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Q1 Correlating Structure and Function of Metal Nanoparticles for Catalysis

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ABSTRACT

This paper summarizes several studies correlating the structure and function of nanoparticle catalysts. Three types of alloy nanoparticles are considered, random alloy, core@shell and alloy-core@shell structures. In the first two cases, the focus is to build theoretical models to understand previous experimental results. In the latter case, calculations play a greater role in leading the development of nanoparticle catalysts. We demonstrate that iteration between theory and experiment can facilitate an understanding of nanoparticle catalysts and reduce the time and effort involved in the design of new catalysts.

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1. Introduction

The science and technology of catalysis is particularly important at this time due to the energy and environmental challenges facing society. Research in the 1990s, showing surprising activity of Au nanoparticles, has largely motivated a search for new catalytic materials on the nano-scale with properties that are different from their bulk counterparts. [1] Another significant factor in the development of new catalysts has been the growth of computing power and improvements in theoretical methods to help understand experiments at the atomic scale and to provide guidelines for catalyst design. Experiments, demonstrating the high activity of nanoparticle catalysts, have inspired the development of theoretical methods for calculating reaction mechanisms and screening for new catalysts. Iterating between theory and experiment is a promising strategy for understanding nanoparticle catalysis and reducing the cost of the development cycle for new catalysts. This paper reviews some of our recent theoretical studies of multi-metallic nanoparticles catalysis, and shows how, with a close coupling to experiment, we are able to refine our models and test our predictions.

Dendrimer-encapsulated nanoparticles (DENs) provide an excellent model system which can be synthesized and characterized at the atomic scale for direct comparison with theory. DENs are synthesized by sequestering metal ions within the interior of, for example, poly(amidoamine) (PAMAM) dendrimers, followed by chemical reduction of the metal-ion/dendrimer complex with a reducing agent such as borohydride. [2–5] Two features of DENs make them a good model system for correlating theory and experiment. First, their size, composition,

and structure can be precisely controlled. [6,7] Second, the dendrimers stabilize the encapsulated nanoparticles and provide a handle for linking them to an electrode surface, but they do not interfere significantly with reactions on the particle surface. [8]

Fig. 1 illustrates the synthetic routes to form random alloy [9,7, 10–12], core-shell [13–16], and alloy-core@shell DENs [17]. Random alloy DENs are prepared by a co-complexation method, where two types of metal cations are reduced simultaneously to form an alloy particle. Core@shell nanoparticles are produced by a sequential reduction or underpotential deposition (UPD) of a shell metal onto the core. Galvanic exchange, which is also known as redox displacement, is an elegant technique which can then be used to replace reactive elements in the DENs with more noble ones, [18] increasing the variety of shells that are available for the DENs synthesis.

Alloy nanoparticles have a broad range of applications for many catalytic processes. In this paper we focus on the oxygen reduction reaction (ORR). The ORR is the cathode reaction of proton-exchange membrane fuel cells. It involves at least two elementary processes, O₂ dissociation and the subsequent removal of the dissociated species by further reduction to H₂O. ORR activity can be measured experimentally using electrochemical techniques, including cyclic voltammetry (CV) and rotating disk voltammetry (RDV). Theoretically, the ORR activity of a surface is understood to correlate with the O binding energy. Pioneering work by Nørskov and co-workers have established a volcano-shaped correlation between the O binding energy and ORR activity. [20,21] On the strong-binding side of the volcano, oxygen species over-bind to the catalyst surface and limit the kinetics of product formation. On the weak-binding side of the volcano the reaction is limited by oxygen dissociation and adsorption. Pt offers the optimal tradeoff of the pure metals and the peak of the volcano corresponds

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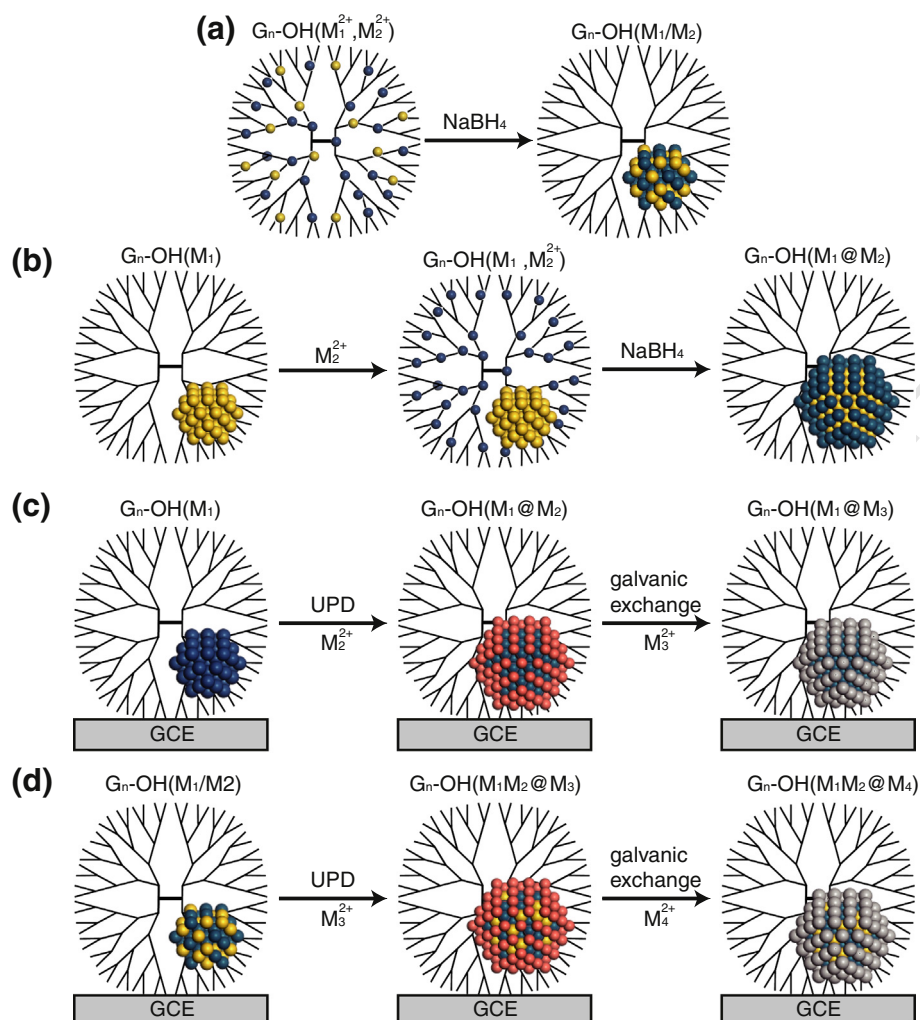


Fig. 1. Routes to synthesize different metallic DENS, including: (a) random alloy, (b) core@shell via sequential reduction, (c) core@shell and (d) alloy-core@shell via underpotential deposition and subsequent galvanic exchange.

83 to an oxygen binding energy which is slightly weaker than on a
84 Pt(111) surface. The underlying reason that oxygen binding is a
85 good reactivity descriptor is that there is a Brønsted-Evans-Polanyi

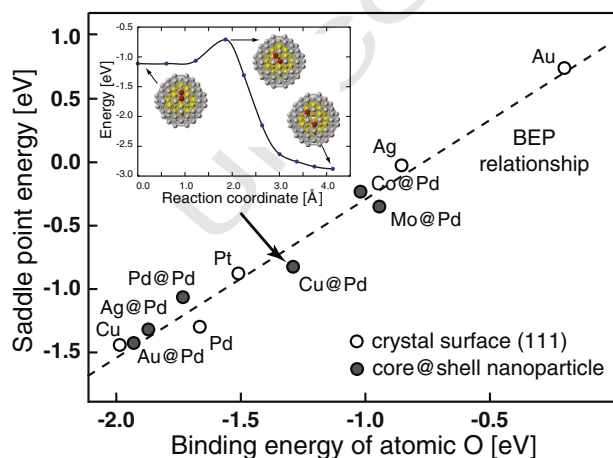


Fig. 2. The saddle point energy for oxygen dissociation on Pd-shelled particles and single-crystal surfaces plotted as a function of O binding energy. The linear trend is a BEP relationship. Particles with barriers and binding energies near Pt(111) are promising catalysts for the ORR. Reproduced with permission from Ref. [19].

(BEP) correlation between the binding and transition state energies, 86
so that a single descriptor can describe both limits. In Fig. 2, Tang *et al.* 87
show the BEP relationship between the O₂ dissociation barrier 88
and O binding energy for a 79 atom Pd-shelled nanoparticle (NP79) 89
and single-crystal (111) transition metal surfaces. [19] Thus a similar 90
trade off between the dissociation barrier and weak product binding 91
is expected for ORR on (111) facets of small size nanoparticles. 92

In the following, we consider several nanoparticle alloys and seek to 93
find structures with oxygen binding energies, and hence ORR activities, 94
that approach or exceed that of Pt. 95

2. Random Alloy Nanoparticles 96

The random alloy structure is one of the most conventional forms of 97
bimetallics, where two elements are randomly or nearly randomly 98
dispersed in the material. Random alloy DENS can be synthesized by the 99
aforementioned co-reduction method shown in Fig. 1(a). A number of 100
random alloys DENS, including Pd/Au, Pd/Cu, Pd/Pt and Au/Ag, in the 101
size range of 1–2 nm have been successfully synthesized. [11,10,7,12, 102
9], The catalytic properties of a random alloy nanoparticle can be 103
tuned by adjusting the ratio of the component elements. Studies on 104
large particles (which behave similar to bulk) have revealed that adding 105
small amounts of metals which bind oxygen strongly (e.g. Co, Ni and 106
Cu) can lower the oxygen binding to more noble metals (Pt or Pd) and 107
improve their ORR activity. [22–25] 108

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