Size-controlled syntheses and hydrophilic surface modification of Fe₃O₄, Ag, and Fe₃O₄/Ag heterodimer nanocrystals[†]

Xiaomin Li,^a Honglei Si,^a Jin Zhong Niu,^a Huaibin Shen,^a Changhua Zhou,^a Hang Yuan,^b Hongzhe Wang,^{*a} Lan Ma*^b and Lin Song Li*^a

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High-quality, monodisperse, and size-controlled Fe₃O₄, Ag, and bifunctional Fe₃O₄/Ag heterodimer nanocrystals (NCs) have been synthesized successfully. In the synthesis of Fe_3O_4 NCs, dodecanol was chosen as the substitute of 1,2-hexadecanediol and "size control" was achieved by simply adjusting the proportion among the ligands instead of utilizing seed-mediated growth. In the synthesis of Ag NCs, organometallic silver acetylacetonate (Agacac) was used as precursors and tunable particle size could be easily obtained by adjusting the reaction temperatures. By using different sized Fe₃O₄ NCs as seeds, Fe_3O_4/Ag heterodimer NCs with particle sizes tuned from 5 to 16 nm for Fe_3O_4 and 4 to 8 nm for Ag were successfully synthesized and superparamagnetism were maintained. We found that the size of Ag attached on the Fe_3O_4 NCs relied on the size of Fe_3O_4 seed. UV-vis absorption spectra and TEM investigations revealed that the bigger the Fe_3O_4 NCs seed used, the bigger the Ag NCs that were obtained from the heterodimer NCs. In addition, we demonstrated that all of these NCs were successfully transferred into water by surface modification with biocompatible carboxylic acid groups, which made them meet the basic requirement for biolabeling and biomedical applications.

Introduction

Nano-sized materials have attracted a great deal of attention from researchers in various areas for their fundamental size- and shapedependent novel magnetic, optical, and other unique properties.¹⁻³ Magnetic nanocrystals (NCs) such as iron oxide, manganese oxide, and noble metal NCs such as Au and Ag are especially important for their potential applications in fields of high-density magnetic storage, magnetic resonance imaging (MRI), molecular adsorption, and catalysts, chemical sensing, biological applications.⁴⁻¹⁷ Recently, various heterostructured NCs composed of noble metal and magnetic oxide have been synthesized, for the purpose of merging the properties of different materials and creating the possibility for new multifunctional applications.¹⁸⁻²² For example, live cells can be manipulated using an applied magnetic field and imaging with two-photon fluorescence microscopy under assistance of such multifunctional heterostructured NCs.²⁰ In addition, the metal-magnetic multifunctional heterostructured NCs could also be used in multimodal biological detections: noble metals for chip-based biosensing and magnetic resonance contrast effects of superparamagnetism.²²

There are many methods for the synthesis of monodisperse magnetic nanocrystals.23-25 Among them, the most successful and common strategy is the thermolysis of organometallic precursors in complex organic solvent systems reported by Sun et al.24 Take

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Fe₃O₄ NCs as an example: 4 nm nearly monodisperse Fe₃O₄ NCs could be synthesized by using ferric acetylacetonate as the precursor in the presence of 1,2-hexadecanediol, oleylamine, and oleic acid in phenol ether. By the introduction of seed-mediated growth method, larger monodisperse magnetite nanoparticles of up to 20 nm in diameter could be synthesized. For the synthesis of noble metal NCs, water-soluble noble salt precursors were commonly used. For example, Ag NCs were synthesized by thermal decomposition silver nitrate in octadecylamine (ODA) has been reported by Li group.26 Based on the very successful syntheses of magnetic and noble metal NCs, synthesis of magnetic noble metal heterodimer NCs was well developed as well. As far as we know, the investigations on magnetic metal heterodimer NCs are mainly focused on the morphology-controlled syntheses, the particle size related effects between the magnetic and noble metal NCs on the synthesis of heterodimer has rarely been discussed.

Here we report on the size-controlled syntheses of monodisperse Fe_3O_4 (4–20 nm), Ag (4–9 nm), and bifunctional Fe_3O_4/Ag heterodimer NCs. In the synthesis of Fe₃O₄ NCs, dodecanol was chosen as the substitute of 1,2-hexadecanediol and "sizecontrol" was achieved by simply adjusting the ratio of different ligands instead of seed-mediated growth. For the synthesis of Ag NCs, organometallic silver acetylacetonate (Agacac) was chosen as precursor and particle size could be tuned easily by adjusting the reaction temperatures. By using differently sized Fe₃O₄ NCs as seeds, Fe₃O₄/Ag heterodimer NCs with particle sizes tuned from 5 to 16 nm for Fe₃O₄ and 4 to 8 nm for Ag were successfully synthesized and the superparamagnetism was maintained. In our synthesis, we found that the size of Fe₃O₄ seed determined the size of attached Ag NCs of the herterodimer. UV-vis absorption spectra and TEM investigations revealed that the bigger the Fe₃O₄

^aKey Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng, 475004, P. R. China. E-mail: whz@henu.edu.cn, lsli@henu.edu.cn

^bGraduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, P. R. China. E-mail: malan@sz.tsinghua.edu.cn

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NCs seed used, the bigger the Ag NCs obtained for the final heterodimer NCs. Furthermore, size-distribution, magnetization behaviors, and optical properties of the as-prepared Fe₃O₄/Ag heterodimer NCs were investigated in detail. In order to make those NCs suitable for biomedical applications, surface modification with biocompatible carboxylic acid group was carried out and Fe₃O₄, Ag, and Fe₃O₄/Ag were all transferred into water successfully. This makes such NCs suitable for further conjunction with biomolecules, such as antibodies, proteins, peptides, and nucleic acids and can serve as new building blocks for the next generation of multimodal biomedical applications including bioseparation, sensing, and imaging.

Experimental

Chemicals

Oleic acid (OA, 90%), oleylamine (OAM, 70%), 1-octadecene (ODE, 90%), and iron acetylacetonate (Fe(acac)₃, 97%) were obtained from Aldrich. 2,4-Pentanedione (98%), triethylamine (99%), hexanes (analytical grade), methanol (analytical grade), ethanol (analytical grade), and acetone (analytical grade) were purchased from Tianjin Chemical Reagents Co. Ltd. Silver nitrate (AgNO₃, 99.8%) were obtained from Beijing Chemical Reagents Co. Ltd. All the chemicals were used as received without any further purification.

Typical synthesis of Fe₃O₄ NCs

For the synthesis of 12 nm Fe₃O₄ NCs, Fe(acac)₃ (0.3532 g, 1.0 mmol) was mixed with ODE (10 mL), OA (0.2825 g, 1.0 mmol), OAM (0.8025 g, 3.0 mmol) and dodecanol (0.5590 g, 3.0 mmol), then heated to 270 °C under stirring and nitrogen flow for an hour. Ultimately, a clear black solution containing Fe₃O₄ NCs was obtained and the resulting NCs were purified with acetone, methanol and hexanes. Fe₃O₄ NCs with different particle sizes of 4 nm, 15 nm, and 20 nm can also be synthesized, with different reactants ratios of Fe(acac)₃ : OA : OAM : dodecanol equal to 0.5:2:3:3, 2:1:3:3, 2:0.5:3:3, respectively.

Typical synthesis of Ag NCs

For the synthesis of 9 nm Ag NCs, Agacac (0.0207 g, 0.1 mmol) was mixed with 5 mL OAM and heated to 200 °C under stirring and nitrogen flow for half an hour. Finally, a clear dark brown solution containing Ag NCs was obtained and the resulting NCs were purified using the same procedure as Fe_3O_4 NCs. The strategies for the synthesis of 4 nm Ag NCs were the same but the reaction temperature was set to 110 °C.

Typical synthesis of Fe₃O₄/Ag heterodimer NCs

For the synthesis of 12 nm Fe₃O₄-6 nm Ag heterodimer NCs, acetone (10 mL) was added to 3.5 mL (~0.1 mmol) reaction solvent of Fe₃O₄ NCs. A black solid was precipitated and collected by centrifugation and then redispersed in a mixture of 0.1 mmol Agacac (0.0207 g) and 5 mL OAM. The reaction mixture was heated to 110 °C and maintained 5 h under stirring and nitrogen flow. The initial black solution turned to yellowish brown, which meant the formation of Fe₃O₄/Ag heterodimer NCs. Upon cooling

to room temperature, acetone (10 mL) was added to the reaction mixture to precipitate the heterodimer NCs. A dark yellowish brown solid was collected by centrifugation at 16 000 rpm. The final product could be easily redispersed in hexanes or toluene for storage. The strategies of synthesis of 15 nm Fe₃O₄/7.5 nm Ag and 5.5 nm Fe₃O₄/4.5 nm Ag heterodimer NCs are the same as the synthesis of 12 nm Fe₃O₄/6 nm Ag heterodimer NCs with different sizes of Fe₃O₄ being used as seeds.

Characterization

Transmission electron microscopy (TEM) studies were performed using a JEOL JEM-100CX II microscope with an accelerating voltage of 100 kV. High resolution transmission electron microscopy (HRTEM) observations were performed with a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV, accompanied by selected area electron diffraction (SAED) studies. TEM samples were prepared by placing a drop of the nanocrystal solution onto a carbon coated copper grid. Phase determination of the products was carried out by a Philips X'Pert Pro X-ray diffractometer using Cu-K α radiation ($\lambda = 1.54$ Å). Room temperature UV-vis absorption and PL spectra were measured with an Ocean Optics spectrophotometer (mode PC2000-ISA). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet AVATAR 360 spectrometer. X-Ray photoelectron spectrum (XPS) measurements were performed on an AXIS ULTRA X-ray photoelectron spectroscope, using monochromatised Al K α radiation with an anode voltage of 15 kV and emission current of 3 mA. The magnetic measurements were performed with a Lake Shore 7410 at room temperature.

Results and discussion

Synthesis of Fe₃O₄ NCs

The synthesis of magnetic NCs with controlled sizes has long been of scientific and technological interest because of their broad applications. For all applications, synthesis techniques which provide precise control over NCs grain sizes and size distributions are crucial in that the particles have uniform physical and chemical properties. However, the preparation of magnetic NCs with the desired size and acceptable size distribution without particle aggregation has consistently been aspired after. Recently, we reported a chemical synthesis of manganese oxide NCs in multi-ligands systems (the mixture of oleylamine, oleic acid, and dodecanol).²⁵ That was the first time to use inexpensive dodecanol as the substitute of expensive 1,2-hexadecanediol. Here we successfully extended this approach to synthesize high quality Fe_3O_4 NCs and the size of Fe_3O_4 NCs can be well controlled from 4 to 20 nm.

In the multi-ligands system for the synthesis of Fe_3O_4 NCs, it was found that all reaction conditions include reactant ratios and temperatures have important influences on size and size distribution of as-synthesized NCs (Fig. S1, ESI[†]) in the multiligands system we chose for the synthesis of Fe_3O_4 NCs. Take the amount of OA for example: when the molar ratio of $Fe(acac)_3$: OA : OAM : dodecanol was set to 1:0.5:3:3, 1:1:3:3, and 1:2:3:3, monodisperse 16 nm, 12 nm, and 5 nm Fe_3O_4 NCs were synthesized, respectively (Fig. S1). That is to say, as the

concentration of OA in ODE increased, the particle size of the monodisperse NCs decreased systematically. This might originate from excessive OA attach on the surface of the Fe₃O₄ NCs, which restricted continuous growth of the NCs. As shown in Fig. S1, we did a series of control experiments to investigate the relationships between size, size distribution of the Fe₃O₄ NCs, and the reactant ratios (or temperatures). It was found that the amounts of OA and Fe(acac)₃ played important roles for the control of NCs sizes. Furthermore, it was found that OAM, the same as OA, could also influence the size of the as-synthesized NCs. As the concentration of OAM in ODE increased, the size of the monodisperse NCs decreased systematically. But there was a point quite different from OA, when the concentration of OAM decreased to less than 0.3 mmol per 10 mL ODE, only NCs with broad size distribution, or lumpish particles aggregation were obtained. Dodecanol was used as reducing agent, which may not have an important effect on particle size and size distribution. So, an excess amount of dodecanol was used in our synthesis. Reaction temperature, another parameter in our synthesis, was set at 270 °C. If the temperature was set higher or lower than 270 °C, the synthesized NCs with broad size distribution was obtained. To sum up, the amounts of OA and Fe(acac)₃ played most important roles in the control of NCs sizes. So, the size-control of Fe₃O₄ NCs was achieved mainly by adjusting the amounts of OA and Fe(acac)₃ here.

Conducted by the method mentioned above, monodisperse Fe_3O_4 NCs with sizes in 4–20 nm range were synthesized successfully. Typical transmission electron microscopy (TEM) images of the as-synthesized NCs with average diameters of 20 nm, 15 nm, 12 nm, and 4 nm are presented in Fig. 1A–D, respectively. As can be seen from the TEM images, the NCs generally self-assembled into a monolayer on the carbon substrate of the TEM grid without the formation of aggregates. The as-prepared Fe_3O_4 NCs could be easily dispersed in various organic solvents, such as hexanes, chloroform, or toluene, and shows ferrofluidic behavior under an



Fig. 1 TEM images of as-synthesized Fe_3O_4 NCs: (A) 20 nm, (B) 15 nm, (C) 12 nm, and (D) 4 nm. (E) Selected area electron diffraction (SAED) pattern acquired from (A). (F) High-resolution TEM image of a single 20 nm Fe_3O_4 NCs.

external magnetic field (Fig. S2B, ESI[†]). The selected area electron diffraction (SAED) patterns showed six distinct rings and the calculated d-spacings matched well with interplanar distances of face-centered cubic (fcc) Fe₃O₄ (Fig. 1E). The structure of a single nanocrystal was studied by high-resolution TEM (HRTEM). Fig. 1F shows the HRTEM image of an isolated 20 nm Fe₃O₄ NCs. The clear lattice fringes indicate that the particle is a single crystal.²⁷ The distance between two adjacent planes is 2.53 Å, which corresponds to the (311) plane of the fcc structured Fe₃O₄.

The X-ray diffraction (XRD) study shows that the assynthesized Fe_3O_4 NCs have a fcc structure and the peak width of the diffraction pattern is size dependent. Fig. 2 depicts the XRD patterns of as-prepared Fe_3O_4 NCs with different sizes. The positions and relative intensity of all diffraction peaks match well with (220), (311), (400), (422), (511), (440), and (533) planes of standard Fe_3O_4 powder diffraction data (JCPDS, 85–1436), respectively. The sizes of Fe_3O_4 NCs estimated from Scherrer's formula are consistent with that determined by statistical analysis based on TEM images.



Fig. 2 X-Ray diffraction patterns of Fe_3O_4 NCs with various sizes: 20 nm, 15 nm, 12 nm, and 4 nm from top to bottom, respectively.

In order to make as-prepared Fe_3O_4 NCs suitable for biomedical applications, surface modification is required for the transfer of hydrophobic products to water. Following the surface modification method reported by our group recently,²⁸ the as-prepared Fe_3O_4 NCs were further transferred into water successfully (Fig. S2, ESI†). The obtained water-soluble NCs was modified by biocompatible carboxylic acid groups which were ideal for binding to biomolecules, such as antibodies, proteins, peptides, and nucleic acids.

Synthesis of Ag NCs

The synthesis of Ag NCs was conducted by one-pot method, and Agacac was introduced to synthesize Ag NCs. OAM was chosen for the preparation of Ag NCs because it can be used not only as a surface-capping agent, but also as a reducing agent. In a typical synthesis, a mixture of 0.1 mmol Agacac and 5 mL OAM was add into 25 mL beaker and then heated to 200 °C with stirring under a nitrogen flow. The color of the solution changed from colorless to light yellow and finally became dark brown, indicating the formation of Ag NCs. By this approach, Ag NCs with tunable sizes were easily synthesized by adjusting the reaction temperature. Fig. 3A and B show typical TEM images of Ag NCs with average diameters of 4 and 9 nm, which were prepared at 110 °C and 200 °C, respectively. It can be seen that the Ag particles have a narrow size distribution and the sizes of particles are influenced by the reaction temperature forcefully. Different from the synthesis



Fig. 3 TEM images of Ag NCs synthesized using Agacac as precursor at 110 $^{\circ}$ C (A) and 200 $^{\circ}$ C (B). (C) SAED pattern acquired from (B). (D) High-resolution TEM image of a 9 nm Ag NCs.

of Fe₃O₄ NCs, the ratio among the reactants has an inconspicuous influence on the size of Ag NCs. As can be seen in Fig. S3,† B and D are TEM images of aliquots taken at 30 min and 5 h when the reaction temperature was set at 200 °C. It was found that by extending the reaction time the sizes of the particles were nearly the same and the size distribution did not show any change. So the size-control of Ag NCs discussed here was achieved just by adjusting the reaction temperatures.

The phase identification of as-synthesized Ag NCs was obtained from electron diffraction and X-ray diffraction. Fig. 3C is a SAED pattern acquired from 9 nm NCs assembly. Table 1 displays the measured lattice spacing based on the rings in the diffraction pattern and compares them to the known lattice spacing for bulk Ag along with their respective (*hkl*) indexes (JCPDS, 04–0783). The XRD patterns of as-synthesized Ag NCs are shown in Fig. S4.† From the XRD pattern, the peaks at 38.2°, 44.3°, 64.4°, and 77.5° correspond to the (111), (200), (220), and (311) reflections of fcc structured Ag, which is in accordance with the result of SAED pattern. The inset shows the photographs of as-prepared Ag NCs before and after transfer into water by surface modification (Fig. S4). The HRTEM images reveal the highly crystalline nature with an interplanar spacing of 2.04 Å, which corresponding to (200) planes of fcc structured Ag NCs (Fig. 3D).

Synthesis of Fe₃O₄/Ag heterodimer NCs

On the base of the synthesis of size-controlled Fe_3O_4 and Ag NCs, we tried our best to extend the work to synthesize Fe_3O_4/Ag heterodimer NCs and achieved a great success.

In a typical synthesis, the Fe_3O_4 NCs of a desired size were first synthesized as described above. Heterodimer NCs were then formed by reducing Agacac in OAM under the presence of pre-synthesized Fe_3O_4 seed NCs. TEM investigations of as-

Table 1 Measured lattice spacing, d (Å), based on the rings in Fig. 3C and standard atomic spacing for Ag along with their respective *hkl* indexes from the PCPDFWIN database.

	Ring					
	1	2	3	4	5	6
d/Å Ag/Å hkl	2.35 2.36 111	2.05 2.04 200	1.47 1.45 220	1.25 1.23 311	0.92 0.94/0.91 331/420	0.82 0.83 422

prepared Fe₃O₄/Ag heterodimer NCs confirmed that our synthetic strategy is effective. By using differently sized Fe₃O₄ NCs as seeds, Fe_3O_4/Ag heterodimer NCs with particle sizes tunable from 5 to 16 nm for Fe₃O₄ and 4 to 8 nm for Ag were successfully synthesized. Fig. 4A and B shows TEM images of Fe₃O₄/Ag heterodimer NCs with Fe_3O_4 at around 16 nm and 5 nm, respectively, and Ag at around 8 nm and 4 nm, respectively. In the TEM images, the Ag particles often appear black and Fe₃O₄ are light colored, which is partly because Ag has a higher electron density and allows fewer electrons to transmit. The SAED pattern (Fig. 4C) shows a few distinct diffraction rings and their calculated d-spacings match well with the major d-spacings of fcc structured Fe₃O₄ and fcc structured Ag. Fig. 4D is a typical HRTEM image of a heterodimer NCs with Fe₃O₄ at 5 nm and Ag at 4 nm. The distance between two adjacent planes in Fe_3O_4 is measured to be 2.53 Å, corresponding to (111) planes in the fcc structured Fe_3O_4 and that in Ag is 2.04 Å, resulting from a group of (200) planes in fcc structured Ag. More HRTEM images for different sized heterodimer NCs are shown in Fig. S5, ESI[†].



Fig. 4 TEM images of 16 nm Fe₃O₄/8 nm Ag (A) and 5 nm Fe₃O₄/4 nm Ag (B) heterodimer NCs. (C) SAED pattern acquired from A (the rings signed with black and red words correspond to Fe₃O₄ and Ag, respectively). (D) High-resolution TEM image of a single 5 nm Fe₃O₄/4 nm Ag heterodimer NCs.

The crystalline nature of the heterodimer NCs can also be characterized by XRD investigations. Fig. 5A shows representative XRD patterns of the heterodimer NCs with Fe₃O₄ at around 16 nm (5 nm) and Ag at 8 nm (4 nm). The positions and relative intensity of all diffraction peaks match well with standard Fe₃O₄ and Ag powder diffraction data, indicating that the synthesis yields fcc structured Fe_3O_4 and fcc structured Ag. It can be seen that the peaks of minor particle-sized heterodimers (red curve) are broader than the peaks of bigger heterodimers (green curve). To obtain more information on the components of heterodimer NCs, X-ray photoelectron spectroscopy (XPS) was introduced. As shown in Fig. 6, we examined the Fe 2p, O 1s, and Ag 3d of the sample, respectively. The Fe 2p core levels are split into $2p_{1/2}$ and $2p_{3/2}$ components, which is due to the spin-orbit coupling (Fig. 6B). It can be seen that the shake-up satellite signal at 719.0 eV is very weak (almost disappeared), which further proves that the product combined with Ag NCs is Fe_3O_4 rather than γ -Fe₂O₃.²⁹ The O 1s spectrum is shown in Fig. 6C. The observed peak is asymmetric with a shoulder on the higher binding energy side, indicating more phases of O element. There maybe three phases of O element contribute to the O 1s spectrum: O element in Fe₃O₄



Fig. 5 (A) X-Ray diffraction patterns of 16 nm $Fe_3O_4/8$ nm Ag and 5 nm $Fe_3O_4/4$ nm Ag heterodimer NCs. The bottom lines represent the XRD patterns of fcc structured of bulk Fe_3O_4 (black) and Ag (blue). (B) Hysteresis loops of 5 nm Fe_3O_4 , 5 nm $Fe_3O_4/4$ nm Ag, and 16 nm $Fe_3O_4/8$ nm Ag heterodimer NCs at room temperature.



Fig. 6 XPS survey, Fe 2p, O 1s, and Ag 3d spectra of 5 nm Fe $_3O_4/4$ nm Ag heterodimer NCs.

NCs, O element in organic ligand, and contamination oxygen from air. The binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ for Ag NCs were 373 eV and 367 eV with a peak splitting of 6 eV, which was consistent with the standard reference XPS spectrum of Ag.

The interaction between the nanoscale Ag and Fe₃O₄ leads to a change of magnetization behavior of the Fe₃O₄ NCs. Fig. 5B shows the hysteresis loops of 5 nm Fe_3O_4 NCs, 5 nm $Fe_3O_4/4$ nm Ag, and 16 nm Fe₃O₄/8 nm Ag heterodimer NCs measured at room temperature. It can be seen that 5 nm Fe₃O₄ NCs were superparamagnetic and magnetization (M) value was ~24 emu g⁻¹ at an applied field (H) of 18 kOe, which was lower than the saturation magnetization value of bulk magnetite (~90 emu g⁻¹). Like 5 nm Fe₃O₄ NCs, the 5 nm Fe₃O₄/4 nm Ag heterodimer NCs were superparamagnetic too. But the magnetization value of 5 nm $Fe_3O_4/4$ nm Ag heterodimer NCs was ~10 emu g⁻¹ which was much smaller than that of 5 nm Fe₃O₄ NCs alone. In addition, we compared the magnetization values of different size of Fe₃O₄/Ag heterodimer NCs and found the magnetization value increased with the size increase of Fe_3O_4/Ag heterodimer NCs at same applied field (H) (Fig. 5B).

The combination of Fe₃O₄ and Ag can also lead to the change of optical properties of the Ag NCs. In order to investigate the influence of Fe₃O₄ NCs on the heterodimer NCs, a series of experiments were performed with and without the participation of Fe₃O₄. Fig. 7B shows the UV-vis spectra of the results. Once Ag NC attached to Fe_3O_4 , it showed a broader absorption feature at 414 nm (green line), a ~5 nm red-shift from the absorption feature compare to pure Ag NCs which was prepared at the same reaction conditions without Fe₃O₄. Comparing the absorption change of different sized of Ag NCs (Fig. 7A), it was found that the maxima absorption center was proportional to the size of Ag NCs which was consistent with the literature.³⁰ So we conclude that the "redshift" after the combination with Fe₃O₄ may result from the bigger size of Ag NCs that were obtained when integrated with Fe₃O₄. To further make it clear how Fe₃O₄ NCs influence the growth of Ag NCs, the average particle diameters of the heterodimer NCs were estimated by statistical analysis of the TEM images and the results were shown in Fig. 8. It was found that when integrated with Fe₃O₄, the average particle diameter of Ag NCs was greater than the Ag NCs from synthesis without Fe₃O₄. The result is consistent with inference obtained from UV-vis spectra shown in Fig. 7. With the sizes of Fe_3O_4 change from 16 nm to 12 nm and 5 nm, the sizes of combined Ag NCs change from 8 nm to 6 nm and 4 nm, respectively, as shown in Fig. 8A-E. That is to say, the bigger Fe₃O₄ NCs were used the heterodimer NCs with the bigger Ag NCs were obtained.



Fig. 7 UV-vis absorption spectra of Ag NCs with different sizes (A) and $16 \text{ nm Fe}_3O_4/8 \text{ nm Ag heterodimer NCs (B)}$.



Fig. 8 TEM images and particle size distribution analysis of the typical samples of 16 nm $Fe_3O_4/8$ nm Ag (A, B), 12 nm $Fe_3O_4/6$ nm Ag (C, D), and 5 nm $Fe_3O_4/4$ nm Ag (E, F) heterodimer NCs.

The heterodimer NCs were capped with a hydrophobic layer, such that they were soluble in organic nonpolar solvents (such as hexanes, toluene and chloroform). In order to make these NCs useful for biological applications, phase transfer experiments were conducted, and the NCs were finally rendered water-soluble. The phase transfer experiments and results are shown in Fig. S6, ESI[†]. The obtained water-solubility NCs were modified by biocompatible carboxylic acid groups which were ideal for conjugating with biomolecules, such as antibodies, proteins, peptides, and nucleic acids. With such high water-solubility and biocompatibility, the as-prepared NCs potentially can serve as a new nanoplatform technology for the next generation multimodal biomedical applications including bioseparation, sensing, and imaging.

Conclusions

In summary, monodisperse size-tuneable Fe₃O₄, Ag, and bifunctional Fe₃O₄/Ag heterodimer NCs have been synthesized with a facile solution route. In the synthesis of Fe₃O₄ NCs, dodecanol was chosen as the substitute of 1,2-hexadecanediol and "sizecontrol" was achieved by simply adjusting the proportion among the multi-ligands without any seed-mediated growth method. In the synthesis of Ag NCs, organometallic silver acetylacetonate (Agacac) was chosen as precursor and tunable sizes were easily obtained by adjusting the reaction temperatures. Under the conductions of the syntheses of Fe_3O_4 and Ag NCs, Fe_3O_4/Ag bifunctional heterodimer NCs with particles sizes tuned from 5 to 16 nm for Fe_3O_4 and 4 to 8 nm for Ag were successfully synthesized. The current synthetic procedure is very simple, lowcost, and highly reproducible. As-prepared hydrophobic Fe₃O₄, Ag and bifunctional Fe_3O_4/Ag heterodimer NCs were successfully transferred into water and modified by carboxylic acid groups which are ideal for conjugating with biomolecules. With such high water-solubility and biocompatibility, the as-prepared NCs provide the potential to serve in many multifunctional biomedical applications, such as multimodal imaging and detection probes.

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