

Combination of 4-ATP Coated Silver Nanoparticles and Magnetic Fe₃O₄ Nanoparticles by Inverse Emulsion Method

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Abstract: 4-Aminothiophenol (4-ATP) functionalized silver nanoparticles and magnetic Fe₃O₄ nanoparticles were combined in a bi-functional nanocolloids which were covered by an approximately 5nm SiO₂ layer by inverse emulsion method in order to apply to biomedicine. High saturated magnetization M_s indicated that the colloids are easy to be controlled by external magnetic field, while the characteristic Surface Enhanced Raman peak positions of 4-ATP absorbed on the metal particles were occurred without any alterations, which significantly predicted attractive applicability of the colloids for biomedical labeling.

Keywords: Multifunctional nanoparticles, Fe₃O₄ nanoparticles, Ag nanoparticles, Inverse micro emulsion, SERS

1. Introduction

In biomedical applications, morphological structures of nanomaterials are used to be designed to have size-compatibility and large total binding surface areas. Some metal materials have been controlled into different shapes [1,2] in order to apply to in situ imaging diagnosis and plasmonic photo thermal therapeutics [3,4]. Semiconductors in different structures such as nanowire [5], nanosphere [6] and tetrapods [7] are employed as docking matrix to increase the sensitivity of sensors. In some classic labeling therapies, centrifugation was used to wash the redundant chemicals, of which the mechanical force would conduct lacks of bioactive cover from the surface of the materials. The progress somewhat decrease the sensitivity of the detection or of the diagnosis method and core-shell structures, which was usually the labeling shell that covered the magnetic colloids [8,9], were found to

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be one solution for this problem. Beside the particles would be a fine marker by itself, it is possible to purify them by magnetic separator then the sensitivity of the detection can be increased. Core-shell structures are also revolutionized to increase appropriate physical and chemical properties. Polymer coats, indeed, were usually used as functionalizing agent to make the target colloids have well biocompatibility, such as polyethylene glycol [10-14]. Later, some semiconductor coats have been improved onto photo luminescent shell to increase the luminescence and/or to decrease the harmful effect [15-17]. In other applications, metal and silica shell [18,19] were used for protect the core materials. Metal shell such as gold [18], moreover, was employed for deposition of the metal-sulfur linkage with bioactive molecules [20-22]. However, it is unfavorable that the synthesis method of such as core-shell structure referred tight conditions and expertise laboratory craftsmanship. In this paper, a simple method of inversed micro emulsion was used to create bi-functional nanocolloids which can act like core-shell structures nanoparticles: can act as labeling agent in biomedical application, biocompatible and also can be purified by magnetic separator.

Despite the fact that Surface Enhanced Raman (SER) technique was a very young technique, but it is used to be a good technique for analytical and biomedical applications. When the molecular vibrations are close to the Plasmon surface of the metal nanocolloids, the Raman signal is enhanced to 10^5 - 10^6 times [23,24]. This phenomenon has been successfully applied to distinguishing the carcinomas segments from normal cell segments without any labeling agents [25,26]. The scattering signal is sensitively enhanced when the molecules are close to the metal colloids surface, which was used in studying the molecular phase transmission [27,28] or in molecular detection [29-32]. Besides, the characteristic SER signals of bioactive molecules on surface of metal colloids were investigated and used as labeling mediator to detect the DNA of cancer cells [33,34]. , As the result, SER signal of some organic molecules on metal surface could be designed into nanomaterials as a labeling domain such as the SER signal of 4-Aminothiophenol (4-ATP) functionalized on silver nanoparticles.

In this study, we used the inverse micro emulsion method to cover the 4-aminothiophenol-linked silver nanoparticles (Ag-4ATP) with Fe_3O_4 magnetic particles by amorphous SiO_2 matrix. Magnetics property prevented the orientate ability in order to applied to magnetic separation, while individual SER scattering of as-prepared colloids had been investigated to expose their labeling capacity.

2. Experiment and method

All the initial chemicals $\text{FeCl}_2\cdot\text{H}_2\text{O}$ cast No. 1.03861.1000, FeCl_3 cast No. 8.45124.1000, polyvinylpyrrolidone (PVP) cast No. 5295-100GMCN, Sodium borohydride (NaBH_4) cast No. 1.06371.0100, Tetraethyl orthosilicate (TEOS) cast No. 8.00658.1000, silver acetate (AgCH_3COO) cast No. 8.01504.0100 and 4-aminothiophenol (4-ATP) cast No. 8.41602.0005 were purchased from MERCK, Germany and were purity checked before being used.

Synthesis of Ag-4ATP nanoparticles

Silver nanocolloids were synthesized by wet chemical reduction method using NaBH_4 with the present of surface activator PVP. NaBH_4 was added to Ag^+ ion solution at 0.01M concentration to have bottom-up nanoparticles growth.

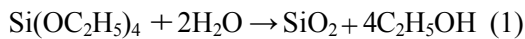
The solution was vigorously magnetic stirred for 30 min. before 4-ATP being embraced. After 8h continuously stirring, the covalent S-Ag linkages were formed between the nanocolloids surface with the 4-ATP molecules [35,36]. The Ag-4ATP colloids containing solution was purified by centrifugation and was stored under room temperature.

Synthesis of Fe₃O₄ nanoparticles

Magnetic nanoparticles were synthesized by co-precipitation [37,38]. Fe²⁺/Fe³⁺ with 1:2 molar rates from the two chloride salts were diluted to 0.01 M/0.02 M concentration while PVP was present to restrain the particle size. The solution was vigorously stirred and kept warm at 60oC before NH₄OH 30% being added to have the black color precipitation. The solution was purified by magnetic separation with ethanol and distilled water several times to decontaminate the auxiliary chemicals.

Synthesis of Ag-4ATP/Fe₃O₄/SiO₂ particles

The inverse micro emulsion was created by mixing hydrophobic phase of toluene and hydrophilic phase that was made from the mixture of Ag-4ATP solution after 4 month storage and Fe₃O₄ solution right after synthesis. Under sonic bath, different mass rates of Ag-4ATP/Fe₃O₄ were moderated for 2 hours before TEOS was being added to react with water in solution to form SiO₂ coat that cover both type particles as in reaction (1) [39,40]. Silicate in amorphous conformation created a boundary thin film, which covered the initial nanoparticles.



The morphological structures of the Ag-4ATP, Fe₃O₄ and the as-prepared Ag-4ATP/Fe₃O₄/SiO₂ colloids were observed by transferred electron microscope - TEM (JEOL- JEM1010). Magnetics properties of the samples were characterized by physical property measuring system (PPMS EVERCOOL II, Quantum Design) under vibrating sample mode (VSM). All three samples were dried and the optical properties were investigated by Raman micro-spectroscope (Lab RAM HR800, HORIBA).

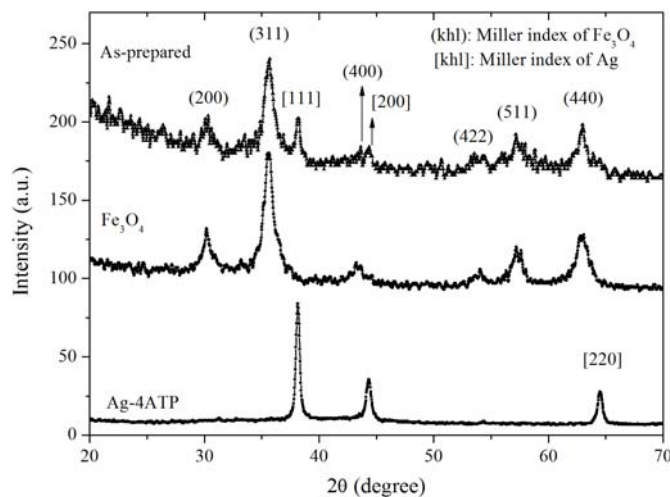


Fig.1. X-ray diffraction of as-prepared Ag-4ATP, Fe₃O₄ and Ag-4ATP/Fe₃O₄/SiO₂ as-prepared nanocolloids.

3. Results and discussion

Typical X-ray patterns of Ag-4ATP, Fe_3O_4 and as-prepared Ag-4ATP/ Fe_3O_4 / SiO_2 colloids are showed in Fig. 1. The obtained peaks of the Ag-4ATP and Fe_3O_4 mostly agree with the standard spectra of JDSPS cast No. 04-0738 closet packed silver, and of the JDSPS cast No. 19-0629 magnetite materials. The spectrum on the top reveals that both the magnetite crystals and silver crystals occurred in the Ag-4ATP/ Fe_3O_4 / SiO_2 superior colloids. These results together with TEM images in Figure 2 indicate that the as-prepared colloids were synthesized successfully.

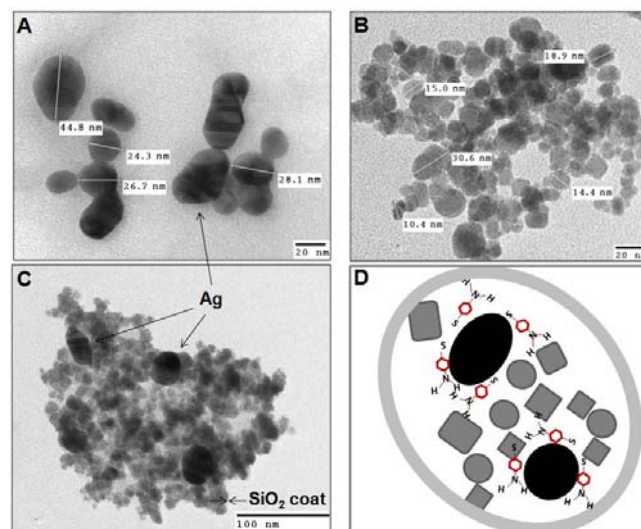


Fig. 2. TEM image of Ag-4ATP nanoparticles (A), Fe_3O_4 magnetic nanoparticles (B), as-prepared complex nanocolloids (C) and schematic graph of the colloid (D).

Figure 2 illustrates the TEM images of Ag-4ATP (A), Fe_3O_4 (B) and the combined multifunctional colloids (C). The figure 2A demonstrates the big sizes of more than 20 nm of Ag-4ATP particles. The twin-effect occurred on Ag nanoparticles agreed with our early result, which was experienced with gold nanoparticles where the large size of the metal particles could be explained by the Ostwald ripening under low concentration of surface activator molecules [41]. However, this reflects a good signal to recognize the present of the silver particles in the combined colloids (Fig. 2C). Figure 2B demonstrates that the sizes of the magnetic nanoparticles are quite unique and distributed from 10 nm to 15 nm (Fig. 2B), which are recognizably distinguished from the silver colloids. It can be seen in Fig. 2C a thin silicate SiO_2 layer that covers the whole colloids, which has approximately 5nm thickness. Fig. 2D is the schematic model of the colloids in Fig. 2C. With the sizes ranged from 150 nm to 200 nm, the combined colloids in Fig. 2C are not homogenous, but with the size equivalent to that of the cells of about micrometers, they are still small enough to be applicable as cell labeling agents.

The SER signal is attracted as characteristic signal that would coordinate the positions of the metal particles [33,34], hence, would be employed in fingerprinted diagnosis. Figure 3 shows the Raman scattering patterns of Ag-4ATP, Fe₃O₄ and of the combined Ag-4ATP/Fe₃O₄/SiO₂ at the region from 900 cm⁻¹ to 1700 cm⁻¹ (A) and from 200 cm⁻¹ to 800 cm⁻¹ (B), respectively. The exhibition of the individual broadband resonance of Fe₃O₄ lattice occurs at about 668 cm⁻¹ only in the case of Fe₃O₄ dried sample (Fig. 3B) and disappears in association with the signal of Ag-4ATP when being grouped in the combined colloids. Besides, the characteristic vibrations of 4-ATP on the surface of the silver nanoparticles were exclusively observed as shown in Fig. 3A, which agreed with early published results as shown in Table 1[20-22].

Table 1. Observed Raman peaks of Ag-4ATP and their suggested vibrations

Measured (cm ⁻¹)	Published (cm ⁻¹)	Suggested vibration
1581	1590	$\nu_{CC+\gamma NH^*}$
1478	1490	$\nu_{CC+\delta CH}$
1443	1435	$\nu_{CC+\delta NH^*}$
1393	1392	$\nu_{CC+\delta CH+\gamma NH^*}$
1305	1294	ν_{NC}
1190	1178	δCH
1145	1144	ν_{CC}
1079	1081	$\nu_{SH+\nu NH}$
1007	1003	$\gamma_{CC} + \gamma_{CCC}$

The usually observed results indicated that the signals of the contiguous vibrations on metal surface were significantly enhanced, and became minor as far as these linkages are. Almost the vibration peaks exhibited when the 4-ATP molecules adhered onto the silver surface [40]. In this study, most issued peaks were perceptible (Table 1), which revealed that the 4-ATP molecules tacked close to silver surface when being dried or when being grouped in 4ATP/Fe₃O₄/SiO₂ colloids as schematically represented in Fig. 1D.

In addition, all the core particles were isolated from the external environment by a approximately 5 nm thickness SiO₂ coat, which firstly have protected the inside materials from chemical effects; secondly the SER signal of the Ag-4ATP are individually observed from strange exterior molecular vibrations; and thirdly should conjugate with APTES to form free amine groups (-NH₂) to be bio-compactable [37,38]. Consequently, the SER signal of this specific structure defines an unchanged marker that applicable to labeling and diagnostic imaging. Furthermore, in order to apply the as-prepared colloids in fast diagnostic imaging, the Raman spectrum would be monitored into more slender interval that only the high and recognizable peaks at 1145 cm⁻¹ or at 1443 cm⁻¹ should reduce the observation time.

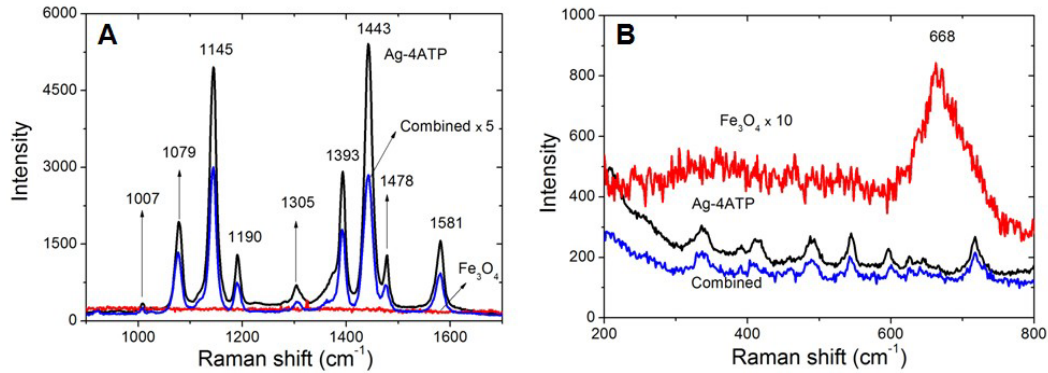


Fig. 3. Raman spectra of Ag-4ATP, Fe_3O_4 and of the combined Ag-4ATP/ Fe_3O_4 / SiO_2 dried sample in region from 900 cm^{-1} to 1700 cm^{-1} (A) and from 200 cm^{-1} to 800 cm^{-1} (B).

The magnetic measurements in Figure 4 established superparamagnetic property of the as-prepared colloids with comparatively high magnetization. A very small coercivity has been found despite that the Fe_3O_4 were associated in colloids (inset of Fig.4).

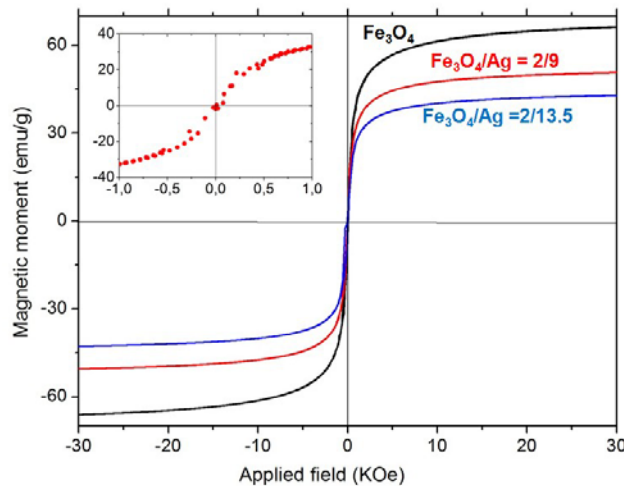


Fig. 4. Magnetization of the Fe_3O_4 and of the combined colloids samples with different initial Fe_3O_4 /Ag-4ATP volume ratios.

Those colloids can be separated by magnetic separators as shown in Figure 5 for 15 minutes. The saturated magnetization M_S of Fe_3O_4 particle was 61.2 emu/g and decreased depending on the amount of the initially added Ag-4ATP (Fig. 4). Therefore, the fraction of the SiO_2 was predetermined due to the unchanged amount of water and added TEOS, hence, the observed saturated magnetization might indicate the proportion of Fe_3O_4 in combined colloids. The calculations showed that the initially added percentage of Fe_3O_4 were 75.0% and 66.7% , while the measurements gave 83.3% and 70.6% respectively, which indicated that nearly 80% amount of initial Ag-4ATP was taken into multifunctional nanoparticles. However, the non-magnetic part was discarded during the magnetic purification.

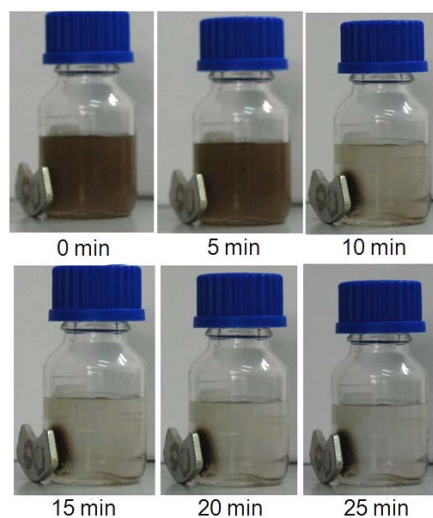


Fig. 5. Orientation of the as-prepared Ag-4ATP/Fe₃O₄/SiO₂ particles by magnetic separator.

4. Conclusion

In conclusion, in order to design a new applicable material, we established a simple and low-cost method to synthesize multifunctional nanocolloids, which based on the magnetic Fe₃O₄ and Ag-4ATP particles. The magnetic property of colloids showed that they still remained super-paramagnetic material which are very easy to be collected by magnetic separators. Besides, the optical property impacted the extraordinary applicability of the as-prepared colloids from their individual SER spectrum. The high and narrow peaks at 1145 cm⁻¹ and at 1443 cm⁻¹ are attracted to be an excellent signaling agent for biomedical labeling, which are not influenced by external materials, such as chemicals or other organic substances. Therefore, the colloids were planned to be employed for fast diagnostic imaging using scanning micro Raman spectroscopy.

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