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Synthesis of Composite Particles with Fe_3O_4 core and Ag Shell for the Development of Fingerprints

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The Fe_3O_4 -core and Ag- shell (Fe_3O_4@Ag nanoeggs) were prepared through the encapsulation of 3-aminopropyltriethoxysilane-coated magnetite nanoparticle in nano-Ag shell by a simple chemically controlled procedure. The Fe_3O_4@Ag nanoeggs were characterized by scanning electron microscopy, transmission electron microscopy, UV-vis spectrum and superconducting quantum interference device magnetometer, respectively. A detailed analysis is provided of how the hydrolysis and condensation of 3-aminopropyltriethoxysilane and the pH value are vital in fabricating the Fe_3O_4@Ag nanoeggs. The prepared Fe_3O_4@Ag nanoeggs possessed uniform size, improved monodispersity, stability against aggregation and high magnetization, which were utilized for the detection of latent fingerprints deposited onto different surfaces. The experimental results showed that the latent fingerprints developed with the Fe_3O_4@Ag nanoeggs powders exhibited excellent ridge details with minimal background staining.

Key Words : Fe_3O_4@Ag nanoeggs, Superparamagnet, Hydrolysis, Condensation, Latant fingerprints

Introduction

Latent fingerprints, which are present but invisible at a crime scene, are the most common form of fingerprint evidence in identification and generalized proof of identity.[1] In order to visualize a latent print, the application of physical or chemical techniques are required.[2] Fine, dry fingerprints powders are routinely used in the field of forensic fingerprint detection.[3] However, this type of technique is limited in many aspects, especially in health and safety, selectivity, sensitivity.

Although, multifunctional magnetic nanoparticles, such as the core-shell nano- Au or nano-Ag combined with magnetic nanoparticles, which have many potential applications in various fields such as catalysis, biomedicine, magnetic resonance imaging, data storage, and environmental remediation.[4-10] However, aggregation and precipitation of the nanoparticles often limited their application.[11] To fabricate multifunctional magnetic nanoparticles with good dispersity, Lee group[12] reported that TEOS was applied to protect the nanocrystals against agglomeration between the Fe_3O_4 nanoparticles. Subsequently 3-aminopropyltriethoxysilane (APTES) was used as a silane coupling agent to modify the surface of the Fe_3O_4@SiO_2 microspheres, and leave the terminal-NH_2 groups for nano-Au immobilization. Core-shell Fe_3O_4@Au nano-composites[13] were prepared by layer-by-layer strategy based on the alternative assembly of oppositely-charged polyelectrolytes on to the colloial templates. Caruntu's and O'Connor's groups[14] and Quanguo He group[15] have reported that APTES was hydrolyzed and condensed in the presence of Fe_3O_4 nanoparticles in ethanol under heating, resulting in silica-coated amine functionalized Fe_3O_4 nanoparticles. Then, the Fe_3O_4@Au nano-composites were prepared *via* sonolysis of a solution mixture of $HAuCl_4$ and APTES-coated Fe_3O_4 nanoparticle with further drop-addition of sodium citrate. However, the complex preparation process, irregular core-shell structures and poor magnetic response have not been well solved in these reports.

In this study, the hydrolysis and condensation of APTES was completed in acidity. Then, Fe_3O_4 nanoparticles were functionalized by the as-prepared APTES at room temperature. After that, the Fe_3O_4@Ag nanoeggs were prepared through the encapsulation of APTES-coated Fe_3O_4 in nano-Ag shell. The Fe_3O_4@Ag nanoeggs have been fabricated through such simple, inexpensive method, and the as-obtained nanoeggs were allowed to detect the latent fingeprints deposited onto different surfaces. Successful results were obtained with detailed fingerprints offering a good contrast due to the Fe_3O_4@Ag nanoeggs with high magnetization and well-defined structure. Moreover, in comparison with commercial magnetic fingerprint powders, the Fe_3O_4@Ag nanoeggs exhibit health and safety, high selectivity, sensitivity as well as easiness of use in the forensic research arena, and hence are potentially useful in a broader range of applications.

Experimental

Materials. 3-Aminopropyltriethoxysilane, $NH_3 \cdot H_2O$ and $NaBH_4$ were obtained from Sigma. NaOH, CH_3COOH, HCl, $FeCl_3$, $FeCl_2$ and $AgNO_3$ were purchased from Chemical Reagent Co, Sichuan, China. All other chemicals employed were of analytical grade and used as received, doubly distilled water was used throughout the experiments.

Instruments. The scan electron microscopy (SEM) images of the particles were obtained in a field emission scanning

electron microscopy (FE-SEM LEO 1530). The UV-vis spectrum was performed on a U-3310 (Hitachi LTD, Japan). Magnetic measurements were carried out using a superconducting quantum interference device magnetometer (HH-15 VSM, Nanking University Instrument Co., China). The detecting fingerprints was performed on a Video Spectral Comparator vsc 5000 (Foster and Freeman. LTD). Transmission electron microscopy (TEM) was performed on a FEI Tecnai G20 (FEI Co., America).

Synthesis of the Fe_3O_4 Nanoparticles. The Fe_3O_4 nanoparticles were first prepared following a method reported by the Yu-Chie Chen's method with slight modification.[19] Briefly, a coprecipitation of ferric and ferrous chlorides (Fe/Fe ratio = 2.6) in 2.0 M HCl were added slowly into 1.5 M NaOH solution under vigorous stirring for 80 min at 80 °C and then was allowed to cool to room temperature in a nitrogen atmosphere. The resulting black product was washed several times with ethanol and dried at 60 °C for 6 h. The Fabrication of Fe_3O_4@Ag nanoeggs was following a method reported by our previously method with major modification.[17]

Fabrication of the APTES-modified Fe_3O_4 Nanocomposites. For the functionalization of Fe_3O_4 nanoparticles with APTES, 1.0 mL Fe_3O_4 nanoparticles (~2.1 mg of Fe_3O_4 /mL nanoparticles of ethanol) were dispersed in 8 mL ethanol for 2 h. After that, 9.15 mL APTES (0.45 mL of APTES mixtured with 0.6 mL 25% CH_3COOH or 0.6 mL 25% $NH_3{\cdot}H_2O$ in 8 mL of ethanol), which was hydrolyzed and condensed under water bath vigorous stirring for 0.5 h, were added to the thus obtained Fe_3O_4 nanoparticles (9.15 mL). The mixture solution reacted under water bath vigorous stirring for 1.5 h. Then the precipitates were separated from the solution by a permanent magnet and washed repeatedly with ethanol for three times to remove the excess APTES, and redispersed in 8 mL of ethanol. The concentration of the APTES-modified Fe_3O_4 nanospheres was about 12.0 mg of Fe_3O_4/mL.

The Fabrication of Fe_3O_4@Ag Nanoeggs. Ag nanoparticles were synthesized according to the reported procedure[18] with slight modification. Then, the 8 mL solution of APTES-modified Fe_3O_4 nanoparticles was mixed with 8 mL of the Ag nanoparticle solution (as seeds), and an adsorption time of 2 h was allowed. The excess Ag seeds were removed by three repeated magnetic separations, and then the particles were redispersed in 8 mL of ethanol. Eventually, a solid shell of Ag was formed onto the Ag-modified Fe_3O_4 magnetic nanocomposites by reducing aliquots of $AgNO_3$ (0.35 mL, 0.1 mM) with $NaBH_4$ (0.024 mL, 0.1 mM) in aqueous solution, the final products were collected by magnetic separation and dissolved in distilled water.

Results and Discussion

The Characterization of Different Nanoparticles. Observation by the SEM showed that the APTES-Fe_3O_4 nanoparticles obtained were dispersed, and nearly spherical in shape with an average diameter of 250 nm except a few big nanoparticles (Fig. 1(a)), and the Ag-modified Fe_3O_4 nanocomposites (Fig. 1(b)) were larger (for about 280 nm) than APTES-Fe_3O_4 nanoparticles. Figure 1(c) indicated that the Fe_3O_4@Ag nanoeggs microphores possess spherical shape with smooth surface, diameter of ~290 nm, more uniform size and morphology as well as excellent dispersibility than the Fe_3O_4@Au nanoeggs reported by Quanguo He.[13] It showed that the formation of the shell of Ag was accomplished by reducing $AgNO_3$ using $NaBH_4$. This reduction chemistry has been found effective in making a uniform coating layer on Fe_3O_4 nanocomposites.[19,20]

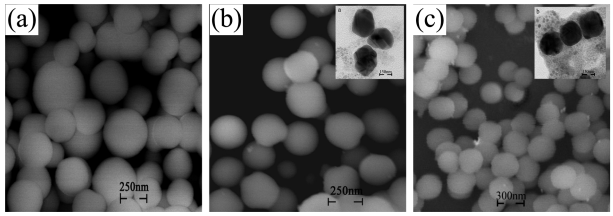


Figure 1. SEM of the APTES-coated Fe_3O_4 nanoparticles (a), Ag-modified Fe_3O_4 nanocomposite (b) and Fe_3O_4@Ag nanoeggs (c). (Inset)TEM images of the Ag-modified Fe_3O_4 (b) and Fe_3O_4@Ag nanoeggs (c).

The representative TEM images of the Ag-modified Fe_3O_4 and Fe_3O_4@Ag nanoeggs were shown in Figure 1 insert. Compare with the Fe_3O_4@Ag nanoeggs (Fig. 1(b) insert), the Ag-modified Fe_3O_4 (Fig. 1(c) insert) possess the relatively poor size uniformity, which was similar to the SEM results.

UV-vis Spectroscopy and Superparamagnetic Characteristic. To further analyze the surface composition of different nanoparticles, UV-vis spectroscopy characterization was employed.[20,21] Figure 2 confirmed the presence of Ag as the shell of the nanocomposite. Initial scans of APTES-coated Fe_3O_4 nanoparticles produced featureless spectra indicating an absence of surface plasmon resonance (Fig. 2(a)), when a layer of Ag seeds were attached onto APTES-coated Fe_3O_4 nanoparticles, an absorption peak developed at 385 nm (Fig. 2(c)). However, the peak was shifted to 425 nm (Fig. 2(b))

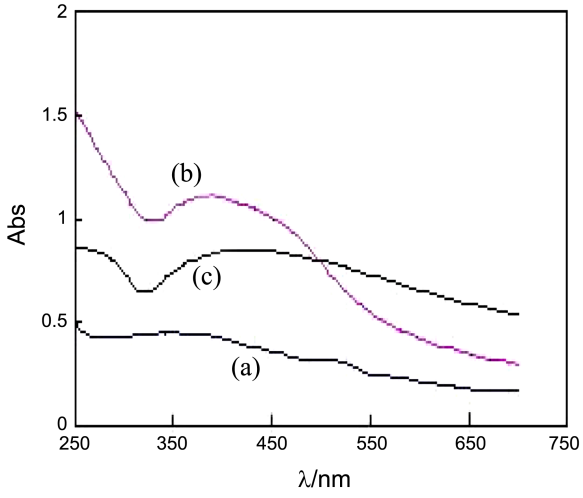


Figure 2. Uv-vis absorption spectra of APTES-coated Fe_3O_4 nanoparticles (a), Fe_3O_4@Ag nanoeggs (b) and Ag-modified Fe_3O_4 nanoparticles (c).

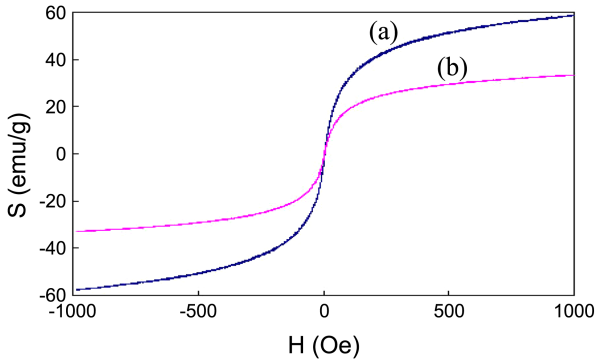


Figure 3. Magnetization curves of Fe_3O_4 nanoparticles (a) and Fe_3O_4@Ag nanoeggs (b).

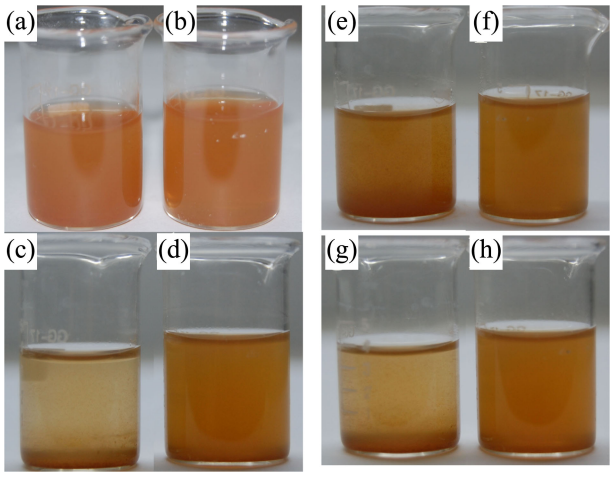


Figure 4. The APTES - Fe_3O_4 nanoparticles (in alkalescence) (a and c) and the APTES - Fe_3O_4 nanoparticles (in acidity) were dissolved in ethanol (b and d), respectively. The Fe_3O_4@Ag nanoeggs were dissolved in distilled water (e and g) or ethanol (f and h), respectively.

and broadened, owning to the particle-to-particle interactions which resulted from the higher packing density of the Ag particles after the deposition of Ag onto Ag-coated Fe_3O_4 nanoparticles.

Superparamagnetic Characteristic. The magnetic behavior of Fe_3O_4@Ag nanoeggs is of importance for practical applications, and it is controlled in a straightforward fashion through the amount of Fe_3O_4 nanoparticles or $NaBH_4$.[21] Increasing the concentration of Fe_3O_4 nanoparticles attributed to much larger nanoparticles with higher magnetism. Meanwhile, the increase of $NaBH_4$ resulted in the thick shell of Ag on the Fe_3O_4 nanoparticles possessing much slighter magnetism. Therefore, 1.0 mL of 2.11 mg/mL Fe_3O_4 nanoparticles and 24 μL of 0.1 mM $NaBH_4$ were adopted for the fabrication of Fe_3O_4@Ag nanoeggs while keeping all other parameters fixed.

Magnetic characterization using a magnetometer at 300 K showed that the Fe_3O_4 nanoparticles were superparamagnetic at room temperature before and after surface modification. The saturation magnetization of Fe_3O_4 nanoparticles, Fe_3O_4@Ag nanoeggs were 60.8 (Fig. 3(a)) and 34.3 emu/g (Fig. 3(b)), respectively. Due to the additional cell that is extraordinary thin outside the Fe_3O_4 nanoparticles, the Fe_3O_4@Ag nanoeggs exhibited higher magnetism comparison to the Fe_3O_4@Au nanoeggs,[22,14] slightly weaker magnetism compared to the Fe_3O_4 nanoparticles.

The Hydrolysis and Condensation of APTES. The Fe_3O_4 nanoparticles, which were prepared by coprecipitation of ferrous and ferric ions with $NH_3 \cdot H_2O$ or NaOH, spontaneously aggregated to form magnetic clusters. Thus, it is generally required to protect the nanocrystals against agglomeration by inorganic and /or organic stabilizers.Several papers have reported that TEOS or chelating solvents[12-15] was selected to prevent particles agglomeration. Subsequently, the silica or chelating solvents-coated Fe_3O_4 nanoparticles were further functionalized with APTES, in which APTES were usually hydrolyzed and condensed in the presence of the as-prepared Fe_3O_4 nanoparticles in alkalescence under heating. In our previous work, silica-coated Fe_3O_4 nanoparticles were achieved by two ways under room temperature.[17] One was injecting sol-gol which was hydrolyzed and condensed into the Fe_3O_4 nanocrystals, the other one was hydrolyzing and condensing of sol-gol in the presence of the as-prepared Fe_3O_4 nanoparticles. We have testified that nanoparticles achived by the first method have predefined size and shape, and improved monodispersity, which makes the first method to be used for the following research.

According to the Stber process, the hydrolysis and condensation of APTES was usually completed in alkalescence.[12] However, we found that APTES can be hydrolyzed and condensed in either acidity or alkalescence. In this case, APTES were hydrolyzed and condensed in acidity and alkalescence, respectively. After that, the APTES were employed as surface-capping in order to prevent the agglomeration between Fe_3O_4 nanoparticles, and left the terminal $-NH_2$ groups available for Ag seeds immobilization. The as-prepared APTES - Fe_3O_4 nanoparticles (in alkalescence) and the APTES - Fe_3O_4 nanoparticles (in acidity) were solubilized in ethanol, respectively, as shown in Figure 4(a, b), both forming brown solution. However, we can see that the APTES - Fe_3O_4 nanoparticles (in alkalescence) completely aggregated after the ultrasonication stopped for 15 min (Fig. 4(c)), while the APTES - Fe_3O_4 nanoparticles (in acidity) can be remained stable in ethanol for more than 190 min (Fig. 4(d)) after the ultrasonication stopped. Therefore, the Fe_3O_4@Ag nanoeggs (the hydrolysis and condensation of APTES in acidity) were selected for the following works.

The Colloidal Stability of the Fe_3O_4@Ag Nanoeggs. The Colloidal stability of the nanoparticles often limited their application.[11] The Fe_3O_4@Ag nanoeggs were dissolved in ethanol and distilled water, respectively. As shown in Figure 4(e, f), both of the Fe_3O_4@Ag nanoeggs possess high monodispersity. However, we can see that the Fe_3O_4@Ag nanoeggs completely aggregated in distilled water after the ultrasonication stopped for 30 min (Fig. 4(g)), while the Fe_3O_4@Ag nanoeggs can be remained suspended in ethanol for more than 150 min (Fig. 4(h)) after the ultrasonication stopped.

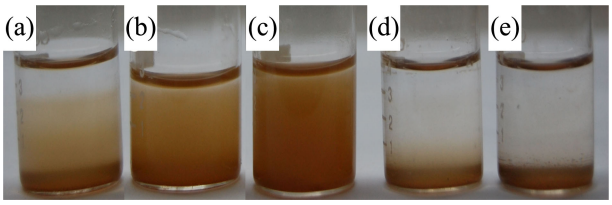


Figure 5. Different pH of Fe_3O_4@Ag nanoeggs suspension: (a) 3.0, (b) 4.5, (c) 6.0, (d) 7.5, (f) 9.0.

The Influence of the Solution pH. It is important to note that the Fe_3O_4@Ag nanoeggs was significantly influenced by PH.[23] We found the negatively charged Fe_3O_4@Ag nanoeggs (negative due to the absorption of stabilizing borohydride) have high solubility and colloidal stability in ethanol (pH 6.0) (Fig. 5(c)). The pH of the Fe_3O_4@Ag nanoeggs were adjusted by CH_3COOH or NaOH. As the pH was decreased from 4.5 to 3.0, the negative surface charge would be deprotonated, and the particles would become neutral in charge and precipitate gradually from solution (Fig. 5(a), (b)). However, it was found that the Fe_3O_4@Ag nanoeggs aggregated immediately with an increase of pH from 7.5 to 9.0 (Fig. 5(d), (e)). The reason is probably that the Fe_3O_4@Ag nanoeggs are hydrophobic, the binding of Fe_3O_4@Ag nanoeggs with Fe_3O_4@Ag nanoeggs to the surface of modified Fe_3O_4 nanoparticles may be facilitated by hydrophobic interactions, which resulted in the increased size of Fe_3O_4@Ag nanoeggs and poor spherical morphologies of core/shell particles. After that, the Fe_3O_4@Ag nanoeggs in different pH were collected by magnetic separation and dry to obtained the Fe_3O_4@Ag nanoeggs powders.

Detection of Fingermarks Using the Fe_3O_4@Ag Nanoeggs in Powder form. Fingerprint powdering remains the most usual technique for the detection of fingerprints.[24] The technique relies on the mechanical adherence of powders to the moisture and/or oily components of the skin ridge deposits,[25] and the excess powder should then be removed by dusting the surface with a gentle tapping, brushing and blowing. Therefore, the size and shape of which have a large influence on the amount of adhesion they have to the fingerprint.[26] Meanwhile, the fingerprint specialists' exposure while working at a crime scene to powder formulations could be a potential health hazard except magnetic fingerprint powders. For the magnetic fingerprint powders are specifically useful that only the magnetic powders touch the fingerprint ridges,

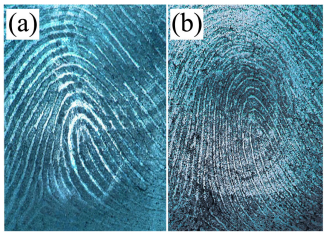


Figure 6. The fingerprints developed with Fe_3O_4@Ag nanoeggs (Figure 6(a)) and Ag-modified Fe_3O_4 nanocomposites (Figure 6(b)) powders, respectively.

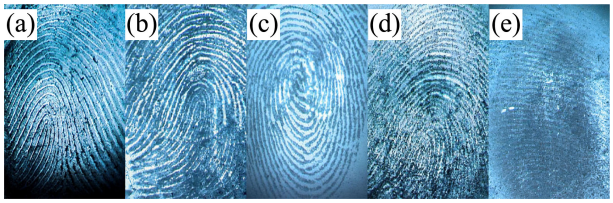


Figure 7. The fingerprints detection on glass surfaces treated with the Fe_3O_4@Ag nanoeggs powders prepared in pH 3.0-9.0 accordingly.

while the excess powders can be removed by the magnetic brush.[24] Therefore, the magnetic powders are healthy and safe for fingerprints experts.

The magnetic property of the powders of the Fe_3O_4@Ag nanoeggs (Fig. 6(a)) or Ag-modified Fe_3O_4 nanocomposites (Fig. 6(b)) was tested by using a magnetic brush. The powders of the Ag-modified Fe_3O_4 nanocomposites or Fe_3O_4@Ag nanoeggs were found to be strongly attached to the brush. However, the Fe_3O_4@Ag nanoeggs powders produced significantly less background development due to smooth and uniform Ag surfaces, resulting in good contrast between the fingerprints and the substrate than the Ag-modified Fe_3O_4 nanocomposites powders. Because the Fe_3O_4@Ag nanoeggs powders possess more uniform size and nano-Ag shell exterior, they hold great promise for high absorption of the proteins in fingerprint systems.

The Fe_3O_4@Ag nanoeggs in powder form prepared in pH 3.0, 4.5, 6.0, 7.5 and 9.0 were used to detect the fingerprints (Fig. 7(a), (b), (c), (d) and (e)), and the fingerprints can be viewed directly (Fig. 7(a), (b) and (c)), due to more clear ridge details. However, the fingerprints treated with the Fe_3O_4@Ag nanoeggs prepared in higher pH value (Fig. 7(d), (e)) which have greater powder intensity with maximum background development result from the larger size of Fe_3O_4@Ag nanoeggs in spherical shape.

Comparison experiment with commercial magnetic Fe_3O_4 powders were performed on non-porous or porous surfaces such as glass, ceramic, paper and polyethylene bags surfaces.

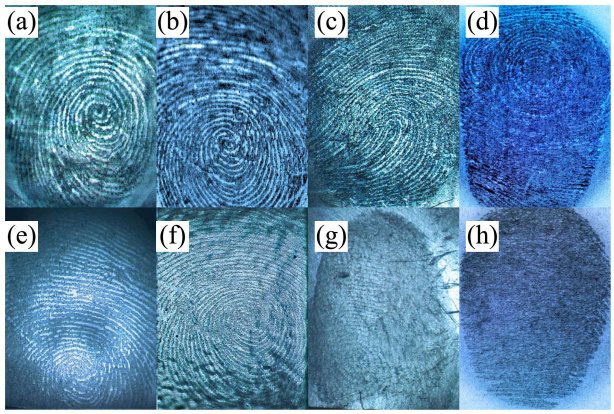


Figure 8. The fingerprints on glass, porcelain enamel, polyethylene pieces and paper surfaces developed with Fe_3O_4@Ag nanoeggs powders (Figure 8(a)-(d)) and commercial magnetic Fe_3O_4 powders (Figure 8(e)-(h)).

The average particle size of the Fe_3O_4@Ag nanoeggs was approximately 290 nm, while those of the commercial magnetic powders were found to be about 119.7 and 82.3 μm, respectively.[27] The Fe_3O_4@Ag nanoeggs showed excellent ridge details with minimal background staining on glass, porcelain enamel, polyethylene pieces and paper surfaces (Fig. 8(a)-(d)), which lead to a better overall contrast for smaller particle adhere more effective to fingerprint residue than commercial magnetic Fe_3O_4 powders on the same surfaces (Fig. 8(e)-(h)). Compared with our previous paper,[17] the present work was low-cost, in spite of both of them produced prints with good definition.

Conclusion

In conclusion, the Fe_3O_4@Ag nanoeggs were prepared through the encapsulation of APTES-coated Fe_3O_4 in nano-Ag shell, which possess a spherical shape with a smooth surface and a more uniform size, high monodispersity and magnetization. The thus obtained Fe_3O_4@Ag nanoeggs can be widely applied to the development of latent fingerprints on different surfaces. The results showed that the Fe_3O_4@Ag nanoeggs are much effective and convenient for workers to detect latent fingerprints in both the powder and the particle suspension forms.

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