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Review

Development of functional nanostructures and their applications in catalysis and solar cells

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The development of functional nanostructured materials, which show unique and versatile characteristics, is highly desirable for important applications, such as catalysis and solar cells. In this review, we first summarize our recent studies on the synthesis of nanohybrid catalysts (such as bimetallic and binary metal oxide nanostructures) and their catalytic behavior in diverse catalytic reactions. We then present our recent developments on plasmonic nanostructures (Au and Ag), and demonstrate and discuss how they may be explored for enhancing photocatalysis and solar cell performance. Subsequently, we describe our work on the synthesis of semiconductor nanocrystals, also known as quantum dots, and their application in solar cells. Besides traditional wet chemical method, we also introduce an alternative, physical method, pulsed laser ablation, toward synthesizing these nanostructures with a unique

Abbreviations: NPs, nanoparticles; AB, ammonia borane; PLAL, pulsed laser ablation in liquid; 1D, one-dimensional; SPR, surface plasmon resonance; NRs, nanorods; SERS, surface enhanced Raman scattering; OSCs, organic solar cells; QDs, quantum dots; PL, photoluminescence; NIR, near infrared; UV, ultraviolet; vis, visible; 4-NP, 4-nitrophenol; MO, methyl orange; TEM, transmission electron microscopy; HRTEM, high-resolution transmission electron microscopy; EDS, energy dispersive X-ray spectroscopy; STEM, scanning transmission electron microscopy; NTs, nanotubes; HAADF, high angle annular dark field; NYF, $NaYF_4$:Yb^{3+}, Er^{3+}, Tm^{3+}; $O_2^{-\bullet}$, superoxide anion radicals; BFO, $BiFeO_3$; PV, photovoltaic; P3HT, poly(3-hexylthiophene-2,5-diyl); PCBM, [6,6]-phenyl-C_{61}-butyric-acid-methyl-ester; CTAB, cetyltrimethylammonium bromide; PEDOT:PSS, poly(3,4-ethyl-enedioxythiophene):poly(styrenesulfonate); PCE, power conversion efficiency; *J–V*, current density–voltage; ITO, indium tin oxide; J_{sc}, short-circuit current; PVP, poly(vinylpyrrolidinone); EELS, electron energy loss spectroscopy; FDTD, finite-difference time-domain; RIU, refractive index unit; PLD, pulsed laser deposition; XRD, X-ray diffraction; TMS, bis(trimethylsilyl)sulfide; OLA, oleylamine; OA, oleic acid; CNTs, carbon nanotubes; SWCNTs, single-walled carbon nanotubes; MWCNTs, multi-walled carbon nanotubes; CB, conduction band; V_{oc}, open-circuit voltage; *FF*, fill factor; NBs, nanobelts; N_{LP}, laser ablation pulses; NH-HJs, nanohybrid heterojunctions; VB, valence band; FTO, fluorine doped tin oxide; SEM, scanning electron microscopy; QY, quantum yield; SILAR, successive ionic layer adsorption and reaction; ODE, octadecene; PBS, phosphate buffered saline; MV^{2+}, methyl viologen; IPA, isopropyl alcohol.

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Quantum dots
Catalysis
Solar cells

"bare and clean" surface, highly relevant to catalytic, plasmonic and photovoltaic applications. Finally, perspectives on future advances of nanostructured catalytic and plasmonic materials as well as quantum dots are outlined.

1. Introduction

During the past few decades, the design and synthesis of functional nanomaterials have attracted considerable attention, because they show novel properties and/or significantly improved properties and thus high potential for various applications, including catalysis [1], solar energy [2], and so on. These novel properties or immensely changed properties are largely affected by the dimension and shape of nanomaterials as well as the way nanocomponents are assembled. For example, ultrasmall nanoparticles (NPs) can show quantum confinement effect and large surface-to-volume ratios, leading to unique or largely improved optical and catalytic behavior [3]. The strong dependence of the property of nanomaterials on their structural parameters offers new and ample opportunities for tuning material properties, especially beneficial for highly demanding applications. Driven by these high promises, the development of functional nanomaterials with well controlled yet different chemical compositions, sizes and morphologies has indeed constituted an important research area in fundamental nanomaterials science [4–6]. Among various types of nanomaterials under investigation, nanostructured hybrid catalysts, plasmonic metal nanostructures and quantum dots have been recognized as three of the most promising materials for energy-related applications, such as solar cells.

Bimetallic NPs and binary oxide nanostructures represent a specific type of hybrid materials, based solely on metals or metal oxides. They have found applications in diverse fields of catalysis [7–9], sensing [10–13], biomedical diagnosis and therapy [14–16], energy storage and conversion [17–19], and so on. Considerable research efforts have been devoted to synthesizing them, because they can exhibit enhanced properties, or even additional functions as compared to individual components. As we know, the performance of a catalyst is highly related to its size, structure, shape, composition, and so on. Besides these, synergetic or cooperative effects between different components and/or active sites in one complex catalyst can possibly endow the composite catalyst with much improved catalytic properties [20]. For example, Xu et al. reported a surfactant aided co-reduction process to synthesize a series of bimetallic RhNi alloy NPs and their behavior in the dehydrogenation of aqueous hydrazine borane [21]. They found that alloying Rh and Ni induces a strong synergistic effect and Rh_4Ni alloy NPs show higher catalytic activity than Rh/Ni NPs at other ratios, and pure Rh and Ni NPs. Beyond enhancing catalytic activity, the combination of different metals or metal oxides into a single structure may increase stability or selectivity as well. For instance, Pt NPs are known as the most efficient catalyst for oxygen reduction reaction, whereas they suffer from poisoning [22]. Zhang and co-workers systematically studied Au clusters modified Pt NPs for the oxygen reduction reaction [23]. After 30,000 cycles of the durability test, the Au/Pt/C catalyst exhibits a negligible loss in the electrochemically active surface area, suggesting a remarkable improvement in the issue of poisoning. In addition to above advantages, multifunctionality can also be achieved by incorporating different components. For instance, Au/Co core/shell NPs were fabricated by a one-step seed-mediated growth route at room temperature under ambient atmosphere within a few minutes [24]. Due to the presence of magnetic Co component, Au/Co core/shell NPs show magnetically recyclable capability following the dehydrogenation reaction of ammonia borane (AB). So far, tremendous advances have been achieved in the synthesis of bimetallic and binary oxide nanostructures by adopting various strategies. Among these synthetic approaches, wet chemical or solution-phase based methods, such as co-reduction and co-thermal decomposition, are currently widely used [25,26]. In these methods, the size, structure, shape and composition of synthesized hybrid nanostructures can be well controlled by a careful selection of solvents, metal precursors, capping agents, reductants, temperature, time of reaction, and so on. For example, for forming a core/shell bimetallic structure, homogeneous nucleation and non-uniform shell growth can be avoided to a great extent through reducing the coexistence of cations and anions of shell materials in solution. Furthermore, such synthesized products are usually crystalline and do not require any post-annealing treatment. Meanwhile, the scale-up of synthesis is also simple for many cases, highly relevant to industrial applications. However, the surface features of most nanostructures prepared by wet chemical approaches are not optimal for catalysis due to the existence of surface stabilizing molecules or tightly adsorbed reaction residues, which exert a "barrier" effect on catalysis. From this point of view, a method that can yield NPs with relatively "bare and clean" surfaces is highly desired for catalysis. Recently, a physical method based on the use of a pulsed laser has drawn a lot of attention. For example, in the case of pulsed laser ablation in liquid (PLAL), NPs are synthesized via laser ablation of a solid target placed in a liquid medium without any addition of chemicals [27,28]. The unique, relatively "bare and clean" surface of NPs prepared by this PLAL approach makes them an excellent candidate for catalytic applications.

Plasmonic metal nanostructures, such as Au and Ag, have prompted tremendous research interest in the past decade because of their unique surface plasmon resonance (SPR). SPR is the result of the resonant oscillation of conduction electrons at metal/dielectric interface excited by incident light and confined to metallic nanostructures [29]. It is reflected by two most prominent features, largely amplified local electric fields near the nanostructure's surface and the appearance of intense absorption and/or scattering. These attributes have initially mainly been explored for surface enhanced Raman scattering (SERS) [30] and very recently fueled the emergence of two highly promising fields, plasmon enhanced photocatalysis [31] and plasmon enhanced photovoltaics (PVs) [32]. In these newly rising fields, plasmons are anticipated to increase exciton generation rate, enhance light trapping or simply boost the number of "useful" charge carriers by hot electron injection [33,34]. Rapid advances of these new fields largely benefit from the recent progress in the synthesis of plasmonic nanostructures. Various synthesis methods, such as salt reduction, polyol process, seed-mediated growth and light-mediated synthesis, have been developed and employed [35]. They can yield nanostructures, in a controlled fashion, with various sizes and geometries, which exhibit widely varying optical responses [35]. Correspondingly, the relationship between SPR and nanostructures' size and shape has been extensively investigated [36–39]. For example, the plasmon resonance of Au nanospheres shows a red shift with the increase of their size. One-dimensional (1D) Au nanorods (NRs) exhibit longitudinal and transverse resonances, distinctly different from zero-dimensional Ag nanospheres [40]. Moreover, it was found that SPR was also affected by dielectric environments [41]. Such tunability offers vast latitude for tuning plasmon resonance frequency and patterns to meet the needs of specific applications, such as