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Review

A review of significant factors in the synthesis of hetero-structured dumbbell-like nanoparticles

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ABSTRACT

This paper reviews several important factors that influence the synthesis of dumbbell-like nanoparticles, which can significantly enhance the catalyst activity in catalytic combustion. The dumbbell-like nanoparticles discussed in this article refer to a hetero-structure with two nanoparticles of different materials in contact with each other. This nanostructure can be considered as a special intermediate between individual spherical nanoparticles and a core-shell nanostructure. Therefore, the synthesis of dumbbell-like nanoparticles is more difficult than other structures. The controllability of the synthesis process, the nanoparticle size and size distribution, and the morphology of the final products depend on many factors: the seed size and size ratio could be used to influence the controllability of epitaxial growth. The component sizes and size distribution could be varied by carefully controlling the reaction temperature and reaction time. The morphology of the dumbbell-like nanoparticles is closely related to the solvent polarity, the precursor ratio, the lattice mismatch between the two components, and the surfactant concentration. Some related synthesis methods are also briefly introduced in each section to facilitate understanding. This summary will benefit the development of new dumbbell-like nanoparticles with various components, which have great potential in catalytic combustion of more dysoxidizable gases.

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1. Introduction

A dumbbell-like nanoparticle consists of a strongly interacting hetero-structure with one nanoparticle at one end and another at the other end. The two different functional nanoparticles in intimate contact with each other look like a dumbbell (Fig. 1(a)) [1]. In some articles, particles with this type of structure are also called peanut-like particles [2]. This kind of binary hybrid nanoparticles are of interest because of their unique electronic [3–7], magnetic [8–10], optical [11–14], and catalytic [15,16] properties, which are not present in the indi-

vidual component nanoparticles. These properties result from the electronic communication across the junction between the two components. In contrast to other structures such as core-shell nanoparticles, in which the core and its interface is surrounded by the shell, in dumbbell-like nanoparticles the two functional surfaces of the two components and their active interface are all exposed; this enhances their catalytic activity and their usefulness as multifunctional probes for diagnostic and therapeutic applications [17,18]. Because the relative positions of each component in dumbbell-like nanoparticles can be fixed, a coordinated distribution between the two components

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Fig. 1. (a) Transmission electron microscopy (TEM) image of the Ag-Fe₃O₄ dumbbell-like nanoparticles (reproduced with permission from Ref. [1]); (b) TEM image of flower-like Au-Fe₃O₄ nanoparticles (reproduced with permission from Ref. [3]); (c) Fe₃O₄-Au-Fe₃O₄ ternary hybrid nanoparticles (reproduced with permission from Ref. [2]).

in catalytic combustion of CO [1,19] and other gases is possible, and sintering can thus be minimized. For example, Au nanoparticles are normally chemically inert and do not catalyze the CO oxidation reaction, but show high catalytic activity after they are deposited on a metal-oxide support [20,21]. This enhancement in catalytic activity is believed to result from the electron transfer between the oxide support and the adjacent Au nanoparticles [22–24]. In a dumbbell-like structure, the catalytic nanoparticles can not only have a better junction effect because they are in intimate contact within each pair but they are also stable at higher temperatures because of their coordinated distribution and fixed positions [25].

Dumbbell-like nanoparticles can be considered as an intermediate between individual component nanoparticles and core-shell nanoparticles. Dumbbell-like nanoparticles are generally synthesized by epitaxial growth of one component nanoparticle on another component nanoparticle, which is called the seed nanoparticle. This is similar to the procedure of synthesizing core-shell nanoparticles, but the nucleation must be controlled appropriately to make the nucleation anisotropically centered on one specific crystal plane around the seeding nanoparticles, which is different from the uniform distribution in core-shell structures. Therefore, heterogeneous nucleation must be promoted and homogeneous nucleation must be suppressed for the successful synthesis of dumbbell-like nanoparticles.

One of the benefits of this special structure and strong interface interactions is that both components in the structure can be modified by electron transfer across the interface, making dumbbell-like nanoparticles highly active at relatively low temperatures for the catalytic oxidation of some exhaust gases, such as CO. Unfortunately, because of the particularity of the structure and the stringent requirements for an appropriate nucleation described above, only a few dumbbell-like nanoparticles have been successfully synthesized to date, including Au(Ag, Pt, Pd)-Fe₃O₄(Co₃O₄) [2,3,17,25–28], Au-PbS(PbSe) [2], FePt-CdS [11], and Cu-Ag [29]; most of these contain noble metal nanoparticles and magnetic nanoparticles. The application of dumbbell-like nanoparticles to the catalytic combustion of gases is limited to very few studies, almost all of which focus

on CO oxidation, which can be oxidized by many other catalysts at very low temperatures, even dozens of degrees below zero [30]. Therefore, the advantages of dumbbell-like nanoparticles cannot be fully appreciated by studying the catalytic oxidation of CO. Other gases including CH₄, which are more difficult to oxidize catalytically at relatively low temperatures, have not been studied using these catalysts. This research gap is mostly owing to the difficulty in synthesizing dumbbell-like nanoparticles using a wide variety of chemical elements. Therefore, it is necessary to know what the difficulties are and what factors can influence the synthesis results.

In this review we have summarized some significant factors that influence the preparation of dumbbell-like nanoparticles, which might be helpful in the development of dumbbell-like nanoparticles composed of other chemical elements. These new structures might show higher catalytic activity and could be used for the catalytic combustion of other gases.

2. Influence of nanoparticle size on the controllability of epitaxial growth

2.1. Influence of seed size

Smaller metal particles with a higher specific surface area and larger contact region with the reactants would not only enhance the catalytic activity, but could also facilitate the synthesis of dumbbell-like nanoparticles if used as seed nanoparticles [31–36].

Wang's group [25] introduced a general approach to noble metal-metal oxide dumbbell-like nanoparticles through organic solvothermal synthesis (Scheme 1). During the seed-mediated growth, after thermal decomposition, metal oxides oxidized from metal carbonyls grown over the noble metal seeds, followed by oxidation in air. They succeed in preparing nanoparticles with diverse materials, including the noble metals Au, Ag, Pt, or Au-Ag alloys and oxides of Fe or Co, which all exhibited enhanced catalytic activity toward CO oxidation. They pointed out that monodisperse seeding nanoparticles with the right size and surface were crucial in making dumbbell-like nanoparticles. The larger particles tended to precipitate as the

Scheme 1. Seed-mediated growth for noble metal-metal oxide nanoparticles. Reproduced with permission from Ref. [25].

metal oxide nanoparticles grow on them. To have good control of the epitaxial growth, the seed sizes should be below 10 nm.

2.2. Influence of size ratio

In another synthesis of exchange-coupled nanocomposite magnets through nanoparticle self-assembly by Zeng et al. [37], hexane dispersions of FePt and Fe₃O₄ nanoparticles with selected concentrations, volumes, and sizes were mixed under ultrasonic agitation, followed by evaporation of the hexane or addition of ethanol. Ultimately, these two kinds of nanoparticles were converted into FePt-Fe₃O₄ nanocomposites. They fixed the mass ratio of Fe₃O₄ and FePt to 1:10 but the sizes were different, and the TEM images of the resulting binary assemblies are shown in Fig. 2 [37]. We can see that when the sizes of Fe₃O₄ and FePt were both 4 nm, almost one Fe₃O₄ nanoparticle was connected with one FePt nanoparticle (Fig. 2(a)); when the Fe₃O₄ nanoparticle was enlarged to 8 nm, each large nanoparticle of Fe₃O₄ was surrounded by 6–8 small FePt nanoparticles (Fig. 2(b)). It follows logically that, because the mass ratio was fixed, a larger Fe₃O₄ nanoparticle should be in contact with more FePt particles. However, when the size of the Fe₃O₄ particles was changed to 12 nm, a clear phase segregation appeared between the two components (Fig. 2(c)). It is apparent that the particle size ratio has a great impact on the ordering of nanoparticles [38] and the structure formed.

3. Influence of reaction temperature on component size

We have already discussed that the seed size could influence the nanoparticle ordering and determine the successful formation of dumbbell-like structures. The sizes of the components in a dumbbell-like structure could also be influenced by the reaction temperature.

Table 1

Average size of Au nanoparticles synthesized at different temperatures. Reproduced with permission from Ref. [39].

Reaction temperature (°C)	Average Au NP size (nm)
2	9.5
10	8.1
15	7.3
20	6.4
25	5.3
35	3.3
40	2.4

3.1. Influencing the size of noble metal seed

The reaction temperature could influence the sizes of noble metal seeds [3,25,28,39]. For example, in Wang's experiment [25] mentioned above, they mixed platinum acetylacetonate [Pt(acac)₂, "acac" refers to acetylacetonyl], 1-octadecene (ODE), oleylamine, and oleic acid, then the hexane solution of Fe(CO)₅ was quickly injected into the hot mixture solution at 180 °C. After heating the solution to 200 °C and keeping it at that temperature for 1 h before cooling to room temperature, they obtained 3-nm Pt nanoparticles; if the Fe(CO)₅ solution was injected at 160 and 120 °C they obtained 5- and 7-nm Pt nanoparticles, respectively.

In a facile synthesis of monodisperse Au nanoparticles reported by Peng's group [39], they used oleylamine (OAm) as a nanoparticle stabilizer, *tert*-butylamine-borane complex as a reducing agent, and tetralin as solvent. They prepared Au nanoparticles through a burst nucleation with sizes tunable from 1 to 10 nm by carefully controlling the reaction temperature at which the reducing solution was injected into the precursor solution. The reaction temperatures and the resulting sizes of the Au nanoparticles are listed in Table 1 [39]. It is apparent that there is a linear correlation between the reaction temperature and the nanoparticle size. This formation of Au nanoparticles can be explained by the classic La Mer theory [40,41]: injection of the reducing agent into the precursor solution at a relatively high temperature results in the burst nucleation consuming most of the precursors, leading to fast nucleation and growth processes, and ultimately produces smaller Au nanoparticles.

Fig. 2. TEM images showing binary nanoparticle assemblies. (a) Fe₃O₄(4 nm):Fe₅₈Pt₄₂(4 nm) assembly; (b) Fe₃O₄(8 nm):Fe₅₈Pt₄₂(4 nm) assembly; (c) Fe₃O₄(12 nm):Fe₅₈Pt₄₂(4 nm) assembly. All with a fixed mass ratio. Reproduced with permission from Ref. [37].

3.2. Influencing the size of metal oxide nanoparticle

Even though the size of the metal oxide nanoparticles is not normally tuned by changing the reaction temperature, it has been observed that, in the synthesis of magnetite nanoparticles using thermal decomposition of the metal precursor [42,43], the metal oxide nanoparticles were bigger as the temperature increased, which is different from the noble metal seeds mentioned above. The thermal decomposition procedure is similar to epitaxial growth of metal oxide nanoparticles on noble metal seeds for the synthesis of dumbbell-like nanoparticles [1]. In the synthesis of Fe_3O_4 nanoparticles reported by Sun et al. [42] (Scheme 2), they mixed $\text{Fe}(\text{acac})_3$, 1,2-hexadecanediol, oleic acid, oleylamine, and phenyl ether, and then heated the mixture to 200 °C. The reaction mixture was then heated to reflux at 265 °C and 4-nm nanoparticles were obtained. However, when they changed the phenyl ether to benzyl ether (which has a higher boiling temperature than phenyl ether) and changed the reflux temperature to 300 °C, they obtained 6-nm nanoparticles.

3.3. Influencing the size distribution

The reaction temperature could also have a strong influence on the size distribution during the epitaxial nucleation and growth process of the metal oxide on noble metal seeds. In a typical synthesis of magnetic-metallic ($\text{XFe}_2\text{O}_4\text{-Au}$, $\text{X} = \text{Fe}, \text{Mn}, \text{Co}$) dumbbell-like nanoparticles, Shi's group [2] pointed out that an inappropriate temperature-rise period would give a much broader size distribution of the nanoparticles. They used a two-stage heating strategy to synthesize hybrid nanoparticles, including $\text{Au-Fe}_3\text{O}_4$ dumbbell-like nanoparticles. The dumbbell-like nanoparticles were prepared by decomposition of iron acetylacetonate ($\text{Fe}(\text{acac})_3$) on the surface of Au nanoparticles in octyl ether, with the presence of oleic acid and oleylamine. Octyl ether is a high-boiling-point solvent; as such, the mixture could be heated to 205 °C and kept at that temperature for 2 h before heating to reflux at a temperature as high as 300 °C. If the reaction mixture was heated to 300 °C directly, a wide size distribution of the dumbbell-like nanoparticles resulted. A temperature of 200 °C was first used for 2 h because it is slightly higher than the decomposition temperature of

$\text{Fe}(\text{acac})_3$, which was used as the precursor of Fe_3O_4 . At this temperature the concentration of free metal ions was not so high, resulting in heterogeneous nucleation and slow growth of the nuclei during this period. After the reaction mixture was heated to reflux at a relatively high temperature of approximately 300 °C, those nuclei grew substantially. Thus, the two-stage temperature could separate the nucleation and growth process of the metal oxide nanoparticles on the noble metal seeds.

This relationship between the temperature and size distribution was also reported by Sun's group [42] in the synthesis of monodisperse magnetite (Fe_3O_4) nanoparticles, using a similar strategy of high-temperature solution phase reaction of $\text{Fe}(\text{acac})_3$ with 1,2-hexadecanediol in the presence of oleic acid and oleylamine. They obtained Fe_3O_4 nanoparticles with a size distribution of 4 to 15 nm when the temperature was raised rapidly from room temperature to reflux; and they succeeded in preparing monodisperse Fe_3O_4 nanoparticles with good size control of 4 or 6 nm using the same two-stage temperature procedure at two different reflux temperatures.

4. Influence of reaction time on component size

4.1. Influence at a liquid-liquid interface

In contrast to the most common methods to produce dumbbell-like nanoparticles using organic solvents [2,3,27], Gu's group [17] introduced a new method to create dumbbell-like nanostructures at a liquid-liquid interface between an organic solvent and an aqueous solution. At this interface, nanoparticles could self-assemble to form "colloidosomes", and every nanoparticle forming the colloidosomes would be partially exposed. Heterogeneous reaction takes place on these exposed surfaces to produce dumbbell-like nanoparticles composed of two distinct nanospheres. In a typical synthesis of $\text{Ag-Fe}_3\text{O}_4$ dumbbell-like nanoparticles, they dissolved the as-prepared nanoparticles of Fe_3O_4 [43] into an organic solvent (e.g., dichlorobenzene, dichloromethane, hexane, or dioctyl ether) to form a solution, and then the solution was added into an aqueous solution of silver nitrate. The mixture was treated under ultrasonic emulsification to form a stable emulsion [44,45] of the two solutions. The dumbbell-like nanoparticles were obtained after 30 min, as illustrated in Scheme 3 [17].

The nucleation of the Ag on Fe_3O_4 nanoparticles was observed using TEM. As shown in Fig. 3 [17], the size of the Fe_3O_4 nanoparticles was 8 nm (Fig. 3(a)) before the nucleation of Ag. After a reaction period of 10 min, the Ag spheres appeared on the surface of the Fe_3O_4 nanoparticles and had a size of 3 nm (Fig. 3(b)); when the reaction was stopped after 30 min the Ag spheres had grown to 5.5 nm (Fig. 3(c)) but the size of the Fe_3O_4 nanoparticles did not change during the reaction period.

This can be explained by the formation process of the Ag nanoparticle. Because the Fe_3O_4 nanoparticle was not completely covered by the surfactant molecules, only a few $\text{Fe}(\text{II})$ sites could act as the catalytic center for the reduction of Ag^+ , i.e., the Fe_3O_4 nanoparticle was used for seeding an Ag nanoparticle. Further reduction of Ag^+ could take place at the initial

Scheme 2. Organic phase process for making monodisperse Fe_3O_4 nanoparticles. Reproduced with permission from Ref. [42].

Scheme 3. Formation of dumbbell-like nanoparticles at a liquid–liquid interface. Reproduced with permission from Ref. [17].

Fig. 3. TEM images of (a) the as-prepared Fe_3O_4 nanoparticles and the Fe_3O_4 -Ag heterodimers (b) after reaction for 10 min and (c) after the reaction was stopped at 30 min. Reproduced with permission from Ref. [17].

Ag nucleation sites. Therefore, the diameter of the Ag nanoparticles increased with the reaction time as they grew on the Fe_3O_4 seeds.

4.2. Influencing difference between liquid–liquid interface formation and burst nucleation

Interestingly, in the synthesis of Au nanoparticle seeds reported by Peng et al. [39], the size of the Au nanoparticle was not dependent on the reaction time. They used a *tert*-butylamine-borane complex as a reducing agent and hydrogen tetrachloroaurate(III) hydrate as a precursor in tetralin and oleylamine to produce monodisperse Au nanoparticles. They removed the same amount of the reaction mixture at different reaction times during the 1-h reaction process, and found little size change. This may be because the reaction rate was different to the nucleation of Ag on Fe_3O_4 . In this synthesis, the burst nucleation occurred immediately and consumed most of the precursors after the reducing agent was injected; thus, the nucleation and growth processes were very fast and independent of the reaction time. That is to say, depending on the actual synthesis method, the reaction time may have an influence on the component size or not.

5. Influence of reaction solvent polarity on the morphology

The morphology of the nanoparticles in a dumbbell-like structure is more important than the size. This is also a more challenging synthetic process. The most common influencing factor that differentiates the dumbbell-like nanoparticles from ordinary spherical or core-shell nanoparticles is the polarity of solvent used in the reaction.

5.1. Electron transfer in dumbbell-like structure formation

The formation of a dumbbell-like nanoparticle results from the epitaxial growth of one component nanoparticle on another component nanoparticle. A suitable electron transfer results in dumbbell-like structures instead of core-shell structures. For example, in the synthesis of Au- Fe_3O_4 dumbbell-like nanoparticles, as the Fe_3O_4 nanoparticles nucleate on Au nanoparticles, the polarized plane [3] induces a change in the charge at the interface, and the free electrons from the Au nanoparticles will compensate for that charge change. However, one Au nanoparticle only has a limited amount of electrons, so the compensation could only take place at only one facet of the Au nanoparticle, resulting in electron deficiency at other facets, which is not suitable for multi-nucleation. Therefore, only dumbbell-like structure can be produced. If the Au nanoparticle has more electrons to compensate for the charge at the plane, the nucleation of Fe_3O_4 nanoparticles on Au seeds would occur at more facets of the Au nanoparticle. These extra electrons could be offered by more polar solvent in the synthesis.

5.2. Influence of solvent polarity

Yu et al. [3] prepared dumbbell-like Au- Fe_3O_4 nanoparticles with 1-octadecene as solvent in the presence of oleic acid and oleylamine. They heated the mixture to reflux at a temperature of approximately 300 °C for the decomposition of iron pentacarbonyl over the surface of the Au nanoparticles, and then the mixture was oxidized at room-temperature in air, as illustrated in Scheme 4. After they changed the solvent from octadecene to diphenyl ether, which has a higher polarity, they obtained flower-like Au- Fe_3O_4 nanoparticles (Fig. 1(b)) [3].

Scheme 4. Synthesis of Au-Fe₃O₄ dumbbell-like nanoparticles using Fe(CO)₅. Reproduced with permission from Ref. [3].

The research of Shi's group [2] is further proof of the influence of solvent polarity on the formation of dumbbell-like nanoparticles. They prepared dumbbell-like nanoparticles through the decomposition of Fe(acac)₃ on the surfaces of Au nanoparticles in octyl ether, with the presence of oleic acid and oleylamine. When the solvent was changed to benzyl ether and phenyl ether, which contain aromatic rings and are good electron donors, core-shell particles were produced using the same procedure that resulted in dumbbell-like nanoparticles in octyl ether. If the solvent polarity was between octyl ether and benzyl ether or phenyl ether, such as octadecene, a mixture of dumbbell-like and core-shell structures was obtained. To further investigate this influence, they stopped the reaction half-way in phenyl ether or benzyl ether and obtained flower-like particles with several Fe₃O₄ "petals" surrounding the Au core. Core-shell particles should be ultimately produced if the reaction is not terminated. This observation is in accordance with the formation principle mentioned at the beginning of this section: high polarity solvents could give more electrons and contribute to the formation of additional Fe₃O₄ nuclei on the Au surface. Several Fe₃O₄ nuclei on the Au nanoparticle would result in a flower-like structure, and as these nuclei increase in size they would fuse together to form a shell, giving the final core-shell structure. However, if a solvent with mostly saturated hydrocarbon chains is used, further nucleation would not be possible after a single Fe₃O₄ nucleus is formed, because these solvents could not give enough electrons.

6. Influence of precursor ratio on nanoparticle size and morphology

6.1. Influencing the nanoparticle size

The size of dumbbell-like nanoparticles could be controlled by varying the molar ratio of one component to the seed component. In their research on using dumbbell-like PtPd-Fe₃O₄ nanoparticles for electrochemical detection of H₂O₂, Sun et al. [46] obtained different sizes of Fe₃O₄ nanoparticles by controlling the molar ratio of Fe(CO)₅ to Pt-Pd seeds, in which Fe(CO)₅ acted as the precursor of Fe. PtPd-Fe₃O₄ nanoparticles formed through controlled nucleation and growth in 1-octadecene in the presence of oleylamine and oleic acid followed by oxidation in air. But this influence of the precursor ratio on nanoparticle size was limited. Under some conditions the change in the precursor ratio could even affect the nanoparticle structures rather than the nanoparticle sizes [47].

6.2. Influencing the morphology in the presence of sulfur

Shi et al. [2] prepared binary and ternary hybrid nanocrystals

by spontaneous epitaxial nucleation and growth of other components onto seed nanoparticles in organic solutions at a high temperature. Dumbbell-like nanostructures were present in the binary hybrid nanocrystals. Although they synthesized Au-Fe₃O₄ dumbbell-like nanoparticles, even though Fe₃O₄ formed on gold nanoparticles all the time, they did not distribute evenly on every gold nanoparticle. They found that when a smaller amount of gold seeds than usual was used, a mixture of free Fe₃O₄ nanoparticles and dumbbell-like structures was produced.

They also prepared Au-PbS and Au-PbSe dumbbell-like nanoparticles [2]. For the synthesis of Au-PbS dumbbell-like nanoparticles, PbO and oleic acid were first mixed in trioctylamine and heated to 120 °C to form a Pb-oleate complex, then the mixture of the Pb-oleate complex was cooled to about 100 °C. A hexane solution of Au nanoparticles was then injected into the solution, followed by the addition of a sulfur solution in oleylamine and phenyl ether. The reaction mixture was heated to 150 °C and kept at that temperature for 1 h. For the synthesis of nanoparticles with different morphologies, they kept the PbO:S ratio at 3:1 while changing the amount of Au nanoparticles. When the ratio of Au:sulfur was 1:10, they obtained dumbbell-like nanoparticles (Fig. 4(a)); when the amount of Au nanoparticles was lowered to an Au:sulfur ratio of 1:20, they obtained ternary hybrid nanoparticles of Fe₃O₄-Au-Fe₃O₄, in which every Au nanosphere was connected with two PbS nanospheres on opposite sides (Fig. 4(b)).

6.3. Influencing difference between sulfur and solvent polarity

It is clear that the precursor to seed ratio can influence the morphology of the resulting dumbbell-like Au-PbS nanoparticles. In contrast to the thermal decomposition of an Fe precursor for the formation of Au-Fe₃O₄, in which the morphology was mostly influenced by the polarity of the solvent, the changes in solvent did not affect the morphology of the Au-PbS hybrid particles. Using different solvents with the same Au to precursor ratio, Shi's group [2] synthesized Au-PbS nanoparticles with the same morphology. This was caused by the addition of sulfur; in the synthesis process sulfur tended to be adsorbed onto the surface of Au, and at the same time sulfur would react with the Pb-oleate complex. Thus, the element of sulfur was needed by both Au and Pb-oleate simultaneously, and the competition finally resulted in the combination of PbS and Au through the nucleation of PbS on the surface of Au. In this way both the Pb-oleate complex and Au were satisfied. So

Fig. 4. Different morphologies with an Au:S ratio of (a) 1:10 and (b) 1:20. Reproduced with permission from Ref. [2].

in the presence of sulfur, the competition and combination of the two components dominate while the electron density has a very minor influence on the nucleation of PbS on the surface of Au. Sulfur plays the role of fusing the nanoparticles together. Regardless of what solvent was used in the synthesis, the morphology is mostly determined by the amount of precursor reacting with the seed nanoparticles.

When the dumbbell-like Au-Fe₃O₄ nanoparticles were heated to 150–200 °C in the presence of elemental sulfur, each pair of the S-modified Au nanoparticles at that high temperature would fuse together to give the Fe₃O₄-Au-Fe₃O₄ ternary hybrid nanoparticles (Fig. 1(c)) [2]. PbS-Au-Fe₃O₄ nanoparticles could also be made by the reaction of Au-Fe₃O₄ nanoparticles with a Pb-oleate complex in the presence of elemental sulfur.

7. Influence of lattice mismatch on morphology

In addition to the polarity of the reaction solvent, the lattice mismatch between the two components is another critical factor in the successful synthesis of dumbbell-like nanoparticles.

7.1. Influence on epitaxial growth

Most of the dumbbell-like nanoparticles are prepared through epitaxial growth of one component nanoparticle on another component nanoparticle. It is commonly believed that in most cases the lattice mismatch between the two components should be below 5% for epitaxial growth to occur [48]. That is why Au and Ag (lattice mismatch: 0.2%), Pt and Pd (lattice mismatch: 0.85%) and other noble metals which have little lattice mismatch with each other have been widely reported for the synthesis of bimetallic nanocrystals with a core-shell structure [47]. With little lattice mismatch, epitaxial growth is more easily to occur and one metal component can have more chances to grow on another metal component, giving core-shell nanoparticles. As mentioned in the above sections, the preparation of dumbbell-like nanoparticles is similar to that of core-shell nanoparticles. Both of them can be synthesized through seeded growth involving preferential growth on a preformed seed surface. Seeded growth is widely used for its advantages in structural control and variety [48,49]. In seeded growth there are two patterns: homogeneous growth and heterogeneous growth. In homogeneous growth the whole seed surface acts as the nucleation site, but in heterogeneous growth, the growth can only occur on part of the seed surface [49–52]. These two patterns could often influence the shape and structure of the final nanoparticles. Core-shell nanoparticles are mostly generated from homogeneous growth and dumbbell-like nanoparticles form mostly as a result of heterogeneous growth [3,53–57]. For the preparation of dumbbell-like nanoparticles, heterogeneous growth could possibly occur when the lattice mismatch is not too large to break the epitaxial growth, which will produce individual nanoparticles, but should still be larger than that of homogeneous growth, which always generates core-shell nanoparticles. The different conditions for these two growth patterns are generally accept-

ed by many researchers and have been proven by a large amount of experimental results [3,49–57].

7.2. Experimental evidence of the influence of lattice mismatch

Zhang et al. [26] prepared Ag-Fe₃O₄ heterodimeric nanoparticles through epitaxial growth of Ag on Fe₃O₄ seeds in nonpolar solution. Silver acetate [Ag(ac)] was used as the Ag precursor and mixed with the as-prepared Fe₃O₄ nanoparticles in oleylamine and toluene. The reaction mixture was heated to 80 °C and kept at that temperature for 8 h. The Ag nanoparticles grew on the Fe₃O₄ nanoparticles giving dumbbell-like nanoparticles. The authors pointed out that the large lattice mismatch between Ag (FCC, $a = 4.08$ Å) and Fe₃O₄ (FCC, $a = 8.40$ Å) could result in the formation of the non-symmetric heterodimer structure instead of the centrosymmetric core-shell type structure. This is similar to the Au-Fe₃O₄ nanoparticles, where the authors [3] believed that the structure was derived from the epitaxial growth of Fe₃O₄ on Au seeds because Au has an FCC structure with $a = 4.08$ Å, whereas Fe₃O₄ has a cubic structure with $a = 8.35$ Å, which is almost exactly double. Even though Jin's group [47] succeeded in synthesizing Pd@Cu core-shell nanocubes through epitaxial growth, the Cu atoms initially nucleated on only a few of the many faces of the Pd seed. Furthermore, the final Pd seed was rarely located in the center of each core-shell structure, which was a result of the large lattice mismatch (7.1%) between Pd and Cu.

Another experiment conducted by Gu et al. [11] further demonstrates the strong influence of lattice mismatch on the formation of dumbbell-like nanoparticles. They reported a one-pot chemical synthesis method for generating dumbbell-like heterodimer nanoparticles by taking advantage of lattice mismatching and selective annealing at a relatively low temperature. First, amorphous CdS was deposited on the surface of FePt nanoparticles forming a metastable core-shell structure. The CdS could be transform from an amorphous to a crystalline state by heating the core-shell nanoparticles to 280 °C. When they were dispersed in solution, the FePt@CdS core-shell nanoparticles evolved into dumbbell-like nanoparticles composed of CdS and FePt nanocrystals, and had sizes of less than 10 nm. This was attributed to the incompatible lattices of FePt and CdS and the help of the surface tension. Scheme 5 [11] illustrates the typical synthetic route of the change from core-shell to a dumbbell-like structure.

From the high-resolution TEM images, they found that the

Scheme 5. The change from a core-shell to dumbbell-like structure. Reproduced with permission from Ref. [11].

dumbbell-like nanoparticles were almost monodisperse after the reaction was completed. The diameters of the FePt parts remained at 2.5 nm and the CdS parts had diameters of about 3 to 4 nm. The selective area electron diffraction image of the dumbbell-like nanoparticles gave the rings that originated from the zinc blende phase of CdS ({111}, {220}, and {311} planes) and the disordered FCC phase of FePt ({111}, {200}, {220}, and {311} planes). They concluded that the key factors in making dumbbell-like nanoparticles are the lattice mismatch and the phase transition. That is why they failed to produce large amounts of well-defined FePt@S and FePt@CdS core-shell nanoparticles.

7.3. Influencing mechanism of lattice mismatch and method to overcome this influence

The reason for the influence of lattice mismatch may be explained from the system energy [58]. For two components that have a larger lattice mismatch, it is hard to form the bond between them because that requires more energy. Therefore, if they are combined in a dumbbell-like structure, the interface between them will be smaller and the system energy can thus be lower. If the lattice mismatch is smaller, the interface energy is not so high and it is possible to form a core-shell structure. That is why noble metals or semiconductors easily form core-shell structures, whereas dumbbell-like structures are easily formed between noble metals and semiconductors.

It is also worth noting that the addition of foreign ions (such as Ag^+ ions) may overcome the lattice mismatch in some reactions. The added foreign ions could form a sacrificial metal layer on the surface of the seed particles, and then another metal will replace the sacrificial metal through under-potential deposition (UPD) [59]. In the controlled overgrowth of Pd on Au nanorods, Jing et al. [60] introduced Ag^+ and H_2PdCl_4 into colloidal Au nanorods in the presence of cetyltrimethylammonium chloride or cetyltrimethylammonium bromide at 30 °C, and then added ascorbic acid as the reducing agent to initiate the Ag-UPD guided deposition of Pd. When the concentration of Ag^+ was low, continuous conformal Pd shells were overgrown on the Au nanorods; with the increase of the Ag^+ concentration, small cavities started to form at the Au-Pd interfaces; after the Ag^+ concentration was sufficiently high, segregated Pd islands started to form on the Au nanorods. It is believed that foreign ions, such as Ag^+ , play crucial roles in the growth control and various Au nanostructures can be made using this strategy during the seed-mediated growth processes [61–63].

In this Ag^+ -mediated Pd overgrowth, the sacrificial Ag monolayer formed on the Au nanorod first, and then reacted with PdCl_4^{2-} ions through galvanic replacement. After that the Ag layer was consumed but continuously regenerated in the solution. With the co-reduction and co-deposition of Ag and Pd, Pd successfully grew on the Au nanorods. Another example using sacrificial material for the synthesis of Au-CdSe is discussed in the next section.

8. Influence of surfactant concentration on morphology

We discussed above that the reaction solvent could influence the morphology of dumbbell-like nanoparticles because different solvents with different polarities have various abilities to give electrons. A surfactant could also influence the morphology of dumbbell-like nanoparticles. The Au-CdSe nanoparticles synthesized by Carbone's group [64] could provide proof. Even though the CdSe in the Au-CdSe nanoparticles was rod-like, the formation of the matchstick-like nanocrystals is still worth understanding for the synthesis of dumbbell-like nanoparticles. It is not easy to grow Au domains onto specific locations of CdSe nanoparticles, so the authors performed a two-step reaction to obtain Au-CdSe. First, they synthesized PbSe-CdSe nanoparticles, in which PbSe was located at the tips of the CdSe nanorod. The PbSe was used as a sacrificial material in the next step. Second, these PbSe nanoparticles were replaced by Au nanoparticles using the Au(III):surfactant complex, which was prepared by dissolving HAuCl_4 , *n*-dodecylamine (DDA) and didodecyltrimethyl-ammonium bromide (DDAB) in toluene by sonication. When the Au(III) amount was not too high, Au-CdSe-Au nanodumbbells were formed. Upon reaction with excess Au(III), the CdSe nanorods became thinner and shorter, and the Au nanoparticles were only located on one end of the CdSe nanorod (Fig. 5(a)) because of intraparticle Ostwald ripening mechanism, which can lead to the dissolution of the most unstable metal patches.

What is important is that by varying the concentration of the surfactants that bind to the gold surface, the author could change the morphology of the Au-CdSe nanoparticles. For example, with the Au(III):surfactant complex lacking DDA, they obtained a disordered network of nanorod chain-like segments (Fig. 5(b)), in which individual dumbbells fused with each other owing to the interaction and coalescing of the Au nanoparticles. With the surfactant containing only DDAB, the Au metal could still deposit on CdSe by an efficient reaction with PbSe sacrificial domains. The DDAB served as a reducing agent for Au(III), and the DDA served as a surface stabilizer for the gold nanoparticles. Without DDA, nanocrystal precipitation would happen and the gold metal nanocrystals would be destabilized, forming the fused hybrid nanocrystals.

In several of the methods [2,3,25,42] discussed in this review, oleylamine and oleic acid were frequently used as protective ligands. In actual fact, oleic acid was mostly used to enhance the reducing power of some reducing agents [65], and oleylamine served as the real stabilizing surfactant. Using only oleic acid might result in a sticky product that is difficult to purify [42].

Fig. 5. Structural images of asymmetric semiconductor-gold hetero-structure (a) and fused Au-CdSe nanoparticles (b) by changing the concentration of the surfactants. Reproduced with permission from Ref. [64].

9. Conclusions

With unique electronic, magnetic, optical, and catalytic properties, the dumbbell-like nanoparticles have great potential for the development of highly active catalysts for energy conversion and highly sensitive delivery probes for biomedical applications. However, in the field of catalytic combustion, the application of dumbbell-like nanoparticles is very limited. Only easily oxidized gases such as CO have been catalyzed using dumbbell-like nanostructured catalysts. The catalytic combustion of other gases at lower temperatures, such as methane, which is more difficult to oxidize, has yet to be achieved. This is because the components used to synthesize dumbbell-like nanoparticles are very limited. Because of the limitations of the current synthesis methods, only a few elements have been used in the past, and even with these elements it is not easy to successfully synthesize the dumbbell-like structure.

Many factors can influence the result in the synthesis of dumbbell-like nanoparticles. The control of the epitaxial growth could be affected by the seed size and size ratio; a smaller seed size and size difference between the two components is favorable for the control of the reaction. The reaction temperature and reaction time should be carefully controlled based on the properties of the reaction materials to obtain dumbbell-like nanoparticles with an appropriate component size and size distribution. The morphology of the dumbbell-like nanoparticles, which is most important for the unique physical and chemical properties, could be influenced by a variety of factors, such as the polarity of the reaction solvent, the ratio of the precursors correlating with the two components in the dumbbell-like structure, the lattice mismatch between the two materials of the dumbbell-like nanoparticles, and the surfactant concentration used in synthesizing the dumbbell-like nanoparticles. In addition to those factors, suitable precursors and reducing or oxidizing agents, the operating environment, and many other factors can determine the result in the synthesis of dumbbell-like nanoparticles. It will be meaningful to discover other synthetic methods to obtain dumbbell-like nanoparticles consisting of more element species and to study the applications of this uniquely structured catalysts for the catalytic combustion of more gases.

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Graphical Abstract

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A review of significant factors in the synthesis of hetero-structured dumbbell-like nanoparticles

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This article reviews some significant factors in the synthesis of dumbbell-like nanoparticles, including seed size and size ratio, reaction temperature and time, solvent polarity, precursor ratio, lattice mismatch, and surfactant concentration.

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异质哑铃型纳米颗粒合成中的关键因素

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摘要: 哑铃型纳米颗粒由一种包含强相互作用的异质结构成, 它两端是不同物质的纳米颗粒。这两种不同功能的纳米颗粒紧密相连, 形成一种哑铃形的外观。这种结构的纳米颗粒在电子、磁性、光学及催化等方面有着不同于单一组分纳米颗粒的独特性质, 因此受到人们广泛关注。哑铃型纳米颗粒的这些独特性质是由两种物质交界面处的电子转移引起的, 得益于较强的界面相互作用, 两种物质都可以通过界面处的电子转移得到改良, 使得这种结构的催化剂在较低温度下催化氧化有机废气时活性很高。以CO氧化反应为例, Au纳米颗粒通常情况下对该反应没有催化活性, 但是被负载到金属氧化物上面以后, 却表现出了很高的催化活性。这正是氧化物载体与Au纳米颗粒之间电子传输的结果。

通常在核壳结构中, 核心物质以及两种物质的交界面都被外壳所包裹, 而哑铃型结构当中的两种物质的功能面以及它们之间活泼的交界面均可以充分地暴露在反应物中, 从而极大提升了其催化效果。这种独特的结构优势也在疾病诊断与治疗中的多功能探针上得到了广泛应用。由于哑铃型结构的两种物质的纳米颗粒相对位置是固定的, 当用作催化剂时可以发挥出很好的抗烧结性能, 还可使这两种物质更协调地均匀分布。因此哑铃型结构催化剂不仅催化活性更高, 而且在较高温度下具有较高的稳定性。

哑铃型结构可以看作是独立纳米颗粒与核壳型纳米颗粒之间的一种中间状态,它通常是由一种物质的纳米颗粒在另一种种子颗粒上面经过外延生长得到的.这与核壳结构纳米颗粒的合成很相似,但是必须准确地控制成核过程,使得成核可以各向异性地发生在种子颗粒的某一个晶面上.而在核壳结构的合成中,这一成核过程是均匀分布的.所以在制备哑铃型结构纳米颗粒时,很重要的就是要促进非均质成核,同时抑制均相成核.

由于哑铃型纳米颗粒的特殊结构,在制备时想要准确控制上述成核条件是非常困难的,所以到目前为止,仅有很少种类的物质可以被制成哑铃型结构,比如Au(Ag, Pt, Pd)-Fe₃O₄(Co₃O₄), Au-PbS(PbSe), FePt-CdS和Cu-Ag等,这些物质中大多数都是由贵金属纳米颗粒和磁性纳米粒子组成的.哑铃型纳米颗粒由于受限于物质种类,它在催化氧化方面的应用也被局限在了很少一部分气体上,如CO.而通过其它很多种催化剂已经可以在较低温度(甚至零下数摄氏度)下实现CO催化氧化.因此,哑铃型结构的优势在CO催化氧化中并不能得到很好利用和体现,而用于甲烷等一些在较低温度下更难氧化的气体的催化氧化尚未见报道.这正是由合成多种多样的哑铃型纳米颗粒的巨大困难所致.因此,找到合成哑铃型纳米颗粒的困难所在以及合成过程中的一些重要影响因素非常有意义,这将帮助我们使用更多的物质合成出一些新的哑铃型纳米颗粒,进而利用其高催化活性,使得更多难以氧化的气体在较低温度下被氧化.

本文总结了合成哑铃型纳米颗粒时的多种影响因素,并介绍了相关的一些合成方法.种子颗粒的尺寸以及两种颗粒之间的尺寸比例可以影响制备过程中外延生长的可控性,颗粒尺寸以及两种颗粒的尺寸差别越小,反应越容易控制.反应温度和反应时间需要根据反应物的性质进行精确控制才可以得到合适的尺寸以及较好的粒径分布.而两种不同的物质最终能不能形成哑铃型结构则是由很多种因素决定的,比如反应溶剂的极性、两种物质之间的晶格错配度以及反应中所用乳化剂的含量.除此之外,合适的前驱体、氧化还原剂以及操作环境等都可以影响哑铃型纳米颗粒的合成结果.

关键词: 哑铃型纳米颗粒; 催化剂合成; 催化燃烧; 催化氧化

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