

Solution Preparation and Properties of Au@Fe₃O₄ Nanospheres

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Abstract-Due to its excellent magnetic and catalytic properties and its biocompatibility, Au@Fe₃O₄ has been widely used in biomedical applications, such as tumor treatment. In this study, Au@Fe₃O₄ nanospheres were prepared using polyethylene glycol as the dispersant. Different weight ratios of Fe₃O₄ to Au were tested in order to obtain evenly coated Au@Fe₃O₄ nanospheres. The structural and magnetic properties were investigated with transmission electron microscopy, scanning electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, and vibrating-sample magnetometry. We found that the Au@Fe₃O₄ nanospheres were well coated when the weight ratio of Fe₃O₄:Au was 3:8. Moreover, the Au@Fe₃O₄ nanospheres showed a high saturation magnetization of 54 emu/g, indicating their potential for use in numerous biomedical applications.

Keywords- Au@Fe₃O₄; Nanospheres; Magnetism; Nanocomposite Particles

I. INTRODUCTION

It is well known that the presence of tumors has become a common health issue in modern society, from which an ever-increasing number of people are suffering. Many treatments have been devised, such as surgical removal, chemotherapy, and radiation therapy. Of these methods, chemotherapy is extremely important [1-4]. In chemotherapy, Au@Fe₃O₄ nanospheres are often used as nanodrug carriers, due to their beneficial magnetic properties and biocompatibility [5-10].

Numerous methods of Au@Fe₃O₄ synthesis have been investigated [11-20]. For example, Ola S. Ahmed synthesized Au@Fe₃O₄ using chemical co-precipitation with the reduction of polyethylene imine (PEI) [16]. In another study, A. Pariti synthesized Au@Fe₃O₄ using a single-step hot-injection precipitation method [17]. In addition, Heng Yu synthesized Au@Fe₃O₄ using the decomposition of Fe(CO)₅ on the surfaces of the Au nanoparticles, followed by oxidation in a 1-octadecene solvent [20]. However, some problems still exist. For example, Au particles often barely cover flocculent Fe₃O₄ grains, or Fe₃O₄ nanospheres are too small to be coated by Au particles.

To obtain high-quality Au@Fe₃O₄ nanospheres in this study, Fe₃O₄ nanospheres were prepared using polyethylene glycol (PEG) as the dispersant. As a result, the produced Fe₃O₄ nanospheres were well shaped, with sphere diameters of 300-400 nm. Au@Fe₃O₄ was then synthesized by the epitaxial growth of Au on the Fe₃O₄ seeds. The large Fe₃O₄ nanospheres could be thoroughly coated by Au particles with sphere diameters of 30-50 nm. We obtained high-quality Au@Fe₃O₄ nanoparticles with a 3:8 weight ratio of Fe₃O₄:Au.

II. EXPERIMENTAL

A. Materials

Chlorogold acid (HAuCl₄•4H₂O), sodium citrate (NaC₆H₅O₇•2H₂O), ferric chloride (FeCl₃•6H₂O), sodium acetate (NaAc), polyethylene glycol (PEG200), ethylene glycol (C₂H₆O₂), and ethyl alcohol (C₂H₆O) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were of analytical grade, and distilled water was used throughout the experimental

process.

B. Preparation of Fe_3O_4

First, 1.35 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 40 mL of $C_2H_6O_2$. Next, 3.6 g NaAc and 1.0 g PEG200 were added while stirring for 30 min. Then, the solution was placed into the reaction kettle to preserve for 10 hours at 200 °C. Finally, the solution was cooled to room temperature and washed three times with C_2H_6O , then dried at 60 °C for 10 hours.

C. Synthesis of $Au@Fe_3O_4$

The Fe_3O_4 and 0.03 g of $NaC_6H_5O_7$ were dissolved in 200 mL of distilled water and dispersed for 5 minutes using an ultrasonic oscillator. The solution was heated to boiling with vigorous stirring, and 20 mL $HAuCl_4$ solution was quickly added. Then, the solution was stirred for 2 hours, washed three times with C_2H_6O , centrifuged at 4500 rev/min for 20 minutes, and dried at 80 °C for 10 hours. During the experiment, different quantities of Fe_3O_4 (0.01 g, 0.03 g, and 0.05 g) were added to obtain high-quality $Au@Fe_3O_4$.

D. Characterization

X-ray diffraction (XRD) analysis of the samples was conducted on a Rigaku D/MAX-RC diffractometer with Ni-filtered Cu-K α radiation ($V = 50$ KV, $I = 80$ mA). The morphologies and microstructures of the products were investigated by scanning electron microscopy (SEM, Hitachi SU-70). Transmission electron microscopy (TEM) was performed on a JEM-1011 transmission electron microscope with a field emission gun operating at 100 KV. Elemental analysis of the samples was conducted using an electron-dispersive spectrometer unit attached to the Hitachi SU-70 SEM. Fourier-transform infrared spectroscopy (FT-IR) analysis of the samples was conducted with a BRUKER TENSOR 37 FT-IR spectrometer using KBr pellets. Static magnetic properties were measured by vibrating sample magnetometer (VSM, 7410).

III. RESULTS AND DISCUSSION

A. TEM Analysis

1) TEM of Fe_3O_4 Nanospheres

The microstructure of the Fe_3O_4 nanospheres was observed by TEM, as shown in Fig. 1. In Fig. 1(a), the Fe_3O_4 nanoparticles appear flocculent, aggregating in patches with diameters of approximately 10 nm. The image in Fig. 1(b) depicts Fe_3O_4 nanospheres under higher magnification, revealing obvious structures. The Fe_3O_4 nanospheres appear as homogeneous spheres with diameters of approximately 300-400 nm, much larger than those of nanospheres prepared without a dispersant or by the co-precipitation method [21-22]. This difference may have been caused by the use of PEG200 as the dispersant, which facilitated the formation and dispersion of the Fe_3O_4 nanospheres.

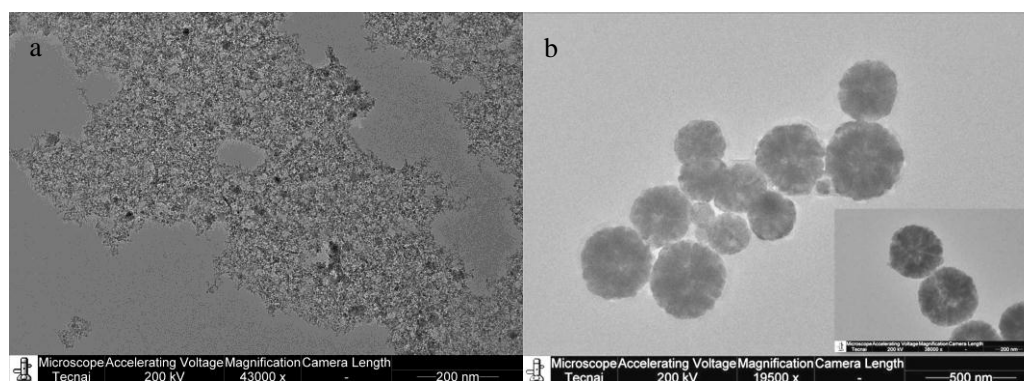


Fig. 1 TEM images of pure Fe_3O_4 nanospheres (a) without dispersant and (b) using PEG as the dispersant

2) TEM of $Au@Fe_3O_4$ Nanospheres

The microstructure of the $Au@Fe_3O_4$ nanospheres was observed by TEM, as shown in Fig. 2. The larger and

lighter-colored nanospheres are Fe_3O_4 , and the smaller and darker-colored nanospheres are Au. The microstructure of the $\text{Au@Fe}_3\text{O}_4$ nanospheres varied with the quantity of Fe_3O_4 . In Fig. 2(a), the amount of Fe_3O_4 is so large that the Au particles cannot fully coat the Fe_3O_4 surfaces, resulting in the appearance of bare Fe_3O_4 nanospheres. In Fig. 2(c), the amount of Fe_3O_4 is so low that the Au particles gather on the surfaces of the Fe_3O_4 nanospheres. In contrast, Fig. 2(b) shows that the amount of Fe_3O_4 is appropriate and that the Au particles can evenly coat the surfaces of the Fe_3O_4 nanospheres. As can be observed in Fig. 2(b), the surfaces of the Fe_3O_4 nanospheres are well coated by Au nanoparticles. Thus, when the weight ratio of $\text{Fe}_3\text{O}_4\text{:Au}$ is the optimal value of 3:8, high-quality $\text{Au@Fe}_3\text{O}_4$ nanospheres can be obtained. Fig. 2 also shows that the diameters of the Fe_3O_4 and Au nanospheres are 300-400 nm and 30-50 nm, respectively.

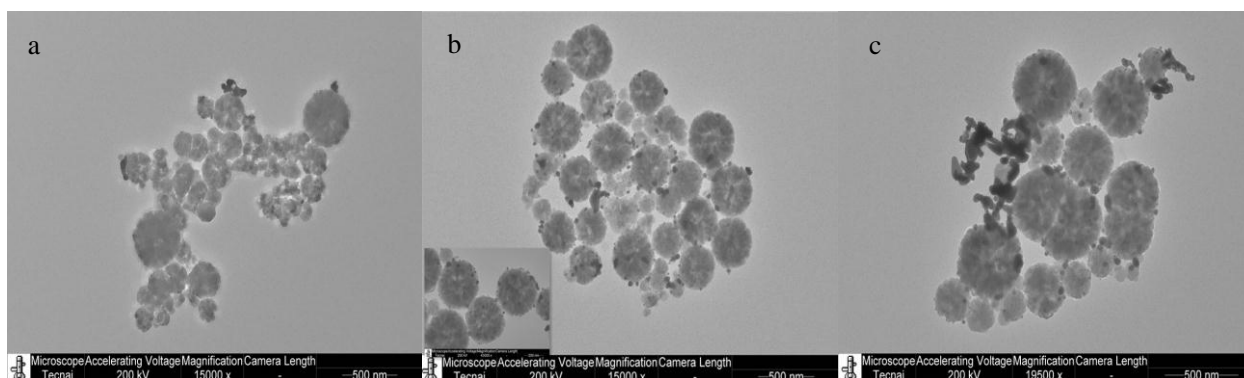
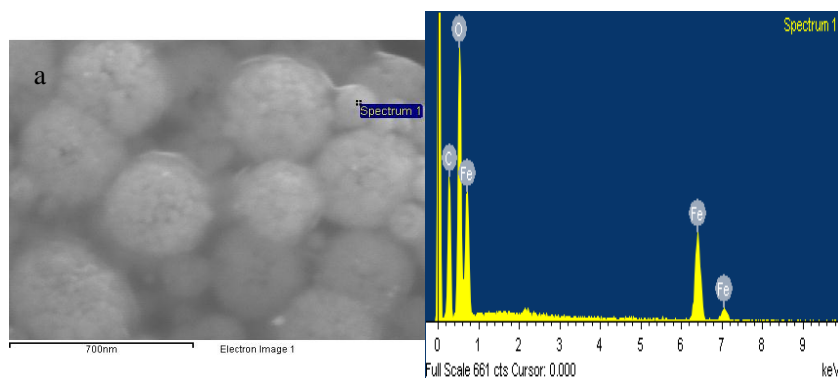


Fig. 2 TEM images of $\text{Au@Fe}_3\text{O}_4$ when (a) 0.05 g, (b) 0.03 g, and (c) 0.01 g of Fe_3O_4 was added

B. EDX Analysis

Elemental composition was investigated by EDX, as shown in Fig. 3. The EDX spectrum corresponding to the sample in Fig. 3(a) indicates that it was mainly composed of Fe and O, resulting in the formation of Fe_3O_4 nanospheres. The additional appearance of C may result from the probe breaking down the samples during EDX testing. Similarly, the EDX spectrum corresponding to the sample in Fig. 3(b) reveals that it was mainly composed of Fe, O, and Au. No other impurity was detected, indicating that Au successfully coated the surfaces of the Fe_3O_4 nanospheres, and that $\text{Au@Fe}_3\text{O}_4$ nanospheres were obtained.



| Element | Weight% | Atomic% |
|---------|---------|---------|
| C K | 27.11 | 42.93 |
| O K | 38.01 | 45.19 |
| Fe K | 34.88 | 11.88 |
| Totals | 100.00 | |

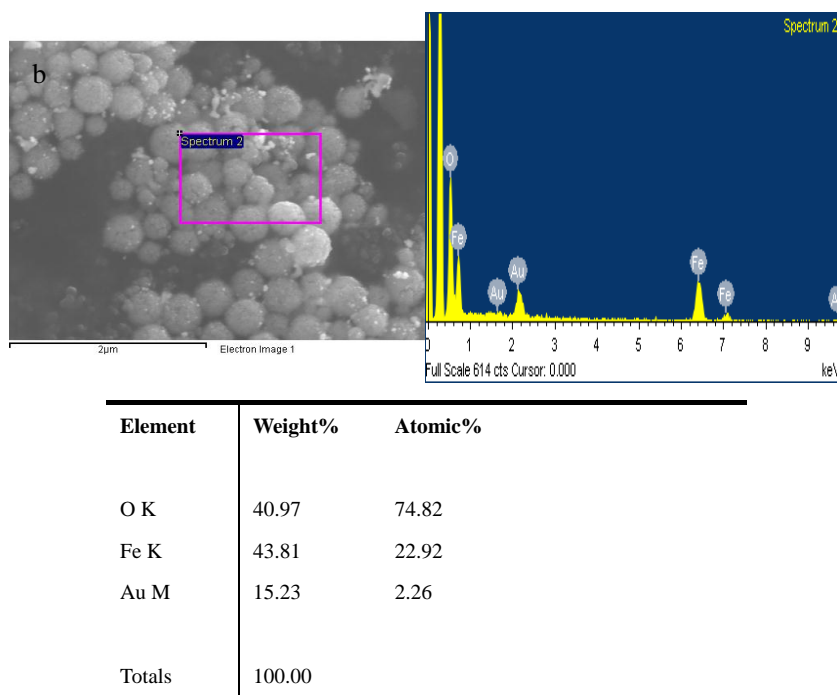


Fig. 3 EDX spectra of (a) Fe_3O_4 and (b) $\text{Au@Fe}_3\text{O}_4$ nanospheres when 0.03 g of Fe_3O_4 is present

C. SEM Analysis

The microstructures of $\text{Au@Fe}_3\text{O}_4$ and Fe_3O_4 were also observed by SEM, as shown in Fig. 4. As shown in Fig. 4(a), the pure Fe_3O_4 nanospheres have smooth surfaces and are monodispersed, with diameters of approximately 300-400 nm. In contrast, the $\text{Au@Fe}_3\text{O}_4$ powders in Fig 4(b), (c), and (d) contain irregular particles with sizes ranging from approximately 30-50 nm to 300-400 nm. By relating these particles to the EDX spectra, the large nanospheres with diameters of 300-400 nm may be identified as Fe_3O_4 nanospheres, and the small particles with diameters of 30-50 nm as Au nanoparticles.

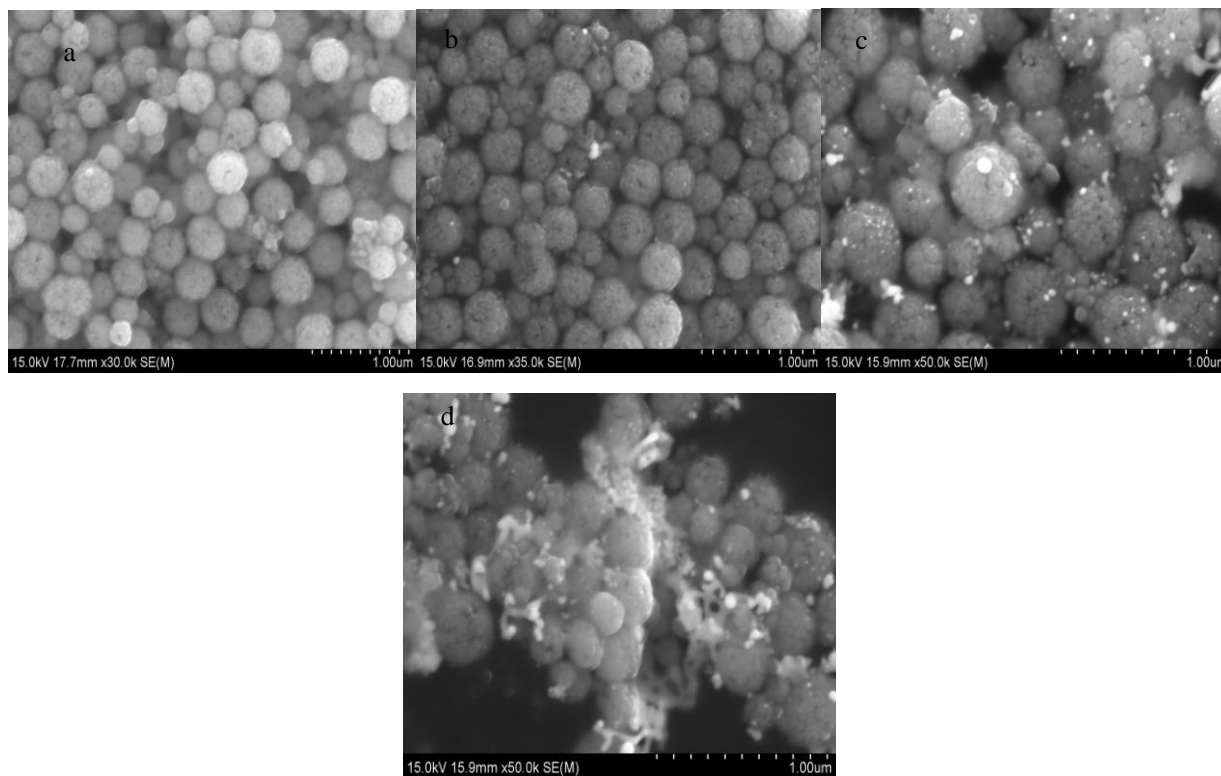


Fig. 4 SEM images of (a) pure Fe_3O_4 and (b-d) $\text{Au@Fe}_3\text{O}_4$ when (b) 0.05 g, (c) 0.03 g, and (d) 0.01 g of Fe_3O_4 is present

Comparing Fig 4(b) and (c) with Fig. 4(d), it is obvious that there are many bare Fe_3O_4 nanospheres in Fig. 4(b) and numerous Au particles gathered on the surfaces of the Fe_3O_4 nanospheres in Fig. 4(d), while the Fe_3O_4 nanospheres are uniformly coated by Au particles and well dispersed in Fig. 4(c). These observations result from the quantity of Fe_3O_4 nanospheres being excessive in Fig. 4(b), insufficient in Fig. 4(d), and appropriate in Fig. 4(c). The conclusion derived from TEM that the optimal weight ratio of Fe_3O_4 :Au is 3:8 was thus verified by SEM.

D. FTIR Analysis

The chemical bonds were investigated by FTIR. The FTIR spectra of (a) Fe_3O_4 and (b) $\text{Au@Fe}_3\text{O}_4$ are given in Fig. 5. The absorption bands at 649.33 cm^{-1} and 431.56 cm^{-1} can be associated with the Fe=O bond of Fe_3O_4 [23]. In contrast to the FTIR spectra of pure Fe_3O_4 , the two peaks decrease in the spectrum of $\text{Au@Fe}_3\text{O}_4$, which indicates that the Au nanoparticles had coated the surfaces of the Fe_3O_4 nanospheres. The other peaks primarily belong to the ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$) that was used as the solvent.

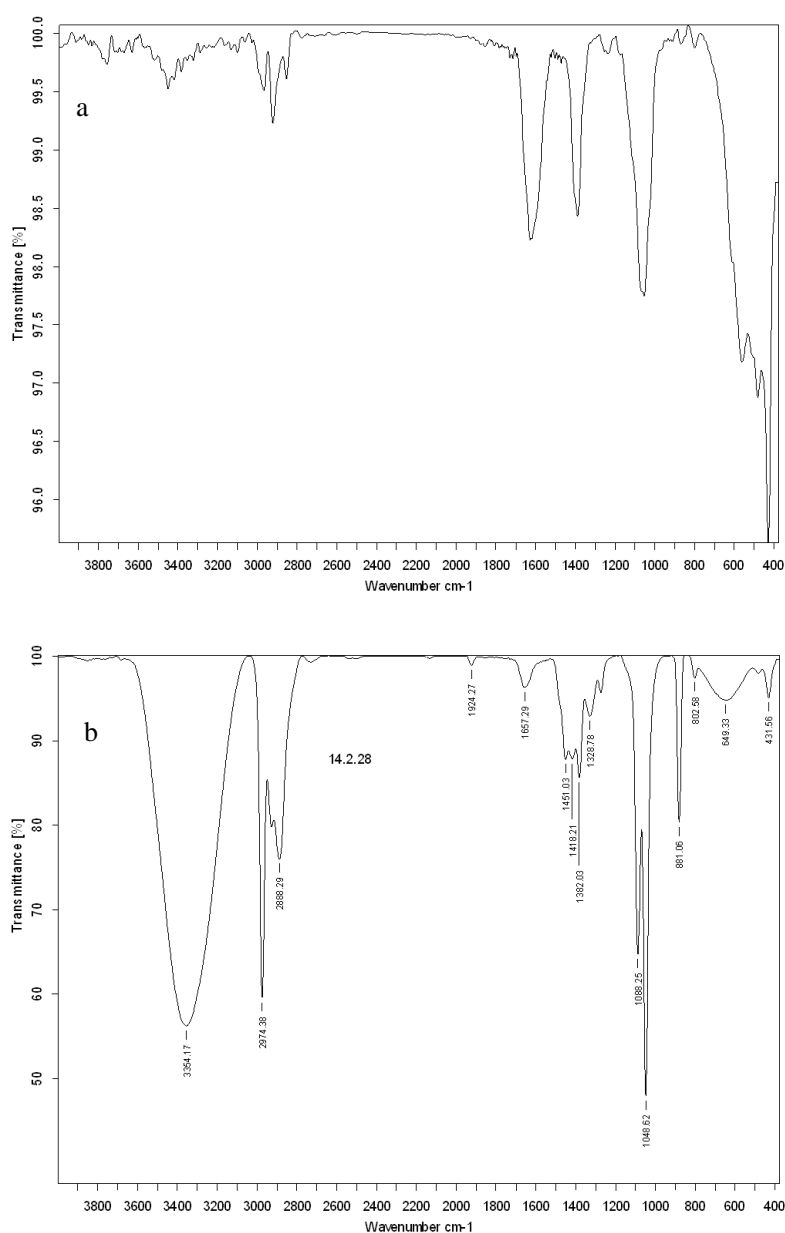


Fig. 5 FTIR spectra of (a) Fe_3O_4 and (b) $\text{Au@Fe}_3\text{O}_4$ when 0.03 g of Fe_3O_4 is present

E. X-Ray Diffraction Analysis

The compositions and phases of pure Fe_3O_4 (black trace) and $\text{Au@Fe}_3\text{O}_4$ (pink trace) obtained by XRD are depicted in Fig. 6. The triangles and circles indicate the characteristic peaks of Fe_3O_4 and Au, respectively. The XRD spectra of $\text{Au@Fe}_3\text{O}_4$ exhibit the characteristic peaks of both Au and Fe_3O_4 , suggesting that the surfaces of the Fe_3O_4 nanospheres were coated by Au particles.

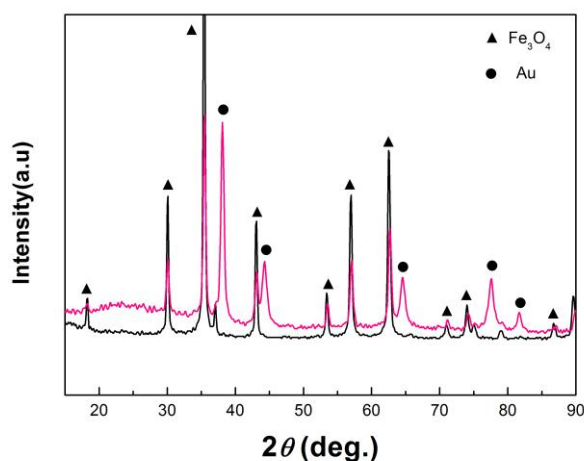


Fig. 6 XRD patterns of Fe_3O_4 (black trace) and $\text{Au@Fe}_3\text{O}_4$ when 0.03 g of Fe_3O_4 is present (pink trace)

F. VSM Analysis

The magnetic properties of the samples were investigated by VSM, as shown in Fig. 7. Both samples demonstrate stronger magnetism with negligible coercivity and remanence at room temperature. The saturation magnetization of Fe_3O_4 is 85 emu/g. Due to the Au particles coating the surfaces of the Fe_3O_4 nanospheres, the magnetization of $\text{Au@Fe}_3\text{O}_4$ decreases to 54 emu/g, which is higher than the 40 emu/g previously reported [18]. In addition, the $\text{Au@Fe}_3\text{O}_4$ nanocomposites were tested in water by placing a magnet near the bottle, as shown in Fig. 7(b). The samples were quickly attracted to the magnet, demonstrating their excellent magnetic responsivity. The $\text{Au@Fe}_3\text{O}_4$ nanocomposites still exhibit strong magnetization, indicating their suitability for magnetic targeting and separation in numerous biomedical applications.

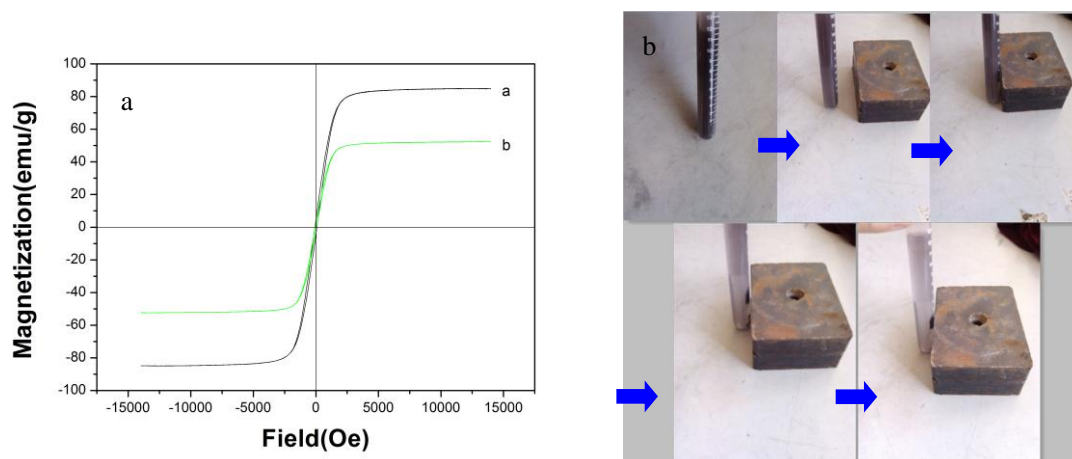


Fig. 7 (a) Room temperature magnetization curves of Fe_3O_4 (trace a); $\text{Au@Fe}_3\text{O}_4$ when 0.03 g of Fe_3O_4 is present (trace b)

(b) Separation process of $\text{Au@Fe}_3\text{O}_4$ when 0.03 g of Fe_3O_4 is present

IV. CONCLUSIONS

In summary, Au@Fe₃O₄ nanospheres were successfully synthesized with PEG as the dispersant. The diameters of the Fe₃O₄ nanospheres were approximately 300-400 nm, which was large enough to be coated by Au particles of 30-50 nm diameter. When the weight ratio of Fe₃O₄:Au was 3:8, well-shaped and evenly coated Au@Fe₃O₄ nanospheres were obtained. The Au@Fe₃O₄ nanospheres were strongly magnetized, with a saturation magnetization value of approximately 54 emu/g, indicating their potential for use in numerous biomedical applications, including as nanodrug carriers targeting tumors in chemotherapy.

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