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Magnetic nanoparticles separation based on nanostructures ☆

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Abstract

This study describes a magnetic array, which consists of depositing Fe nanowires on a porous alumina membrane. Such a device can be used as a planar magnetic separator. Its performance for the collection of Fe_3O_4 nanoparticles is experimentally shown. For magnetization of such iron nanowires in the vertical direction, we propose equations to calculate the theoretical absorption ratio.

Keywords: Magnetic separation; Magnetic nanorod array; Planar separator

1. Introduction

Magnetic separation techniques, playing an important role in molecular biology, have been paid more and more attention due to the increasing utilization of reagents containing magnetic labels [1–3]. The most attractive advantage of using magnetic separation is the simplicity of manipulation. Once the target biological cells or molecules are immobilized on magnetic nanoparticles, these target biomolecules can be separated from a sample solution, flexibly manipulated in various reagents, and easily transported to a desired location by controlling magnetic fields produced by a permanent magnet or an electromagnet [4,5]. However, as biochemical experiments are now done at molecular levels with the emergence of micro total analytical system (μTAS), it is a challenging task to avoid inconsistencies between relatively large separators and increasingly small volumes of samples [6].

Recently, Jin-Woo Choi et al. [7] proposed a planar separator prototype using planar inductance with a permalloy as the ferrocore. The planar separator has the advantages of compactness, design flexibility and easy integration over conventional separators that are generally composed of specifically placed permanent magnets or magnetizable wire matrices combined with a uniform magnetic field [8,9]. However, high-field gradients require high geometric curvature, which seems incompatible with the design of devices. For example, membranes of magnetic metals, prepared by electroplating or sputtering, are often exploited as separators with magnetization by a uniform magnetic field. However, due to the shape anisotropy, the produced gradient is not satisfying.

Actually, more and more nanostructures with unique and exotic properties are found due to their size and shape. This could lead to novel applications in industry [10,11]. In this paper, we propose a new type of separator with vertically arranged Fe nanowire arrays. Compared with the existing planar separators, our device offers advantages of high-field gradients, large-scale treatment, low-cost fabrication and no heat generation. The latter feature is very important for practical applications because the heat produced by separators may be potentially harmful to biomolecules [12].

In this article, the polydispersed magnetite nanoparticles (about 40 nm in diameter) are chosen as objects to be separated from colloidal suspensions. For nanoscaled particles, the Brownian motion will no more be negligible, which requires strong enough magnetic fields, and field gradients to overcome the influence of Brownian motion.

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Therefore, the planar separator based on magnetic nanowire arrays, seems particularly useful to capture such small particles due to the nanometric diameters of nanowires.

2. Theoretic background

A magnetic force exerted on a nanoparticle in an inhomogeneous magnetic field, can be expressed by $F_m = \frac{1}{2} V_m(\chi_p - \chi_f)/\mu_0 \nabla B^2$, where V_m is the volume of a magnetic nanoparticle, χ_p and χ_f are the susceptibility of particles and fluidic medium, respectively, B is the magnetic flux density and μ_0 is the permeability of free space [13]. As far as separator equipment is concerned, the generation of high-field gradients is a key issue since the field intensity is achieved by an externally exerted uniform field. The magnetic nanowire array is fabricated via electrochemical deposition of Fe into channels of alumina films, which exhibit parallel alignment normal to the substrate plane. Therefore, along axis of the magnetized nanowires, high-field gradients can be generated due to such large aspect ratios. The configuration of porous alumina films is shown in Fig. 1. Macroscopically, it behaves as a compact film, having the thickness of Al substrate. In practical applications, the uniform magnetic field is applied vertically to the film, as it is interesting for planar films to generate high magnetization fields in the normal direction.

A single magnetized nanowire can be regarded as an annular current it is often macroscopically called magnetization current. According to Ampere's molecular current viewpoint, the magnetic field generated by a magnetized rod is identical to a electrified solenoid. Hence, in a plane, the nanowire can be regarded as an annular. Generally, the pore density of porous alumina film is so high (10^9–$10^{11}\,cm^{-2}$ [14]) that the annular currents can be considered as continuous distributions. Then due to the effect resulting from mutual neutralization of annular currents with reverse directions, all annular currents will be reduced to one annular current, i.e. to a single nanowire with high magnetization, somewhat similar to the mechanism of magnetization in a magnet. According to Refs. [15,16], the flux produced by the magnetic film is just like that of a bar magnet along the length direction. The field distribution of nanowires array film has an advantage of good anisotropy in z-direction over that of magnetically metallic membranes, prepared by electroplating.

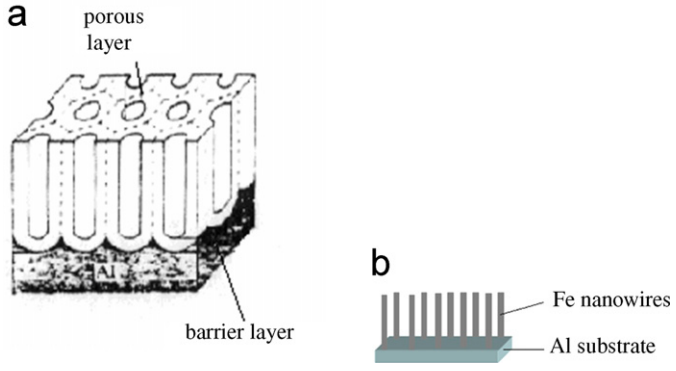

Fig. 1. (a) Is a morphological sketch of a porous alumina film, and (b) is a morphological sketch of metal nanowires deposited in the channels of an alumina film. The black rods mean Fe nanowires.

For nanoscaled colloidal suspensions, magnetic nanoparticles separation behaves as a statistical mechanics process due to thermal fluctuations. Supposing that one nanowire is one absorptive centers at the film surface and the energy of one captured particle is $-\varepsilon_0$, the equilibrium absorptive ratio is

$$\rho = \frac{\overline{N}}{N_0}, \tag{1}$$

where $\overline{N}$ is the captured particle number in equilibrium and N_0 is the total number of absorptive centers. Regarding the suspension as thermal source and particle source, the captured particles can be considered as a system exchanging particle and energy with source, which complies with grand canonical distribution. When N particles are captured, the energy of system is $-N\varepsilon_0$. Considering that N particles in N_0 absorptive positions have $N_0!/N!(N-N_0!)$ permutations, the systematic grand canonical partition function and the average captured particle number are expressed in Eqs. (2) and (3), respectively:

$$X = \sum_{N=0}^{N_0} e^{\beta(\mu+\varepsilon_0)N} \frac{N_0!}{N!(N_0-N)!} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0} \tag{2}$$

$$\overline{N} = -\frac{\partial}{\partial\alpha} \ln\, \Xi = kT \frac{\partial}{\partial\mu} \ln\, \Xi = \frac{N_0}{1 + e^{-\beta(\varepsilon_0+\mu)}}, \tag{3}$$

where $\alpha = -\beta\mu$, β is the Lagrange's unknown factor, which is determined by $(kT)^{-1}$. Here, k is Boltzmann's constant and T is the absolute temperature. μ is the chemical potential of the system. At equilibrium, it is identical to that of the source, namely the suspension. Using Eq. (3), we obtain the absorptive ratio

$$\rho = \frac{\overline{N}}{N_0} = \frac{1}{1 + e^{-\beta(\varepsilon_0+\mu)}}. \tag{4}$$

Eq. (4) reveals that the trapping process will consequentially reach equilibrium and the trapping efficiency depends on temperature, magnetization, and the chemical potential of suspensions.

3. Experimental section

The porous alumina template was prepared by electrochemical anodization of a 0.1 mm thick Al disk as the anode, using a pure graphite plate as a cathode [14]. The set up is shown in Fig. 2. The voltage was set to 20 V DC using 0.3 M sulfuric acid as electrolyte. Typically, the experiment was carried out for 10 h. After the formation of an alumina film on the surface of the Al substrate, the Al disk was maintained but the electrolyte was removed and replaced by a 5 wt% phosphoric acid solution, applied during one more hour to form larger pores. When it finished, the

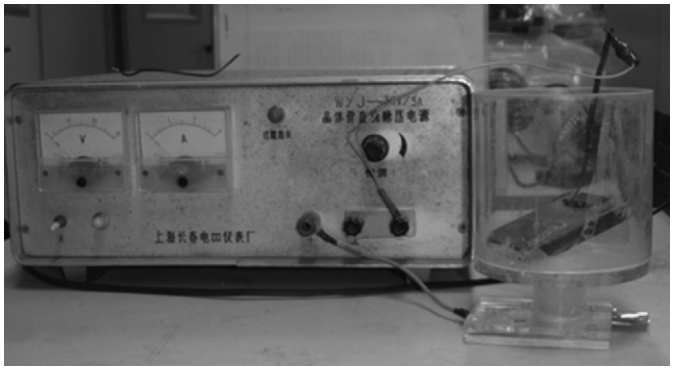

Fig. 2. The set up of fabricating alumina film and magnetic array. The aluminum disk was placed in the bottom of the tank and connected with the anode of power supply (red column). The cathode of power supply (black column) was connected with the graphite plate.

phosphoric acid solution was poured out and the film was also fixed in the tank. The film, and the reaction tank was washed with distilled water for several times.

The preparation of Fe nanowires was based on the same set-up, but the DC voltage was replaced with AC voltage and the sulfuric acid electrolyte was replaced with the mixed solution consisted with $120\,g\,L^{-1}$ $Fe_2SO_4\cdot 7H_2O$, $45\,g\,L^{-1}$ boracic acid and $1.0\,g\,L^{-1}$ vitamin C. Using the graphite plate as counter-electrode and setting the voltage on 20 V, 50 Hz AC, the Fe^{2+} were reduced into Fe and confined to the wire-like shape by the channels of alumina template. The reaction time was correlative to the length of formed nanowires, and in our experiments, it was about 10 min. The Fe nanowires array was characterized by scanned electron microscopy (SEM) and the removed Fe nanowires were characterized by transmission electron microscopy (TEM) . The removal of the Al substrate and alumina template was achieved by treating the disk in a saturated KOH solution at 60 °C. After Al and alumina were both dissolved, the solution was separated by centrifugation in 3000 r/min and washed with distilled water. Such treatments were repeated for several times until the pH value of solution was approximately equal to 7.

The magnetic separation experiments were done in a glass tank ($40\times 30\times 6\,mm^3$). The porous film was fixed at the bottom by cyanoacrylate adhesive. The objects to be separated were glutamic acid capped magnetite nanoparticles with mean diameter of 40–50 nm, which were prepared in our lab and dispersed in water [17]. A peristaltic pump was employed to drive the highly diluted aqueous suspension to flow into the glass tank. A 0.25 T homogeneous magnetic field generated by an electromagnet was externally applied to the tank with the magnetic flux perpendicular to the magnetic nanowire film. Due to the field gradient from the magnetized nanowires array, the magnetic nanoparticles were captured by the film. This could be observed by naked eye, as the suspension turns limpid. The separation experiment was carried out at different separation times. In each separation time, the supernate was drawn out into a cuvette as sample copy by a syringe. Fe concentrations of all the samples were measured by atomic absorption spectroscopy (polarized zeeman atomic absorption spectrophotometer). We think that Fe signals are due to Fe_3O_4 nanoparticles, therefore the remnant Fe in supernate could characterize the separation efficiency.

Simultaneously, after the separation experiment, the porous alumina film was observed by SEM and the elemental analysis for a selected area was performed by energy-dispersive X-ray spectrograph (EDX) to investigate Fe content absorbed on the film surface. The porous alumina film with Fe deposition before separation was characterized for comparison.

4. Results and discussion

The morphological SEM image of alumina template surface is shown in Fig. 3 which reveals the high density of channels of porous alumina film. TEM photos of Fe nanowires after the removal of template and substrate are shown in Fig. 4, where the diameter of nanowires is about 15 nm and the length is about several micrometers, respectively. Based on these data, the aspect ratio can be calculated to be above 100, exhibiting the strong geometrically magnetic anisotropy. So it may well be inferred that the film will be easily magnetized along the direction normal to its surface while an ordinary ferruginous slice is often hard to be magnetized in this direction due to the large demagnetization factor on disk-like shape. The magnetic characterization of magnetic nanowire arrays is shown in Fig. 5, from which the ferromagnetism of Fe–Al_2O_3–Al, corresponding to the ternary system consisting of nanowire, template and substrate is documented.

The Fe concentration–time curve is shown in Fig. 6. There is a sharp decline after 5 min, predicating that equilibrium is reached after maximum 5 min. The absorptive ratio, which is up to 90%, is calculated using the final concentration in supernatant divided by the original

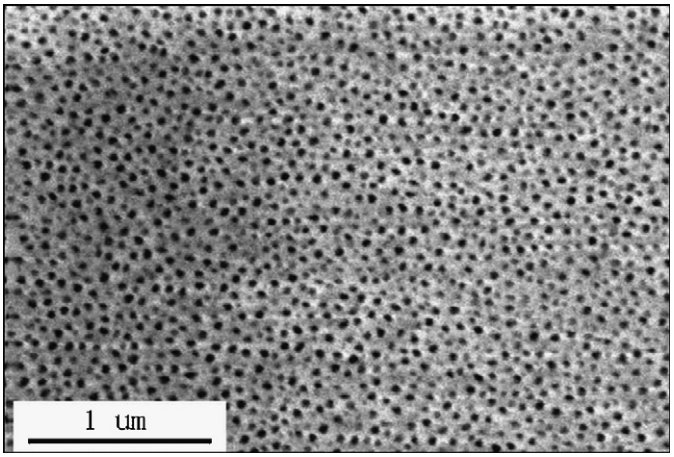

Fig. 3. SEM image of porous alumina film without Fe deposition.

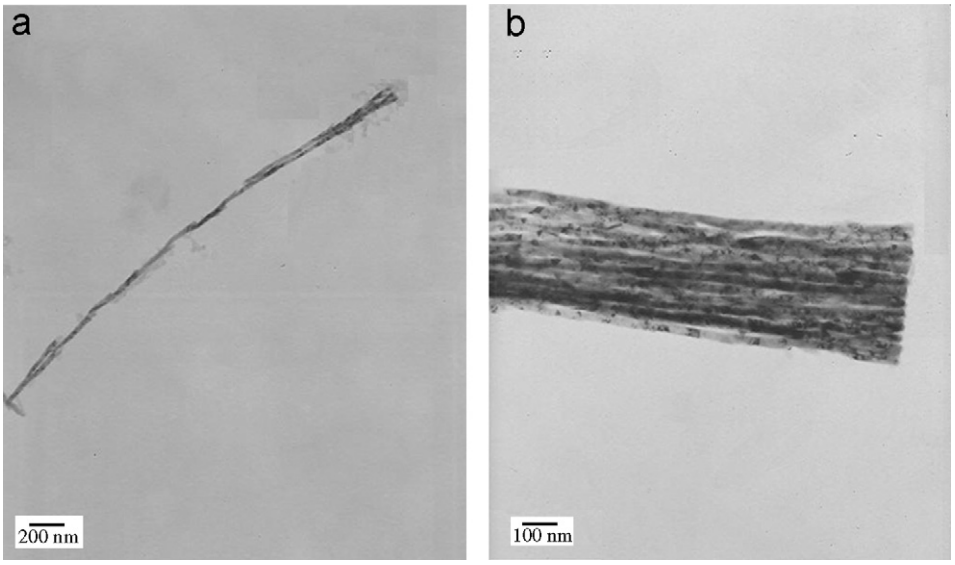

Fig. 4. (a) Is the TEM image of a single wire and (b) is the TEM image of aligned wires.

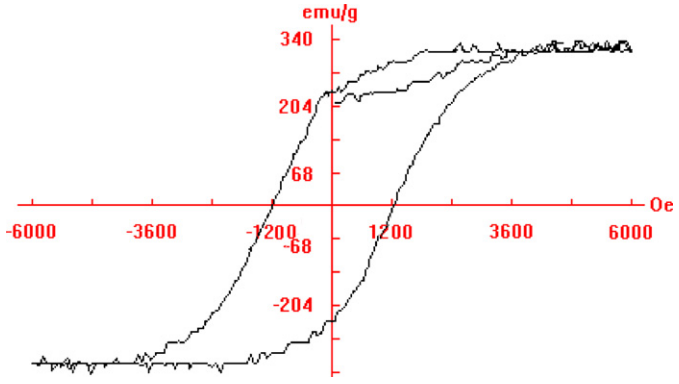

Fig. 5. Magnetic hysteresis of Fe–Al_2O_3–Al ternary system. The magnetization is perpendicular to the surface.

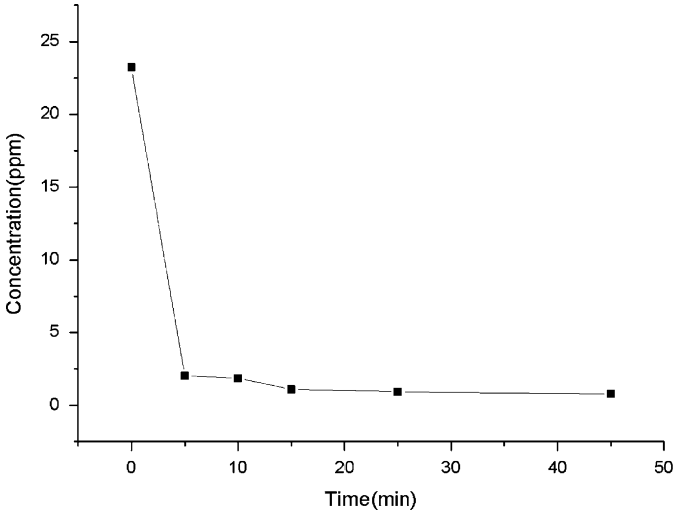

Fig. 6. Fe concentration vs. time curve (under room temperature). The parameter in *y*-axis represents the Fe concentration in different samples measured by atomic absorption spectroscopy and the parameter in *x*-axis is separation time.

concentration in the suspension. From Eq. (4), it is seen that 100% separation of magnetic nanoparticles is impossible and once the equilibrium arrives, the absorptive ratio is independent of time. Thermal fluctuations contribute to irregularities in the concentration curve (Fig. 6). These are consistent with our experimental results. From the experimental point of view, these phenomena can be explained by the theory proposed by Takayasu [18], where the size of nanoparticles plays an important role in the capturing process. In our experiments, the pure iron disk was also experimentalized for comparison with magnetic array film. Also, the colloidal suspension was experimentalized under a uniform magnetostatic field in the absence of magnetic array film or other ferromagnetic components. The results show no significant particulate separation is observed under both cases. This is because that the adequate field gradient fails to be generated. For the former, the shape anisotropy diminishes the gradient too weakly to exert forces on nanoparticles. For the latter, there exists only uniform magnetic field, under which the magnetic forces on the nanoparticles are zero.

Another interesting result comes from EDX experiments. As illustrated in Fig. 7, before adsorption, no Fe peak is found while 2 weak Fe peaks are found after adsorption, indicating that Fe is not fully deposited into the channels of the used alumina film while the Fe peaks result from the nanoparticles captured into the surface of film. Because of the larger size of nanoparticles than that of the channels, there remain vast nanoparticles without entering the channels. A typical SEM photo is shown in Fig. 8. These phenomena suggest applications in biosensors, that the difference of Fe content in surface can be exploited to characterize the amount of adsorbed particles, offering a novel approach for the biological detection and measurement of biological affinity.

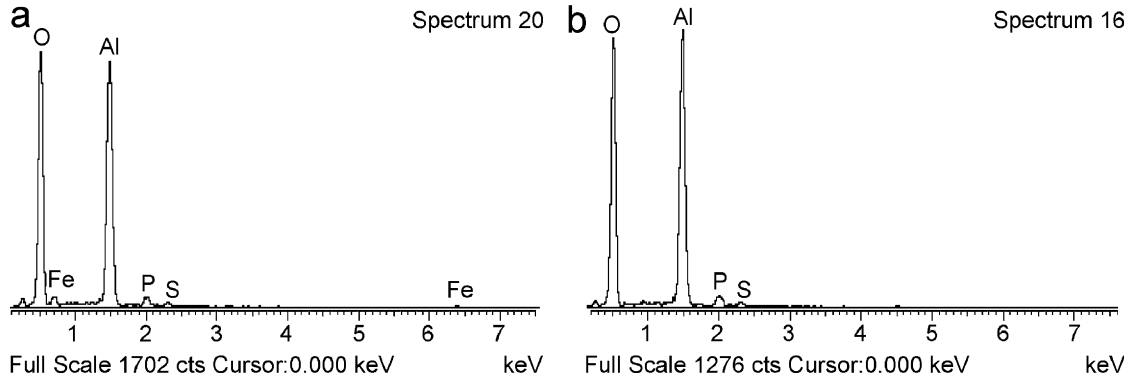

Fig. 7. (a) Is EDX spectrum after adsorption. Two weak Fe peaks are visible. No Fe peaks are revealed in the reference EDX spectrum (b).

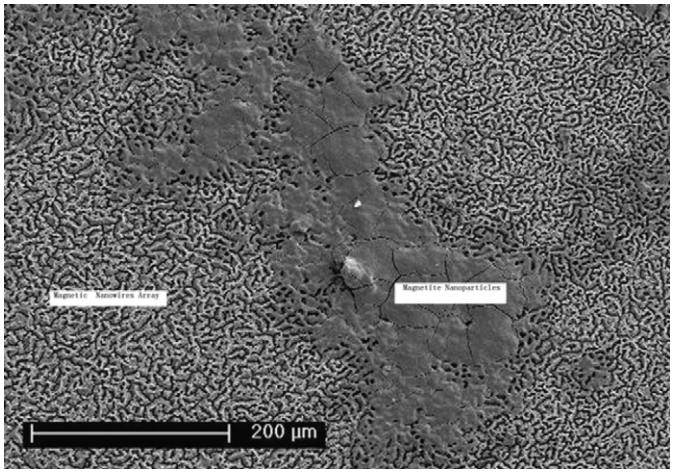

Fig. 8. SEM image of magnetic nanowires array after separation.

5. Conclusion

A matrix with a planar separator based on magnetic nanowire arrays has been proposed. The magnetic nanowire arrays were fabricated electrochemically and characterized by TEM and SEM. The separation efficiency is characterized by the functional curve between Fe concentration and separation time. The Fe-deposited alumina film is macroscopically seen as a film but the easily magnetized direction in our case is normal to the flake while it is the difficultly magnetized direction of ordinary ferromagnetic film. Since Al can be electroplated on many substrates with different morphologies, the application of this porous alumina films would be very promising.

Due to the complexity of nanowires array system, the investigation of quantitative relationship between separated particles number and field gradient, as well as the quantificational description of separation process with statistical theory will be our next challenges.

We believe this fundamental study helps to realize technological applications, which is the key issue in nanoscience development.

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