Article

Study on Magnetic and Plasmonic Properties of Fe$_3$O$_4$-PEI-Au and Fe$_3$O$_4$-PEI-Ag Nanoparticles

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Abstract: Magnetic–plasmonic nanoparticles (NPs) have attracted great interest in many fields because they can exhibit more physical and chemical properties than individual magnetic or plasmonic NPs. In this work, we synthesized Au- or Ag-decorated Fe$_3$O$_4$ nanoparticles coated with PEI (Fe$_3$O$_4$-PEI-M (M = Au or Ag) NPs) using a simple method. The influences of the plasmonic metal NPs' (Au or Ag) coating density on the magnetic and plasmonic properties of the Fe$_3$O$_4$-PEI-M (M = Au or Ag) NPs were investigated, and the density of the plasmonic metal NPs coated on the Fe$_3$O$_4$ NPs surfaces could be adjusted by controlling the polyethyleneimine (PEI) concentration. It showed that the Fe$_3$O$_4$-PEI-M (M = Au or Ag) NPs exhibited both magnetic and plasmonic properties. When the PEI concentration increased from 5 to 35 mg/mL, the coating density of the Au or Ag NPs on the Fe$_3$O$_4$ NPs surfaces increased, the corresponding magnetic intensity became weaker, and the plasmonic intensity was stronger. At the same time, the plasmonic resonance peak of the Fe$_3$O$_4$-PEI-M (M = Au or Ag) NPs was red shifted. Therefore, there was an optimal coverage of the plasmonic metal NPs on the Fe$_3$O$_4$ NPs surfaces to balance the magnetic and plasmonic properties when the PEI concentration was between 15 and 25 mg/mL. This result can guide the application of the Fe$_3$O$_4$-M (M = Au or Ag) NPs in the biomedical field.

Keywords: Fe$_3$O$_4$-PEI-M (M = Au or Ag) nanoparticles; plasmonic; magnetic

1. Introduction

At present, magnetic nanoparticles (NPs) have attracted great interest in many fields, such as bearing drugs [1,2], radionuclides [3,4], hyperthermia [5–7], active magnetic field targeting [8–10], protein purification [11–13], biosensors [14,15], and catalysis [16–18]. Researchers also further modify the surface of magnetic NPs with antibodies or proteins to expand their applications [19–21]. As such, Sohn et al. combined iron oxide nanoparticles with glucose transporter 1 antibody for vascular therapy [19]. Gawali et al. prepared magnetic nanoparticles conjugated with bovine serum albumin protein for magnetothermal therapy [21]. Unfortunately, magnetic NPs can easily aggregate, and it is difficult for them to couple with biomolecules due to the lack of functional groups, which limits the applications of magnetic nanomaterials [22]. In order to overcome these shortcomings, metal or metal oxide shells were coated on the surface of the magnetic nanomaterials to decorate the nanoparticles [23]. Noble metals (Au, Ag) are considered to be the most ideal coating material due to their unique optical properties, localized surface plasmon resonance (LSPR), high stability, biocompatibility, and easy surface functionalization [24–27]. Magnetic–plasmonic NPs, consisting of plasmonic metal materials (Au or Ag) coated onto

the surfaces of magnetic NPs, can exhibit more physical and chemical properties than individual magnetic or plasmonic NPs, such as magnetic, plasmonic, biological, compatibility, chemical stability, and physicochemical properties [28–31]. They are considered as effective candidate materials for catalysts [32], sensors [33], antibacterial materials [34], cancer detection [35], and medical applications [36]. Therefore, it is of great significance to combine magnetic NPs with noble metal materials to generate nanoparticles that simultaneously exhibit both excellent magnetic and plasmonic characteristics. This has been the focus of many researchers in recent years. In 2020, Kou et al. prepared flower-shaped Fe_3O_4-Au NPs and found that the magnetic properties gradually decreased by increasing the amount of Au seeds [37]. Aarthi et al. synthesized Fe_3O_4/Ag NPs and studied the surface-enhanced Raman scattering (SERS), and the photocatalytic and antibacterial activities of the nanoparticles [38]. Oguzlar studied Fe_3O_4 and Fe_3O_4@Ag NPs to improve the oxygen sensitivity of ruthenium dyes [39]. In 2021, Du et al. synthesized Fe_3O_4@Au core-shell NPs and studied both the magnetic and optical properties derived from the Fe_3O_4 NPs and the Au nano-shells [40]. Salimi et al. prepared Au-Fe_3O_4 NPs and studied the nano-morphology and formation process of the Au-Fe_3O_4 NPs [41]. In 2022, Lv et al. prepared the Fe_3O_4@Au NPs, which showed LSPR absorption in the near-infrared region [42]. Mikoliunaite et al. prepared Fe_3O_4@Ag NPs and found that their plasmonic resonance could be varied from 470 to 800 nm by changing the volume of the Ag colloid solution [43]. In 2023, Ravichandran et al. synthesized Fe_3O_4/Ag NPs and studied the dye removal rate of the Fe_3O_4/Ag NPs in the presence of a reducing agent [44]. According to the above works, most of the research on Fe_3O_4-M (M = Au or Ag) NPs was limited to a single particle type or physical property, and studies on the relationships between the coverage of the plasmonic metal NPs on the magnetic NPs surfaces and both the magnetic and plasmonic properties are lacking. Therefore, it is important to systematically investigate the magnetic and plasmonic characteristics of Fe_3O_4-M (M = Au or Ag) NPs.

In this work, we prepared the Au- or Ag-decorated Fe_3O_4 nanoparticles coated with PEI (Fe_3O_4-PEI-M (M = Au or Ag) NPs) using a simple method. Fe_3O_4 NPs were synthesized through a co-precipitation method, and plasmonic metal (Au or Ag) NPs were prepared using a chemical reduction method. Fe_3O_4 NPs and plasmonic metal NPs were mixed at room temperature to form Fe_3O_4-PEI-M (M = Au or Ag) NPs. In this process, positively charged PEI was assembled onto negatively charged Fe_3O_4 through electrostatic self-assembly. Then, negatively charged plasmonic metal NPs were electrostatically bound to the positively charged PEI-coated Fe_3O_4 NPs, resulting in a formation of Fe_3O_4-PEI-M (M = Au or Ag) NPs (Scheme 1). The density of the plasmonic metal NPs coated on the Fe_3O_4 NPs was adjusted by controlling the concentration of polyethyleneimine (PEI), and the effects of the plasmonic metal NPs' density on the magnetic and plasmonic properties of the Fe_3O_4-PEI-M (M=Au or Ag) NPs were studied. The relationships between the coating density of the plasmonic metal NPs and both the magnetic and plasmonic properties were established. This work can provide guidance for the application of Fe_3O_4-M (M = Au or Ag) NPs in the biomedical field.

Scheme 1. Schematic of the preparation of Fe_3O_4-PEI-M (M = Au or Ag) nanoparticles.

2. Materials and Methods

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and ammonium hydroxide (28–30% NH_3) were obtained from Merck (Shanghai, China). Polyethyleneimine (PEI, branched, $M_w \approx 10,000$ g/mol), sodium hydroxide (NaOH), chloroauric acid ($HAuCl_4$), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) were obtained from Aladdin (Shanghai, China). All chemicals were used as received with no further purification.

2.2. Synthesis of Fe₃O₄ Nanoparticles

Fe_3O_4 nanoparticles were synthesized through a co-precipitation method [45]. A total of 4.25 g of $FeCl_3 \cdot 6H_2O$ and 2 g of $FeCl_3 \cdot 6H_2O$ were added to 200 mL of ultrapure water. In an oxygen-free environment, the mixture was heated to 70 °C with stirring at 800 rpm and maintained at this temperature for 1 h. A total of 10 mL of ammonia solution (25% wt) was added into the mixture. A black precipitate was produced, indicating the formation of Fe_3O_4 NPs. The resulting solution was stirred for another 15 min. The nanoparticles were purified by means of magnetic separation five times and then redispersed in 200 mL of ultrapure water for further use.

2.3. Synthesis of Au Nanoparticles

Au nanoparticles were synthesized through $NaBH_4$ reduction of chloroauric acid [29]. Firstly, 0.5 mL of 0.01 M $HAuCl_4$ was mixed with 0.5 mL of a 0.01 M trisodium citrate solution. Then, the mixture was added into 18 mL of ultrapure water and stirred at 1200 rpm. A total of 0.5 mL of an ice 0.04 M $NaBH_4$ solution was quickly added with vigorous stirring at room temperature. When the solution turned pink, indicating the formation of Au NPs, the solution was allowed to stand for 2 h. The particles were collected by centrifugation at 14,000 rpm for 10 min. The Au nanoparticles were stored in the fridge until further use.

2.4. Synthesis of Ag Nanoparticles

Ag nanoparticles were prepared through the $NaBH_4$ reduction of silver nitrate [46]. Briefly, 10 mL of a 1 mM $AgNO_3$ solution was mixed with 0.8 mL of 40 mM sodium citrate solution used as stabilizer. A total of 0.2 mL of an ice 0.06 M $NaBH_4$ solution was added into the mixture, and the mixture was stirred at 1200 rpm for 15 min. After the solution turned dark yellow, indicating the formation of Ag NPs, the Ag nanoparticles were collected by means of centrifugation at 14,000 rpm for 10 min. The Ag nanoparticles were stored in the fridge until further use.

2.5. Synthesis of Fe₃O₄-PEI-M (M = Au or Ag) NPs

Firstly, 2 mL of the Fe_3O_4 NPs suspension (1 mg/mL) was mixed with 20 mL of the PEI solution. After 60 min of ultrasonic treatment, the mixture was left to stand for half an hour [47]. Subsequently, magnetic separation was employed for washing the nanoparticles. The PEI-coated Fe_3O_4 NPs were finally redispersed in 2 mL of ultrapure water. Then, the 0.5 mL PEI-coated Fe_3O_4 NPs solution was mixed with 4.5 mL of the plasmonic metal (Au or Ag) NPs solution. The mixture was continuously stirred at 2000 rpm for 45 min. Finally, the Au- or Ag-decorated Fe_3O_4 nanoparticles coated with PEI were collected by magnetic separation and washed with ultrapure water three times. By varying the concentrations of the PEI solution, the adhesion density of the plasmonic metal NPs on the Fe_3O_4 NPs surfaces could be changed.

2.6. Electric Field Simulation

To investigate the plasmonic properties of nanoparticles, the electric field distributions of the nanoparticles were simulated using the finite element method with the commercial software COMSOL 5.5. The excitation beam was a plane wave polarized along the x-axis

with the plasmonic resonance wavelength of the nanoparticle, and the permittivities of Au and Ag were taken from the experimental data of Johnson and Christy [48]. The mesh size was set to 2 nm.
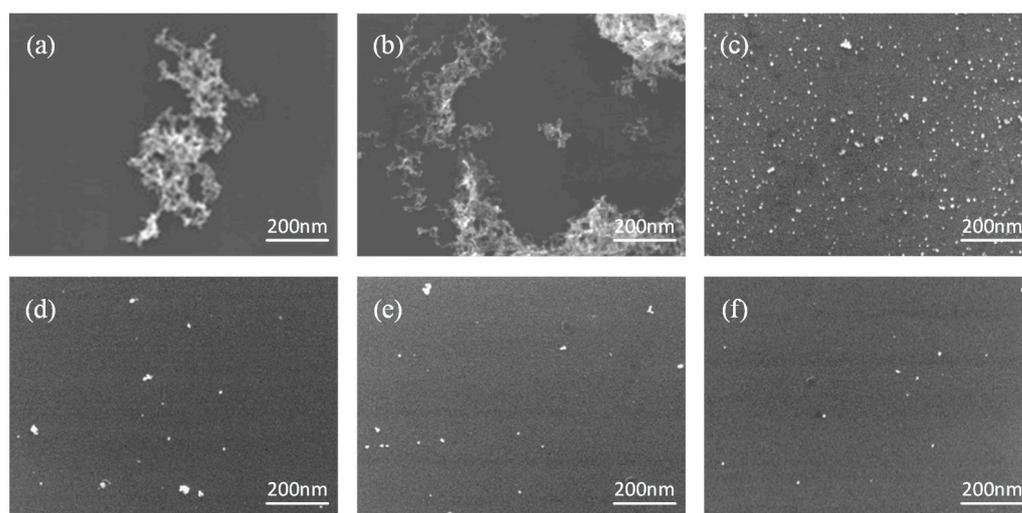
2.7. Characterization

The morphology and structure of the nanoparticles were observed by scanning electron microscopy (SEM, JSM-7000F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan). Hydrodynamic diameter and zeta-potential measurements were carried out using dynamic light scattering (DLS, Delsa, Palmdale, CA, USA). The crystalline structure of the nanoparticles was analyzed by X-ray powder diffraction (XRD, D8 ADVANCE, Bruker, Bremen, Germany). UV–visible absorption spectra were obtained using a UV–vis spectrophotometer (Cary 5000, Agilent, Santa Clara, CA, USA). Magnetization measurements of the nanoparticles were performed using a vibrating sample magnetometer (MPMS-squid VSM-094, Quantum Design, San Diego, CA, USA).

3. Results and Discussion

3.1. Study on the Plasmonic Metal Nanoparticles

3.1.1. Au Nanoparticles

To prepare suitable Au nanoparticles for coating Fe_3O_4 NPs' surfaces, we investigated the influence of the reducing agent ($NaBH_4$) concentrations on the Au nanoparticles. Figure 1 shows the SEM images of the Au NPs synthesized with $NaBH_4$ concentrations ranging from 4 to 0.04 M. We found that the synthesized Au nanoparticles formed agglomerates with an average diameter of about 12 nm when the $NaBH_4$ concentration was 4 M (Figure 1a). With a decrease in the $NaBH_4$ concentration from 4 to 0.04 M, the Au NPs became more diffuse, and the particle size became more uniform. When the $NaBH_4$ concentration was 0.04 M, the average diameter of the Au NPs was about 10 nm, as shown in Figure 1f, and there was excellent dispersion, which was beneficial for attachment on the Fe_3O_4 NPs' surfaces. Figure 1 shows that the particles size increased and more easily agglomerated with the increase in $NaBH_4$ concentration. This is attributed to the over-reduction of $HAuCl_4$ in the case of excessive amounts of reducing agent [49,50].
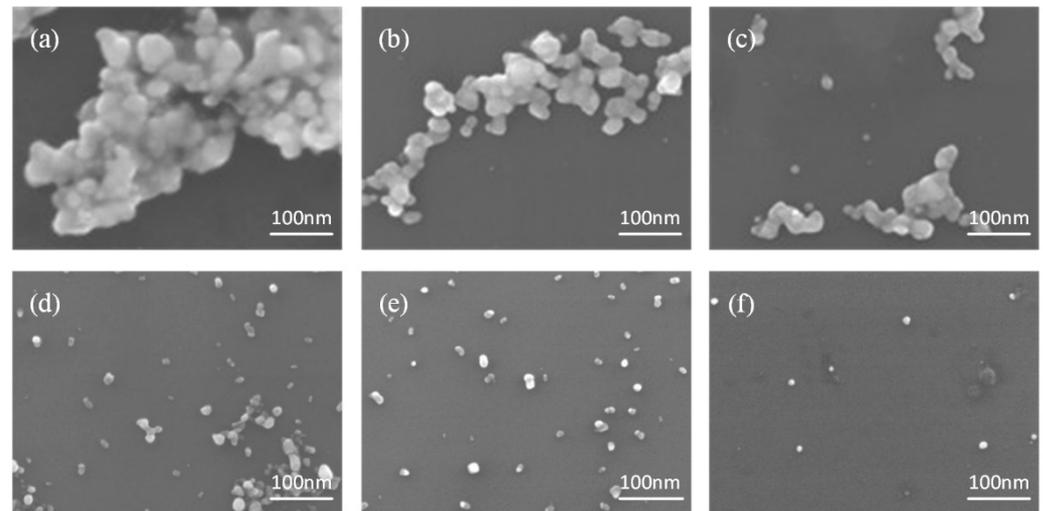

Figure 1. SEM images of the Au NPs prepared with (**a**) 4 M, (**b**) 2 M, (**c**) 1 M, (**d**) 0.4 M, (**e**) 0.08 M, and (**f**) 0.04 M $NaBH_4$ solution.

3.1.2. Ag Nanoparticles

In addition, we also investigated the Ag NPs, which were prepared using trisodium citrate as a stabilizer and $NaBH_4$ to reduce $AgNO_3$. Figure 2 shows the SEM images of the Ag NPs prepared with different $NaBH_4$ concentrations. We found that the synthesized

Ag nanoparticles formed agglomerates with an average diameter of about 25 nm when the $NaBH_4$ concentration was 8.5 M (Figure 2a). With a decrease in the $NaBH_4$ concentration from 8.5 to 0.06 M, the Ag NPs became more diffuse, and the size became more uniform [51]. This was due to more Ag atoms being produced with the increase in $NaBH_4$ concentration [49]. When the concentration of $NaBH_4$ was 0.06 M, the average diameter of the Au NPs was about 10 nm, as shown in Figure 2f, and there was excellent dispersion, which is desirable for the further preparation of Ag-decorated Fe_3O_4 NPs.

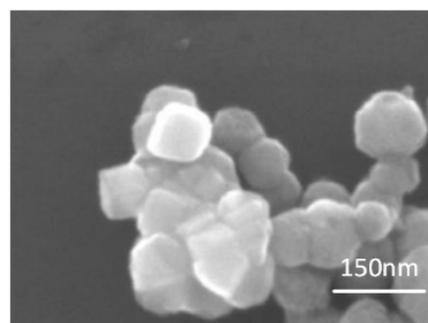**Figure 2.** SEM images of the Ag NPs prepared with (**a**) 8.5 M, (**b**) 0.85 M, (**c**) 0.43 M, (**d**) 0.17 M, (**e**) 0.08 M, and (**f**) 0.06 M $NaBH_4$ solution.

3.2. Study on the Properties of the Fe_3O_4-PEI-Au Nanoparticles

3.2.1. Fe_3O_4-PEI-Au Nanoparticles

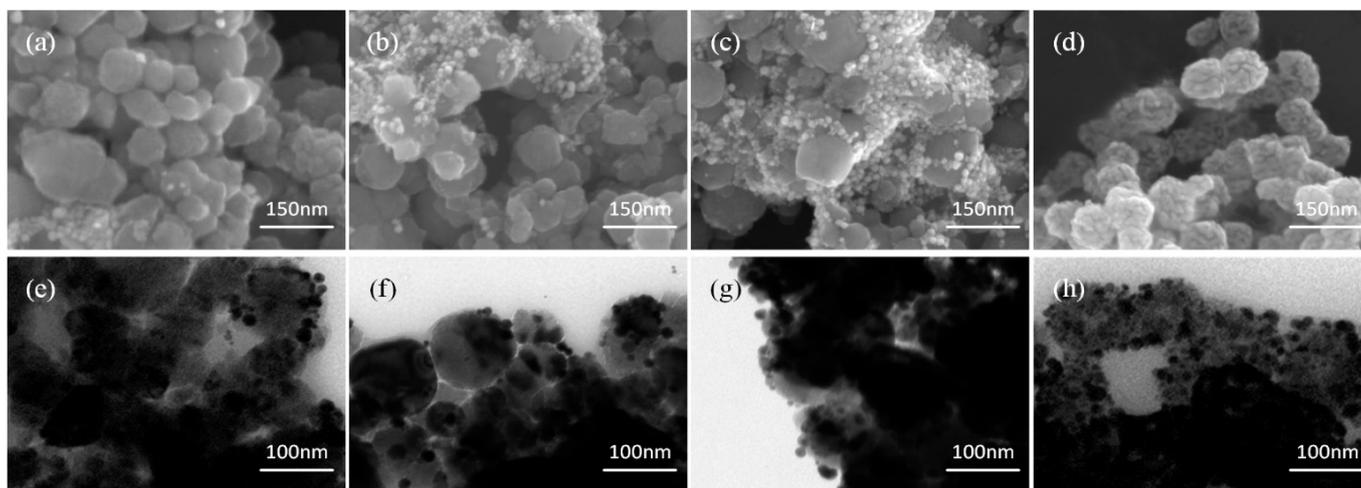In order to explore the magnetic and plasmonic properties of the Au-decorated Fe_3O_4 nanoparticles, we synthesized the Fe_3O_4-PEI-Au NPs with different densities of Au NPs on the Fe_3O_4 NPs surfaces. Figure 3 shows the SEM image of the Fe_3O_4 NPs, and the average size was about 80 nm in diameter.

Figure 3. SEM image of the Fe_3O_4 NPs.
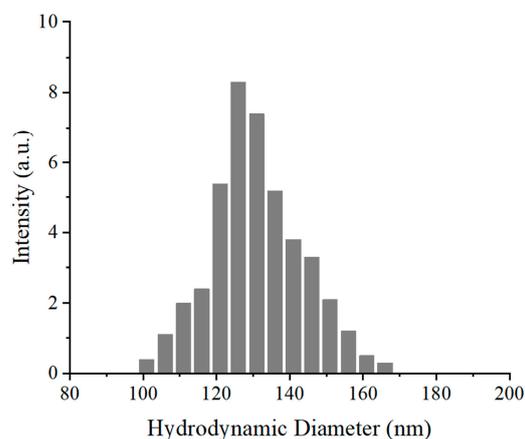
The coating density of Au NPs on the Fe_3O_4 NPs surfaces was controlled by changing the PEI concentration. PEI is used as a bonding material. It is a water-soluble cationic polymer which contains amino and imino groups in each polymer chain. When the polymer PEI is dispersed in aqueous solution, each polymer chain is positively charged due to the amino and imino groups [52]. When the Fe_3O_4 NPs are immersed in a PEI solution, positively charged PEI is assembled onto the negatively charged Fe_3O_4 through electrostatic self-assembly, leading to the formation of a stable polyelectrolyte layer. Subsequently, the negatively charged Au NPs are easily electrostatically bound to the positively charged PEI-coated Fe_3O_4 NPs, resulting in a formation of the Fe_3O_4-PEI-Au NPs [53]. Figure 4

shows the SEM and TEM images of the Au-decorated Fe_3O_4 NPs treated with different concentrations of PEI solutions. It shows that 10 nm diameter Au NPs were attached to the surfaces of 80 nm diameter Fe_3O_4 NPs. DLS measurements depicted that the hydrodynamic diameter of the Fe_3O_4-PEI-Au NPs is about 131 nm (shown in Figure 5), and the zeta potential is around +18.4 mV. When the Fe_3O_4 NPs were treated with a 5 mg/mL PEI solution, a small amount of Au NP was coated on the Fe_3O_4 NPs' surfaces, as shown in Figure 4a,e. With an increase in the PEI concentration from 5 to 35 mg/mL, the coating density of the Au NPs gradually increased, and thus the coverage of the Au NPs on the Fe_3O_4 NPs surfaces increased. This is attributed to a greater amount of NH_2 groups provided by PEI that can adsorb more Au NPs with an increase in the PEI concentration.

Figure 4. SEM images of the Fe_3O_4-PEI-Au NPs treated with (**a**) 5, (**b**) 15, (**c**) 25, and (**d**) 35 mg/mL PEI solution. The corresponding TEM images of the Fe_3O_4-PEI-Au NPs treated with (**e**) 5, (**f**) 15, (**g**) 25, and (**h**) 35 mg/mL PEI solution.
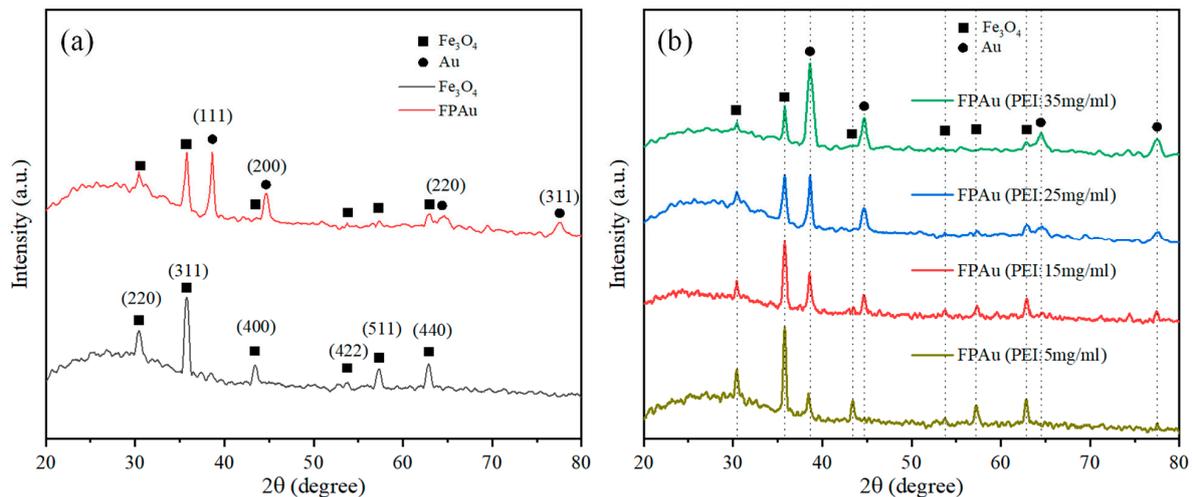

Figure 5. Hydrodynamic diameter distribution of Fe_3O_4-PEI-Au NPs (PEI: 35 mg/mL).

3.2.2. X-ray Diffraction (XRD) Analysis

An X-ray diffractometer was used to characterize the crystal structures of the Fe_3O_4 and Fe_3O_4-PEI-Au NPs. As shown in Figure 6a, the XRD spectrum of Fe_3O_4 showed six diffraction peaks at 2θ values of 30.43°, 35.78°, 43.44°, 53.79°, 57.34°, and 62.89°, corresponding to the diffraction peaks located at (220), (311), (400), (422), (511), and (440). All these diffraction peaks correspond to the face-centered cubic structure of Fe_3O_4. Compared to that of Fe_3O_4, the XRD spectrum of the Fe_3O_4-PEI-Au NPs exhibited additional peaks at 38.62°, 44.67°, 64.61°, and 77.62°, which match well with the (111), (200), (220), and (311) faces of Au. This result is consistent with that reported in the literature [54]. Therefore, the

X-ray diffraction spectra further confirmed that Au NPs were successfully loaded onto the Fe_3O_4 NPs surfaces. In addition, in Figure 6b, it is implied that with an increase in the PEI concentration, the characteristic peak intensities of the Au NPs gradually increased, while the characteristic peak intensities of the Fe_3O_4 NPs gradually decreased. This is because of the increase in the density of Au NPs coated on the Fe_3O_4 NPs surfaces. No peaks of other impurities were detected in the XRD spectra, indicating a high purity of the materials.
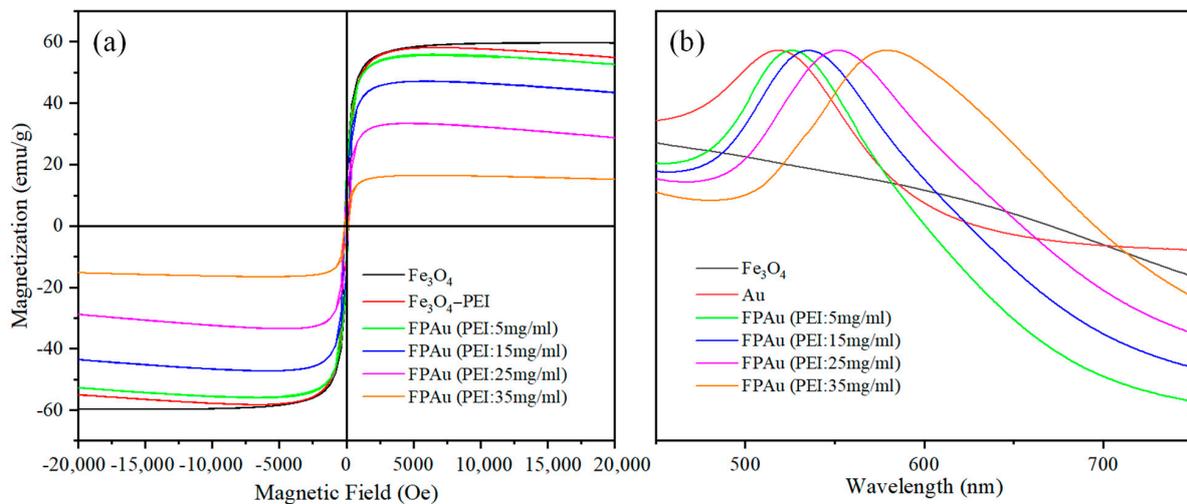

Figure 6. XRD spectra of the (**a**) Fe_3O_4 and Fe_3O_4-PEI-Au (FPAu) NPs, and (**b**) Fe_3O_4-PEI-Au (FPAu) NPs treated with 5~35 mg/mL PEI solution.

3.2.3. Analysis of Magnetic and Plasmonic Properties

Firstly, the magnetic properties of the Fe_3O_4-PEI-Au NPs with different coverages of the Au NPs on the Fe_3O_4 NPs surfaces were studied. Figure 7a exhibits the hysteresis loops of the Fe_3O_4-PEI-Au NPs with different Au NP densities, controlled by using different PEI concentrations (the magnetic field scanning range was 20,000 g at 300 K). All the curves for the Fe_3O_4 and Fe_3O_4-PEI-Au NPs have similar shapes. The saturation magnetization of the Fe_3O_4 NPs was 60 emu/g, which is same as that of Fe_3O_4 NPs in a previous study [55]. After treatment with the PEI solution, the saturation magnetization of the Fe_3O_4-PEI NPs decreased to 57 emu/g. This value is a little smaller than the one previously reported for PEI-coated Fe_3O_4 NPs [56]. This may be due to the agglomeration of particles and the interaction between them [55]. Furthermore, for the Fe_3O_4-PEI-Au NPs, when the PEI concentration increased from 5 to 35 mg/mL, the Au NP coating density increased, and the saturation magnetization of the Fe_3O_4-PEI-Au NPs decreased from 55 to 16 emu/g, as shown in Table 1. The reduction in saturation magnetization of the Fe_3O_4 NPs due to the introduction of plasmonic metal NPs could be demonstrated in reference [54]. Therefore, with the increase in the density of the Au NPs on the Fe_3O_4 NPs surfaces, the shielding effect of the Au NPs on the Fe_3O_4 NPs increases.
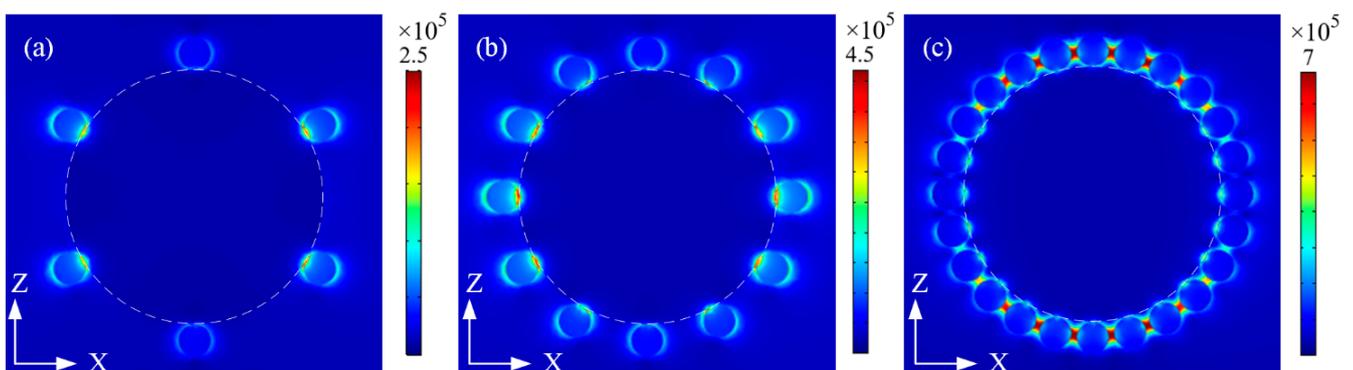
Table 1. Absorption peak wavelength and saturation magnetization of the Fe_3O_4, Au, Fe_3O_4-PEI-Au nanoparticles treated with different PEI concentrations.

	Fe_3O_4	Au	Fe_3O_4-PEI-Au PEI: 5 mg/mL	Fe_3O_4-PEI-Au PEI: 15 mg/mL	Fe_3O_4-PEI-Au PEI: 25 mg/mL	Fe_3O_4-PEI-Au PEI: 35 mg/mL
Absorption peak (nm)	/	519	526	535	552	578
Saturation magnetization (emu/g)	60	/	55	46	31	16

Figure 7. (**a**) Hysteresis loops and (**b**) normalized absorption spectra of the Fe_3O_4 and $Fe_3O_4-PEI-Au$ (FPAu) NPs treated with 5~35 mg/mL PEI solution.

Due to Fe_3O_4-PEI-Au NPs with different Au NP densities exhibiting different magnetic and plasmonic properties, we also investigated the plasmonic properties of the Fe_3O_4-PEI-Au NPs. Figure 7b shows the absorption spectra of the Fe_3O_4-PEI-Au NPs with different Au NP densities. The Fe_3O_4 NPs had no absorption peak in the visible region, which is consistent with the result from a previous study [57]. The absorption peak of the Au NPs was located at 519 nm. When the PEI concentration increased from 5 to 35 mg/mL, the Au NP coating density increased and the absorption peak of the Fe_3O_4-PEI-Au NPs red shifted from 526 to 578 nm (shown in Table 1) because of the decrease in the gap distance between the Au NPs. To further investigate the influence of the Au NP coating density on the enhanced electric field of the nanoparticles, three-dimensional models of the Fe_3O_4 nanoparticle decorated with different Au NP densities were built. Many researchers calculated electric field characteristics by quantum method [58], or classical method [59,60]. Here, the electric field distributions were simulated using the finite element method with the commercial software COMSOL 5.5. Figure 8 shows the electric field distributions of Au-decorated Fe_3O_4 NPs with Au NP coating densities ranging from sparse to dense. It was observed that with an increase in the Au NP coating density, the electric field became stronger, and the plasmonic coupling between the adjacent nanoparticles became stronger, indicating that the plasmonic properties were enhanced.
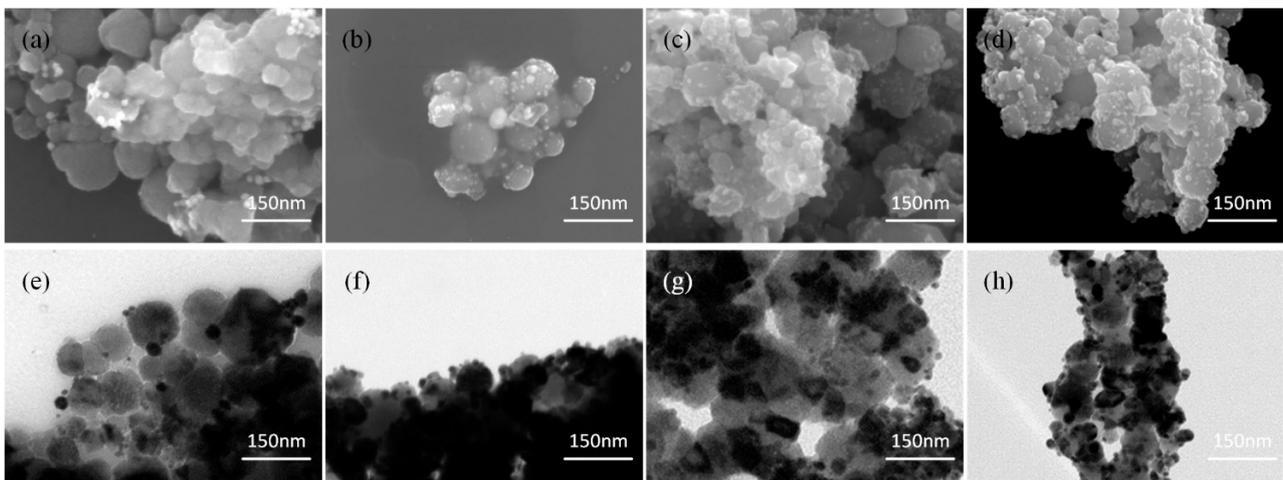

Figure 8. Electric field distributions of the Fe_3O_4 NP coating with Au NPs of (**a**) sparse, (**b**) medium, and (**c**) dense.
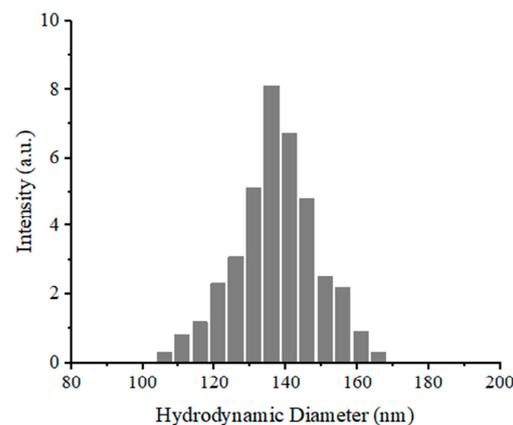
3.3. Study on the Properties of the Fe₃O₄-PEI-Ag Nanoparticles

3.3.1. Fe₃O₄-PEI-Ag Nanoparticles

According to Figure 7b, the plasmonic resonance peak of the Fe₃O₄-PEI-Au NPs is located at about 526 nm. However, when a shorter wavelength of plasmonic resonance is needed, Fe₃O₄-PEI-Ag NPs are more suitable; thus, we also need to study their magnetic and plasmonic properties. Here, we synthesized Fe₃O₄-PEI-Ag NPs using the same methods that were utilized to prepare the Fe₃O₄-PEI-Au NPs. Similarly, positively charged PEI binds to negatively charged Fe₃O₄ by electrostatic self-assembly, and negatively charged Ag nanoparticles combine with positively charged PEI-coated Fe₃O₄ nanoparticles to form Fe₃O₄-PEI-Ag NPs. Figure 9 shows SEM and TEM images of the Ag-decorated Fe₃O₄ NPs treated with PEI concentrations ranging from 5 to 35 mg/mL. It was observed that 10 nm diameter Ag NPs were attached to the surface of 80 nm diameter Fe₃O₄ NPs. DLS measurements show that the hydrodynamic diameter of the Fe₃O₄-PEI-Ag NPs is about 137 nm (as shown in Figure 10) and the zeta potential is around +19.1 mV. When the Fe₃O₄ NPs were treated with a 5 mg/mL PEI solution, a small amount of Ag NP was coated on the Fe₃O₄ NP surfaces, as shown in Figure 9a,e. When the concentration of PEI increased from 5 to 35 mg/mL, the coverage of the Ag NPs on the Fe₃O₄ NPs surfaces increased gradually. This is because of the greater amount of NH₂ groups provided by the PEI leading to an increased number of Ag NPs attached on the Fe₃O₄ surface with the increase in PEI concentration.
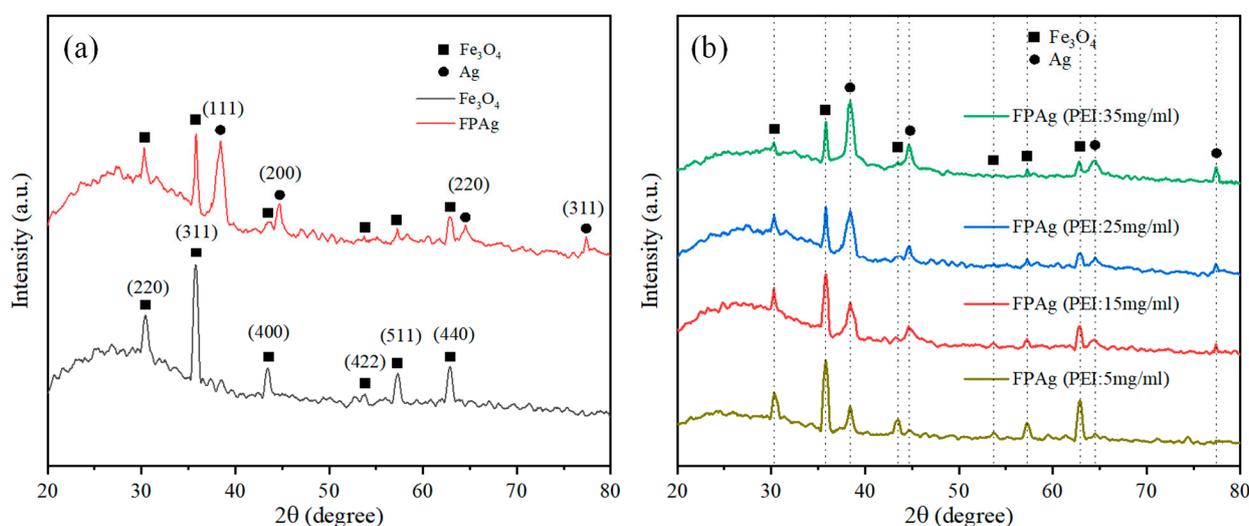

Figure 9. SEM images of the Fe₃O₄-PEI-Ag NPs treated with (**a**) 5, (**b**) 15, (**c**) 25, and (**d**) 35 mg/mL PEI solution. The corresponding TEM images of the Fe₃O₄-PEI-Ag NPs treated with (**e**) 5, (**f**) 15, (**g**) 25, and (**h**) 35 mg/mL PEI solution.

Figure 10. Hydrodynamic diameter distribution of Fe₃O₄-PEI-Ag NPs (PEI: 35 mg/mL).

3.3.2. X-ray Diffraction Analysis

The crystalline structures of the Fe_3O_4 and Fe_3O_4-PEI-Ag NPs were characterized using an X-ray diffractometer. As shown in Figure 11a, the positions and relative intensities of all diffraction peaks are in good agreement with the standard Fe_3O_4 and Ag NP diffraction peaks. Compared to the Fe_3O_4 NPs, there were four more main peaks in the Fe_3O_4-PEI-Ag NP spectrum, which can be clearly observed at 2θ values of 38.42°, 44.63°, 64.53°, and 77.38°, corresponding to the reflection of the (111), (200), (220), and (311) crystal planes of Ag [61]. Therefore, the X-ray diffraction spectra further confirmed that Ag NPs were successfully loaded on the Fe_3O_4 NPs surfaces. In addition, Figure 11b shows that, with an increase in the PEI concentration, the characteristic peak intensities of the Ag NPs gradually increased, while that of the Fe_3O_4 NPs gradually decreased. This is because of the increase in the density of Ag NPs coated on the Fe_3O_4 NPs surfaces. No peaks of other impurities were detected in the XRD spectra, indicating high purity of the materials.
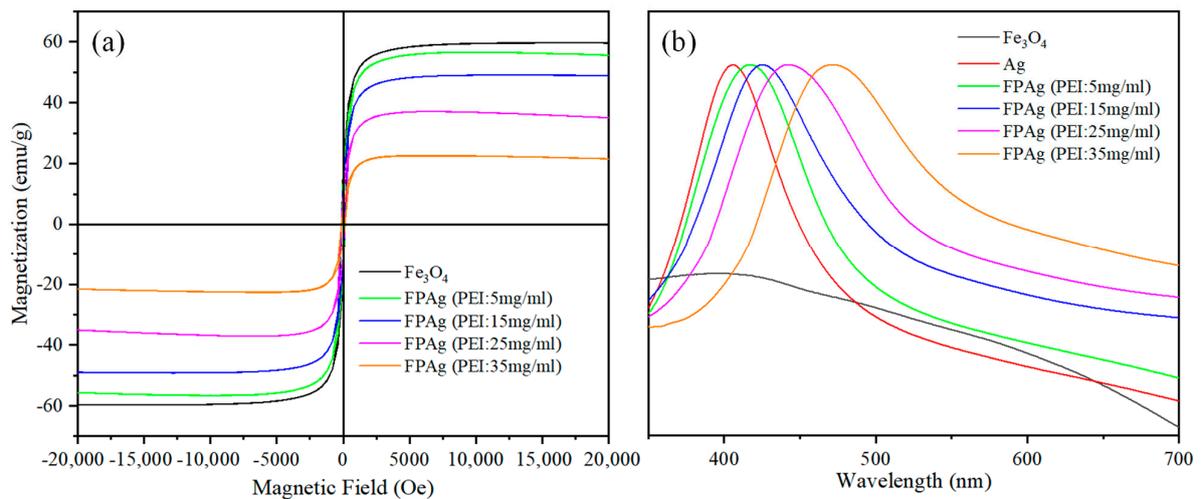

Figure 11. XRD spectra of the (**a**) Fe_3O_4 and Fe_3O_4-PEI-Ag (FPAg) NPs, and (**b**) Fe_3O_4-PEI-Ag (FPAg) NPs treated with 5~35 mg/mL PEI solution.

3.3.3. Analysis of Magnetic and Plasmonic Properties

Figure 12a illustrates the hysteresis loops of the Ag-decorated Fe_3O_4 NPs treated with different PEI concentrations. It can be observed that the curves of the Fe_3O_4 and Fe_3O_4-PEI-Ag NPs exhibit similar trends. The saturation magnetization of the Fe_3O_4 NPs was 60 emu/g. When the PEI concentration increased from 5 to 35 mg/mL, the Ag NP coating density increased, and the saturation magnetization of the Fe_3O_4-PEI-Ag NPs decreased from 56 to 22 emu/g, as shown in Table 2. Therefore, with an increase in the Ag NP density, the shielding effect of the Ag NPs coated on the Fe_3O_4 NPs increases.

Table 2. Absorption peak and saturation magnetization of Fe_3O_4, Ag, and Fe_3O_4-PEI-Ag nanoparticles treated with different PEI concentrations.

	Fe_3O_4	Ag	Fe_3O_4-PEI-Ag PEI: 5 mg/mL	Fe_3O_4-PEI-Ag PEI: 15 mg/mL	Fe_3O_4-PEI-Ag PEI: 25 mg/mL	Fe_3O_4-PEI-Ag PEI: 35 mg/mL
Absorption peak (nm)	/	406	417	425	442	472
Saturation magnetization (emu/g)	60	/	56	49	36	22

Figure 12. (a) Hysteresis loops and (b) normalized absorption spectra of the Fe_3O_4 and $Fe_3O_4-PEI-Ag$ (FPAg) NPs treated with 5~35 mg/mL PEI solution.

Figure 12b shows the absorption spectra of the Ag and Fe_3O_4-PEI-Ag NPs. It shows that 10 nm Ag NPs had a plasmonic absorption peak of 406 nm. When the PEI concentration increased from 5 to 35 mg/mL, the absorption peak of the Fe_3O_4-PEI-Ag NPs red shifted from 417 to 472 nm with the increase in the Ag NP coating density (Table 2). This is due to the decrease in the gap distance between the Ag NPs. To further study the effect of Ag NP coating density on the enhanced electric field of the nanoparticles, the electric field distributions were simulated using the finite element method. Figure 13 illustrates the electric field distributions of Ag-decorated Fe_3O_4 NPs with varying Ag NP coating densities ranging from sparse to dense. It was found that, as the coating density increased, the electric field became stronger. Therefore, according to the analysis of the magnetic and plasmonic properties of Au- or Ag-decorated Fe_3O_4 NPs treated with different PEI concentrations, as shown in Figure 7, Figure 8, Figure 12, and Figure 13, it is implied that when the PEI concentration is low, such as 5 mg/mL, the coverage of plasmonic metal NPs on the surface of Fe_3O_4 NPs is minimal. This results in a weak shielding effect of plasmonic metal NPs, leading to a strong magnetic field intensity but a weak plasmonic intensity in Fe_3O_4-PEI-M (M = Au or Ag) NPs. Conversely, when the PEI concentration is high (such as 35 mg/mL), the coverage of the plasmonic metal NPs is too large, the shielding effect of the plasmonic metal NPs is strong, the magnetic intensity becomes weak, and the plasmonic intensity becomes strong. Therefore, when the PEI concentration is between 15 and 25 mg/mL, there is an optimal coverage of the plasmonic metal NPs on the Fe_3O_4 NP surfaces to balance the magnetic and plasmonic properties.

Figure 13. Electric field distributions of the Fe_3O_4 NP coating with Ag NPs of (a) sparse, (b) medium, (c) dense.

4. Conclusions

In conclusion, we synthesized Fe_3O_4-PEI-M (M = Au or Ag) NPs using a simple method. The density of the plasmonic metal NPs coated on the Fe_3O_4 NPs surfaces was adjusted by controlling the PEI concentration. We investigated the effects of the Au or Ag NP coating density on the magnetic and plasmonic properties of the Fe_3O_4-PEI-M (M = Au or Ag) NPs. We found that, for the Fe_3O_4-PEI-M (M = Au or Ag) NPs, with an increase in the plasmonic metal NP density, the saturation magnetization decreased, the plasmonic intensity increased, and the plasmonic absorption peak was red shifted. When the concentration of PEI was between 15 and 25 mg/mL, Fe_3O_4-PEI-M (M = Au or Ag) NPs exhibited both excellent magnetic and plasmonic properties. The relationships among the coating density of the plasmonic metal NPs and both magnetic and plasmonic properties were established. This work can provide guidance for the application of Fe_3O_4-M (M = Au or Ag) NPs in the biomedical field.

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