Synthesis, Processing, Assembly and Activation of Core- Shell Structured Gold Nanoparticle Catalysts

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Abstract. This paper describes recent progress of an investigation of the synthesis, processing, assembly and activation of gold nanoparticles that are of potential interest to fuel cell catalysis. Core-shell type gold nanoparticles of a few nanometer core size with organic monolayer encapsulation are highlighted. The activation of the core-shell nanoparticle assemblies towards nanostructured catalyst for potential fuel cell catalytic reactions is discussed. The understanding of the control factors in terms of nanocrystal size and interparticle spatial properties has important implications to the design of highly active nanogold catalysts for practical applications.

Introduction

The development of the ability to harness the large surface area-to-volume ratios and the unique surface properties of nanoparticles in the <10 nm size range, especially in heterogeneous catalysis, is a major driving force in both fundamental research and practical applications of nanoparticle catalysts. It is this size range over which metal particles undergo a transition from atomic to metallic properties. The study of this unique aspect was indeed inspired by the discovery of the high catalytic activity of nanosized gold towards CO oxidation (1-4). Gold is traditionally considered catalytically inactive as a practical catalyst, but this property is completely changed when the size is reduced to a few nanometers. There are two major challenges for developing nanometer-sized particles as catalysts: 1) the control of sizes and compositions, and 2) the prevention of the aggregation propensity of nanoscale materials. The recent exploration of core-shell type nanoparticles, which can be broadly defined as core and shell of different matters in close interaction, including inorganic/organic, inorganic/inorganic, organic/organic, or inorganic/biological combinations (5-7), provides intriguing pathways to address these challenges. The use of such nanoparticles as building blocks towards catalytic materials takes advantage of diverse attributes, including size monodispersity, processibility, solubility, stability, self-assembly capability, and unique optical, electronic, magnetic, and chemical/biological properties.

In this report, we focus on the study of one particular class of core-shell nanoparticles, gold nanocrystal cores (1-6 nm diameters) encapsulated with organic monolayer shells. The understanding of the synthesis, processing, assembly and activation is geared towards the exploration of nanostructured catalysts. For more comprehensive overviews of gold nanoparticles in catalysis, readers are referred to several recent reviews and articles, including those in earlier issues of *Gold Bulletin* (3-4, 8-13).

Because of the lack of ability to control size, shape, surface, and interparticle spatial properties, the structure-activity relationships of many commercial catalysts are poorly understood. Recent progress in nanotechnology has led to new synthetic or processing routes to prepare nanoparticles and new analytical tools for probing nanostructure. Consider the assembly of pre-engineered nanoparticles onto a desired support platform (Scheme 1) (14). The use of a planar substrate is desired for fundamental studies using modern surface analytical tools (e.g., STM or AFM), whereas the use of high-surface-area support materials is important for practical applications. The nanoparticles can be assembled using molecular wires or linkers, and then activated for a catalytic reaction ($R \rightarrow P$). The activation may involve partial or

Scheme 1

A schematic illustration of assembly and activation of core-shell nanoparticles as catalysts on planar substrate and high-surface-area support materials. The R-to-P process illustrates a catalytic reaction from reactant to product

complete removal of the shell molecules. It is thus important to develop fundamental understanding of the precise control of size, shape, and interparticle spatial properties in the processing, assembling, activation and catalytic reactions. Issues related to each of these aspects are discussed in the following subsections.

Experimental

The experiments described in this paper include synthesis and processing of core-shell gold and alloy nanoparticles, assembly of the nanoparticle on desired supporting substrates, and characterization of the structures and morphologies. This section briefly outlines some of the experimental aspects. Details will be referred to the relevant references in the subsequent sections.

Gold nanoparticles of 2-nm core size encapsulated with alkanethiolate monolayer shell ($\text{Au}_{2\text{-nm}}$) were synthesized by standard two-phase method. Briefly, AuCl_4^- was first transferred from aqueous HAuCl_4 solution to toluene solution by phase transfer reagent (tetraoctylammonium bromide). Thiols (e.g., decanethiol, DT) were added to the solution at a 2:1 mole ratio (DT/Au), and an excess of aqueous NaBH_4 was slowly added for the reaction. The produced DT-encapsulated Au nanoparticles (~ 1.9 nm) were subjected to solvent removal, and cleaned using ethanol. Different molecular linkers were used to assemble the nanoparticles. For example, using 1,9-nonanedithiol (NDT) as a crosslinking agent, the nanoparticles were assembled on an electrode surface as an ensemble of the shell-linked particles via an exchange-crosslinking-precipitation route. Briefly, a substrate was immersed into a hexane solution of DT-capped nanoparticles and NDT with controlled concentrations for 1–24 hours. During the immersion, the NDT-DT exchange reaction was followed by crosslinking,

leading to nucleation and growth of a nanoparticle thin film on the substrate, i.e., $\text{NDT-Au}_{2\text{nm}}$. The thickness of the film was controlled by immersion time. The films were thoroughly rinsed with the solvent and dried under argon. Films ranging from 1 to 20 equivalent number of particle layers were estimated from quartz-crystal microbalance measurements.

Several types of support materials were used for the thin film preparation. Glassy carbon (GC) disks (geometric area: 0.28 cm^2), polished with $0.03\text{ }\mu\text{m}$ Al_2O_3 powders, and carbon black powders (C) were mainly used for electrochemical and AFM measurements. Gold thin films evaporated on Cr-primed glass slides were used as substrates for infrared reflectance spectroscopic characterization. The surfaces were pre-cleaned by immersion in 1:3 H_2O_2 (30%)- H_2SO_4 (conc.) solution and rinsing in deionized water and ethanol. For electrochemical quartz-crystal nanobalance (EQCN) experiments, 10 MHz gold-coated quartz crystal piezoelectrodes (geometric area: 0.20 cm^2) were used as substrates.

The cyclic voltammetry, rotating disk electrode, and EQCN measurements were performed at room temperature. All experiments were performed in three-electrode electrochemical cells. All electrolytic solutions were de-aerated with high purity argon or nitrogen before the measurement. All potentials are given with respect to the reference electrode of Ag/AgCl saturated KCl. A Multimode NanoScope IIIa equipped with an E scanner was utilized for imaging. We used TappingMode AFM, which allowed imaging at minimum disruption of the nanostructures. The XPS measurements were made using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system uses a focused monochromatic $\text{Al K}\alpha$ x-rays (1486.7 eV) source for excitation. The collected data were referenced to an energy scale with binding energies for $\text{Cu } 2p_{3/2}$ at $932.67 \pm 0.05\text{ eV}$ and $\text{Au } 4f$ at $84.0 \pm 0.05\text{ eV}$.

Synthesis and Processing

In general, the preparation of naked metal nanoparticles on supports using traditional approaches is advantageous in terms of the exposure of the nanocrystal surface sites to catalytic reactions. Co-precipitation, deposition-precipitation, ion-exchange, impregnation, and successive reduction and calcination have been widely used (3, 4, 15). Nanoparticles of different metals supported on oxides, carbon, nanotubes, polymers or dendrimers, and organic monolayers have been reported. For gold nanoparticle catalysts, the use of TiO_2 and Fe_2O_3 support materials has also been demonstrated to be most effective (1, 2, 6). A disadvantage is however the lack of control over size, shape and stability. It is especially difficult to process the nanoparticles once produced. Stabilizing the surface by capping it with a shell of organic molecules can lead to controllable size, shape and surface properties. The shell, while enhancing stability against aggregation of nanocrystals, is however, an inherent disadvantage because of the blocking of surface sites.

The two-phase synthesis protocol developed by Schiffrin and co-workers (16-17) is now widely used for fabricating stable and soluble gold and alloy nanoparticles of a few nanometers in core diameter, which is briefly described in the Experimental section. The nanocrystal cores can be re-sized or re-shaped in a solution by a thermally-activated processing protocol developed recently in our laboratory (18-19). Briefly, the processing starts from the pre-synthesized nanoparticles (1-2 nm) in concentrated solutions and molten salt solutions by thermally inducing desorption of capping molecules, coalescence of nanocrystal cores and re-encapsulation. This process produces different particle sizes (3-10 nm) with high monodispersity. An example is shown in Figure 1. It is known that melting starts at the surface layer where the solid core is in equilibrium with the surrounding liquid shell. The temperature-correlation of melting predicts that the lowering of melting point is inversely proportional to the particle size (18). In comparison with a melting temperature of 1320 K for bulk gold, gold particles of 2.5 nm diameter are predicted to

melt at ~ 500 K. The surface melting temperature could be even lower, and the temperature change is also related to the capping-dominated surface tension. The driving force for coalescence of two particles is the reduction in free energy through a reduction in surface area (i.e., increase of size). The exothermic process due to a significant increase of temperature within the particle (20) could be extremely important in the coalescence process by reducing the coalescence time by as much as a few orders of magnitude. Gold and alloy nanoparticles in the 1-10 nm range have been successfully prepared using this thermal processing protocol (18-19, 21-24).

Assembly

The effective assembly of gold-based nanoparticles on planar surfaces is important for probing the detailed nanostructure with advanced analytical surface tools (e.g., STM and AFM), whereas the dispersion on carbon support materials is essential for practical fuel cell application. While the use of molecular linkers such as α,ω -functionalized thiols has been demonstrated for stepwise layer-by-layer assembly of nanoparticles (25-26), we recently developed a simple and effective pathway (27, 28). This exploits the surface exchange (28) and interparticle-crosslinking reactivities of monolayer-capped nanoparticles towards an assembly, termed as one-step exchange-crosslinking-precipitation route (Figure 2). One example is the exchange of α,ω -functionalized alkyl thiols, e.g., 1,9-nonanedithiol (NDT), with decanethiolates (DT) capped on gold nanoparticles, which is followed by crosslinking leading to nucleation and growth of a 3D network thin film. Another example involves hydrogen-bonding of carboxylic acid functionalized alkyl thiols, e.g., 11-mercaptoundecanoic acid (MUA). The DT-MUA exchange reaction was followed by hydrogen-bonding into a thin film. The preparation procedure is briefly described in the Experimental section.

We have demonstrated controllable assembly of the NDT- and MUA-linked gold nanoparticles of different core sizes on

Figure 1

Left: A scheme illustrating the thermally-activated core-shell processing of nanoparticles. Right: A TEM micrograph for the processed gold nanoparticles (5.6 ± 0.4). Insert: HRTEM showing the crystallinity of nanocrystal

Figure 2

Left: Schemes illustrating the assembly of core-shell gold nanoparticles by molecular linkers (An example for X-X: 1,9-nonanedithiol (NDT); and for X-Y: 11-mercaptopundecanoic acid (MUA)). Right: A TEM micrograph showing the NDT-linked gold nanoparticles ($\text{Au}_{2\text{-nm}}$) on carbon black (Vulcan C-72R)

planar substrates (27, 28). Figure 2 shows TEM micrograph for the NDT-linked gold nanoparticles of $\sim 2\text{-nm}$ core size ($\text{Au}_{2\text{-nm}}$) on carbon black (30-50 nm spheres) support. The assembly displays individually-isolated character and well-dispersed spatial property. It is important to note that the relative ratio of the capping vs. assembling molecules depends on the extent of exchange (27-29). The electronic conductivity and nanoporous properties of these nanostructured films depend on the particle core size and linker chain length. The interfacial reactivity and mass fluxes can be fine-tuned chemically or electrochemically (30, 31). The latter is desired for achieving catalytic access through the nanostructured pores in a way similar to zeolite pores. There are also other types of interparticle mediation or assembly chemistry which are viable for manipulating the interparticle spatial property, including polymeric matrix (32) and multidentate thioether ligands (33).

Catalytic Activation

To explore the catalytic activity of the core-shell gold nanoparticles, a key issue is to find an effective means towards activation so that the nanocrystal surface sites are accessible by the reactant. For CO and methanol oxidation, we found that the application of a polarization potential at $\sim +800\text{ mV}$ (vs. Ag/AgCl , Sat'd KCl) to the assembled catalysts, a process termed as electrochemical activation (34, 35, 36), could induce the activation of the assembled gold catalysts, as evidenced by the observation of CO or methanol oxidation waves. Using an electrochemical quartz-crystal nanobalance (EQCN) (36, 37) which is highly sensitive to interfacial mass fluxes (0.1 ng), the detected mass change corresponds to an equivalency of 80-90% loss of the thiolates in the catalyst film. By XPS analysis of S(2p) and O(1s) spectral regions (38), the relative change of sulfur and oxygen before and after the

Table 1

XPS-determined relative surface composition for as-prepared and electrochemically activated nanoparticles on HOPG substrate. (38)

Catalyst	Treatment	%S	%O
NDT- $\text{Au}_{2\text{-nm}}$	as-prepared	8.2	0.3
	electrochemically activated	2.1	10.7
MUA- $\text{Au}_{2\text{-nm}}$	as-prepared	2.7	3.7
	electrochemically activated	0.7	7.6

electrochemical activation (Table 1) provide quantitative information to assess the surface reconstitution. On the basis of the relative oxygen to sulfur ratios on the activated gold nanocrystals, the thiolates (DT and MUA) are largely removed and the detected oxygen is largely from the surface oxides. Spectral deconvolution of the Au(4f) bands revealed a combination of Au(0) and Au(I)/(III) (e.g., Au_2O_3 , or $\text{Au}(\text{OH})_x$) components after the removal of thiolates.

AFM studies (36) of the activated nanoparticle assembly revealed insignificant change in particle size and interparticle spatial property at least within the resolution limit. This is indicative of the effective isolation of individual nanoparticles before and after the catalytic activation even though there is a rearrangement of the nanostructured particles. On the basis of the recent proposal for catalytic oxidation of CO on oxide (e.g., TiO_2 or Fe_2O_3)-supported Au catalyst and surface oxygen ad-atom on gold (13), the structure of the activated core-shell catalysts can be hypothesized as nanocrystal cores with a partial oxide encapsulation (Scheme 2). The uptake of oxygen forming gold oxides leads to the formation of pores, which could then be operative for admitting reactant or releasing product, and allowing catalysis to occur at the peripheral (interfacial) areas between core and shell involving Au or $\text{Au}^{\delta+}$ species. In the activated core-shell nanoparticle

Scheme 2

A schematic illustration of the electrochemical activation of the core-shell gold nanoparticles towards a nanocrystal with the partial encapsulation and the formation of surface oxides. The large gray circle stands for O, and the small dark circle stands for Au in an oxidized state

case, the partial opening of the capping/linking nanostructure and the formation of surface oxides on the gold nanocrystals are operative as a result of the removal of shell molecules. In comparison with the relatively inert surface properties of bulk gold, the tendency of gold oxide formation on nanocrystal surface is another indication that the surface properties could be completely changed as a result of the size shrinkage.

Thermal treatment of the nanostructured catalysts provides another means to the catalytic activation. One advantage over electrochemical activation is the elimination of the use of electrolytes. Calcination of catalysts is well documented for catalyst pretreatment. The thermolysis of metal-carboxylate bridged gold nanoparticles (39) for preparing conductive films and the calcination of surfactant-capped Pt/Ru nanoparticles (40), for preparing catalysts are some of the recent examples. A key question is how particle size, interparticle spatial, and surface properties evolve controllably. An AFM examination of the individual nanoparticles (Figure 3A) reveals that the average particle

size shrinks after thermal activation. The shrinkage is due to the removal of the capping shell molecules (Figure 3B), which is consistent with the core-shell size feature, i.e., 2 nm core size and 1.5 nm shell. Our on-going work further examines the size evolution of the nanoparticles after treatments at different temperatures, different time lengths, and on different substrates.

In a recent AFM study (41) of a NDT-linked Au nanoparticle film on mica before and after heating at 225°C (corresponding to complete desorption of the capping decanethiolates), we found that the outline of individual particles was better resolved, and the chain-like nanoparticle feature remained intact though there was a slight increase in particle size. The relatively small changes in particle size and interparticle feature have demonstrated that the interparticle spatial property could be controlled even if there is a local sintering from the overlapped nanoparticles. The thermally-activated Au particles were found to exhibit catalytic activity toward methanol oxidation (41) similar to the activity observed for electrochemical activation (35, 36).

The particle size and spatial properties are dependent on loading of nanoparticles and annealing temperature. For ~50% loading of Au_{2-nm} nanoparticles on Vulcan-72R carbon, the TEM image obtained after thermal activation at 300°C showed a subtle increase of the particle size from ~2 nm to ~3.5 nm. The size increase for samples with lower loading is smaller than that for the higher loading case. While thermal treatments have been applied to nanoparticle systems, including surfactant-capped Pt/Ru (40) and metal-carboxylate linked Au (39) nanoparticles, there is limited fundamental understanding on how the nanoscale morphology is thermally evolved in a controllable way. Theoretically, there are two possible pathways for thermally-induced sintering and coagulation, a) sintering of small particles into larger-sized particles, and b) agglomeration of small particles into coagulated cluster (42). The driving force

Figure 3

(A) In-situ AFM images for DT-capped Au_{2-nm} on mica before (a) and after (b) thermal activation (225°C, 30 min). Cross-section view corresponds to the line drawn. (B) A scheme illustrating the thermal removal of the organic shell from the core-shell nanoparticle

for sintering can be described by the basic Gibbs-Thompson (G-T) relation. A recent model study (43) demonstrated that the dependence of this energy on particle size is much stronger than that predicted with the usual G-T relation. The size distribution depends on the interplay between the interparticle distances (density) and the thermal mobility of metal atoms on the surface. Work on a detailed delineation of the temperature, surface free energy, and particle size in the heating treatment is in progress.

Electrocatalytic Oxidation of Methanol and Reduction of Oxygen

Fuel cells operating by electrochemical oxidation of hydrogen or methanol fuels at the anode and reduction of oxygen at the cathode are attractive power sources due to their high conversion efficiencies, low pollution, lightweight and high power density. While methanol offers the advantage of easy storage and transportation in comparison with hydrogen fuel cell, its energy density (~ 2000 Wh/kg) and operating cell voltage (0.4 V) are much lower than the theoretical energy density (~ 6000 Wh/kg) and the thermodynamic potential (~ 1.2 V). The poor activity of the anode catalysts and inefficient activity or issue related to "methanol cross-over" at the cathode electrode are associated with the loss of about one-third of the available energy at the cathode and the other one-third at the anode. Extensive studies have been focused on Pt-group metals (Pt+Pd+Rh+Ru+Ir (PGM)) for both anode and cathode catalysts. A major problem is the poisoning of Pt by CO-like intermediate species (44, 45). Recently, oxide-supported gold nanoparticles in the <10 nm size range have emerged as one of the best catalysts for CO oxidation (1-4, 46), and for water gas shift reaction in reforming stage using 5 nm Au on Fe_2O_3 (10). Whether the unique properties of gold nanoparticles can be exploited for addressing these problems is a focus area of our work.

Table 2 shows the electrocatalytic activities observed from studies of Au-based nanoparticle catalysts for methanol oxidation and oxygen reduction. The data serve as relative comparisons of the different catalyst preparations. For the electrochemically-activated gold nanoparticles assembled on glassy carbon electrode (first two entries) (35), the anodic wave is observed at $+200\sim 350$ mV for the oxidation of methanol in alkaline electrolyte, which closely matches the potential for Au oxide formation. This observation suggests an electrocatalytic mechanism by which oxidation of methanol is mediated by surface oxide redox species. It was also found that the anodic current exhibited a linear increase with methanol concentration, whereas the cathodic wave decreased with methanol concentration (35). This is again

supportive of the electrocatalytic mediation mechanism. In EQCN measurement, a mass wave was detected corresponding to this current wave. This implies an initial product release followed by formation of surface oxygenated species, which is in part attributed to the reduction of nanocrystal's surface oxygenated species or oxides, and in part to release of solvent or anions (OH^-) from the nanostructure. The surface reaction likely involved the formation of a hydrated metal oxide phase (e.g., $\text{Au}_2\text{O}_3 \cdot n\text{H}_2\text{O}$).

A comparison of the electrocatalytic activity between the thermally activated (Table 2 third entry) and the electrochemically activated (Table 2 first entry) gold catalysts indicated that the anodic current density for the former is twice as large as the latter. In addition, the observation of two overlapping anodic waves for the thermally activated catalysts indicates the existence of at least two different catalytic sites. These findings suggest that the nature of the catalytic surface sites is dependent on the activation treatment.

The catalytic activity is also dependent on the nature of the initial molecular linkers. MUA-linked $\text{Au}_{2-\text{nm}}$ is not only activated more easily than NDT-linked $\text{Au}_{2-\text{nm}}$, but also displays a higher electrocatalytic activity, as evidenced by the peak potential of the oxidation wave being slightly lower ($+280$ mV) and peak current larger (by a factor of ~ 2) than those for NDT-linked $\text{Au}_{2-\text{nm}}$ (Table 2 first two entries). This difference is intriguing because it demonstrates the influence of the linker molecular structure on the final catalytic activity. The increased activity is likely due to the presence of a large open framework for easy access of alkaline electrolytes and the higher solubility of MUA than NDT upon the potential-induced desorption.

Gold-based alloy nanoparticles also served as a model catalyst system to explore its potential bifunctional catalytic properties that are well known for PtRu catalyst (45, 47, 48). Consider for example the viability of a AuPt catalyst for methanol oxidation, in which Pt functions as main hydrogenation or dehydrogenation sites, and Au together with Pt help to speed up the removal of poisonous CO species. For O_2 reduction on Pt, the strong adsorption of OH forming Pt-OH often causes inhibition of the reduction. Table 2 included observations of several AuPt nanoparticle catalysts for methanol oxidation and oxygen reduction (49). For NDT-linked AuPt nanoparticles assembled on planar glassy carbon electrode, two anodic waves were observed for methanol oxidation upon the thermal activation. These two waves, A and B, correspond to reaction sites of Au and Pt, respectively. In addition, the current density for wave-B was found to increase with the relative amount of Pt component. The two metal components in the nanoparticles are likely phase-segregated.

Table 2

Electrocatalytic properties of several activated nanoparticle catalysts on GC electrodes in 0.5 M KOH + 3 M methanol or Saturated O₂, and in 0.5 M H₂SO₄ + 3 M methanol or Saturated O₂ (from cyclic voltammetric data)

Catalyst	N _L ^{f)}	Electrooxidation of Methanol		Electroreduction of Oxygen	
		i _{pa} (μA/cm ²)	E _{pa} (mV) ^{c)}	i _{pc} (μA/cm ²)	E _{pc} (mV) ^{c)}
^{a)} NDT-Au ₂ -nm /GC	5	82	+226	-	-
^{a)} MUA-Au ₂ -nm /GC	5	149	+206	-	-
^{b)} NDT-Au ₂ -nm /GC	5	166	+206	-	-
^{b)} NDT-AuPt /GC	~10	148 (A) ^{d)}	320 (A) ^{d)}	-	-
		912 (B)	-50 (B)	-	-
^{b)} (AuPt/C) /GC	^{g)} 12 μg/cm ²	1820	-155	1360	-243
		360 ^{e)}	675 ^{e)}	1040 ^{e)}	+292 ^{e)}
^{b)} (AuPt/TiO ₂ /C) /GC	^{g)} 12 μg/cm ²	10630	-96	1500	-210
		850 ^{e)}	671 ^{e)}	1800 ^{e)}	+387 ^{e)}

a) Electrochemically activated; b) thermally activated; c) E_{pa} and E_{pc}: vs. Ag/AgCl (Sat'd KCl) d) Two anodic wave were observed: A closely matches the oxidation at Au component, whereas B corresponds to that on Pt component; e) the supporting electrolyte was 0.5 M H₂SO₄. f) N_L: number of equivalent layers. g) metal loading. Other notes: The Au/Pt molar ratio: 73:27, for the last three entries was determined by DCP-AES analysis, (loading on C: ~10 %). Carbon (C): Vulcan-72 (Cabot Corporation). Scan rate: 50 (first three 4 entries), and 100 (last 2 entries) mV/s. (-) not measured.

The preparation of carbon-supported Au or AuPt nanoparticles is aimed at evaluating the electrocatalytic activity of the catalysts in fuel cells. Nanoparticle-loaded carbon with or without TiO₂ (~20 nm) particles (Table 2 last two entries) was examined in preliminary experimental testing. The carbon-supported catalysts were activated by thermal treatment. In both cases, a single wave was detected for the AuPt (ratio 73:27) alloy composition, implying the operation of alloy, not segregated components, in the catalytic reaction. The observation of the much higher activity for methanol oxidation at AuPt/TiO₂(~10%)/C than that at AuPt/C indicates a contribution of the promoter TiO₂. The catalyst also showed catalytic activity in acidic electrolyte. In view of the fact that previous studies of the bulk form of AuPt alloy have not shown catalytic activity for methanol oxidation in acidic electrolytes, this preliminary finding provided interesting opportunities for studying the binary nanoparticle catalysts. Furthermore, the catalyst was found to be active towards CO oxidation in preliminary experiments. For O₂ reduction, a mixed process of 2e⁻ and 4e⁻ reductions was also detected using the carbon-loaded AuPt catalyst (49). A further assessment of the alloying composition, particle size and support effect should provide insights into the intriguing Au-based bifunctional catalytic mechanism.

Conclusion and Future Prospectus

In conclusion, we have shown that gold and its alloy nanoparticles of controlled size and composition can be produced by combining capping-based synthesis and

thermally-activated processing protocols. We have also demonstrated that the assembly of such nanoparticles on appropriate support materials after electrochemical or thermal activation presents new opportunities to prepare nanostructured catalysts for fuel cell catalysis. The catalytic activation involved controlled removal of the shell materials and reconstitution of the nanocrystal surface composition. The electrocatalytic oxidation of CO and methanol and the electrocatalytic reduction of oxygen are just a few examples of the catalytic reactions being explored for these nanoparticle catalysts. The delineation of the particle size, alloy composition and support materials properties with the catalytic activity of gold-based nanoparticles is part of our on-going work. It is important to note that the fundamental insights into these control parameters should be applicable to many other explorations of nanoparticles in catalysis. The insights could also form the basis of many new technologies for purification of air, long duration space travel, control of emissions from automobile exhausts, and microsensors.

While explorations of gold nanoparticle catalysts have shown great promises in fuel cell catalysis, the question of whether nanostructured gold nanoparticles can be eventually used as practical fuel cell catalysts that are compatible with existing PGM catalysts has not yet been answered. Such an answer will certainly require in-depth fundamental insights into the full controllability of size and surface composition of the nanoscale gold during the catalytic activation and reaction. The rapid development of gold-based nanotechnology will help enormously in the exciting advent towards gold "catalyst-by-design".

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References

- 1 M. Haruta, *Catal. Today*, 1997, **36**, 153
- 2 M. Haruta, M. Date, *Appl. Catal. A*, 2001, **222**, 427
- 3 G.C. Bond, D.T. Thompson, *Gold Bull.*, 2000, **33**, 41
- 4 G.C. Bond, *Gold Bull.*, 2001, **34**, 117
- 5 A.C. Templeton, W.P. Wuelfing, R.W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27
- 6 R.M. Crooks, M.Q. Zhao, L. Sun, V. Chechik, L.K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181
- 7 D.R. Rolison, *Science*, 2003, **299**, 1698
- 8 C.W. Corti, R.J. Holliday, D.T. Thompson, *Gold Bull.*, 2002, **35**, 111
- 9 A. Ueda, M. Haruta, *Gold Bull.*, 1999, **32**, 3
- 10 D. Andreeva, *Gold Bull.*, 2002, **35**, 82
- 11 R. Grisel, K.J. Weststrate, A. Gluhoi, B.E. Nieuwenhuys, *Gold Bull.*, 2002, **35**, 39
- 12 D.T. Thompson, *Gold Bull.*, 1998, **31**, 111 & 1999, **32**, 12
- 13 L.D. Burke, P.F. Nugent, *Gold Bull.*, 1998, **31**, 39
- 14 C.J. Zhong, M.M. Maye, *Adv. Mater.*, 2001, **13**, 1507
- 15 K.J. Klabunde, R.S. Mulukutla, in *Nanoscale Materials in Chemistry*, ed. K.J. Klabunde, John Wiley & Sons, Inc., New York, 2001, pp.223.
- 16 M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* 1994, 801
- 17 M.J. Hostetler, J.E. Wingate, C.J. Zhong, J.E. Harris, R.W. Vachet, M.R. Clark, J.D. Londono, S.J. Green, J.J. Stokes, G.D. Wignall, G.L. Glish, M.D. Porter, N.D. Evans, R.W. Murray, *Langmuir*, 1998, **14**, 17
- 18 M.M. Maye, W.X. Zheng, F.L. Leibowitz, N.K. Ly, C.J. Zhong, *Langmuir*, 2000, **16**, 490
- 19 M.M. Maye, C.J. Zhong, *J. Mater. Chem.*, 2000, **10**, 1895
- 20 K.E.J. Lehtinen, M.R. Zachariah, *Phys. Rev. B*, 2001, **63**, art. no. 205402
- 21 L. Han, J. Luo, N. Kariuki, M.M. Maye, V.W. Jones, C.J. Zhong, *Chem. Mater.*, 2003, **15**, 29
- 22 S.W. Chen, *Langmuir*, 2001, **17**, 2878
- 23 N.Z. Clarke, C. Waters, K.A. Johnson, J. Satherley, D.J. Schiffrin, *Langmuir*, 2001, **17**, 6048
- 24 T. Teranishi, S. Hasegawa, T. Shimizu, M. Miyake, *Adv. Mater.*, 2001, **13**, 1699
- 25 D. Bethell, M. Brust, D.J. Schiffrin, C.J. Kiely, *J. Electroanal. Chem.*, 1996, **409**, 137
- 26 M.D. Musick, C.D. Keating, M.H. Keefe, M.J. Natan, *Chem. Mater.*, 1997, **9**, 1499
- 27 F.L. Leibowitz, W.X. Zheng, M.M. Maye, C.J. Zhong, *Anal. Chem.*, 1999, **71**, 5076

References continued on page 102