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Review

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

Qifu Huang, Wenzhi Li *, Qizhao Lin #, Dong Pi, Chao Hu, Chunyu Shao, Haitao Zhang

Department of Thermal Science and Energy Engineering, School of Engineering Science, University of Science and Technology of China, Hefei 230026, Anhui, China

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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.

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 individual 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

* Corresponding author. Tel: +86-551-63600786; Fax: +86-551-63600786; E-mail: liwenzhi@ustc.edu.cn
# Corresponding author. Tel: +86-551-63600430; E-mail: qlin@ustc.edu.cn
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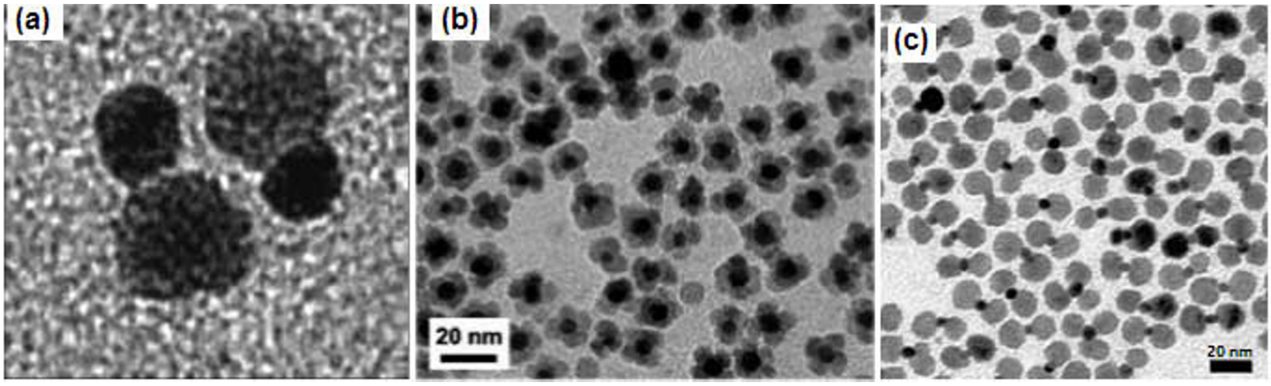

Fig. 1. (a) Transmission electron microscopy (TEM) image of the Ag–Fe_3O_4 dumbbell-like nanoparticles (reproduced with permission from Ref. [1]); (b) TEM image of flower-like Au–Fe_3O_4 nanoparticles (reproduced with permission from Ref. [3]); (c) Fe_3O_4–Au–Fe_3O_4 ternary hybrid nanoparticles (reproduced 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)–Fe_3O_4(Co_3O_4) [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 CH_4, 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