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# Multifunctional Silver Nanoparticles: Synthesis and Applications

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## Abstract

Multifunctional silver nanoparticles have attracted widely due to their potential applications. Based on the properties of individual silver nanoparticles, such as plasmonic and antibacterial properties, silver nanoparticles can become multifunctional by surface modifications with various surfactants or they can be combined in core-shell and composite structures with the magnetic nanoparticles to form bifunctional nanoparticles. After reviewing the methods of synthesis and applications of silver nanoparticles, the chapter describes the synthesis and the properties of the new types of multifunctional silver nanomaterials based on the plasmonic behaviors of silver nanoparticles and the iron oxide  $\text{Fe}_3\text{O}_4$  superparamagnetic nanoparticles. One type is a simple combination of silver nanoparticles and iron oxide nanoparticles in a silica matrix  $\text{Fe}_3\text{O}_4/\text{Ag}-4\text{ATP}@ \text{SiO}_2$ . Other types are the core-shell structured nanoparticles, where  $\text{Fe}_3\text{O}_4$  nanoparticles play as the core and silver nanoparticles are the outer shell, so-called  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-Ag}$  and  $\text{Fe}_3\text{O}_4\text{-Ag}$ . In the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-Ag}$ , silver nanoparticles are reduced on the surface of silica-coated magnetic core, while in  $\text{Fe}_3\text{O}_4\text{-Ag}$ , silver nanoparticles are directly reduced on the amino groups functionalized on the surface of magnetic nanoparticles without coating with silica. Both of types of the multifunctional silver nanoparticles show the plasmonic and magnetic properties similar as the individual silver and iron oxide nanoparticles. Finally, some applications of those multifunctional silver nanoparticles will be discussed.

**Keywords:** Silver nanoparticles, magnetic nanoparticles, plasmonic-magnetic bifunctional, core-shell nanoparticles, multifunctional nanoparticles, combination synthesis, bioapplications

## 1. Introduction: Silver nanoparticles and their properties

Silver was used for long time in human life as jewelry and houseware. It is a transition metal which is soft and has the highest reflectivity. Among its many useful applications, silver also has known as an infection controller from ancient civilizations [1]. In the Han Dynasty in China *circa* 1500 BC, the earliest use of silver for therapeutic purposes was recorded [2]. Silver vessels and plates were commonly used during the Phoenician, Macedonian, and Persian empires [3]. Families of the higher socioeconomic classes during the middle-ages were so acquainted with the usage of silver. The result is that they developed bluish skin discolorations known as argyria,

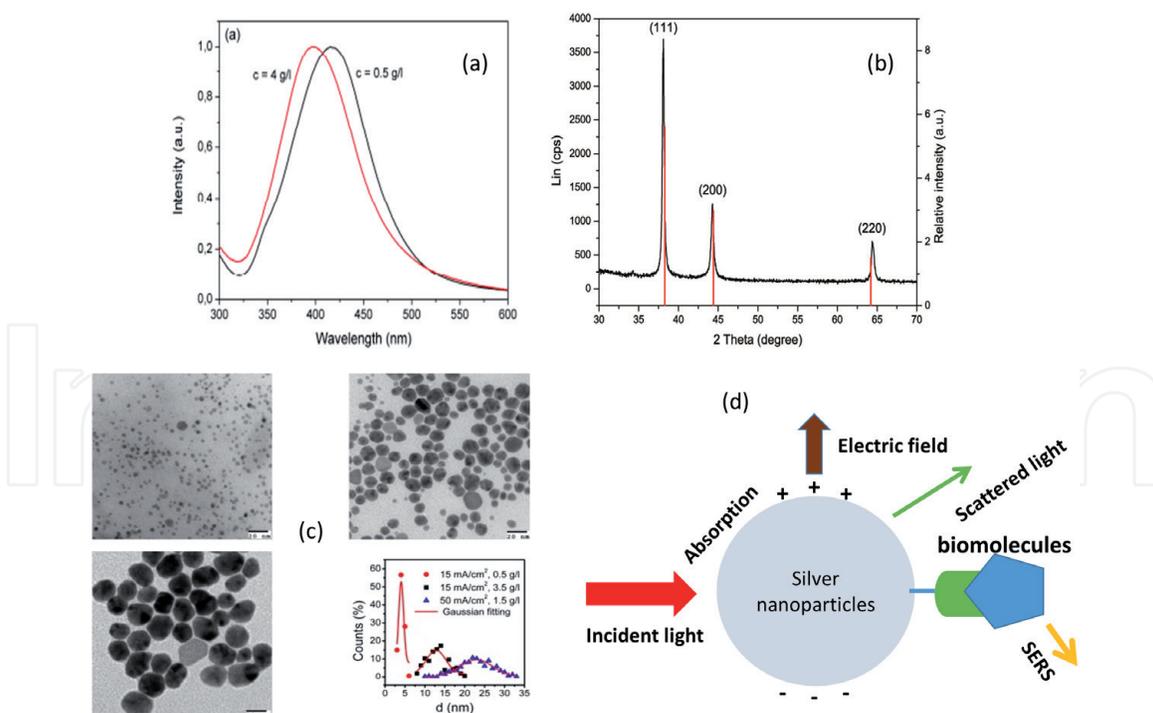
an affliction which may have led to the term 'blue blood' to describe members of the aristocracy [4]. In recent years, silver has gained attention as an antimicrobial agent due to the increase in bacterial antibiotic resistance, along with the development of nanosilver studies opening up the huge potential applications of silver in biomedicine. Today, modern medicine uses medical silver forms, such as silver sulfadiazine, silver nitrate, colloidal silver and/or silver in the nanoparticle form. Applications of the silver nanoparticles can be found in personal care products, home products, medical applications, and agricultural/industrial applications. Silver nanoparticles can be defined as silver particles with the size ranged from 1 to 100 nm. When the size of particles decreases to the nano scale, the surface-volume ratio dramatically increases, then bring the nanoparticles become highly applicable in applications requiring large surface contact, such as catalysis or antibacterial therapeutic. Silver in aqueous solution, or in its monoatomic state ( $\text{Ag}^+$ ), can be biologically active [5]. It is similar to the form of silver sulfadiazine or silver nitrate, which usually be used in wound healing treatments. In nanocrystalline form, silver metallic ( $\text{Ag}^0$ ) also can be biologically active when it releases ions or either in its native form. To date, the mechanisms by which silver acts on bacterial can be listed as follows:

- Silver ions react with the peptidoglycan component and form pores and puncture the bacterial cell wall [6];
- Silver cations enter into the bacterial cell, disrupting metabolic pathways resulting in generation of reactive oxygen species and inhibiting cellular respiration [7];
- In the cell, silver disrupt DNA replication cycle and DNA itself [8, 9].

Using those mechanisms, the wide and ever-expanding applications of silver nanoparticles in medicine, health care, and other daily life activities were developed [10].

In addition to antibacterial applications above, silver nanoparticles are being integrated into products from photovoltaics to chemical sensors due to their unique optical, electrical, and thermal properties. The most interesting property of silver nanoparticles is plasmonic absorption as shown in **Figure 1a**. The plasmons are the oscillations of free electrons in metallic nanoparticles that are excited by incident light as can be illustrated in **Figure 1d**.

The plasmons are the consequence of the formation of a dipole in the nanoparticles due to incident electromagnetic waves, which lead the electrons migrate to restore initial state. The incident electromagnetic waves oscillate forcing the electrons to oscillate at the same frequency as the light, which called resonant frequency. These coupling are called surface plasmon resonance because the free electrons are distributed on the surface of silver nanoparticles and, therefore, the resonant frequency strongly depends on the size and shape of the silver nanoparticles. In experiments, the surface plasmonic absorptions are detected by monitoring the resonant frequency as a function of incident wavelength. **Figure 1a** exhibits the absorption spectra of silver nanoparticles prepared by the sonoelectrochemical method with various concentration of surfactant to control the size of nanoparticles. In **Figure 1a**, two absorption peaks related to two size distributions of silver nanoparticles can be observed. Nanocrystalline silver has the face-centered cubic structure with the X-ray diffraction XRD peaks of (111), (200) and (220) as can be seen in **Figure 1b**. The prepared silver nanoparticles have the transmission electron microscope (TEM) images as shown in **Figure 1c** with size distribution varies when the current changes accordingly. In **Figure 1d**, the schematic structure



**Figure 1.** Silver nanoparticles prepared by sonoelectrochemical method. (a): Absorption spectra of silver nanoparticles (b) XRD pattern of silver nanoparticles (c) TEM images and size distribution of silver nanoparticles (d) schematic illustration of properties of silver nanoparticles.

of functionalized silver nanoparticles is illustrated. As described above, the absorption or the scattering cross-sections describe the intensity of a given frequency to be absorbed or scattered, respectively. The absorptions are due to the collective electrons oscillations to form surface plasmon resonances, which exhibit enhanced near-field amplitude at the resonance wavelength. This near-field is highly localized at the nanoparticles and decays rapidly away from the nanoparticles, though far-field scattering by the nanoparticles is also enhanced by the resonance. Under the effect of incident laser, these resonance increases significantly the intensity of the Raman scattering signals of the vibration of molecules/biomolecules functionalized on the surface of nanoparticles. Observing these enhanced Raman signals under the incident wavelength, the Surface Enhance Raman Scattering (SERS) technique can be used to recognize the vibration of molecules conjugated on the surface of the nanoparticles, then can be applied in bio-labeling. Under a certain incident wavelength, the enhanced Raman signals are sensitive with the shape and size distribution of silver nanoparticles, which can be varied with different method of synthesis.

Silver nanoparticles can be produced from chemical, physical, physicochemical methods, as well as biological or green methods [11–13]. Chemical reduction is the most common approach for synthesis of silver nanoparticles. The reducing agents, such as sodium borohydride  $\text{NaBH}_4$ , sodium citrate ... reduce  $\text{Ag}^+$  to form metallic silver  $\text{Ag}^0$ , which aggregate into oligometric clusters, then form metallic silver particles [14–16]. During the production process, the dispersive nanoparticles need to be stabilized and protected from the agglomeration by using surfactants as protective agents. Those functional comprising surfactants, such as thiols, amines, alcohols, etc. interact with particle surfaces and stabilize particles growth, as well as protect nanoparticles from agglomeration, sedimentation, or losing their surface properties. One of the effective protective agents to stabilize nanoparticles is polymeric compound, such as polyvinyl alcohol, polyethylene glycol, polymethylmethacrylate, etc. Silver nanoparticles were prepared by injecting them with various rates at high temperature up to  $100^\circ\text{C}$  [17].

Microemulsion techniques are effective to synthesize uniform and size controllable silver nanoparticles [18]. The metal precursor and the reducing agent are in two immiscible phases aqueous organic-systems. The interface between the two liquids and the intensity of inter-phase transports affect the rate of the reactions between metal precursors and reducing agents, leading to the metal clusters formation at the interface. The metal clusters are stabilized by coating with stabilizer molecules occurring in the non-polar aqueous medium.

Physical approaches can be used to synthesize silver nanoparticles with advantages of the absence of solvent contamination. Laser ablation is a method to synthesize silver nanoparticles by laser ablation of metallic bulk materials in solution [19]. Evaporation-condensation and arc discharge are also effective physical methods to synthesize silver nanoparticles [20, 21].

Physicochemical approaches, which use a physical method to support chemical reduction, are very effective methods to synthesize silver nanoparticles. Photoreduction is a clean process to fabricate the silver nanoparticles in various mediums, such as cells, emulsion, polymer films, etc. One effective and simple method is the UV-initiated photoreduction, which use the UV light to synthesize silver nanoparticles in stabilizing agents for prevention of the aggregation [22]. Besides, the electrochemical and sonoelectrochemical methods can be used to synthesize silver nanoparticles with controlling the particles size by adjusting electrolysis and ultrasonic parameters [23, 24]. A modified sonoelectrodeposition method was used to synthesize silver nanoparticles [16, 25]. In this modification the cathode is a silver plate, which allows producing silver nanoparticles with the size range of 4–30 nm dispersed in a non-toxic medium. Furthermore, microwave-assisted synthesis provides silver nanoparticles with smaller sizes, narrower size distributions, and a higher degree of crystallization [26].

Biological or green methods need to develop as environmentally and economically friendly processes, which do not use toxic chemicals in the protocol. These methods use organisms, such as prokaryotic bacterial cells, eukaryotic fungi and plants to synthesize silver nanoparticles [27]. Biological methods could be used for synthesis of highly stable and well-characterized nanoparticles. Sizes and morphologies of synthesized silver nanoparticles can be controlled by altering some critical conditions, including pH, mixing speed, light, exposure time, temperature, substrate concentration, buffer strength, biomass and substrate concentration. In these methods, the critical aspects, such as types of organisms, genetical and inheritable properties of organisms, election of the biocatalyst states, enzyme activity, optimal conditions for cell growth and optimal reaction conditions have been considered.

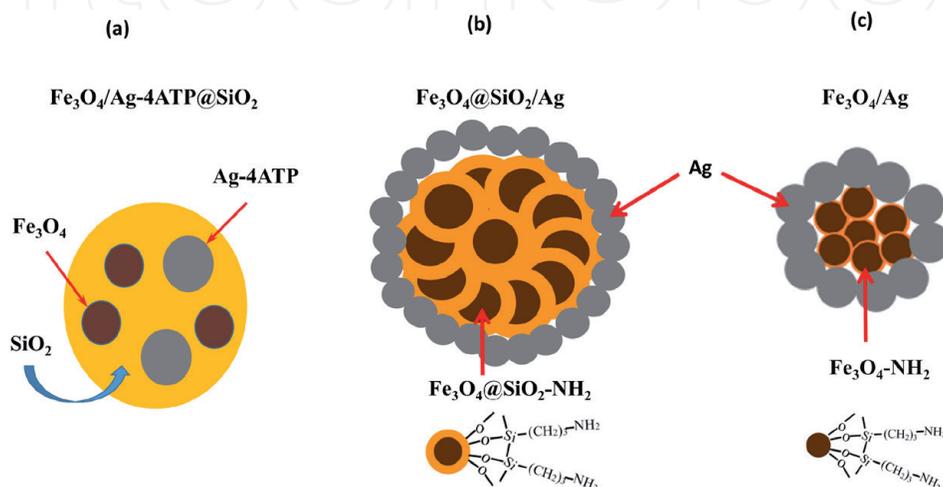
## **2. Multifunctional silver nanoparticles and their applications**

Multifunctional nanoparticles have attracted much interest because of their ability to combine various properties, such as electronic, optical, catalytic, surface enhance, and magnetic properties, by using the combination of individual nanoparticles and/or functionalize the core nanoparticles with appropriate agents [28–31, 15]. Combining of individual nanoparticles enhances functionality or creates new properties compared to those of individual nanoparticles. For instance, nanoparticles with the combination of plasmonic and magnetic properties can be a good candidate for bio imaging, diagnosis and therapy using their plasmonic properties. In parallel, they can be used for targeted drug delivery and magnetic resonance imaging under an external field, as well as allow bio tissues to be targeted and separated with their superparamagnetic properties.

Individual silver nanoparticles are special plasmonic nanoparticles which can be used as an antibacterial agent and/or as the plasmonic agent in biomedicine applications. They can be multifunctional if they are functionalized with appropriate surfactants allowing to apply silver nanoparticles in more than one purpose, such as in labeling together with in therapy. They also can be multifunctional if they can be combined with other individual nanoparticles, such as magnetic or semiconductor nanoparticles, in order to have both the properties/functionalities of individual nanoparticles in the combined one. In this section, some simple combinations of silver nanoparticles and magnetic nanoparticles, which so-called multifunctional silver nanoparticles, will be described.

One type of the magnetic nanoparticles, which most often used for bio applications due to their good superparamagnetic feature and simple in production, is iron oxide  $\text{Fe}_3\text{O}_4$  nanoparticles [28]. During the production, they can be stabilized and more biocompatible by coating with polymers, chitosan, starch and silica, in which silica has shown much higher stability than the other coatings [32]. The amorphous silica shells can also behave as carriers for the immobilization of functional nanoparticles and avoid their aggregation, as well as provide the ability of further functionalizing. In order to combine magnetic nanoparticles  $\text{Fe}_3\text{O}_4$  and silver nanoparticles to form multifunctional silver nanoparticles, silica shell plays an important role, which keeps the stability of bifunctional plasmonic-magnetic nanocomposites. It can be the outer shell of the combination of 4-Aminothiophenol (4-ATP) functionalized silver nanoparticles and magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles as shown in **Figure 2a**, which protect and keep both functionalities of individual nanoparticles [15]. It also can be act as a very thin protection layer of the magnetic core, and then silver ion was observed and reduced on the surface of the silica layer to form plasmonic-magnetic nanocomposites as can be seen in **Figure 2b** [29]. In comparison,  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles are functionalized with 3-aminopropyltriethoxysilance (APTES) and silver nanoparticles are reduced on the amino ( $-\text{NH}_2$ ) groups of this functionalized layer to form multifunctional silver nanocomposites, which have a one-atom thin layer of Si-O on the surface of  $\text{Fe}_3\text{O}_4$  core as can be seen in **Figure 2c** [30, 31].

The magnetic nanoparticles in all listed composites were synthesized by coprecipitation method [28], where  $\text{Fe}^{2+}/\text{Fe}^{3+}$  with 1:2 molar ratio was diluted to 0.01/0.02 M concentration from  $\text{FeCl}_2$  and  $\text{FeCl}_3$ . Polyvinylpyrrolidone (PVP) was used as stabilizer to restrain the nanoparticles size. The mixture was stirred and kept warm at 60–70 °C.  $\text{NH}_4\text{OH}$ , then was added to the warmed mixture to have



**Figure 2.**  
Schematic structure of silver multifunctional nanoparticles.

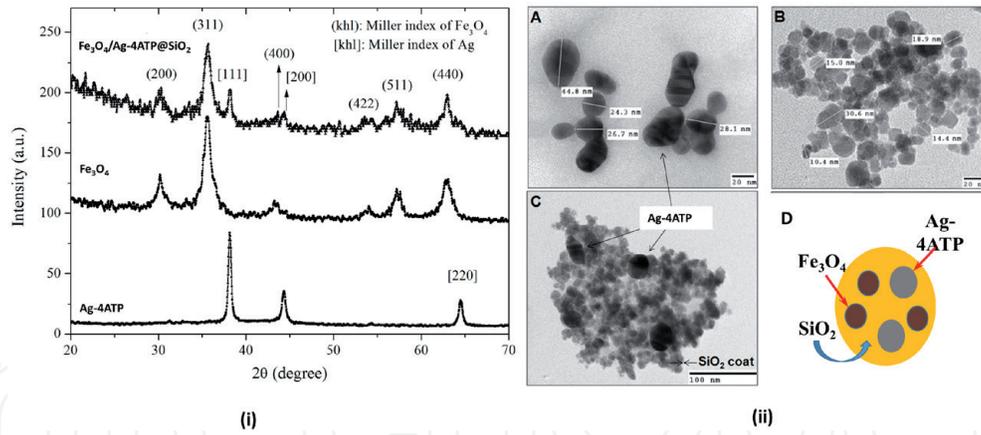
the black color precipitation, which was collected by purification with magnetic separation and washing with ethanol and distilled water. This is the most common and simplest way to produce  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles.

In order to combine plasmonic and magnetic properties of individual nanoparticles, the simplest thinking is to cover both of them in a suitable shell, such as silica. Biocompatible silica layer can be used as stabilizer, as well as the dock for further targeted functionalizing. Inside the silica shell, the silver nanoparticles need to exhibit all the plasmonic behaviors, which are properties of multifunctional silver nanoparticles. To confirm that, the silver nanoparticles were prepared with functionalized 4-ATP, which will be indicator for the surface plasmon resonance, on the surface to form Ag-4ATP nanoparticles [15]. They were produced by reducing silver acetate  $\text{AgCH}_3\text{COO}$  solution at 0.01 M concentration using  $\text{NaBH}_4$  as reductant with the present of PVP as surface activator. The solution was vigorously stirred before 4-ATP was added and the covalent S-Ag linkages were formed between the silver nanoparticles surface and the 4-ATP molecules. The prepared silver nanoparticles functionalized with 4-ATP (Ag-4ATP) was combined with the produced  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles by using inverse micro emulsion method, which was created from the mixing of hydrophobic phase of toluene and hydrophilic phase that was made from the Ag-4ATP and  $\text{Fe}_3\text{O}_4$  aqueous solutions. Under sonic bath, the mixture was moderated for 2 h before adding tetraethyl orthosilicate (TEOS), which react with water in solution to form silica shell. The combination of magnetic and plasmonic nanoparticles in silica shell is symbolled by  $\text{Fe}_3\text{O}_4/\text{Ag-4ATP}@SiO_2$ .

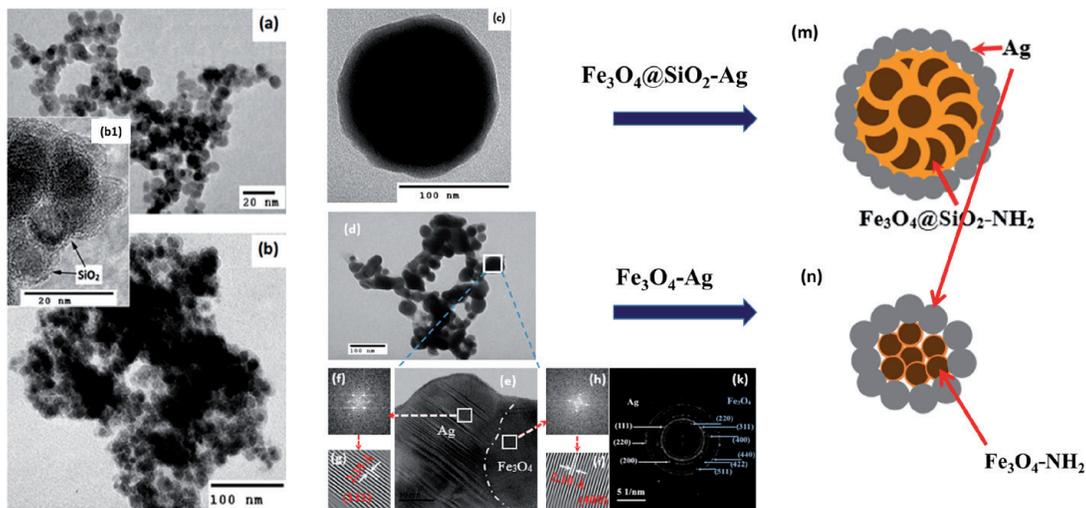
In order to produce plasmonic-magnetic nanocomposites in “core-shell” form,  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were first coated by silica layer, and then were functionalized with APTES. The magnetic nanoparticles were dispersed in water mixed with ammonia solution. TEOS was added into the mixture to form a silica layer on the magnetic nanoparticles. After washing, the collected nanoparticles were functionalized with the amino group by a silanol reaction of APTES in a mixture containing silica-coated magnetic nanoparticles and ammonia  $\text{Fe}_3\text{O}_4@SiO_2-NH_2$ . Finally, the plasmonic-magnetic nanocomposites denoted by  $\text{Fe}_3\text{O}_4@SiO_2-Ag$  were prepared by the reduction of  $\text{AgNO}_3$  onto the surface of amino functionalized magnetic nanoparticles. The reduction of silver ions was carried out in pH of 11 by using sodium borohydride  $\text{NaBH}_4$  as a reducing agent, under the influence of an ultrasonic wave. This method is called ultrasound-assisted chemical method [29].

Magnetic nanoparticles can also be directly functionalized with APTES without coating with silica layer [30, 31]. They were dispersed in ethanol before adding the APTES and  $\text{NH}_4\text{OH}$  with assistance of ultrasound. The next step is the reduction of  $\text{AgNO}_3$  onto the surface of amino functionalized magnetic nanoparticles and the final product denoted by  $\text{Fe}_3\text{O}_4-Ag$  has the structure as expected in **Figure 2c**.

The prepared multifunctional nanoparticles/composites need to be confirmed the structure and morphology by using X-ray diffractometer (XRD) and high resolution TEM (HRTEM). An example can be seen in **Figure 3**, where the XRD patterns in **Figure 3(i)** of Ag-4ATP,  $\text{Fe}_3\text{O}_4$  nanoparticles and the combination of them in silica shell  $\text{Fe}_3\text{O}_4/\text{Ag-4ATP}@SiO_2$  are shown together [15]. They demonstrate that the combination contains both the individual nanoparticles, where the XRD pattern of the combination shows both the characteristic peaks of silver and magnetic nanoparticles. The XRD results of  $\text{Fe}_3\text{O}_4@SiO_2-Ag$  and  $\text{Fe}_3\text{O}_4-Ag$  composites also lead to the similar conclusions [29, 31]. The TEM images in **Figure 3(ii)** conclude that the combination contains both the individual nanoparticles due to the existence of bigger nanoparticles of silver and smaller one of magnetic nanoparticles, in consistence with the results observed from XRD patterns. The pattern D in **Figure 3(ii)** shows the schematic model of the combination in pattern C indicating



**Figure 3.** XRD pattern (i) and TEM images (ii) of the combination of  $\text{Fe}_3\text{O}_4$  and Ag-4ATP nanoparticles in silica matrix.



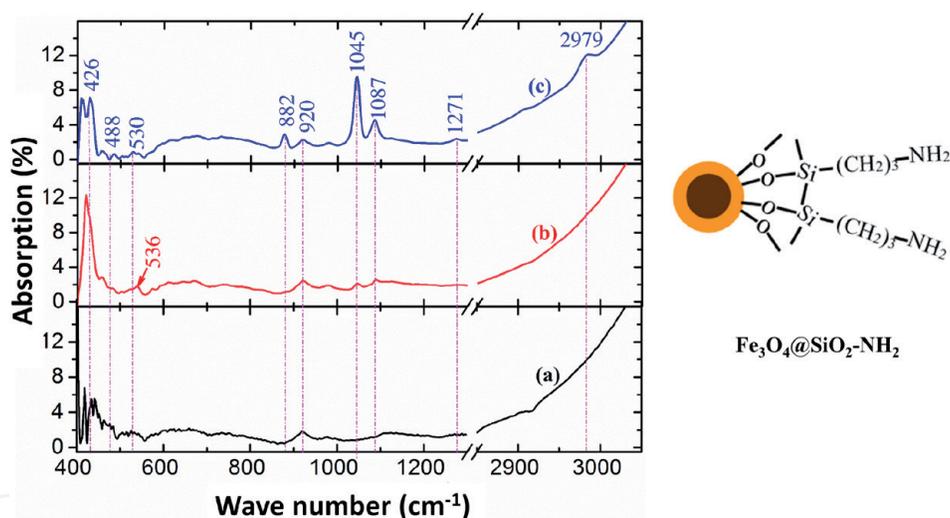
**Figure 4.** TEM and HRTEM images and the schematic structure of core-shell silver multifunctional nanoparticles.

that the combination is covered by a thin layer of silica and have the size of around 150–200 nm, which can be applicable for biomedicine, despite that they are not so homogenous.

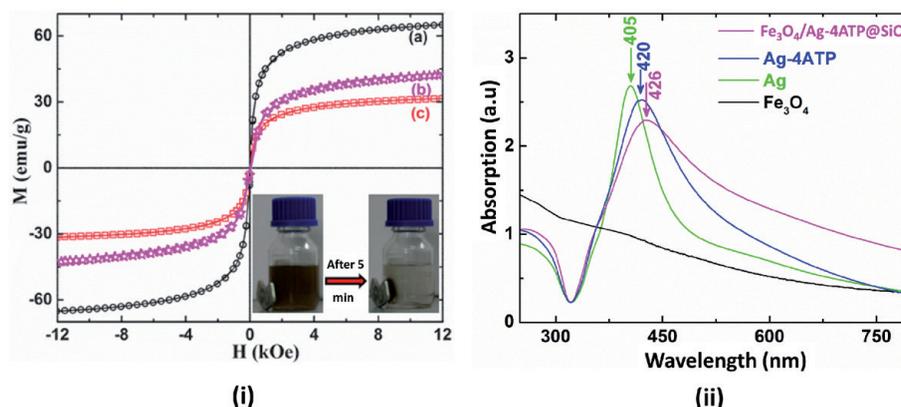
The HRTEM images of plasmonic-magnetic  $\text{Fe}_3\text{O}_4@SiO_2-Ag$  and  $\text{Fe}_3\text{O}_4-Ag$  composites are shown in **Figure 4** [29–31], where the **Figure 4a** shows the image of magnetic core. **Figures 4b** and **4b1** show the TEM and HRTEM image of the magnetic nanoparticles coated with silica  $\text{Fe}_3\text{O}_4@SiO_2$ , respectively, while the **Figure 4c** shows the final composite image after Ag nanoparticles were reduced on the amino groups  $\text{NH}_2$ - around the magnetic core. In this TEM image, two layers can be seen: the inner core is high contrast, which can be the  $\text{Fe}_3\text{O}_4@SiO_2$  nanoparticles, while the outer layer with low contrast can be the silver nanoparticles layer. The outer layer is of thickness of around 10 nm, in consistence with that conducted from XRD results. The possible structure of the nanocomposite  $\text{Fe}_3\text{O}_4@SiO_2-Ag$  with the size of around 150 nm have schematically shown in **Figure 4m**. This possible structure was also strengthened by the XRD results, which also show both the peaks of  $\text{Fe}_3\text{O}_4$  and Ag nanocrystalines [29]. Similarly, the **Figure 4d** shows the TEM images of  $\text{Fe}_3\text{O}_4-Ag$  nanocomposites and the enlarged HRTEM image in **Figure 4e** shows the composites structure, where the crystalline patterns of silver part and  $\text{Fe}_3\text{O}_4$  parts can be clearly seen. The patterns in **Figure 4f** and **g** show the lattice and diffraction images of silver part in composites, while **Figure 4h** and **i** show those of magnetic

crystalline, respectively. The diffraction of the composites can be seen in **Figure 4k** and then the schematic structure of  $\text{Fe}_3\text{O}_4\text{-Ag}$  is illustrated in **Figure 4n**. It is noted that  $\text{Fe}_3\text{O}_4\text{-Ag}$ , which have the magnetic core without the coating of silica shell, have more simple structure than that of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ . In addition, they have the size of around 50 nm which is much smaller than that of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ .

In this type of “core-shell” nanocomposites of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$ , the steps of forming nanocomposites can be checked by using Fourier-Transform Infrared (FTIR) spectroscopy. In the **Figure 5**, one can see the FTIR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and (c)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  functionalized with amino group  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ . All the spectra show the absorption peaks at  $426\text{ cm}^{-1}$  and  $530\text{ cm}^{-1}$  of F-O vibration corresponded to the magnetic core, where peak at  $530\text{ cm}^{-1}$  is broaden and shifted to  $537\text{ cm}^{-1}$  in coated nanoparticles. The peaks at  $1045\text{ cm}^{-1}$  in (b) and (c) can be assigned to stretching vibration of Si-O-Si. The peaks at  $882\text{ cm}^{-1}$ ,  $1087\text{ cm}^{-1}$ ,  $1271\text{ cm}^{-1}$ , and  $2979\text{ cm}^{-1}$  are only observed in  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ , which can be assigned to a twisting vibration of the  $-\text{CH}_2$  group [33, 34], a stretching vibration of C-N [35], a wag vibration of  $-\text{CH}_2$  [33] or a C-N binding vibration [36] and a stretching vibration of  $-\text{CH}_2$  [33, 37, 38], respectively. These indicated that the  $\text{Fe}_3\text{O}_4$  nanoparticles were coated by silica layers, then amino groups were successfully functionalized onto the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles, as schematically shown in right side of the **Figure 5**. In  $\text{Fe}_3\text{O}_4\text{-Ag}$ , the X-ray photoelectron spectroscopy (XPS) results also lead to the same conclusion that the  $\text{Fe}_3\text{O}_4$  magnetic



**Figure 5.** The FTIR spectra of the  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  nanoparticles.

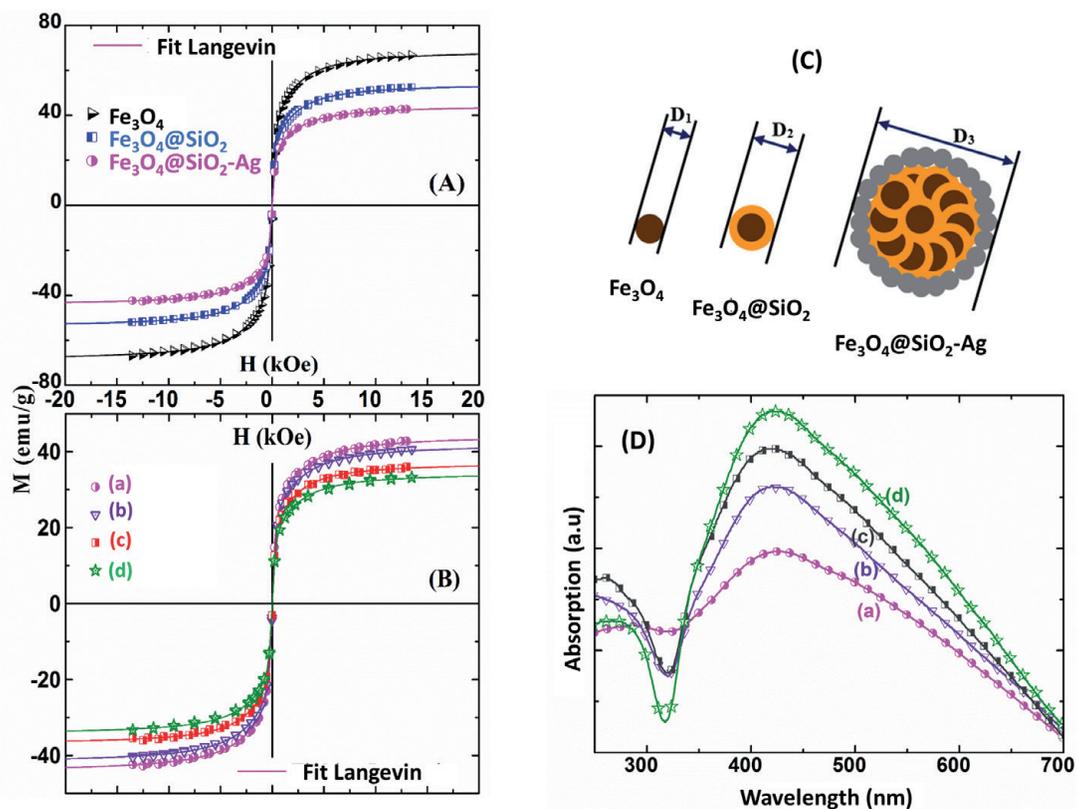


**Figure 6.** Magnetic (i) and optical (ii) properties of  $\text{Fe}_3\text{O}_4/\text{Ag-4ATP}@SiO_2$ .

nanoparticles were successfully functionalized by  $\text{NH}_2$  amino groups, then the Ag reduced on those to form multifunctional silver nanoparticles [30].

In order to confirm the multifunctionalities of nanocomposites, the magnetic and the optical properties of the final product were measured in comparing with those of the individual magnetic and silver nanoparticles. **Figure 6(i)** shows the magnetization curves of  $\text{Fe}_3\text{O}_4$  nanoparticles in (a),  $\text{Fe}_3\text{O}_4/\text{Ag-4ATP}/\text{SiO}_2$  with different ratio of Fe/Ag in (b) and (c), respectively. Both of them show the superparamagnetic properties without the coercivity and applicable in biomedical applications. The magnetization of the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles has highest value of around 64 emu/g under the external field of 12 kOe. The magnetization decreases when the magnetic nanoparticles were combined with non-magnetic Ag-4ATP nanoparticles. When the ratio of Fe/Ag decreases from (b) to (c), the magnetization also decreases, indicating that the combination nanoparticles have magnetic properties as expected from the combined structure and can be used in biomedical applications. The inset shows the ability to be applied in magnetic separation of the multifunctional nanoparticles after 5 min. In parallel, the absorption spectra of  $\text{Fe}_3\text{O}_4$ , Ag, Ag-4ATP and  $\text{Fe}_3\text{O}_4/\text{Ag-4ATP}/\text{SiO}_2$  nanoparticles were shown in **Figure 6(ii)**. The absorption peak of silver nanoparticles was broadened and shifted from 405 nm to 420 nm and then 426 nm, when the silver nanoparticles were functionalized with 4ATP then put into the combination of  $\text{Fe}_3\text{O}_4$  and Ag-4ATP nanoparticles inside the silica matrix.

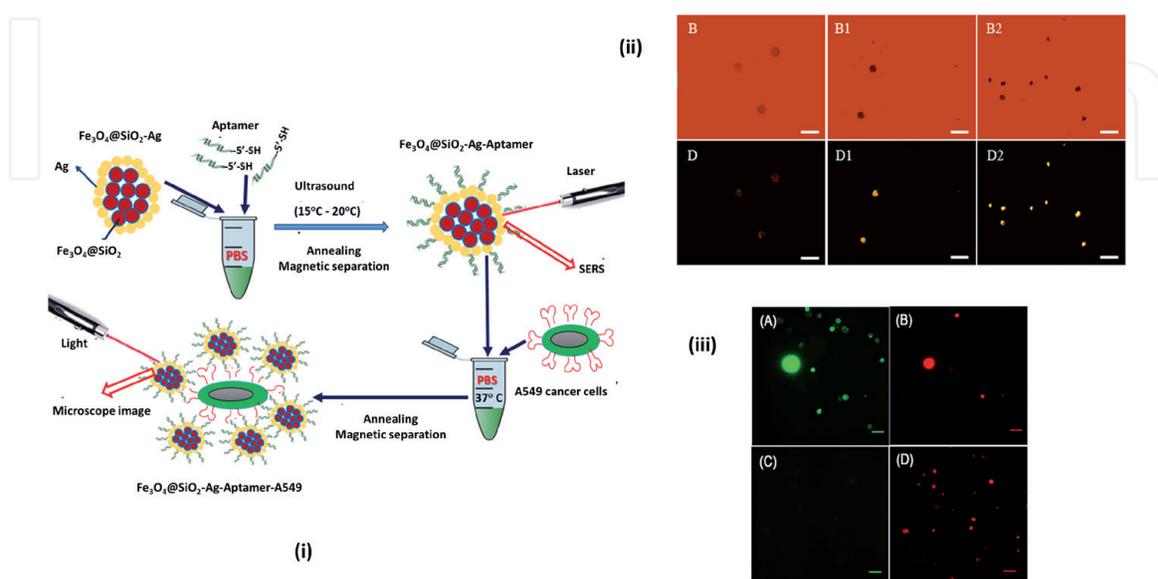
The  $\text{Fe}_3\text{O}_4$  nanoparticles do not show the similar absorption peaks in the spectrum. The combination nanoparticles then have the plasmonic properties same as the individual Ag nanoparticles themselves, therefore, they can be used in labeling or diagnostic applications based on the plasmonic properties.



**Figure 7.** (A) Magnetization curves of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$  nanoparticles (B) magnetization curves of  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$  nanoparticles with various ratios of Fe/Ag (c) schematic structure of from the core to the shell of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$  nanoparticles (D) absorption spectra of  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$  nanoparticles with various ratios of Fe/Ag.

The  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  “core-shell” multifunctional silver nanoparticles also show both the superparamagnetic and the plasmonic properties, which change when the Fe/Ag ratio changes [29]. **Figure 7A** shows the magnetization curves of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  nanoparticles under the external field. The magnetization of those decreases when the core  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were coated with silica, then silver nanoparticles was reduced onto the surface of coated nanoparticles, as schematically shows in **Figure 7C**. When the amount of reduced silver nanoparticles on the surface of coated nanoparticles increases, or, in another words, the ratio of Fe/Ag of the core-shell nanoparticles decreases, the magnetization of those decreases accordingly as shown in **Figure 7B**. In this figure, (a), (b), (c) and (d) denote the magnetization curves of the nanoparticles with the decrease of the ratio Fe/Ag. In consistence, the absorption spectra of those exhibit the increase in the absorption peak of silver nanoparticles as can be seen in **Figure 7D**. Those results also imply that the core-shell nanoparticles combine the plasmonic and magnetic properties, which can be used together in the applications of the multifunctional silver nanoparticles. The  $\text{Fe}_3\text{O}_4\text{-Ag}$  composites, as expected, show the same picture [30, 31].

The plasmonic-magnetic nanoparticles can be applied in the applications which can use both the magnetic and plasmonic properties of them. In order to check the applicability in biomedical applications, the multifunctional silver nanoparticles were or surface modified with aptamer then were checked the modification by SERS using their surface plasmon resonance behavior. The aptamer can help the nanoparticles to conjugate with the cells, such as A549 lung cancer cells. Using the magnetic separator and the superparamagnetic properties of the multifunctional nanoparticles, the cells which conjugated with the nanoparticles can be separated from original sample then can be seen under microscope. This procedure is illustrated in **Figure 8(i)**. The results of using  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  “core-shell” multifunctional nanoparticles to label the lung cancer cells A549 are shown in **Figure 8(ii)**. In this Figure, patterns B and D are bright-field and dark-field microscopy images of only A549 cancer cells. Patterns B1, D1 and B2, D2 show the bright-field and dark-field images of the A549 cells conjugated with  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  after annealing in 1 h and 2 h, respectively. It can be seen that the cells were observed much more clearly.



**Figure 8.**

(i) Schematic procedure of the application of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  nanoparticles (ii) bright (B) and dark (D) field images of A549 cancer cells with and without conjugation with  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Ag}$  nanoparticles (iii) isolation and detection CD34<sup>+</sup> stem cells using  $\text{Fe}_3\text{O}_4\text{-Ag}$  nanoparticles.

The multifunctional silver nanoparticles can also be functionalized with amino groups then connect to antibody of cells through the bridge of EDC catalyst to form  $\text{Fe}_3\text{O}_4\text{-Ag-antiCD34}$  nanoparticles [31]. **Figure 8(iii)** shows the microscopic images of the FITC labeled CD45+ cells (A), the EDC labeled CD34+ cells in the bone marrow samples before being conjugated with the  $\text{Fe}_3\text{O}_4\text{-Ag-antiCD34}$  nanoparticles. Bone marrow is a source of blood stem cells, which contain around 10 million cells/mL, wherein includes 65% CD45+ leukemia cells and 5–7% CD34+ stem cells. After being conjugated with  $\text{Fe}_3\text{O}_4\text{-Ag-antiCD34}$ , (C) shows that no green luminescent CD45+ cells were observed, and (D) shows that only the red luminescent CD34+ cells were isolated from the bone marrow samples. The EDC catalyst enhanced the reaction of the amino group on the surface of  $\text{Fe}_3\text{O}_4\text{-Ag}$  with the carboxyl group of the EDC-antiCD34 antibody molecules [39]. The conjugated product,  $\text{Fe}_3\text{O}_4\text{-Ag-antiCD34}$  nanoparticles, emits red light under the excitation of 494 nm incident light. The fluorescence basically originated from the EDC-fluorophore of the EDC-antiCD34 molecules. By using similar methods, multifunctional silver nanoparticles can be used in many applications, which need the plasmonic and magnetic properties together.

### 3. Conclusion

The chapter told a story about the synthesis and applying the silver multifunctional nanoparticles in the combination of individual silver nanoparticles and  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles. They can be combined in a silica matrix, or the core magnetic nanoparticles were functionalized with various methods and creating the outer shell with silver nanoparticles in order to have the combination of plasmonic and magnetic properties both in once. They can be used similar as individual silver nanoparticles, or individual magnetic nanoparticles with those applications. But the most important of the new type of these materials is that they can use both the properties together in order to enhance the number of possible applications, especially in biomedicine. It is expected that the multifunctionality of nanoparticles will lead them to be used for nano-biosensors and manufacturing nano-devices.

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