# Nanoscale

### Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/nanoscale

#### Nanoscale

Cite this: DOI: 10.1039/c0xx00000x

# ARTICLE TYPE

# Gel-limited synthesis of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres and their SERS applications

Xiaoli Zhang,<sup>a</sup> Chunyu Niu,<sup>a</sup> Yongqiang Wang<sup>a</sup>\*, Shaomin Zhou,<sup>a</sup> Jin Liu<sup>b</sup>

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

Abstract: A novel gel-limited strategy was developed to synthesize dumbbell-like  $Fe_3O_4$ -Ag composite microspheres through a simple one-pot solvothermal method. In such reaction system, a special precursor solution containing oleic, water, ethanol and silver ions was used and transformed into a bulk gel under heating at the very beginning of reaction, thus all the subsequent reactions proceeded in the interior of gel.

- <sup>10</sup> The gel-limited reactions had two advantages, on one hand, the magnetic Fe<sub>3</sub>O<sub>4</sub> microspheres would be fixed in the gel which avoided them to aggregate together; On the other hand, the silver ions stored in the gel could be gradually released and tended to diffuse towards a nearest Fe<sub>3</sub>O<sub>4</sub> microsphere, which favored for the generation of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag structure. From the time-depended experiments under optimal condition, the typical growth process of dumbbell-like structure was clearly demonstrated that a
- <sup>15</sup> silver seed firstly appeared on the surface of single  $Fe_3O_4$  microsphere, which grew bigger slowly and formed a dumbbell-like  $Fe_3O_4$ -Ag structure finally. Moreover, the formation of gel was found to be strongly affected by the ratio of water and ethanol in precursor solution, which further influence the mophologies of  $Fe_3O_4$ -Ag microspheres. Additionally, the effect of lattice match between  $Fe_3O_4$  and Ag on the final products was also proved from control experiments by using template with different surface

<sup>20</sup> crystalline structure. When used as SERS substrate, the final dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag microspheres show fast magnetic separation and selective detection of thiram for the surface capped oleic chain during the growth process.

#### 1. Introduction

The controls on shape, size and composition of particles are very <sup>25</sup> important for the nanomaterials because their chemical and physical properties depend upon these factors greatly.<sup>1</sup> And there have been tremendous developments in the synthetic control of these factors of particles to tailor their properties. Recently, hybrid nanomaterials, combining disparate material components,

<sup>30</sup> provide a powerful strategy for modifying nanomaterials' properties. These hybrids often exhibited grotesque shapes like spherical or cubic core/shell including yolk-like structures, co-joined sphere-sphere or nanorod structures (called Janus particles) with different interfaces (metal-metal, metal-magnet, <sup>35</sup> magnet-semiconductor, et al), nanoparticle-decorated nanowire,

fibres or nanosheet, and more.<sup>2-5</sup>

At present, Janus particles can be regarded as some of the most complicated colloidal particles. Beyond their use as elementary

<sup>a</sup> Key Laboratory for Special Functional Materials of the Ministry of Education, Henan University, Kaifeng 475004, P. R. China.
<sup>b</sup> College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China.
Email: wangyq@henu.edu.cn; Fax: +86 371 63881358; Tel.: +86 371 63881358.
† Electronic Supplementary Information (ESI) is available: [XRD patterns and TEM images of the relevant products]. See http://dx.doi.org/10.1039/b000000x/ building blocks for supraparticular assemblies, they were also <sup>40</sup> very promising with respect to numerous applications by tailoring their compositions.<sup>6, 7</sup> According to their compositions, they were often categorized into three types: polymeric, inorganic, and polymeric-inorganic, and each kind of Janus particles can be spherical, dumbbell-like, snowman-like, cylindrical, disk-like, or <sup>45</sup> any of a variety of other shapes.<sup>8, 9</sup> Among them, due to the versatility of inorganic materials, the Janus particles composed of two or more different inorganic components attracted many researchers' focus and were investigated widely. And more importantly, multifunctional particles could be realized through <sup>50</sup> assembling inorganic materials with different properties, like magnetism, electrics, semiconductivity, optics, optoelectronics, or catalysis, and even new phenomena or properties could be found.<sup>10, 11</sup>

For the early synthesis of inorganic Janus particles, it often <sup>55</sup> required partial coverage of the surfaces of inorganic particles, which is followed by functionalization of the exposed surfaces with other inorganic particles or their precursors like electrostatic deposition, spin-coating or metal evaporation.<sup>12-14</sup> Compared with the above methods, the chemical solution methods were paid <sup>60</sup> much attention to for their simple and low-cost synthesis procedure nowadays.<sup>15-18</sup> For example, Sun et al reported the synthesis of dumbbell-like Au-Fe<sub>3</sub>O<sub>4</sub> NPs via the decomposition of Fe(CO)<sub>5</sub> over the surface of the Au NPs, followed by oxidation in air, where the controlled nucleation and growth of only one  $Fe_3O_4$  on each Au seeded NP was attributed to lattice match and the possible electron transfer between Au and  $Fe_3O_4$ . Followed this report, some other dumbbell-like Pt-Fe<sub>3</sub>O<sub>4</sub> and Ag-Fe<sub>3</sub>O<sub>4</sub> s composite spheres were synthesized by using similar method.<sup>16</sup>

- Later, Xu et al employed ultrasonic emulsification method to synthesize Ag-Fe<sub>3</sub>O<sub>4</sub> at a liquid-liquid interface, where the imperfect coverage of Fe<sub>3</sub>O<sub>4</sub> by surfactant offered few Fe(II) sites to act as the catalytic centre for the reduction of Ag<sup>+</sup> and the
- <sup>10</sup> seeding of the Ag nanoparticle.<sup>18</sup> Recently, the dumbbell-like FePt-Au nanoparticles were reported to be fabricated by heteroepitaxial Au growth on FePt through catalytic effects.<sup>19</sup> Besides, other various types were also synthesized through chemical solution methods, like Fe<sub>3</sub>O<sub>4</sub>-MnO, PS-SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>-<sup>15</sup> SiO<sub>2</sub>, Au-Pd, Fe<sub>3</sub>O<sub>4</sub>-CdSe, FePt-CdS, and Au-CdS and so on.<sup>20-26</sup>

In all the chemical solution methods, the successful synthesis of dumbbell-like particles relied critically on promoting heterogeneous nucleation while suppressing homogeneous nucleation, thus the controlled nucleation and growth during the

- $_{20}$  reaction process was crucial. $^{27}$  It was early reported that gel reaction media was a kind of special and excellent system for its controlled crystal nucleation and growth. $^{28}$  As for the magnetic dumbbell-like particles, the gel system may be attractive because Fe<sub>3</sub>O<sub>4</sub> microspheres could be fixed in the interior of the gel
- <sup>25</sup> evenly and kept isolated against magnetic aggregation during the reaction. Based on the above consideration, a novel gel method was developed to synthesize dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres in our paper. In such gel system, the Fe<sub>3</sub>O<sub>4</sub> microspheres were immobilized in the interior of gel; meanwhile
- <sup>30</sup> the silver ions stored in the gel would be released gradually and then diffused slowly towards a nearest Fe<sub>3</sub>O<sub>4</sub> microsphere in the gel. The investigation of growth mechanism demonstrated the gel reaction system was very successful for the synthesis of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres. Additionally,
- <sup>35</sup> the finally products show selective detection of thiram when used as magnetic separable SERS substrate for surface-capped oleic chain.

#### 2. Experimental section

#### 2.1 Synthesis procedure

#### 40 2.1.1 Synthesis of multicrystalline Fe<sub>3</sub>O<sub>4</sub> microspheres

The Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized by a typical solvothermal method. In a typical synthesis procedure, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.3 g) and CH<sub>3</sub>COONa (3.6 g) were mixed in ethylene glycol (40 ml) under magnetic stirring, followed by the <sup>45</sup> addition of polyacrylic acid (0.2 ml), and then the above mixed solution was sealed in Teflon-lined stainless-steel autoclaves (80 ml) and heated at 220 °C for 6 h. The black product was separated under external magnet and washed several times with distilled water, and then uniform Fe<sub>3</sub>O<sub>4</sub> microspheres were <sup>50</sup> obtained and stored in ethanol for further use.

#### 

The dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres was synthesized in a mixed oleic-ethanol-water system. The detailed <sup>55</sup> synthesis procedure was as follows: oleic acid (0.3 ml) and sodium oleate (0.225 g) were firstly dissolved in 5 ml ethanol, and then aqueous silver nitrate solution (7.5 ml, 0.01 g/ml) was dropped under mechanical stirring. During the above process, white floccules appeared immediately. The as-obtained Fe<sub>3</sub>O<sub>4</sub> <sup>60</sup> microspheres (30 mg, 2.5 ml ethanol) were then added into the above solution under ultrasonically dispersing for 10 minutes. Finally, the mixture was transferred into Teflon-lined stainlesssteel autoclaves (20 ml) and heated at 200 °C for 8 h. The product was separated by using an external magnet and washed by <sup>65</sup> ethanol for several times. The final product was kept in ethanol for further characterizations.

#### 2.2 Characterizations

The morphologies and compositions of the as-prepared products were characterized by field-emission scanning electron <sup>70</sup> microscopy (FESEM, Sirion 200 FEG) at an acceleration voltage of 20.0 kV. Transmission electron microscopy (TEM) observations were performed on a JEOL 2010 electron microscope operating at 200 kV. The phase and the crystallographic structure of the products were investigated by X-<sup>75</sup> ray diffraction (XRD, Philips X' Pert Pro).

#### 2.3 SERS measurements

Thiram was used as Raman probes for the SERS measurements. During the SERS tests, the obtained dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres were firstly dispersed into Thiram <sup>80</sup> solutions (20 ml) with different concentrations for 2 hour, and then were separated and rinsed with ethanol. The thiram-absorbed samples were dropped and assembled on a glass slide substrate under an external magnet. After they dried under atmosphere, the glass slide substrate was characterized for Raman tests. Confocal <sup>85</sup> microscopy Raman Spectrometer (LABRAM-HR) was used with its laser beam at an excitation wavelength of 514.5 nm in this

its laser beam at an excitation wavelength of 514.5 nm in this study. The acquisition time was 3 s for each spectrum. Other pesticides like parathion-methyl and trichlorfon were tested by using the similar method.

#### 90 3. Results and discussion

# 3.1. Characterization of dumbbell-like $\rm Fe_3O_4\text{-}Ag$ composite microspheres.

In our experiment, Fe<sub>3</sub>O<sub>4</sub> microspheres with 480 nm were used as magnetic seeds for the subsequent attachment of silver 95 nanoparticles as seen in Fig. 1a and 1b. The microsphere was composed of a large number of tiny Fe<sub>3</sub>O<sub>4</sub> nanoparticles shown as the magnified image in Fig. 1c. After the gel reaction completed, the morphology of finally obtained samples was characterized by SEM in Fig. 1d, and lots of dumbbell-like structures with 100 different contrasts could be obviously observed, and the dumbbell-like structures were also clearly watched from the corresponding TEM images in Fig. 1e. The spherical part with light colour could be identified as Fe<sub>3</sub>O<sub>4</sub> from the configuration, since it was similar with the original Fe<sub>3</sub>O<sub>4</sub> microspheres in Fig. 105 1b. Meanwhile, the other part attached to the Fe<sub>3</sub>O<sub>4</sub> microspheres showed the dark colour which could be proposed to be Ag parts of the product. Actually, the brightness in the TEM image reflects the intensity of transmitted electrons from different substance and

is proportional to the atomic number (*Z*). In a single dumbbell-<sup>110</sup> like composite microsphere in Fig. 1f, the Ag parts, which have the higher Z compared to the Fe<sub>3</sub>O<sub>4</sub> particles, will have a dark image. Therefore, it can be seen that every Fe<sub>3</sub>O<sub>4</sub> microsphere was attached with a single dark particle, which then could be ascribed to Ag parts. And the Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres <sup>5</sup> were also indentified from the XRD patterns through the

- comparison of products before and after reaction. From the curve a in Fig. S1, all the diffraction peaks in curve a can be attributed to cubic-phase  $Fe_3O_4$  (JCPDS Card, No. 19-629), while the curve b in Fig. S1 showed exactly silver peaks with cubic structure
- <sup>10</sup> (JCPDS Card, No. 4-783) besides those low  $Fe_3O_4$  peaks. These results demonstrated the successful synthesis of dumbbell-like  $Fe_3O_4$ -Ag composite microspheres by using our gel-limited strategy. It was also noticed that the peak intensities of  $Fe_3O_4$  are rather low in comparison with that of silver, probably caused by
- ${}_{15}$  the large lattice stress from the interface of Fe\_3O\_4-Ag and the low crystallinity.  ${}^{29}$



Fig. 1 (a) SEM image of Fe<sub>3</sub>O<sub>4</sub> microspheres, (b) TEM image of Fe<sub>3</sub>O<sub>4</sub> microspheres, (c) TEM image of a single Fe<sub>3</sub>O<sub>4</sub> microsphere, (d) SEM
<sup>20</sup> image of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag microspheres, (e) Magnified SEM image of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag microspheres, (f) TEM image of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag microspheres.

#### 3.2. Investigation of the gel reaction system.

From the above results, dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite <sup>25</sup> microspheres were successfully synthesized by using the gel reaction system. Unlike the previous and traditional reported liquid solution methods, here a quite different reaction system was used, for all the reagents were immobilized in the interior of gel. Thus, the key questions that how and why dumbbell-like <sup>30</sup> Fe<sub>3</sub>O<sub>4</sub>-Ag composite microsphere was formed in the gel reaction system need to be explored in detail, including the growth process, the structure and function of the gel in the reaction.

Time-depended experiments were firstly conducted to investigate the growth process of  $Fe_3O_4$ -Ag composite

<sup>35</sup> microspheres. When the pictures of products at different intervals was taken for comparison, it was surprising that the morphology of each intermediate products exhibited a kind of perfect bulk gel structure, which could be taken out easily from Teflon autoclave without collapse as shown in Fig. 2a-e. Although the size of the

- <sup>40</sup> bulk gels was gradually decreased from Fig. 2a to 2d, they always kept a cylindrical shape, indicating that the reaction proceeded in the interior of gel during the reaction procedure, and the gel finally disappeared at the end of reaction in Fig. 2e. Although the magnetic products in the gels from Fig. 2a to 2d were extracted
- 45 by repeatedly washing and separation for TEM characterization,

there are still some residual organic chemicals in the products which caused the TEM images blurry. However, the contour of the products can still be distinguished from Fig. 2a<sub>1</sub>-2e<sub>1</sub>. At the initial stage (10 min), there is only one small Ag particle attached 50 to a spherical microsphere, and these small particles grew bigger and bigger with the reaction proceeding until the silver ions in solution were completely consumed (8 h), which was proved from the ICP-AES results. In the final product, no separate Ag particles were observed, indicating that the gel reaction system 55 promoted heterogeneous nucleation while suppressing the homogeneous nucleation successfully. From the whole growth process, it can be seen that the reaction was strictly restricted to single Ag particle on each Fe<sub>3</sub>O<sub>4</sub> microsphere, and no other heterogeneous nucleation and growth on Fe<sub>3</sub>O<sub>4</sub> microsphere was 60 found, thus dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres were successfully achieved through a gradual growth process in the gel reaction system.



**Fig. 2** Pictures and TEM images of the intermediate products at different <sup>65</sup> intervals (minute): (a-a<sub>2</sub>) 10; (b-b<sub>2</sub>) 20; (c-c<sub>2</sub>) 60; (d-d<sub>2</sub>) 240; (e-e<sub>2</sub>) 480. (Note: the intermediate products without any treating (a-e) and after repeated washing (a<sub>1</sub>-e<sub>1</sub>)).

It can be seen that the gel didn't collapse during the reaction, but its size decreased from the above results in Fig. 2a-2d, thus 70 the Fe<sub>3</sub>O<sub>4</sub> microspheres were confined in the interior of gel though the whole reaction process. However, whether the gel was critical factor for the formation of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres needed to be further verified. It was lucky to found that the gel system was strongly affected by the 75 ingredient of precursor soltuion, and the morphologies of final

Nanoscale Accepted Manuscript

products changed greatly by varying the ratio of water and ethanol (W/E) in precursor solution. As shown in Fig. 3, especially when pure water or ethanol (W/E = 20:0 or 0:20) was used as solvent, more than one Ag particles could be found s around some Fe<sub>3</sub>O<sub>4</sub> microspheres as exemplarily marked by arrows in Fig. 3. Especially for the product synthesized in pure

- ethanol solution, more Ag particles with smaller size appeared on the surface of the Fe<sub>3</sub>O<sub>4</sub> microspheres in Fig. 3d. Meanwhile, when the mixture of water and ethanol (W/E = 15:5 or 5:15) was
- <sup>10</sup> used as solvent, dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres could be synthesized which is similar with the above product in Fig. 1, however, some tiny silver nanoparticles was found on the big silver particles as marked by arrows in Fig. 3c (W/E = 5:15). The results reflected that the morphologies of final products were
- <sup>15</sup> strongly influenced by the precursor solution. When the intermediate phase was studied, they exhibited different morphologies after the precursor solutions with different ingredients were heated for 10 minutes. As shown in the inset of Fig. 3, not all the precursor solutions were transformed into bulk
- <sup>20</sup> gel. Only the immediate phase from the precursor solution with W/E of 20:0 and 15:5 shown in Fig. 3a and 3b presented the similar gel morphology with that in Fig. 2a, and others either exhibited smaller bulk gel in Fig. 3c or mud without any shapes in Fig. 3d. It was worth mentioning that silver oleate had better
- $_{25}$  soluble in ethanol than in water. Therefore, when pure ethanol was used, the diffusion of  $Ag^+$  ions was faster than that in water (in the form of silver oleate), and then more  $Ag^+$  ions would move towards to the same  $Fe_3O_4$  microsphere at the same time, which would lead to the appearence of more Ag nuclei on the
- $_{30}$  Fe<sub>3</sub>O<sub>4</sub> microsphere as seen in Fig. 4d. When no ethanol was used, most of the final product showed dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag structure, however few Fe<sub>3</sub>O<sub>4</sub> microspheres with two Ag nanoparticles were observed in Fig. 3a, for the distribution of Fe<sub>3</sub>O<sub>4</sub> microsphere were not uniform in such gel system. Through
- 35 the above comparison, it can be easily concluded that the uniform gel was prerequisite and crucial for the formation of perfect dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres.



**Fig. 3** TEM images of the products synthesized by using different 40 precursor solutions with W/E ratio (a) 20:0, (b) 15:5, (c) 5:15 and (d) 0:20. (With inset of their corresponding intermediate products at 10 minutes)

It was interesting to find that the precursor solution was transformed into gel under heating very quickly, as shown in the inset of Fig. 4. A slice of the gel obtained at 10 minutes was cut 45 to investigate the structure by low-angle X-ray diffraction (XRD). The periodical diffraction peaks in degree in Fig. 4a revealed the gel was a kind of lamellar structure, with the interlayer spacing distance about 4.41 nm in the 20 range 4-15°C. When a slice of the gel without adding Fe<sub>3</sub>O<sub>4</sub> was characterized for comparison 50 (the white gel in Fig. 4b), no obvious difference was detected, which indicated the existence of Fe<sub>3</sub>O<sub>4</sub> almost had no influence on the gel system. The above XRD results were similar with the previously reported solution gel structure, where sodium oleate/1octanol/AgNO<sub>3</sub> solution was employed, and the gel was 55 composed of vesicles assembled by silver oleate in a lamellar form.<sup>30</sup> And an earlier research revealed that a lamellar liquid crystalline alignment of vesicles could be formed in sodium oleate/1-octanol/water gel system.<sup>31, 32</sup> Therefore, here silver oleate was proposed to realign into vesicles in the mixture of 60 water and ethanol under heating, with water and ethanol locating inside, and these vesicles further assembled a kind of lamellar array. From the size decreasing phenomenon in the above Fig. 2, it was proposed the silver ions in the form of silver oleate were released and reduced slowly, the continual consumption of silver 65 oleate lead to the destruction of the vesicles while the water and ethanol were discharged. The residual silver oleate may reassemble and maintain the morphology of gel, and this process lasted until all silver ions were used up, which could be deduced from the size decreasing of gel and the increasing amount of 70 solution around it during the reaction process in Fig. 2. In the bulk gel reaction system, the silver ions in the gel were also supposed to diffuse slowly when compared with that in liquid solution, which most probably moved towards a nearest Fe<sub>3</sub>O<sub>4</sub> microsphere for the short diffusion distance. Thus once an Ag 75 seed appeared on the Fe<sub>3</sub>O<sub>4</sub> microsphere, the slow diffusion and reaction rate favoured the heterogeneous growth of single Ag nanoparticle on each Fe<sub>3</sub>O<sub>4</sub> microsphere seen in Fig. 2.



Fig. 4 XRD patterns of gel products (a) with  $Fe_3O_4$  microspheres and (b) <sup>80</sup> without  $Fe_3O_4$  microspheres.

From the above analysis, the gel was thought to be a superior system for the synthesis of dumbbell-like  $Fe_3O_4$ -Ag composite microspheres for two functions in the reaction procedure. One is its limitation of the movement of  $Fe_3O_4$  microspheres during the

reaction, which avoid the aggregation of  $Fe_3O_4$  microspheres from magnetic attraction; the other is its limitation of the release and reduction of  $Ag^+$  ions during the reaction, which was beneficial for the formation of dumbbell-like structure.

# 5 3.4. Lattice match on the formation of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres.

The reason why silver atoms would deposit on the Fe<sub>3</sub>O<sub>4</sub> seeds to form Ag or Au crystals has been explained by the lattice match in many previous reports, where nano-scaled Fe<sub>3</sub>O<sub>4</sub> particles with <sup>10</sup> single crystalline were used in the reaction.<sup>33</sup> The earliest explanation was seen in the synthesis of Fe<sub>3</sub>O<sub>4</sub>-Au structure, for Au has an FCC structure with a = 4.08 Å, and Fe<sub>3</sub>O<sub>4</sub> has a cubic structure with a = 8.35 Å, which is within 3 % of being exactly double.<sup>33</sup> Later, the theory of lattice match was also used to <sup>15</sup> illustrate the formation mechanism in Fe<sub>3</sub>O<sub>4</sub>-Ag or Au system for

- the similar lattice structure between Au and Ag.<sup>29, 34</sup> Here in our experiment, multi-crystalline Fe<sub>3</sub>O<sub>4</sub> microspheres rather than nano-scaled Fe<sub>3</sub>O<sub>4</sub> crystal were used, however the final product still exhibited that only one Ag particle attached on each Fe<sub>3</sub>O<sub>4</sub>
- <sup>20</sup> microsphere. It was proposed that the multi-crystalline  $Fe_3O_4$ microsphere was composed of large amount of tiny  $Fe_3O_4$ nanocrystals, thus these  $Fe_3O_4$  nanocrystals exposed on the surface could also provide depositing point for Ag atoms due to the lattice match. It is not surprising to find when single-crystal
- Fe<sub>3</sub>O<sub>4</sub> microspheres, which was synthesized according to typical solvothermal method by Li et al,<sup>35</sup> was used in the gel reaction system, the final product still exhibited dumbbell-like structure in Fig. 5a. For further comparison, the time-depended experiments were conducted again by using single-crystalline Fe<sub>3</sub>O<sub>4</sub>
  microspheres as seeds, and the growth process in Fig. S2 was similar with that by using multi-crystalline Fe<sub>3</sub>O<sub>4</sub> microspheres in Fig. 2.



Fig. 5 TEM images of products by using different microspheres as seeds <sup>35</sup> in gel reaction system (a) single-crystalline Fe<sub>3</sub>O<sub>4</sub> microspheres, (b)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> microspheres, (c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres and (d) silica colloidal microspheres.

Although the lattice match was used to explain the special

growth of Ag on Fe<sub>3</sub>O<sub>4</sub> very well in the previous reports 40 including our present experiment, no further experimental evidence was reported to prove the lattice match until now. For our experiment, it is convenient to confirm the explanation from another point through using other microspheres with same or different crystalline structures. E.g., the multi-crystalline Fe<sub>3</sub>O<sub>4</sub> 45 microspheres could be treated in different conditions before using as seeds, like heating in nitrogen or air atmospheres, then  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres would be obtained respectively. It is well known that the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> have similar crystalline structure with Fe<sub>3</sub>O<sub>4</sub>, thus they showed similar XRD patterns from curve a so and curve b in Fig. S3, while  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> had a different crystalline structure in curve c in Fig. S3. When the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres were used to replace the multi-crystalline Fe<sub>3</sub>O<sub>4</sub> microspheres in gel system, the dumbbell-like structure was only observed in the final product when  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> microspheres were 55 used in Fig. 5b. And no silver particles were found to be attached to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres. Therefore, this control experiment demonstrated the crucial role of crystalline structure of microspheres in the growth of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres. In addition, when the multi-crystalline Fe<sub>3</sub>O<sub>4</sub> 60 microspheres were further substituted by amorphous silica colloidal microspheres, no dumbbell-like structure was observed in the final product in Fig. 5d. Through the above control experiments, the theory of lattice match was suitable for explaining the prior deposition of Ag atoms on Fe<sub>3</sub>O<sub>4</sub> 65 microspheres, and our results proved again that lattice match was critical factor for the formation of dumbbell-like structure.

# 3.4. Growth mechanism of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres.



70 Fig. 6 Schematic growth procedure of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres.

From the above discussions, there are two main factors during the growth process including lattice match and gel-limited growth. The growth mechanism of the gel-limited system was 75 proposed and illustrated in Fig. 6. (a) After the Fe<sub>3</sub>O<sub>4</sub> microspheres were added into the precursor solution, the mixture was treated ultrasonically to make magnetic Fe<sub>3</sub>O<sub>4</sub> microspheres disperse evenly. (b) Once the precursor solution was heated in autoclave, silver oleate in the solution assembled into vesicles 80 and arrange into lammellar structure, thus the precursor solution transformed into gel quickly in less than five minutes, and magnetic  $Fe_3O_4$  microspheres were immobilized in the interior of gel; (c) The silver oleate in the vesicles would release silver ions under heating, which were then reduced into Ag atoms, and grew on the surface of magnetic  $Fe_3O_4$  microspheres for the lattice 5 match. Meanwhile, more and more vesicles were destroyed with

- the reaction proceeding, thus the size of the gel continually decreased with the water and ethanol discharging outside of gel; (d) With the continual release and reduction of silver ions from the gel, the silver seeds grow bigger and bigger; (e) The reaction
- <sup>10</sup> proceeded until the constituent of the gel (silver oleate) were used up, and then the gel disappeared naturally, for all silver ions were transformed into silver nanoparticles on  $Fe_3O_4$  microspheres. From the illustration, the advantage of gel was obvious for its limit effects on both the movement of  $Fe_3O_4$  microsphere and the
- 15 growth rate of Ag during the reaction process, which favored the synthesis of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres.

#### 3.4. SERS applications.



Fig. 7 SERS spectra of pesticides adsorbed on dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag <sup>20</sup> composite microspheres with different concentrations: (a)  $1 \times 10^{-4}$  M, (b)  $1 \times 10^{-5}$  M, (c)  $1 \times 10^{-6}$  M, (d)  $1 \times 10^{-7}$  M (thiram), (e) parathion-methyl ( $10^{-4}$  M) and (f) trichlorfon( $10^{-4}$  M).

Ag structures with diverse shape have synthesized, and they have been applied as substrates for surface-enhanced Raman <sup>25</sup> scattering (SERS) in the recent years.<sup>36-42</sup> Recently, Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres were focused for their convenient separable properties when used as SERS substrate.<sup>43-45</sup> Here, besides the fast magnetic separation, the dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres prepared in this work are attractive for

- <sup>30</sup> their capped oleate group. It was reported that the silver nanoparticles modified with oleate showed good selectivity towards thiram molecules than other agricultural chemical residues, since the affinity of thiram to the surface of the Ag nanoparticles was strong enough to replace the original oleate
- <sup>35</sup> group.<sup>46</sup> Here the as-obtained dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres were used as SERS substrate to detect thiram in water. As shown in Fig. 7, all the peaks from 400 to 1800 cm<sup>-1</sup> in curve a are attributed to thiram signals according to previous reports, where the main Raman bands could be assigned as
- $_{40}$  following, 564 cm<sup>-1</sup> attributed to vs(CSS), 928 cm<sup>-1</sup> to v(CH<sub>3</sub>N) or v(C-S), 1150 cm<sup>-1</sup> to  $\rho$ (CH<sub>3</sub>) or v(C-N), and 1386 and 1514 cm<sup>-1</sup> to  $\rho$ (CH<sub>3</sub>) or v(C-N), respectively.<sup>47</sup> All feature peaks of thiram band could be clearly observed even at the low level of 10<sup>-</sup>

<sup>7</sup> M in Fig. 7d. Since the dumbbell-like  $Fe_3O_4$ -Ag composite 45 microspheres would aggregate together under external magnet, the contacts between silver particles would bring nano-scaled gaps (so-called "hot spots"),48 when thiram molecules located in these hot spots, strong SERS signals could be observed, therefore the excellent SERS performance of dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag 50 composite microspheres is likely to come from the hot spots under magnetite-induced aggregation. When parathion-methyl and trichlorfon were used as probe molecules, both of them did not show any SERS signals in Fig. 7e and 7f, respectively. Previously reports of SERS revealed that molecules like thiram 55 undergo a surface reaction on silver, and the studies have shown that thiram are chemisorbed dissociative on the Ag surface by cleavage of S-S bonds as shown in Fig. S4a.49 When compared with other two pesticides parathion-methyl and trichlorfon shown in Fig. S4b and 4c, the thiram would bond to the Ag surface 60 through S atom, which had a stronger interaction with Ag surfaces than the original oleate groups, while other two pesticides couldn't replace the surface capped oleate groups, therefore only thiram could be detected in our SERS experiments. Our results validated the selective SERS detection performance 65 of oleic capped silver particles again.<sup>46</sup> Therefore, the present sensing system exhibits a good detecting performance and high selectivity for thiram, and could be applied for the detection of thiram in aqua samples.

#### 4. Conclusion

<sup>70</sup> Dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag composite microspheres were prepared through a simple one-pot solvothermal method in a gel system. The special precursor solution containing oleic, water, ethanol and silver ions was transformed into a bulk gel under heating, which made the reaction limit in the interior of gel including the <sup>75</sup> movement of Fe<sub>3</sub>O<sub>4</sub> microspheres and diffusion of Ag<sup>+</sup> ions. Additionally, the lattice match between Fe<sub>3</sub>O<sub>4</sub> and Ag was proved to be critical factor from control experiments by using different

microspheres with different crystalline structure. Through the detail investigation of the reaction in gel system, a novel gellimited strategy was put forward. Besides, the final dumbbell-like Fe<sub>3</sub>O<sub>4</sub>-Ag microspheres capped by oleic chain show selective detection of thiram when used as SERS substrate and the magnetic property of SERS substrate made the separation conveniently.

#### **85 Acknowledgments**

This work was supported by the Natural Science Foundation of China (No. 51102077, No. 51372070 and No. 41201520), the Scientific Research Foundation of Henan University (No. B2010088 and No. 0000A40409), and Changjiang Scholars and Innovative Research Team in University (No. PCS IRT1126).

#### **References:**

- 1. G. Hodes, Adv. Mater., 2007, 19, 1307.
- 2. G. Loget and A. Kuhn, J. Mater. Chem., 2012, 22, 15457.
- 3. J. Hu, S. Zhou, Y. Sun, X. Fang and L. Wu, *Chem. Soc. Rev.*, 2012, **41**, 95 4356.
- 4. F. Liang, K. Shen, X. Qu, C. Zhang, Q. Wang, J. Li, J. Liu and Z. Yang, *Angew. Chem. Int. Ed.*, 2011, **50**, 2379.

5. S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K. S. Schweizer and S. Granick, *Adv. Mater.*, 2010, **22**, 1060.

#### Nanoscale

100

105

110

115

140

- 6. A. Walther and A. H. Muller, Chem. Rev., 2013, 113, 5194.
- 7. Q. Chen, J. K. Whitmer, S. Jiang, S. C. Bae, E. Luijten and S. Granick, *Science*, 2011, **331**, 199.
- 8. M. Lattuada and T. A. Hatton, *Nano Today*, 2011, **6**, 286.
- <sup>5</sup> 9. L. Yan, N. Popp, S. Ghosh and A. Bo"ker, *ACS Nano*, 2010, **4**, 913. 10. Y. Li, Q. Zhang, A. V. Nurmikko and S. Sun, *Nano Lett.*, 2005, **5**, 1689.
- 11. S. T. Selvan, P. K. Patra, C. Y. Ang and J. Y. Ying, *Angew. Chem. Int. Ed.*, 2007, **46**, 2448.
- 10 12. Y. Lu, H. Xiong, X. Jiang, Y. Xia, M. Prentiss and G. M. Whitesides, J. Am. Chem. Soc., 2003, **125**, 12724.
  - 13. S. Yang, J. Xu, Z. Wang, H. Zeng and Y. Lei, *J. Mater. Chem.*, 2011, 85 21, 11930.
- 14. S. Ye and R. L. Carroll, ACS Appl. Mater. Interfaces, 2010, 2, 616.
- 15 15. A. Ohnuma, E. C. Cho, P. H. Camargo, L. Au, B. Ohtani and Y. Xia, J. Am. Chem. Soc., 2009, 131, 1352.
- 16. C. Wang, H. Yin, S. Dai and S. Sun, Chem. Mater., 2010, 22, 3277.
- 17. Y. Wang, H. Xu, Y. Ma, F. Guo, F. Wang and D. Shi, *Langmuir*, 2011, **27**, 7207.
- 20 18. H. Gu, Z. Yang, J. Gao, C. K. Chang and B. Xu, J. Am. Chem. Soc., 2005, 127, 34.
  - 19. J. Choi, Y. Jun, S. Yeon, H. C. Kim, J. Shin and J. Cheon, J. Am. Chem. Soc., 2006, **128**, 15982.
- 20. M. Li, X. Yu, S. Liang, X. Peng, Z. Yang, Y. Wang and Q. Wang, 25 Adv. Funct. Mater., 2011, 21, 1788.
- 21. P. H. C. Camargo, Y. Xiong, L. Ji, J. M. Zuo and Y. Xia, *J. Am. Chem. Soc.*, 2007, **129**, 15452.
- 22. B. M. Teo, S. K. Suh, T. A. Hatton, M. Ashokkumar and F. Grieser, *Langmuir*, 2011, **27**, 30.
- 30 23. L. Zhang, F. Zhang, W. Dong, J. Song, Q. Huo and H. Sun, Chem. Commun., 2011, 47, 1225.
- 24. K. P. Yuet, D. K. Hwang, R. Haghgooie and P. S. Doyle, *Langmuir*, 2010, **26**, 4281.
- 25. J. Yang, H. I. Elim, Q. Zhang, J. Y. Lee and W. Ji, J. Am. Chem. Soc., 35 2006, **128**, 11921.
- K. S. Lee, R. M. Anisur, K. W. Kim, W. S. Kim, T. Park, E. J. Kang and I. S. Lee, *Chem. Mater.*, 2012, 24, 682.
   C. Wang, C. Xu, H. Zeng and S. Sun, *Adv. Mater.*, 2009, 21, 3045.
- 28. A. R. Patel and A. V. Rao, *Bull. Mater. Sci.*, 1982, **4**, 527.
- <sup>40</sup> 29. J. Huang, Y. Sun, S. Huang, K. Yu, Q. Zhao, F. Peng, H. Yu, H. Wang and J. Yang, *J. Mater. Chem.*, 2011, **21**, 17930.
  30. X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He and Y. Qian, *J. Mater. Chem.*, 2001, **11**, 1775.
- 31. M. Gradzielski, M. Bergmeier, M. Müller and H. Hoffmann, *J. Phys.* 45 *Chem. B*, 1997, **101**, 1719.
- M. Gradzielski, M. Müller, M. Bergmeier, H. Hoffmann and E. Hoinkis, J. Phys. Chem. B, 1999, 103, 1416.
   H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. Sun, 120
- Nano Lett., 2005, **5**, 379.
- <sup>50</sup> 34. T. Zhang, J. Ge, Y. Hu and Y. Yin, *Nano Lett.*, 2007, 7, 3203.
   <sup>51</sup> H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem. Int. Ed.*, 2005, 44, 2782.
   <sup>52</sup> Y. Cao, D. Li, F. Jiang, Y. Yang and Z. Huang, *J. Nanomater.*, 2013, <sup>53</sup> Y. Cao, D. Li, F. Jiang, Y. Yang and Z. Huang, *J. Nanomater.*, 2013, <sup>54</sup> Y. Cao, <sup>55</sup> Y. Cao, <sup>56</sup> Y. Cao, <sup>57</sup> Y. Yang and <sup>75</sup> Y. Yang <sup>57</sup> Y. Cao, <sup>57</sup> Y. Cao, <sup>56</sup> Y. Cao, <sup>56</sup> Y. Cao, <sup>56</sup> Y. Cao, <sup>56</sup> Y. Cao, <sup>57</sup> Y. Yang <sup>57</sup> Yung <sup>57</sup> Y. Yang <sup>57</sup> Y. Yang <sup>57</sup> Yung <sup>5</sup>
- 2013.
  55 37. S. L. Kleinman, R. R. Frontiera, A. Henry, J. A. Dieringer and R. P. Van Duyne, *Phys. Chem. Chem. Phys.*, 2013, 15, 21.
  38. X. Gong, Y. Bao, C. Qiu and C. Jiang, *Chem. Commun.*, 2012, 48, 7003.
- 39. D. Cialla, A. M A Rz, R. E. B O Hme, F. Theil, K. Weber, M. Schmitt<sup>130</sup> 60 and J. U. R. Popp, *Aanl. Bioanal. Chem.*, 2012, 1.
- 40. C. Zhu, G. Meng, Q. Huang, Z. Li, Z. Huang, M. Wang and J. Yuan, J. Mater. Chem., 2012, 22, 2271.
- 41. Z. Li, G. Meng, Q. Huang, C. Zhu, Z. Zhang and X. Li, *Chem.- Eur. J.*, 2012, **18**, 14948.
- <sup>65</sup> 42. X. W. Lou, C. Yuan and L. A. Archer, *Chem. Mater.*, 2006, **18**, 3921.
  43. Y. Ye, J. Chen, Q. Ding, D. Lin, R. Dong, L. Yang and J. Liu, *Nanoscale*, 2013, **5**, 5887.
- 44. L. Yang, Z. Bao, Y. Wu and J. Liu, *Journal of Raman Spectroscopy*, 2012, **43**, 848.
- Y. Q. Wang, K. Wang, B. F. Zou, T. Gao, X. L. Zhang, Z. L. Du and S. M. Zhou, *J. Mater. Chem. C*, 2013, **1**, 2441.
   C. Yuan, R. Liu, S. Wang, G. Han, M. Han, C. Jiang and Z. Zhang, *J. Mater. Chem.*, 2011, **21**, 16264.

47. K. Wang, X. Zhang, C. Niu and Y. Wang, *ACS Appl. Mater*. 75 *Interfaces*, 2014, **6**, 1272.

48. J. M. McMahon, S. Li, L. K. Ausman and G. C. Schatz, J. Phys. Chem. C, 2012, 116, 1627.

49. J. S. Kang, S. Y. Hwang, C. J. Lee and M. S. Lee, *Bull. Korean Chem. Soc.*, 2002, **23**, 1604.

