Magnetic Nanocomposite Multilayers Using Layer-by-Layer Assembly in Nonpolar and Polar Solvent

Younghoon Kim and Jinhan Cho*

School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea

Sanghyo Kim*

College of BioNano Technology, Kyungwon University, Gyeonggi-do 461-701, Korea

Introduction

Magnetic nanoparticles have recently attracted a great deal of attentions due to a number of potential applications such as MRI contrast agents, magnetic separation, nonvolatile memory devices or magnetic cards as well as a fundamental scientific interest.[1-3] The effective use of magnetic nanoparticles in a given application is based on two important factors: the inherent properties of nanoparticles (magnetization, size, etc.) and the ability to tailor their adsorbed amount onto the substrates. It has been reported by several research groups that high temperature decomposition of iron precursors in the presence of capping ligands can induce the high quality particles with facile size control, size uniformity and crystalline in comparison with more traditional coprecipitation/dextran methods[4] or the reduction method in aqueous solution.[5] These nanoparticles obtained from thermal decomposition can be well dispersed in nonpolar solvent due to hydrophobic property of the used stabilizers. Additionally, the particles with negatively charged stabilizers can allow the multiple depositions[6] (i.e., layer-by-layer assembled deposition) between particles and oppositely charged components and resultantly can enhance the intensity of their inherent properties such as magnetization. However, to the best of our knowledge, the facile and efficient method fully satisfying these two factors has not been introduced up to date.

Herein, we introduce the novel and simple method for the fabrication of magnetic nanocomposite multilayers, including the high quality γ-Fe$_2$O$_3$ nanoparticles (MP) by thermal decomposition method and allowing the tailored magnetic properties. 2-bromo-2-methylpropionic acid (BMPA)-stabilized MP in toluene solvent was prepared by exchanging oleic acid with BMPA after initially synthesizing the oleic acid-stabilized MP (OA-MP). The bromo (-Br) groups of BMPA-MP can be covalently bonded with amine (-NH$_2$) groups.[7] Based on this high affinity, it is demonstrated that the magnetic nanocomposite multilayers can be fabricated using BMPA-MP dispersed in toluene and poly(allyamine hydrochloride) (PAH) in water.

Results and Discussion

Using the covalent-bonding between bromo and amino groups, LbL assembly of BMPA-MP (10±3 nm) and PAH was performed on the quartz substrates, and the growth of multilayers was monitored by UV-vis spectroscopy. The uniform growth of the absorbance peak at 250 nm (due to BMPA-MP) indicates that the adsorbed amount of BMPA-MP per bilayer is regular, demonstrating the PAH/ BMPA-MP multilayer growth.

Quartz crystal microgravimetry (QCM) measurements were also conducted to quantify the adsorbed amount of PAH and BMPA-MP in the multilayer films. Based on the mass changes calculated from the frequency changes, the alternate deposition of PAH and BMPA-MP results in $-\Delta F$ of 9 ± 1 (Δm of ~ 159 ng·cm^{-2}) and 36 ± 2 Hz (Δm of ~ 636 ng·cm^{-2} and number density of nanoparticles ~ 3.26×10^{11}/cm^2), respectively. Although it was reported that water-soluble octakis components could be used as a stabilizer exchange of OA-MP through phase transfer method,[8] the transfer rate from OA-MP to octakis-MP is relatively very low. This phe-
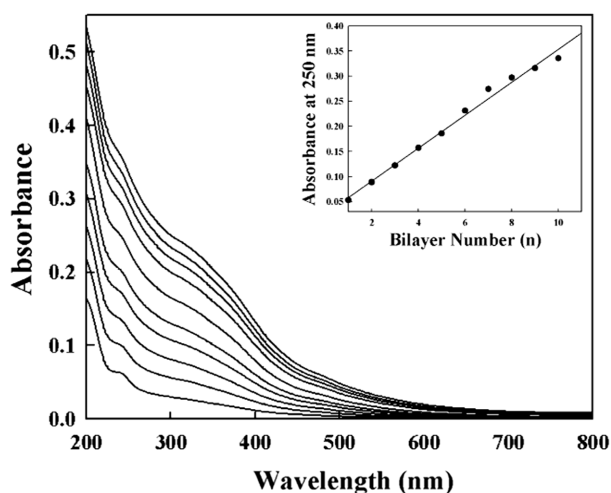

Figure 1. UV-vis absorption spectra of (PAH/BMPA-MP)$_n$ measured with increasing the layer number (n) from 1 to 10. The inset shows the change in absorbance (at 250 nm) as a function of bilayer number.

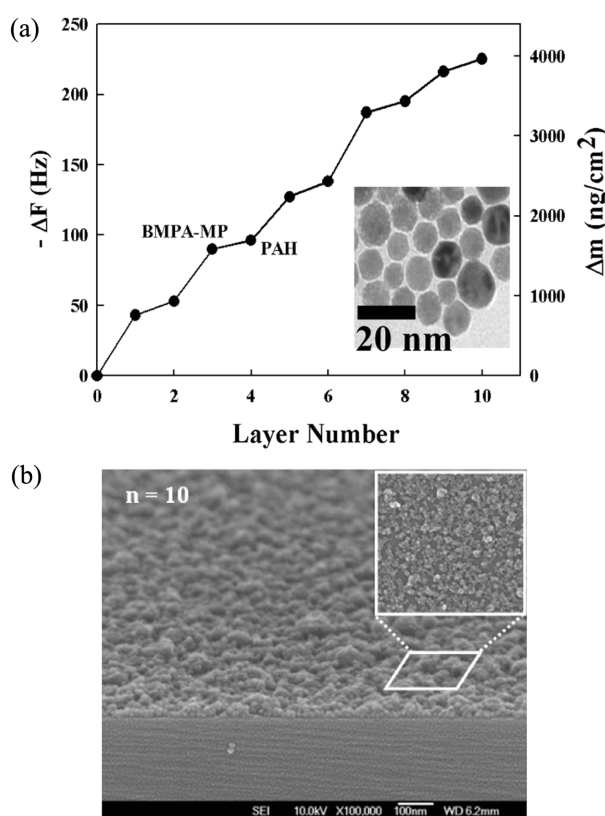*Corresponding Authors. E-mails: jinhan@kookmin.ac.kr or samkim@kyungwon.ac.kr

Figure 3. Magnetization curves of (PAH/BMPA-MP)$_{n=5 \text{ and } 10}$ multilayers measured from vibrating sample magnetometer.

Figure 2. (a) Frequency change of BMPA-MP/PAH multilayers. In this case, mass change per unit area was calculated from frequency change. ΔF (Hz) = -56.6×Δm_A, where Δm_A is the mass change per quartz crystal unit area in ng·cm^{-2}. The inset indicates the TEM image of BMPA-MP dispersed in toluene. (b) The tilted SEM image of (PAH/BMPA-MP)$_{10}$ multilayers.

nomenon resultantly yields the diluted nanoparticle solution, and furthermore the water-soluble MP needs the minute pH control for optimizing the surface charge density of octakis-MP. In general, the surface charge density has a significant effect on the dispersion stability and adsorbed amount of nanoparticles in water solvent (i.e., well-dispersion and low adsorbed amount at high surface charge density and on the other hand, poor-dispersion and high adsorbed amount at low surface charge density). The formation of (PAH/BMPA-MP)$_{10}$ multilayers was further characterized by scanning electron microscopy (SEM). As shown in Figure 2(b), the magnetic nanocomposite multilayer is highly uniform with the root-mean surface roughness of about 2 nm (also measured from atomic force microscopy).

Based on these results, we investigated the magnetization of (PAH/BMPA-MP)$_n$ multilayers with increasing bilayer number (n). The magnetization curves of the (PAH/BMPA-MP)$_{n=5 \text{ and } 10}$ multilayers were completely reversible without coercivity, remanence and hysteresis, indicating the superparamagnetic behavior. It should be also noted that the regular increase of saturated magnetization as a function of
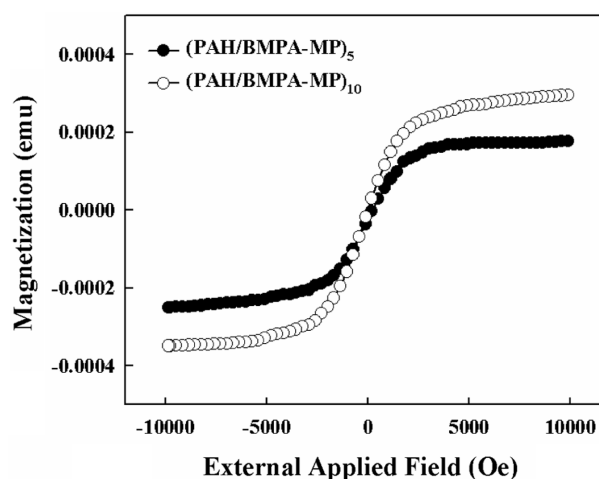
bilayer number is linearly proportional to the total amount of adsorbed BMPA-MP within multilayers and therefore, in the case of the magnetization per gram of adsorbed nanoparticles (data not shown), there was almost complete concord among magnetization curves measured by two different multilayers.[9]

These results imply that magnetic coupling of nanoparticles between adjacent layers is strongly dependent on the long-range magnetostatic interactions during the build-up of multilayers although the magnetic properties of densely packed BMPA-MP in plane are affected by the short-range electron exchange as well as long-range magnetostatic interactions.

In summary, we have demonstrated that the highly uniform (toluene-soluble BMPA-MP/water-soluble PAH)$_n$ multilayers could be fabricated through the covalent bonding interaction between -Br and -NH$_2$ groups, allowing the tailored magnetic property. We highlight that the hydrophobic nanoparticles with various functionalities can be assembled into 3D nanostructures through covalent interaction.

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