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Historical perspective

Noble metal-based bimetallic nanoparticles: the effect of the structure on the optical, catalytic and photocatalytic properties

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ABSTRACT

Nanoparticles composed of two different metal elements show novel electronic, optical, catalytic or photocatalytic properties from monometallic nanoparticles. Bimetallic nanoparticles could show not only the combination of the properties related to the presence of two individual metals, but also new properties due to a synergy between two metals. The structure of bimetallic nanoparticles can be oriented in random alloy, alloy with an intermetallic compound, cluster-in-cluster or core–shell structures and is strictly dependent on the relative strengths of metal-metal bond, surface energies of bulk elements, relative atomic sizes, preparation method and conditions, etc. In this review, selected properties, such as structure, optical, catalytic and photocatalytic of noble metals-based bimetallic nanoparticles, are discussed together with preparation routes. The effects of preparation method conditions as well as metal properties on the final structure of bimetallic nanoparticles (from alloy to core–shell structure) are followed. The role of bimetallic nanoparticles in heterogeneous catalysis and photocatalysis are discussed. Furthermore, structure and optical characteristics of bimetallic nanoparticles are described in relation to the some features of monometallic NPs. Such a complex approach allows to systematize knowledge and to identify the future direction of research.

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1. Introduction

Nanomaterials and nanoparticles (NPs) have one or more dimensions in the nanometer scale (<100 nm) range and subsequently show novel properties from their bulk materials. Bimetallic composite nanoparticles, composed of two different metal elements, attract more attention than monometallic nanoparticles from both scientific and technological viewpoints due to potential unique electronic, optical, catalytic or photocatalytic properties that are absent in the coincident monometallic nanoparticles. It's expected that bimetallic nanoparticles (BNPs) could show not only the combination of the properties related to the presence of two individual metals, but also new properties due to a synergy between two metals. The structure of bimetallic nanoparticles (BNPs) is defined by the distribution modes of the two elements and can be oriented in random alloy, alloy with an intermetallic compound, cluster-in-cluster or core–shell structures. Shape and size of mono- and bimetallic nanoparticles are strictly dependent on the preparation methods and conditions and affects the physicochemical properties of resulted final nanomaterial. Monometallic nanoparticles could be shaped as cubes, tetrahedrons, octahedron, truncated octahedrons, icosahedrons, concave cubes, rods, spheres and even stars, as shown in Fig. 1. Combination of two metals results in much more possibilities in shape and structure due to miscellaneous distribution of each metal within a particle and their various organization, as shown for Pd–Pt nanoparticles in Fig. 2.

Due to huge interest in preparation methods, properties and potential applications of monometallic and bimetallic noble metal-based nanoparticles over the last ten years, a number of review articles have been appeared. Several earlier reviews deal with preparation routes and characterization of mono- and bimetallic NPs [1] including nanoclusters [2], application of NPs in bioanalysis [3], BNPs obtained by wet-chemical methods [4], nanoalloys [5,6], nano zero valent iron/bimetallic NPs for groundwater remediation [7], plasmonic properties of NPs [8], core–shell nanoparticles [9], bimetallic dendrimer-encapsulated nanoparticles (DENs) [10], three layer structures in Au–Pd NPs [11] and surface segregation in bimetallic alloy nanoparticles [12].

Some previous review papers in the area of monometallic nanoparticles have focused on preparation methods, such as using of microemulsion systems [18,19], supercritical fluids [20] and biosynthesis by wide spectrum of organisms [21,22], characterization of NPs [23,24], applications [25,26], toxicity [27,28] and ecotoxicity [29–32]. Due to high potential to application, there are a several papers describing different aspects of silver and gold nanoparticles. Thus, the unique optical and antimicrobial properties together with possible applications and eventual environmental impact of silver nanoparticles were overviewed by Rai et al. [33], Fabrega et al. [34], Hadrup et al. [28], Li et al. [35], Hajipour et al. [36], Ravindran et al. [37], Oćwieja et al. [38] and Wen et al. [39]. Recent advances regarding gold nanoparticles

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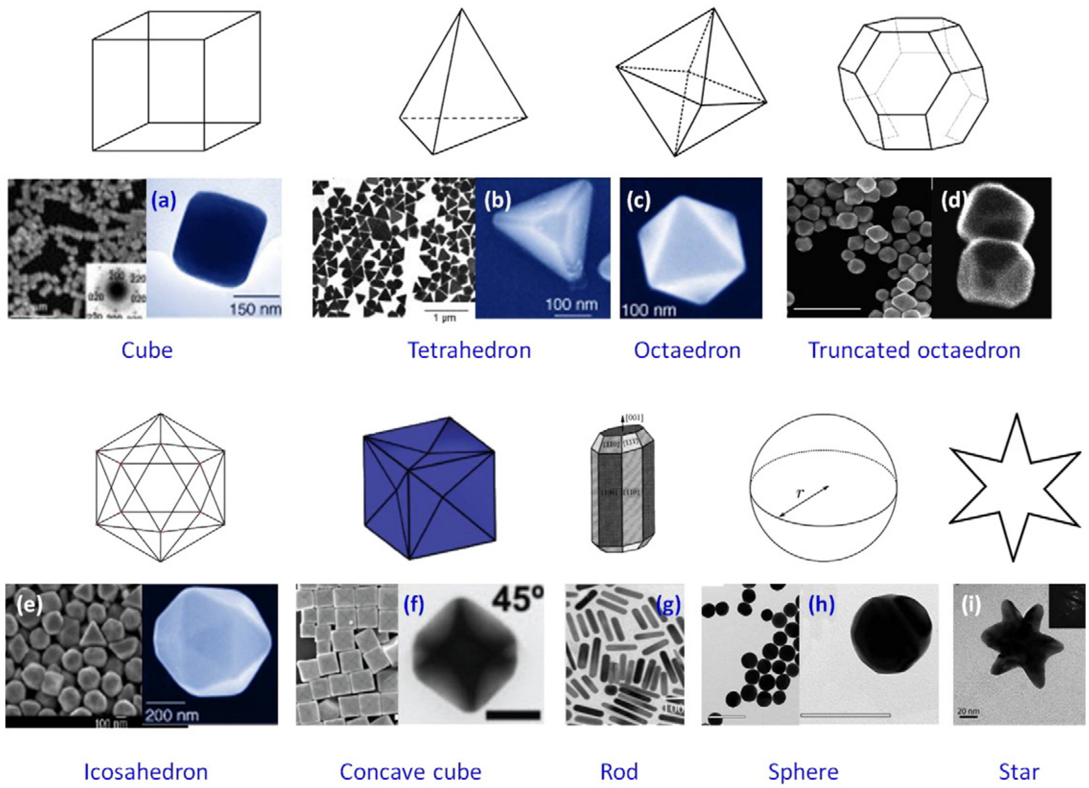

Fig. 1. Examples of gold nanoparticles with different shapes: (a) cubes (Reprinted with permission from Ref. [13]), (b) tetrahedron (Adapted with permission from Ref. [13]), (c) octahedron (Adapted with permission from Ref. [13]), (d) truncated octahedron (Adapted with permission from Ref. [14]), (e) icosahedron (Adapted with permission from Ref. [13]), (f) concave cube (Adapted with permission from Ref. [15]), (g) rod (Adapted with permission from Ref. [16]), (h) spheres (Adapted with permission from Ref. [14]), and (i) star (Adapted with permission from Ref. [17]).

summarized data regarding implementations in catalysis [40], cancer diagnosis and therapy [41–43], applications in targeted drug delivery systems [44], biomolecular probe application [45], gold nanorods-based biosensor [46] and microbial synthesis [47]. Recently a few overviews have been focused on the properties and synthesis routes of inorganic core–shell nanostructure [48] as well as application of core–shell nanoparticles in remediation technologies [49], catalysis [50,51], biomedicine [52], photocatalysis [53] and for energy conversion in low-temperature fuel cells [54].

According to their composition and structure – differing from alloy to core–shell– and composition/structure-dependent features, bimetallic nanoparticles seem to be useful and encouraging group of nanomaterials in catalysis, medicine, photocatalysis, etc. However, the following questions are still open: How do the composition and structure of bimetallic nanoparticles affect the optical properties of BNPs? How does the preparation method and conditions affect the structure of BNPs? What properties of BNPs are crucial in catalysis and photocatalysis? Is it any relation between optical properties of BNPs and photocatalytic activity of BNPs-semiconductors composites?

These aspects are essential to select preparation methods and conditions to prepare BNPs with desired composition, structure and properties appropriate to the application. In view of this, in this review, selected properties, such as structure, optical, catalytic and photocatalytic of noble metals-based bimetallic nanoparticles, are discussed with respect to preparation routes and conditions. Furthermore, the optical characteristics of bimetallic nanoparticles are discussed in relation to the some features of monometallic NPs, while the feasible structures of BNPs are discussed based on the properties of single metals. In our opinion, such a complex approach allows to systematize knowledge and to identify the future direction of research in the field of synthesis and application of bimetallic nanoparticles.

2. Structure of bimetallic nanoparticles

In the late 1980s, it was found that heterogeneous, composite or sandwich colloidal particles have better efficiency than their corresponding single particles. Generally, bimetallic nanoparticles can be categorized into two main groups: core–shell and alloys structures. Depending on the synthetic approach used in the preparation of BNPs, the distribution of each metal within a particle and their organization will vary to adopt either core–shell, random alloy, alloy with an intermetallic compound type or cluster-in-cluster, subclusters, etc., as shown in Fig. 3. It was found that for nanoparticles composed of a few metals, such as bimetallic and trimetallic nanoparticles, the alloying or phase segregation process is strongly dependent on the particle size [56,57].

Mixed A–B nanoalloys may be either ordered (Fig. 3a) or random (i.e., a solid solution, Fig. 3b). Random mixed nanoalloys are often termed “alloyed” nanoparticles in the literature, but also the terms “mixed” or “intermixed” are used. The intermixed pattern is common to many systems. In bulk metals, two kinds of metal elements often provide an alloy structure. If the atomic sizes of two elements are similar to each other, then it will be a random alloy. When the atom sizes are quite different from each other and the mole ratio of the two elements is simple and adequate to the structure, then they form an intermetallic compound. In the case of bimetallic nanoparticles, these kinds of alloy structures seem to be more easily produced than in the case of bulk metals. In fact, it was found that bimetallic nanoparticles between

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