absorbance was monitored for 24 h at a wavelength of 600 nm.

Note that the 600 nm monochromatic light was irradiated near the air-liquid interface. Hence, the absorbance should decrease if precipitation occurs. As shown in Fig. 5, the absorbance slightly increased rather than decreasing, indicating the aqueous dispersion of AET-capped FePt NPs has excellent stability. However, the increase in the absorbance suggests the formation of aggregates, because they increase the Rayleigh scattering. In fact, this sample resulted in precipitation within a couple of days. The as-prepared aqueous dispersion of AET-capped FePt NPs of 0.3mg/mL concentration was very stable, and neither precipitation nor aggregation was observed for a week. In the case of thiol-stabilized semiconductor NPs, the dilution of NP dispersion was found to cause desorption of ligand molecules from NP surfaces resulting in colloidal instability [11]. Hence, the destabilization in the diluted dispersion of AET-capped FePt NPs would also be due to the desorption of the AET ligands from the NP surfaces.

In conclusion, water-dispersible AET-capped FePt NPs were synthesized using a ligand exchange technique. The AET-capped FePt NPs were found to be stable when $\text{pH} < 8$, and the zeta potential was more than +30 mV when $\text{pH} \leq 7$. On the contrary, the AET-capped FePt NPs were

unstable when $\text{pH} \geq 8$, and promptly precipitated. In a pH neutral condition, as-prepared aqueous dispersion of the AET-capped FePt NPs showed excellent stability. However, the dilution destabilized the AET-capped FePt NP dispersion, and the aggregation was enhanced.

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Figure captions

Fig. 1. (a) Oleic acid-capped FePt NPs/hexane (upper phase) and pure water (lower phase); (b) pure hexane (upper phase) and AET-capped FePt NPs/water (lower phase).

Fig. 2. TEM images of (a) oleic acid-capped and (b) AET-capped FePt NPs.

Fig. 3. Zeta potential vs pH for the AET-capped FePt NPs dispersed in water.

Fig. 4. Number-weighted size distribution of the AET-capped FePt NPs dispersed in water. The dotted, dashed, solid, and dashed-dotted lines represent the size distribution of NPs obtained at pH=3.3, 5.3, 7.5, and 9.2, respectively. The inset shows the peak sizes plotted vs pH.

Fig. 5. Temporal change in absorbance of the water dispersion of AET-capped NPs monitored at 600 nm.

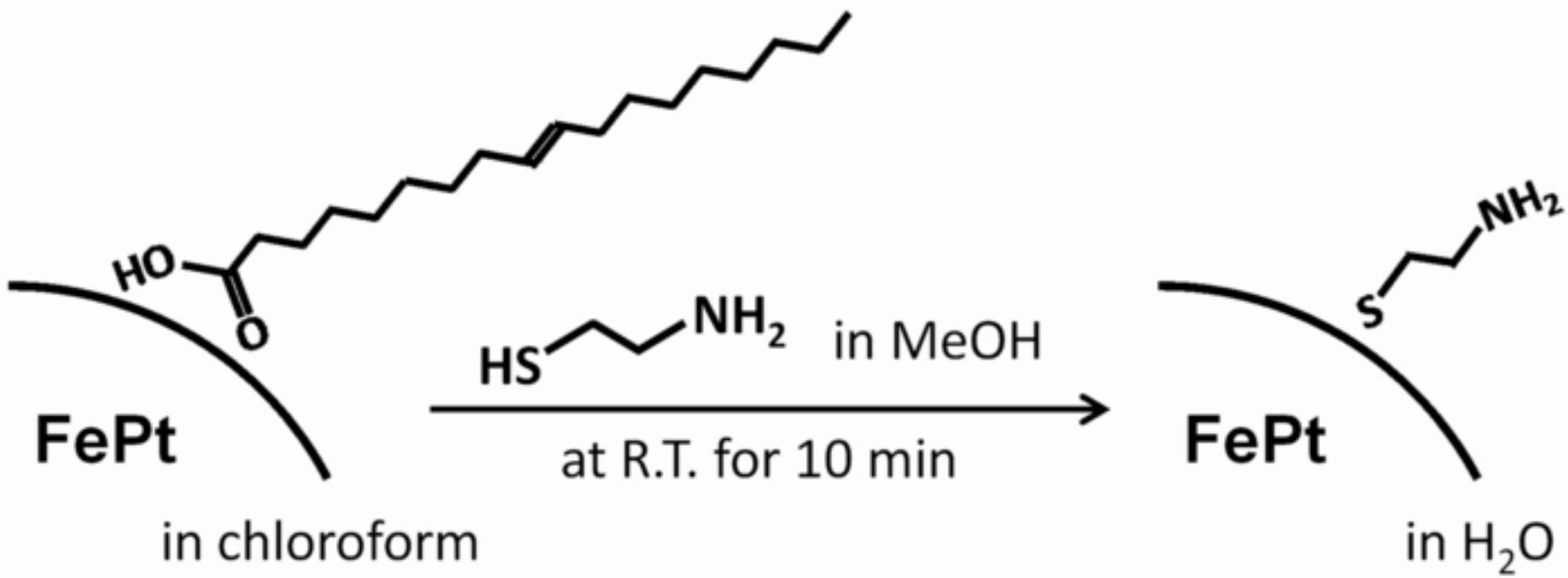


Figure1

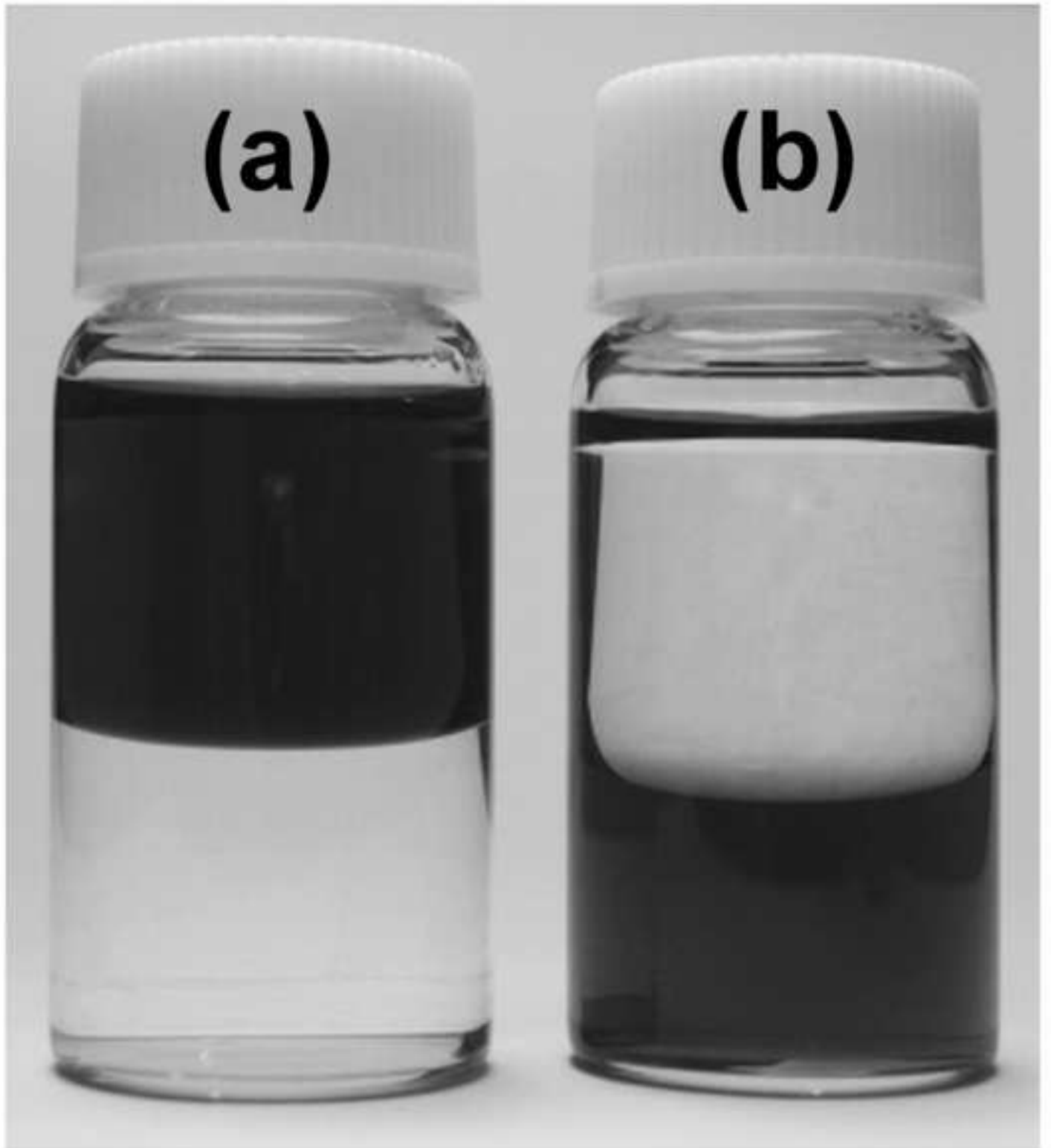


Figure2

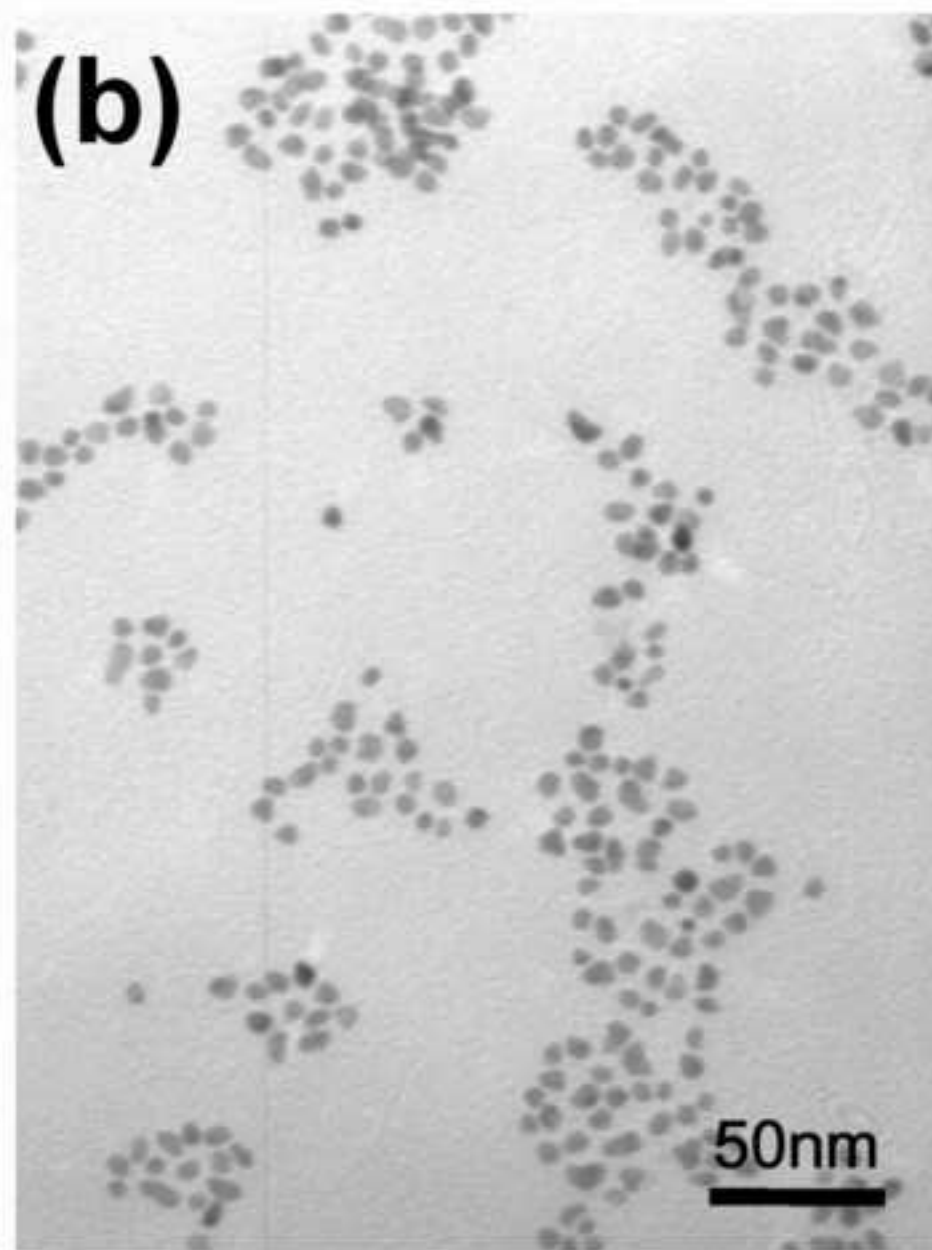
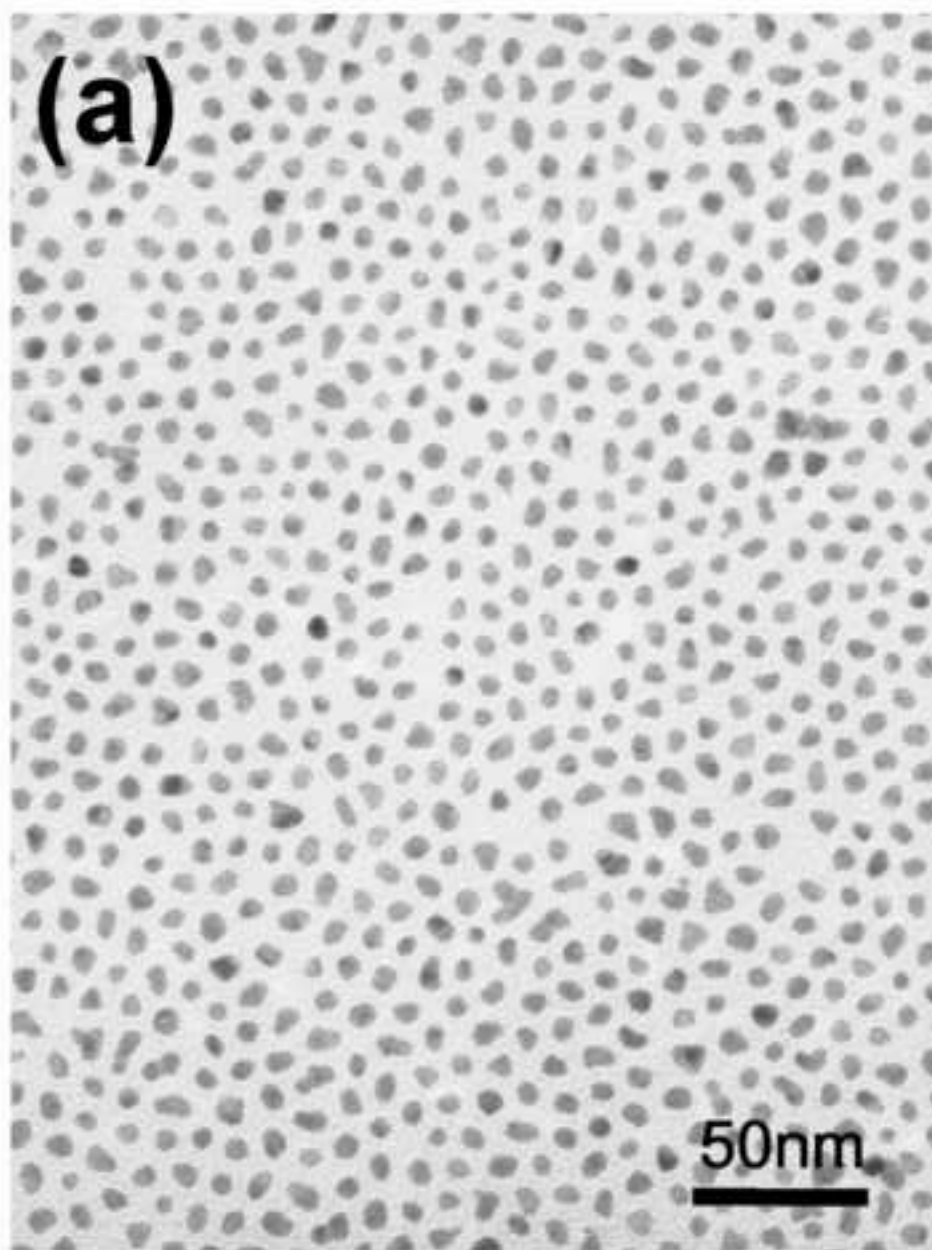


Figure3

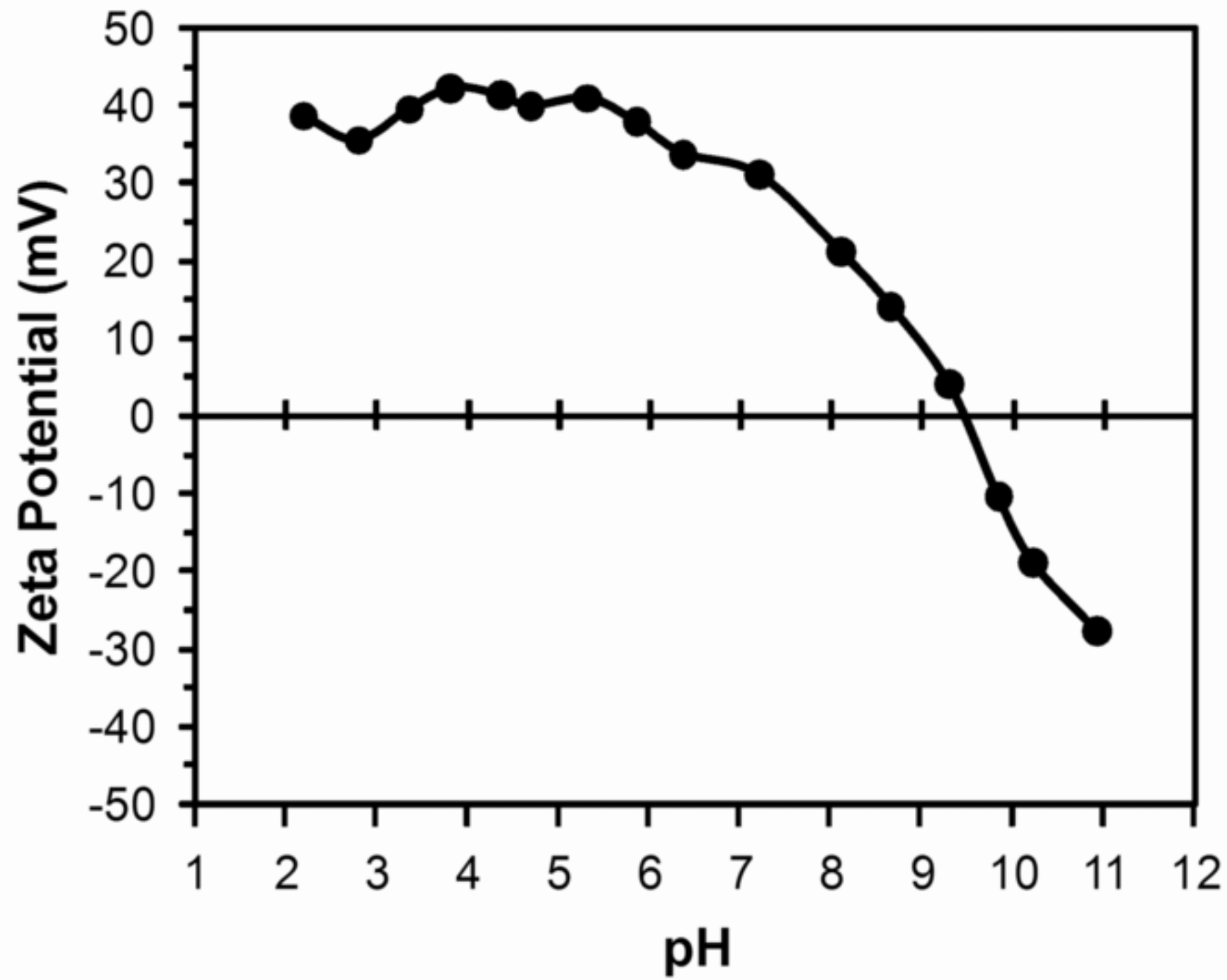


Figure4

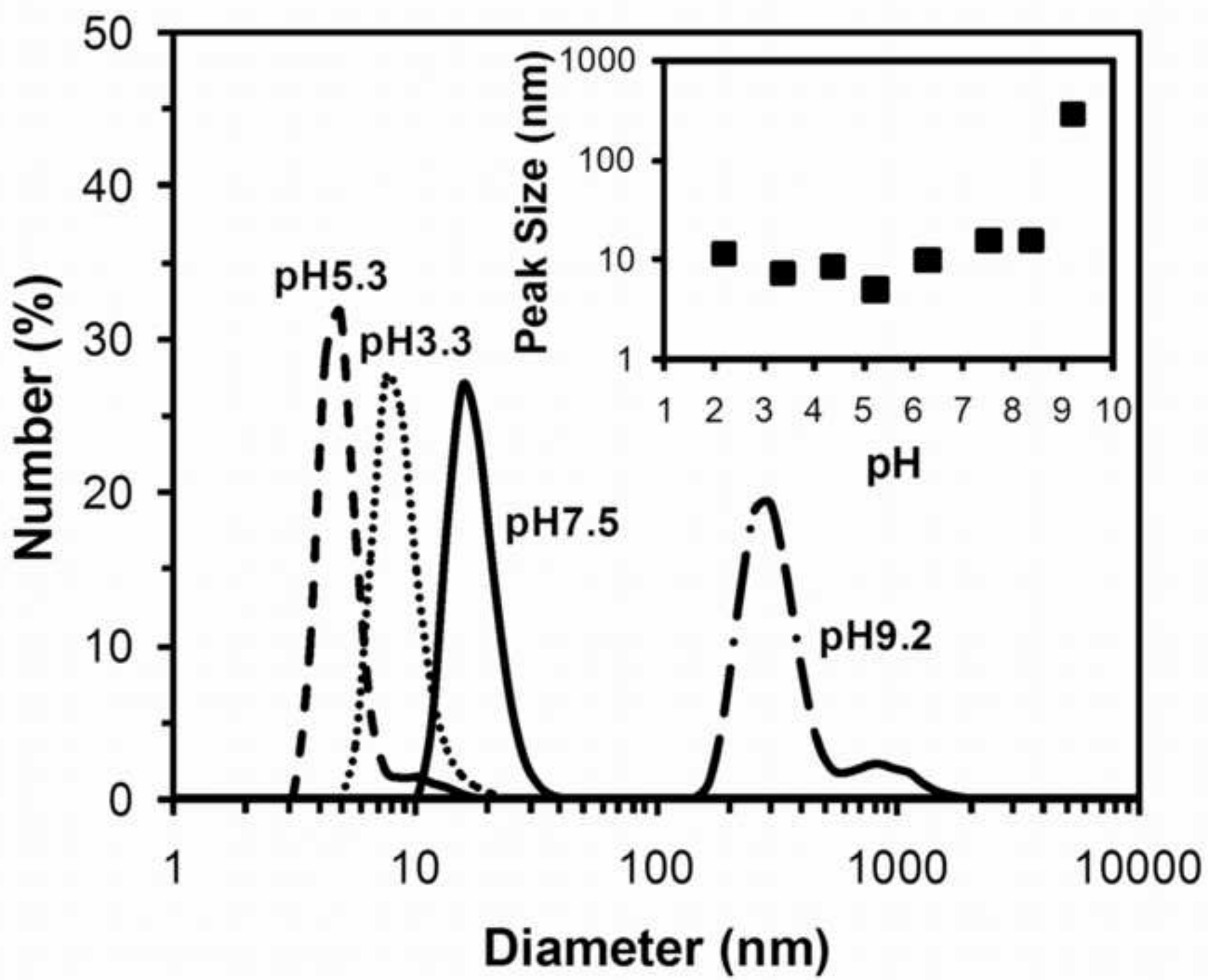


Figure5

