In Situ Transmission Electron Microscopy Observations of the Growth Process of Fe_3O_4 –Ag Nanoparticles

Jing-Hua Liu^{1,2} · Jin-Jun Liu¹ · Qiang Zheng³ · Bao-Ru Bian² · Juan Du^{2,3}

Received: 8 November 2019 / Revised: 7 February 2020 / Published online: 28 April 2020
© The Chinese Society for Metals (CSM) and Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract

The properties of nanocrystals are highly dependent on their morphology, composition and structure. To obtain full control over their properties, the behavior of nanocrystals under external stimuli, such as heat treatment, needs to be understood. Herein, to in situ observe their microstructure and morphology changes, Fe_3O_4 –Ag heterodimers were selected as a model system. Their structural changes after heat treatment were investigated by in situ transmission electron microscopy. A combination of real-time imaging with elemental analysis enabled observation of the transformation of Fe_3O_4 –Ag heterodimers having a loose interface configuration to those with a Janus structure at the atomic scale after heating from room temperature to 600 °C. After incubation at 600 °C for 32 min, two kinds of Janus structures could be seen, including a clear linear interface in the Fe_3O_4 –Ag heterodimers and a semi-crescent-shaped interface between the Ag and Fe_3O_4 nanoparticles (NPs). These dynamic observations provide unique insights into NP growth mechanisms, which are essential for understanding and controlling the structure and morphology of nanoparticles.

Keywords In situ TEM · Fe_3O_4 –Ag heterodimer · Nanoparticle · Janus structure · Interface

1 Introduction

There is a remarkable interest in nanocrystalline metals and alloys due to their excellent strength and unique physical properties. Many types of magnetic metal alloy nanoparticles (NPs) have been explored in the past owing to their interesting practical applications, for example, ultrahigh density recording media [1], permanent nanocomposite magnets

[2–4], drug delivery [5] and biomedical technology sensors [6]. Iron oxide nanoparticles are the most widely researched and commonly used material because of their unique chemical, biological and magnetic properties such as chemical stability, non-toxicity, biocompatibility, high saturation magnetization and high magnetic susceptibility [7–10]. Among all of the iron oxides, it was found that maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) are the most biocompatible, but magnetite (Fe_3O_4) is the most commonly used oxide for biomedical applications [11]. Ag nanoparticles show high electrical conductivity, thermal conductivity, chemical stability, good catalytic activity and enhanced Raman scattering. These properties are beneficial for applications in drug delivery and cancer therapy. Hybrid nanoparticles integrate two or more nanocrystal domains into one single architecture that can have properties not previously present, or that are relatively enhanced versus those of the individual components. These hybrid nanoparticles mainly exist in core–shell and Janus structures. In the core–shell form, the shell can protect the core part from oxidation or prevent the core from agglomeration and help with further functionalization and conjugation to proteins, enzymes, antibodies and anticancer drugs. For the Janus structure, the hybrid nanoparticles connected by the interface and the different components may

Available online at <http://link.springer.com/journal/40195>.

✉ Qiang Zheng
qiangzheng616@hotmail.com

✉ Bao-Ru Bian
bianbr@nimte.ac.cn

✉ Juan Du
jdu-case@hotmail.com

¹ School of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

² CAS Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

³ Institute of Materials, Shanghai University, Shanghai 200444, China

produce a synergetic effect. Performing in situ chemical and structural characterizations are of significant importance for understanding the structure–property relationships and promoting the extensive applications of hybrid nanomaterials [12–15]. Post-annealing specimen characterization is then often employed to determine what has happened to the nanoparticles during the heating stage [16–18]. Such ex situ analysis methods do provide some valuable information, for example, revealing the structure and properties of nanoparticles before and after sintering, but they have no way to deal with temperature-dependent structural and chemical variations, which may not be retained fully after cooling down to room temperature. The in situ characterizations of sintering can also enable real-time observations of compositional and structural evolutions dependent on temperature and time, as demonstrated in some previous reports [19–21]. Fe_3O_4 –Ag heterodimers were selected as a model system for in situ observation of the dynamic growth process during the heating process because of their broad applications in biomedical fields and as a catalyst. The heating process affects the properties of nanocrystals. The hybrid nanomaterials are usually prepared at low temperatures, and their crystallinity is poor, which will affect the magnetic properties of the nanoparticles and their real applications, such as the effect of magnetic therapy. Second, the heating process affects the facets of the nanostructures. The nanocatalysts are typically heated to several hundred degrees to initiate chemical reactions in many catalytic processes, especially for heterogeneous nanocatalysis. Additionally, the catalysis effect depends on different facets of the catalyst. Therefore, in this work, Fe_3O_4 –Ag heterodimers were first synthesized by thermal decomposition, and then their dynamic structure variations and kinetic processes during the heating process were observed in situ by transmission electron microscopy (TEM).

2 Experimental

Hydroxyl iron oxide was dissolved in 1-octadecene, then oleic acid was added, and Ar inert gas was flushed for 20 min in air. After that, the solution was heated to 320 °C at a heating rate of 10 °C min^{−1}, and the dwell time was 60 min. The black product was centrifuged after adding ethanol. The centrifugation process was performed three times, and the product was finally dissolved in hexane. The Fe_3O_4 seed particles were mixed with silver acetate, and both were dissolved in toluene. Then, oleander was added and heated to 70 °C under an argon atmosphere, and the dwell time at 70 °C was 12 h. Finally, the product was kept in toluene for characterization. The in situ imaging of the Fe_3O_4 –Ag growing process was performed in a Tecnai F20 TEM (FEI Ltd., USA) operated at 200 kV, and the beam current density was

10^5 A m^{-2} . All of the recordings were made at a frame rate of five frames per second by using a Gatan Orius 894 camera. To prepare the TEM specimen, the powdered sample was dispersed in alcohol and then dropped onto a carbon film supported on a copper grid. Then, the sample holder was placed on a heating coil made of resistance wire. The thermocouples were connected to the sample holder to monitor the actual temperature. For the in situ TEM observation, the TEM images were recorded throughout the heating process from room temperature to 600 °C. The temperature and how long after the temperature reached the target values were annotated to the TEM images during the in situ TEM observation process. For example, 600 °C–2 min 59 s means that the TEM images were taken at 2 min and 59 s after the temperature reached 600 °C. High-angle annular dark-field-transmission electron microscopy (HAADF-TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED) patterns, fast Fourier transform (FFT) and energy-dispersive spectroscopy (EDS) were applied to characterize the morphology, microstructure, crystal lattice spacing and element distribution of the Fe_3O_4 –Ag NPs.

3 Results and Discussion

3.1 Characterization of Fe_3O_4 –Ag Heterodimers

The TEM images of the synthesized Fe_3O_4 –Ag NPs are shown in Fig. 1a. The obtained Fe_3O_4 –Ag NPs have a good dispersion and spherical morphology, which can be observed in Fig. 1a. After statistical calculation, the size distribution shows that the Fe_3O_4 have a mean size of 11.3 nm with a reasonable standard deviation (σ) of 2.0 nm. There are also unattached Ag NPs beside those attached to the Fe_3O_4 NPs. The mean size of the Ag NPs in the Fe_3O_4 –Ag heterodimers is approximately 3.5 nm, but the unattached small Ag nanoparticles are much smaller than 3.5 nm and will disappear with elongation of the dwell time (reaction time) according to the process of Ostwald ripening (in which larger particles grow at the cost of the smaller ones), as pointed out in Zhang's work [22]. In Ref. [22], by elongating the reaction time from 2 h to 8 h, well-distributed Fe_3O_4 –Ag heterodimeric nanoparticles were obtained, and no unattached Ag NPs were found.

The inset of Fig. 1a is the selected area electron diffraction (SAED) pattern recorded from the Fe_3O_4 –Ag heterodimeric nanoparticles. The SAED patterns show diffraction rings, corresponding to the (200) and (111) crystalline planes of Ag and the (220), (311), (511) and (440) crystalline planes of Fe_3O_4 . Figure 1b gives the HRTEM images of the Fe_3O_4 –Ag heterodimers. The cubic crystal lattice spacing of 0.25 nm and 0.31 nm can be correlated with the standard plane (311) and (220) of Fe_3O_4 [23]. The lattice

Fig. 1 **a** TEM images of the as-synthesized Fe₃O₄-Ag heterodimers, **b** HRTEM images of Fe₃O₄-Ag heterodimers. The insets in **a** and **b** are the SAED patterns for the Fe₃O₄-Ag heterodimers and Fast FFT images for the Ag and Fe₃O₄ nanoparticles, respectively

fringe spacing of 0.21 nm and 0.24 nm displayed in the HRTEM image is consistent with the lattice spacing of the (200) and (111) planes of cubic silver. Additionally, the corresponding fast Fourier transform (FFT) images for the Ag and Fe₃O₄ nanocrystals are shown as insets in Fig. 1b. The results revealed that Fe₃O₄-Ag heterodimers had been successfully synthesized. There are mainly two kinds of interfaces between the Ag and Fe₃O₄ NPs, i.e., the loose interface and the dangling bond interface, because of the mismatch of different crystal lattices and the poor crystallinity of Ag.

3.2 In Situ TEM Observations of the Dynamic Growth of the Fe₃O₄-Ag Heterodimers

Fe₃O₄-Ag heterodimers with free Ag nanoparticles at room temperature resulting from a high Ag/Fe ratio and a shorter reaction time can be seen in Fig. 2a, and they are separately dispersed or connected to the Fe₃O₄ nanoparticles. The inset in Fig. 2a is the statistical analysis of the nanoparticle size distribution of the Fe₃O₄ and Ag, and the specific values can be found in Table 1. In Fig. 2b, the sublimation of Ag nanoparticles that are scattered on the carbon films can be observed during the heating process to 300 °C. When the temperature reached 500 °C, the sublimation of Ag was accelerated as shown in Fig. 2c. The separately scattered Ag nanoparticles completely disappeared, while those connected to the Fe₃O₄ nanoparticles were more stable and tended to become larger. There are two possible reasons for this result. The first is that the separately scattered Ag nanoparticles were completely sublimated. In Ref. [24], the authors pointed out that when the size of the Ag NPs is below 10 nm, the sublimation temperature is lower than 550 °C. In Fig. 2a and b, it

can be seen that some Ag nanoparticles are smaller than 10 nm. Therefore, the sublimation of Ag has happened, according to the conclusions given in Ref. [24]. The other reason for the disappearance of the Ag nanoparticles could be Ostwald ripening, in which smaller Ag nanoparticles disappear, and larger Ag nanoparticles become even larger. This possibility is supported by the increases in the average Ag particle size and the disappearance of the free Ag NPs with smaller particle sizes, as shown in the inset of Fig. 2c and Table 1, and by comparing the data from 300 and 500 °C. The sublimation process occurred in bursts rather than continuously, which is consistent with the results in Ref. [24]. The melting temperature of the nanoparticles has been shown to decrease with decreasing particle size. Additionally, the temperature at which the nanoparticles undergo direct sublimation without melting is lower relative to the bulk materials [25]. When the temperature increased to 600 °C, a few smaller Ag nanoparticles tended to fuse into a larger one, see Fig. 2d. In Fig. 2e, the Ag nanoparticles were completely fused when the temperature was kept at 600 °C for 17 min. In addition, the fusing of Fe₃O₄ nanoparticles is also very serious. As shown in Fig. 2f, the Ag nanoparticles gradually enlarged and tended to form Janus structures with Fe₃O₄ when the temperature rose to 600 °C and dwelled there for 32 min. It was observed that the Ag was absorbed into the Fe₃O₄ particles, and the Fe₃O₄ particles began to fuse.

Table 1 gives the statistical values of the Ag and Fe₃O₄ particles from room temperature (25 °C) to 600 °C. It can be seen that with increasing temperatures, the size of the Fe₃O₄ nanoparticles slightly increases; however, the size of the Ag nanoparticles dramatically increases relative to those at room temperature. This also indicates the dynamic growth

Fig. 2 Selected bright-field TEM images of Fe_3O_4 -Ag heterodimers with free Ag nanoparticles at room temperature (a), at temperatures ranging from 300 to 600 °C (b–f)

Table 1 Statistical particle size of the Ag and Fe_3O_4 NPs from room temperature (25 °C) to 600 °C

	25 °C	300 °C (0 s)	500 °C (0 s)	600 °C (2 min 59 s)
Fe_3O_4 size (nm)	11.3 ± 2.0	11.5 ± 2.3	12.0 ± 2.3	12.1 ± 1.7
Ag size (nm)	3.5 ± 0.5	4.7 ± 0.6	5.3 ± 1.20	6.0 ± 1.0

of Ag nanoparticles and that the Fe_3O_4 nanoparticles are more stable than the Ag nanoparticles.

The morphology and microstructure of Fe_3O_4 -Ag in other regions after dwelling at 600 °C for 32 min were observed, as shown in Fig. 3. Two scenarios can be seen in Fig. 3a: one is that the Fe_3O_4 -Ag has a clear linear interface (red circle), and the other is that the Fe_3O_4 -Ag has a semi-crescent-shaped interface (blue circle). Figure 3b gives the distribution of the elements Fe, Ag and O, in which one oxygen-enriched shell around Fe_3O_4 NPs can be seen, as shown in both red and blue circles. Figure 3c–e gives the individual element distribution for Fe, Ag and O. It can be seen that the Ag and Fe elements have a homogeneous distribution. However, the distribution of the O element is not well distributed, and it is instead enriched for on the outside of the Fe_3O_4 NPs and forms an oxygen-enriched circle on the surface of the Fe_3O_4 NPs.

These different Janus structures between Fe_3O_4 and Ag NPs are ascribed to the differences of the surface/interface energy at different temperatures. Three models have been

proposed to explain the in situ observed structural transformations of the Ag- NiP_x core-shell nanocrystals [14] due to the different ratios of $\gamma_{\text{NiP}_x}/\gamma_{\text{Ag}}$. In this work, the reason why the Fe_3O_4 -Ag heterodimers with a smaller Ag size were initially formed was due to the larger $\gamma_{\text{Fe}_3\text{O}_4}$ compared with that of γ_{Ag} . With increasing temperature, the Ag NPs grew larger and the γ_{Ag} also became larger. The Fe_3O_4 -Ag Janus structure formed, and the ideal form will be a 1:1 ratio of Fe_3O_4 and Ag when γ_{Ag} is equal to $\gamma_{\text{Fe}_3\text{O}_4}$. When γ_{Ag} is larger than $\gamma_{\text{Fe}_3\text{O}_4}$, mixing of Ag and Fe_3O_4 will occur and the Ag will be absorbed into the Fe_3O_4 to lower the total surface energy as shown in the blue circles of Fig. 3a and b.

Figure 4a gives the SAED patterns from a large area of the Fe_3O_4 -Ag nanoparticles after heating at 600 °C for 32 min. The SAED patterns show diffraction rings corresponding to the (200) and (111) crystalline planes of Ag and the (311) and (511) crystalline planes of Fe_3O_4 , respectively. For the Fe_3O_4 -Ag Janus structure with a clear interface shown in Fig. 4b, the HRTEM results showed the three lattice-fringes corresponding to the (200) and the two

Fig. 3 HAADF-TEM image (a) and HAADF-TEM EDS mapping images of Fe, Ag, and O elements (b), and the corresponding elemental maps for Ag (c), Fe (d) and O (e), respectively

Fig. 4 SAED patterns from a large area of the Fe₃O₄-Ag nanoparticles after heating at 600 °C for 32 min (a), HRTEM images of a Fe₃O₄-Ag Janus structure with a clear interface (b) and a Fe₃O₄-Ag Janus structure with a semi-crescent-shaped interface (c). The insets in b and c are FFT images of the Ag and Fe₃O₄ nanoparticles

differently oriented (111) planes of Ag, which means that there are three domains in the Ag NPs. This also proves the dynamic growth of the Ag NPs with increasing temperature, which is consistent with the data in Table 1. The lattice-fringes corresponding to the (400) plane of Fe₃O₄ are also shown in Fig. 4b. The cubic crystal lattice spacing of 0.20 nm and 0.24 nm can be correlated with the standard planes (200) and (111) of Ag. In addition, the lattice fringe spacing of 0.20 nm displayed in the HRTEM image is consistent with the lattice spacing of the (400) plane of Fe₃O₄. The FFT patterns shown as an inset in Fig. 4b further confirm the data of the crystal planes for Ag and Fe₃O₄. For the

Fe₃O₄-Ag Janus structure with a semi-crescent-shaped interface as shown in Fig. 4c, the HRTEM image was taken along the incident beam direction. At the interface, there are no moiré fringes, which come from the overlapped crystals of Ag and Fe₃O₄. A semi-crescent-shape can easily be seen at the Ag and Fe₃O₄ interface. Additionally, the HRTEM results show that there are two lattice-fringes corresponding to it, the (111) crystal plane of Ag and the (311) crystal plane of Fe₃O₄. The lattice fringe spacing of 0.24 nm displayed in the HRTEM image is consistent with the lattice spacing of the (111) plane of Ag. Additionally, the lattice fringe spacing of 0.25 nm displayed in the HRTEM image is

consistent with the lattice spacing of the (311) plane of Ag. The FFT patterns for Ag and Fe_3O_4 further confirm the data of their crystal planes.

4 Conclusion

In summary, in situ TEM observations of the dynamic behaviors of the Fe_3O_4 -Ag heterodimers during heating were conducted in this work. Fe_3O_4 -Ag heterodimers have a loose interface configuration in their original state at room temperature. This kind of hybrid composite shows good stability until 600 °C during the in situ heating process. In situ TEM observations showed a transformation of the Fe_3O_4 -Ag heterodimers having a loose interface configuration at room temperature to a Janus structure at the atomic scale after heating to 600 °C. Additionally, after dwelling at 600 °C for 32 min, two scenarios co-existed. One is the Fe_3O_4 -Ag Janus structure with a clear sharp linear interface, and the other is the Fe_3O_4 -Ag Janus structure with a semi-crescent-shaped interface. Both of the Fe_3O_4 -Ag Janus structures have an oxygen-enriched shell covering the outside of the Fe_3O_4 NPs. These dynamic observations provide unique insights into nanoparticle growth mechanisms, which are important for understanding and controlling the structure and morphology of nanoparticles.

Acknowledgements This work was financially supported by the Zhejiang Provincial Natural Science Foundation of China (No. LD19E010001) and the National Natural Science Foundation of China (Nos. 51771219, 51771095 and 51771220).

References

- [1] S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, *Science* **287**, 1989 (2000)
- [2] C. Rong, H. Zhang, X. Du, J. Zhang, S. Zhang, B. Shen, *J. Appl. Phys.* **96**, 3921 (2004)
- [3] H. Zeng, J. Li, J.P. Liu, Z.L. Wang, S. Sun, *Nature* **420**, 395 (2002)
- [4] W. Yang, W. Lei, Y. Yu, W. Zhu, T.A. George, X.Z. Li, D.J. Sellmyer, S. Sun, *J. Mater. Chem. C* **3**, 7075 (2015)
- [5] C. Xu, Z. Yuan, N. Kohler, J. Kim, M.A. Chung, S. Sun, *J. Am. Chem. Soc.* **131**, 15346 (2009)
- [6] S. Mornet, S. Vasseur, F. Grasset, P. Veverk, G. Goglio, A. Demourgues, J. Portier, E. Pollert, E. Duguet, *Prog. Solid State Chem.* **34**, 237 (2006)
- [7] C. Sun, J.S. Lee, M. Zhang, *Adv. Drug Deliv. Rev.* **60**, 1252 (2008)
- [8] Z. Karimi, L. Karimi, H. Shokrollahi, *Mater. Sci. Eng., C* **33**, 2465 (2013)
- [9] B. Tural, N. Özkan, M. Volkan, *J. Phys. Chem. Solids* **70**, 860 (2009)
- [10] Z.P. Chen, Y. Zhang, S. Zhang, J.G. Xia, J.W. Liu, K. Xu, N. Gu, *Colloids Surf. A* **316**, 210 (2008)
- [11] K. McNamara, S.A.M. Tofail, *Biomedical Applications of Nanomaterials, in Nanomaterials: From Fundamentals to Emergent Applications* (Elsevier, Oxford, 2013)
- [12] A.P. LaGrow, M.R. Ward, D.C. Lloyd, P.L. Gai, E.D. Boyes, *J. Am. Chem. Soc.* **139**, 179 (2017)
- [13] D. Li, Z.L. Wang, Z. Wang, *J. Phys. Chem. C* **121**, 1387 (2017)
- [14] X. Huang, Z. Liu, M.M. Millet, J. Dong, M. Plodine, F. Ding, R. Schlog, M.G. Willinger, *ACS Nano* **12**, 7197 (2018)
- [15] Z. Wei, Z. Zhou, M. Yang, C. Lin, Z. Zhao, D. Huang, Z. Chen, J. Gao, *J. Mater. Chem.* **21**, 16344 (2011)
- [16] Q. Zheng, Z.R. Zhang, J. Du, L.L. Lin, W.X. Xia, J. Zhang, B.R. Bian, J.P. Liu, *J. Mater. Sci. Technol.* **35**, 560 (2019)
- [17] J. He, B. Bian, Q. Zheng, J. Du, W. Xia, J. Zhang, A. Yan, J.P. Liu, *Green Chem.* **18**, 417 (2016)
- [18] B. Bian, J. He, J. Du, W. Xia, J. Zhang, J.P. Liu, W. Li, C. Hu, A. Yan, *Nanoscale* **7**, 975 (2015)
- [19] X. Huang, T. Jones, H. Fan, M.G. Willinger, *Adv. Mater. Interfaces* **3**, 1600751 (2016)
- [20] Y. Jiang, H.B. Li, Z.M. Wu, W.Y. Ye, H. Zhang, Y. Wang, C.H. Sun, Z. Zhang, *Angew. Chem. Int. Ed.* **55**, 12427 (2016)
- [21] A.O. Yalcin, Z.C. Fan, B. Goris, W.F. Li, R.S. Koster, C.M. Fang, A. van Blaaderen, M. Casavola, F.D. Tichelaar, S. Blas, G. van Tendeloo, T.J.H. Vlugt, D. Vanmaekelbergh, H.W. Zanberge, M.A. van Huis, *Nano Lett.* **14**, 3661 (2014)
- [22] L. Zhang, Y.H. Dou, H.C. Gu, *J. Colloid Interface Sci.* **297**, 660 (2006)
- [23] D. Yu, X. Sun, J. Zou, Z. Wang, F. Wang, K. Tang, *J. Phys. Chem. B* **110**, 21667 (2006)
- [24] M.A. Asoro, D. Kovar, P.J. Ferreira, *ACS Nano* **7**, 7844 (2013)
- [25] Q. Jiang, S. Zhang, M. Zhao, *Mater. Chem. Phys.* **82**, 225 (2003)