Nano Today (2011) 6, 240—264

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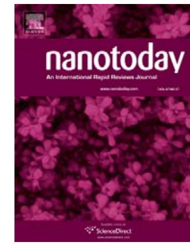

REVIEW

Noble metal nanomaterials: Controllable synthesis and application in fuel cells and analytical sensors

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Received 18 November 2010; received in revised form 25 January 2011; accepted 21 April 2011
Available online 24 May 2011

KEYWORDS
Metal nanomaterial;
Nanocluster;
Nanoelectrocatalyst;
Fuel cell;
Sensor

Summary Nobel metal nanomaterials (NMNs) with interesting physical and chemical properties are ideal building blocks for engineering and tailoring nanoscale structures for specific technological applications. Particularly, effectively controlling the size, shape, architecture, composition, hybrid and microstructure of NMNs plays an important role on revealing their new or enhanced functions and application potentials such as fuel cell and analytical sensors. This review article focuses on recent advances on controllable synthesis and fuel cell and sensing applications of NMNs. First, recent contributions on developing a wet-chemical approach for the controllable synthesis of noble metal nanomaterials with a rich variety of shapes, e.g. single-component Pt, Pd, Ag and Au nanomaterials, multi-component core/shell, intermetallic or alloyed nanomaterials, metal fluorescent nanoclusters and metal nanoparticles-based hybrid nanomaterials, are summarized. Then diversified approaches to different types of NMNs-based nanoelectrocatalysts with the aim to enhance their activity and durability for fuel cell reactions are outlined. The review next introduces some exciting push in the use of NMNs as enhanced materials or reporters or labels for developing new analytical sensors including electrochemical, colorimetric and fluorescent sensors. Finally, we conclude with a look at the future challenges and prospects of the development of NMNs.

Introduction

Nobel metal nanomaterials (NMNs) with interesting size-dependent electrical, optical, magnetic, and chemical properties, as a kind of modish materials, have been intensively pursued, not only for their fundamental scientific interest, but also for their many technological applications [1—12]. At present, size, shape, architecture, composition, hybrid and microstructure of NMNs are several important key parameters in determining, revealing

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1748-0132/$ — see front matter
doi:10.1016/j.nantod.2011.04.007

and enhancing their functions and potential applications [4,5,8—10]. In principle, one can accurately tune the physical and chemical properties of NMNs by controlling any one of these parameters, but the flexibility and scope of change are highly sensitive to some specific parameters. For instance, Au nanoparticles (NPs) have size-dependent surface plasmon resonance (SPR) property and generally exhibit visible SPR absorption whereas gold nanorods (NRs), gold nanocage and hollow gold nanospheres own strong near-infrared (NIR) absorption [2,11,13]. These novel gold nanostructures with NIR absorption are very important for photothermal therapy and bioimaging in the NIR region because blood and soft tissue in the NIR region are relatively transparent in this region, so that collateral damage to surrounding healthy tissue is minimized; Pt nanomaterials with high-index facets or complex morphologies (e.g. dendritic structure) or multi-compositions have been proven to exhibit higher electrocatalytic activities toward small molecule oxidation and oxygen reduction reactions (two key reactions in the field of fuel cell) than the commercial catalysts [14—16]; Ag nanostructures with proper size, complex sharp structure or more edges and corners have higher surface-enhanced Raman scattering (SERS) activity than spherical Ag NPs [17]; certain noble nanoclusters (NCs) (Au, Ag and Pt in particular), consisting of several to roughly a hundred atoms and possessing sizes comparable to the Fermi wavelength of electrons, can exhibit molecule-like properties and strong size-dependent fluorescent emission [18]. Thus, the control of these pivotal parameters provides the good opportunity for enhancing their application potentials in the fields of catalysis, electronics, photography, photonics, sensing, imaging, medicine and information storage, among others [5,16]. To date, diverse methods have been developed to synthesize NMNs in a variety of shapes such as rod, wire, polyhedron, dendrite, dimer, belt, star, and cage, etc. The research on NMNs has been flourishing in the last decades and many research papers as well as some review papers have been dedicated to this topic [1—10]. However, at present, the majority of reviews are centered on the research work of NMNs mainly before 2007. Therefore, a highlight review on latest significant developments of NMNs (including their controllable synthesis and fuel cell and sensing applications) with a particular focus on the last 3 years, will greatly appeal to the broad readership interested in nanochemistry, nanoenergy and nanoanalytical chemistry.

With the increasing environmental concerns and accelerated depletion of fossil fuels, the development of new technology for producing new alternative energy conversion and storage devices such as solar cell, supercapacitor, and lithium ion battery, etc. is very important for solving the present energy crisis [19]. Fuel cell, as an environmentally friendly energy device, has been intensely studied because of their numerous advantages, which include high-energy density, the ease of handling liquid, low environmental impacts and their possible applications to microfuel cell [16]. At present, tremendous research efforts have been dedicated to the fabrication of efficient fuel cells with high performance. In all of the NMNs, Pt and Pt-based nanomaterials are still indispensable and the most effective catalysts for fuel cells. However, one of the major obstacles for fuel cell commercialization is the cost and reliability issues of Pt nanocatalysts used [16]. Thus, design and synthesis of advanced catalysts to meet the requirements of reducing Pt loading amounts and meantime increasing the activity and stability of the Pt-based catalyst is highly desired [20,21]. In order to achieve this goal, some important information, challenges or opportunities should be taken adequately into consideration and are now summarized briefly as follows: (1) the size of Pt-based nanocatalyst should be reduced to a smaller size in order to provide higher electrochemical active area. (2) Controlling the shape of Pt-based catalysts to more complex morphologies (e.g. dendritic morphology) is an important avenue for greatly improving Pt electroactivity. (3) The nanocatalysts had better own high-index facets, which can provide higher activity and stability for fuel cell application. (4) Another interesting route for greatly improving Pt activity and stability is to design Pt-based bimetal or trimetal nanostructures with controlled architectures (e.g. core/shell, alloy and even both). (5) Design high-efficiency non-Pt multi-metal catalysts. (6) Searching new support materials with high conductivity, chemical stability and surface area. (7) Effectively controlling the uniform distribution of NMNs on the advanced supporting materials with high conductivity. Inspired by these significant challenges, many scientists have explored some advanced strategies for obtaining highly active NMNs-based catalysts for fuel cell reactions.

On the other hand, nanoanalytical sensing system is a rising interdisciplinary field, which combines the inherent characteristics of analytical techniques (e.g., high sensitivity, rapid detection and low cost, etc.) with unique electronic, optical, magnetic, mechanical, and catalytic properties of nanomaterials to become one of the most exciting topics [22,23]. Particularly, with the gradual appearance of new or enhanced properties of NMNs, different analytical techniques or strategies have been developed to construct high-sensitivity sensors for detecting diverse targets. Three notable techniques include electrochemical, fluorescent and colorimetric sensing ones, respectively. (1) NMNs-based electroanalytical technique shows the enormous potentials for constructing enhanced platforms for chemical sensing and biosensing. This is because that NMNs can effectively catalyze the redox processes of some molecules of analytical interest due to their high conductivity, large surface area and good surface chemistry property, thus permit an improvement of the analytical performance (lower detection limit and shorter deposition time) of voltammetric techniques in comparison to conventional electrodes [24,25]. (2) NMNs-based NCs, as a new class of fluorophore, can be used as environmentally friendly and biocompatible fluorescence probes for the detection of low-concentration analytes, owing to its low toxicity, inexpensive and good biocompatibility [26,27]. (3) NMNs-based colorimetric methods (the change of SPR of Au or Ag NPs) are also extremely attractive because they can be easily read out with the naked eye, and allow onsite, real-time qualitative or semi-quantitative detection without complicated analytical instruments [28,29]. Therefore, NMNs-based analytical sensing devices exhibit good advantages and potentials for detecting different targets, which have important significance in the aspects of environmental pollution, serious diseases, human health and food safety, etc.