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Supported binary hybrid nanomaterials and their applications

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Hybrid nanostructured materials provide new functionalities not found in their individual pristine nanocomponents. The present review focuses on successful extension from single-component materials to different hybrid nanostructured materials and on their novel applications in chemical sensing, green energy, and advanced manufacturing. Hybridization is performed mainly by electrochemical deposition and a number of advanced dry deposition techniques, including pulsed laser deposition and size-selected magnetron sputtering. Hybrid nanostructured materials are classified into two main categories: A + B systems consisting of two materials of different chemical identities including metal–metal, metal–metal oxide, metal–biomolecule, and metal oxide–metal oxide; and A + A′ systems consisting of one material but with two components of different crystalline phases, with and without dopants, and with and without defects. The novelties and synergistic properties of these hybrid nanomaterials are exploited for the development of emerging applications.

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1. Hybrid nanostructures

Nanotechnology has attracted a lot of recent attention [1], because of its potential applications in catalysis [2,3], information and data storage [4–6], biotechnology and medicine [7], environment and energy [8], and advanced optics and electronics [9,10]. Its impact on our daily life is manifested by increasing commercialization of a wide variety of nanomaterials, especially nanoparticles (NPs), in cosmetic and heath products, green energy, storage media, and electronics. Nanostructured materials are especially interesting because they constitute a new type of materials with nanoscale properties that are very different from those of individual atoms and molecules and of bulk matter. Nanostructured materials have a much larger surface area to volume ratio (or specific surface area) than their bulk counterpart, which along with their quantum size effects forms the basis for their unique physicochemical nanoscale properties.

Hybrid nanostructured materials constructed from more than one component have also attracted increased interest due to their additional functionalities [11–14]. The term "hybrid nanostructure" is commonly used to describe a discrete multi-component nanostructure, which includes multi-metallic systems and alloy NPs [10]. These components could be two (or more) metals, or a metal and an organic or bio-molecule, or a metal and an inorganic material such as a metal oxide. There are a number of important incentives to combine two or more components together to make a composite nanostructure. For instance, the surface chemical properties of a particle can be modified by coating with a second material to improve its colloidal stability or resistance to oxidation [10]. New synergetic effects can be created upon alloy formation of two metals. Additional functionality may also be introduced to a nanostructure for bio-applications, for instance, by attaching an antibody for biological targeting application. There are many different plausible types and morphologies of hybrid nanostructures, with some of the key nanostructures shown schematically in Fig. 1 [10].

Hybrid materials can be divided into two main categories. Type A + B corresponds to two chemically different materials combined together, with each keeping its own chemical identity (formula). Type A + A′ refers to the combination of two components with the same chemical identity but different intrinsic properties (e.g., crystalline phases, amounts or types of defects, or both) or extrinsic properties (e.g., dopants). If the same shape is maintained, the hybrid material can be further divided into core-shell or mixed alloy nanostructures. The core-shell nanostructures could be made up of metal and metal, metal and semiconductor, metal and dielectric, or any other combinations. The order of the core and shell arrangement (e.g., semiconductor core metal shell vs metal core semiconductor shell) could also lead to radically different hybrid core-shell materials. There are even more variations in the different combinations of three materials (A, B, C) into outer shell A, inner shell B, and core C, all of which could exhibit different properties. There are many good literature reviews about bimetallic nanostructures and their properties [15–17]. The mixed alloy nanostructured materials are usually combinations of two metals, while combinations of a metal and a non-metal such as a metal oxide or a biomolecule, e.g. Fe–glucose oxidase hybridization, are also possible [18]. For hybrid materials that are made up of materials with two different shapes, there are also many possible combinations involving, e.g., spherical nanoparticles on wires, rods, walls, and nanoparticles with different shapes. We first consider type A + B materials consisting of two chemically different A and B materials with the same or different shapes, and provide a few examples of typical combinations along with their unique properties. This will then be followed by our discussion on type A + A′ materials.

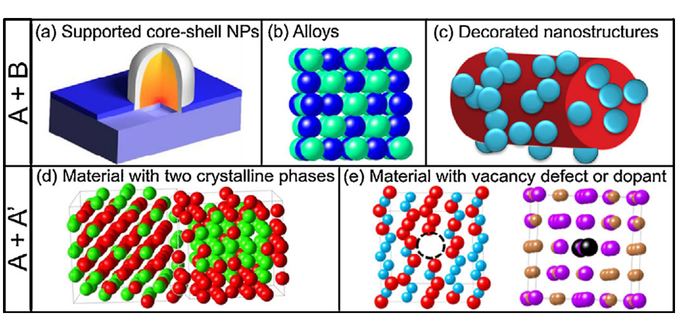

Fig. 1. Examples of common hybrid nanomaterials. Top panel (A + B): (a) Core-shell nanoparticles (NPs), (b) alloy metals, and (c) nanowires or nanorods decorated with metal nanoparticles. Bottom panel (A + A′): (d) Alloy metals with the same composition but different crystalline phases, and (e) metal oxides with vacancy defects (left) or dopants (right).

2. Type A + B materials: binary hybrid materials with two chemically different components

2.1. Metal–metal

Bimetallic NPs belong to a unique class of materials that shows a combination of sometimes very different properties associated with two constituent metals. In many cases, their specific physical and chemical properties are greatly enhanced owing to synergistic effects [19,20]. Based on the mixing pattern, bimetallic NPs can be divided into three main types [9]:

(a) Core-shell alloy NPs (Fig. 2a) consist of a core of one type of material (A) surrounded by a shell of another type of material (B), with possible mixing between the core and the shell materials at their interface.
(b) Segregated alloy NPs or heterostructures [1] (Fig. 2b) consist of segregated A and B clusters or domains, which may share a

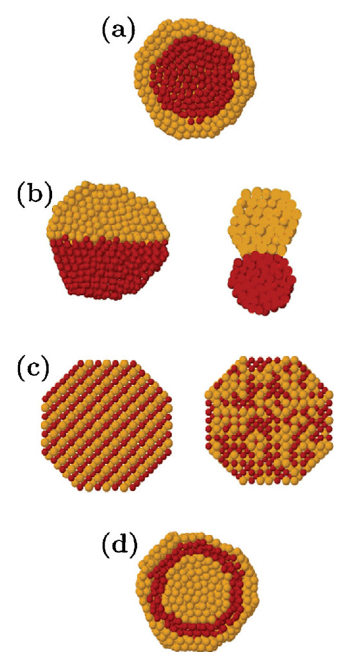

Fig. 2. Schematic representations of three main types of bimetallic nanoparticles of possible mixing patterns: (a) core-shell, (b) segregated, and (c) mixed alloy systems, plus more complex bimetallic systems such as (d) three-shell alloy system.