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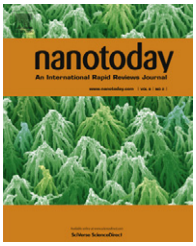

REVIEW

Surface and interface control of noble metal nanocrystals for catalytic and electrocatalytic applications

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Summary Catalysis and electrocatalysis by noble metal (NM) nanomaterials is typically surface and interface-sensitive. Effective surface and interface control over NM nanomaterials provides important foundation for studies of structure-dependent catalysis which is critical to the design of NM nanocatalysts with optimized catalytic performances for practical applications. In this review, we focus on recent progress in developing wet-chemical strategies to control the surface and interfacial structures of NM nanocrystals for catalytic and electrocatalytic applications. Approaches to control the surface structures of NM nanocrystals are first summarized and demonstrated by representative examples. We then focus discussions on how to control three different interfaces (i.e., metal—metal, metal—oxide and metal—organic interface) on the surface of NM nanocrystals. Finally, conclusions and perspectives are given to propose the challenges in catalysis-driven surface and interface control of NM nanocrystals.

Introduction

Over the past decades, noble metal (NM) nanomaterials have attracted increasing research attention for diverse applications in fields of catalysis, biology, and nanotechnology [1—5]. At the length scale of nanometers, the surface-area-to-volume ratio significantly increases, so that surface/facet and interface effects become predominant and even significantly modify the macroscopic properties of the NM nanomaterials to enhance their catalytic performance. Catalysis has been considered as one of the central fields of nanoscience and nanotechnology [6]. In surface science, single-crystal surfaces of metal or metal oxide have been widely adopted by surface scientists as model catalysts or supports to systematically study the effect of surface/interface structure on catalysis reactions, such as ammonia synthesis, isomerization of light alkanes, hydrogenolysis of alkanes, electrocatalysis and so on [7—16]. Well-defined single-crystal catalysts are usually studied by applying physical techniques under ultralow-pressure conditions to gain deep understanding of the factors that influence their catalysis performances, which leads to the pressure and material gaps between many

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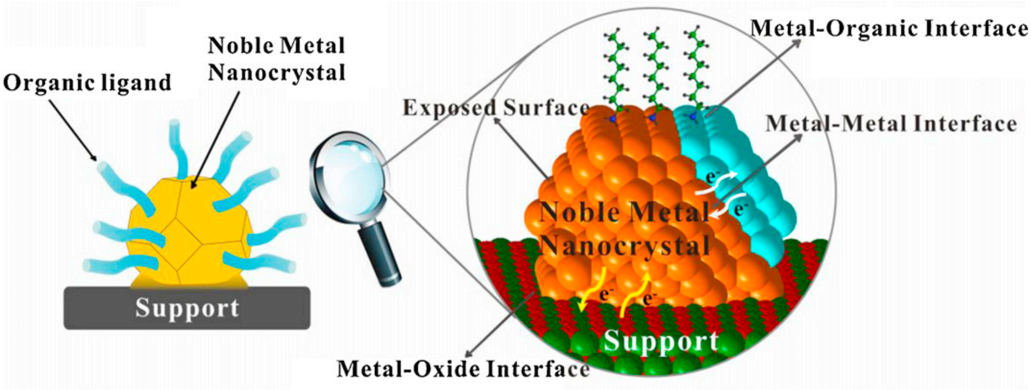

Figure 1 Typical surface and interfacial structures involved in NM nanocrystal-based catalysts.

model catalysis studies and real catalysis [15,17,18]. Owing to the high surface-area-to-volume ratio, nanomaterials with well-define surface/interface structure are ideal materials serving as novel model catalysts to bridge these gaps in heterogeneous catalysis [19—23].

Heterogeneous catalysis occurs with the reactants adsorbed to the surface of a catalyst. When NM nanocrystals are used in heterogeneous catalysis, reactant molecules have to find paths to interact with the catalytic surface of the NM nanocrystals. NM nanocrystals applied in catalysis can be broadly classified into four categories: (1) supportless NM nanocrystals with clean surfaces; (2) supportless NM nanocrystals that are surface-capped by organic species; (3) supported NM nanocrystals with clean surfaces; and (4) supported NM nanocrystals with organic-modified surfaces. Factors that influence their catalytic performances are varied for NM nanocrystal catalysts lying in different categories. In all cases, it has been well-documented that the size, composition, electronic effect (e.g., introducing a second metal to form alloy or intermetallics) and structure of NM nanocrystals are important factors in determining their catalysis.

In this review, we focus on the structural aspects of NM nanocrystal catalysts as shown in Fig. 1. When only structural aspects are taken into account, supportless NM nanocrystals with clean surfaces represent the most ideal catalysts in which surface structure is the only determining factor in their catalysis. That is to say, when their surfaces are clean, the performance of NM nanocrystals depends strongly on their exposed facets. Different facets have exposed atoms with different coordination numbers, and thus exhibit different catalytic properties [24]. Numerous studies that focus on facet-controlled synthesis and facet-dependent catalytic properties on NM nanocrystals have thus been carried out by a large number of research groups [22,25—30]. For face-centered cubic (fcc) metals, the surface energy of different single-crystal facets is increased in the order of $\gamma\{111\} < \gamma\{100\} < \gamma\{110\} < \gamma\{hkl\}$ [31]. As a result, many catalysis reactions are facet dependent. For example, in catalytic hydrogenation of benzene, Bratlie et al. [25] have found that Pt nanocubes exposed with $\{100\}$ facets catalyzed benzene to cyclohexane, while $\{111\}$ and $\{100\}$-bounded Pt nanocuboctahedra resulted in both cyclohexane and cyclohexene, suggesting the same product selectivities obtained on Pt$\{111\}$ and Pt$\{100\}$ single crystals in earlier studies. Tian et al. have successfully applied electrochemical methods to prepare NM nanocrystals for the study of enhanced electrocatalysis by high-index facets [28]. NM nanocrystals prepared by electrochemical methods are probably the closest case to ideal surface-clean NM nanocrystals [28]. It should be noted that most shaped NM nanocrystals prepared by wet-chemical reduction methods are essentially capped by protecting agents. During the studies of facet effect, in some cases, the surface-protecting agents are not taken into account because they do not much influence the catalysis of NM nanocrystals. In other cases, the surface-protecting agents can be cleaned by chemical or physical treatments to exclude their influence on the facet effect studies.

In most cases, the presence of surface-protecting agents is considered deleterious to the catalytic performance of NM nanocrystals and, therefore surface-protecting agents are cleaned out before catalysis. However, many recent studies have demonstrated the important roles of surface-protecting agents (e.g., organic ligands, polymers) in creating metal—organic interfaces that can significantly improve the catalytic performance, both activity and selectivity, of supportless organic-capped nanocrystals. The reported metal—organic interfacial effects are mainly due to the electronic and steric contributions of organic capping on metals [32—40]. Compared with supportless NM nanocrystals, more structural factors are associated with the catalytic performances of NM nanocrystals that are deposited on non-inert supports such as semiconducting oxides or other metals to have new metal—oxide and metal—metal interfaces created. For example, metal—oxide interfaces (e.g., Au—TiO_2, Pt—FeO_x, Au—Fe_3O_4) have been found able to enhance catalysis in CO oxidation [21,41—43], selective oxidation or hydrogenation [44—47], water—gas shift [14,48,49], electrocatalytic H_2O_2 reduction [50,51], etc. The Pt—Au interface can facilitate CO oxidation [52] and also stabilize the Pt electrocatalysts against dissolution under potential cycling regimes [53]. Desired metal—organic interfaces were also built up on many supported NM nanocrystal catalysts by functionalizing the surface of NM nanocrystals with organic modifiers. For example, supported Pt nanocatalysts have been modified by chiral cinchona alkaloids for the enantioselective hydrogenation of α-ketoesters [54—61].