

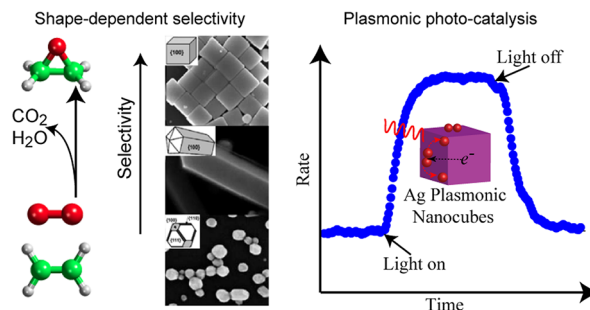
# Catalytic and Photocatalytic Transformations on Metal Nanoparticles with Targeted Geometric and Plasmonic Properties

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## CONSPECTUS



Heterogeneous catalysis by metals was among the first enabling technologies that extensively relied on nanoscience. The early intersections of catalysis and nanoscience focused on the synthesis of catalytic materials with high surface to volume ratio. These synthesis strategies mainly involved the impregnation of metal salts on high surface area supports. This would usually yield quasi-spherical nanoparticles capped by low-energy surface facets, typically with closely packed metal atoms. These high density areas often function as the catalytically active surface sites. Unfortunately, strategies to control the functioning surface facet (i.e., the geometry of active sites that performs catalytic turnover) are rare and represent a significant challenge in our ability to fine-tune and optimize the reactive surfaces.

Through recent developments in colloidal chemistry, chemists have been able to synthesize metallic nanoparticles of both targeted size and desired shape. This has opened new possibilities for the design of heterogeneous catalytic materials, since metal nanoparticles of different shapes are terminated with different surface facets. By controlling the surface facet exposed to reactants, we can start affecting the chemical transformations taking place on the metal particles and changing the outcome of catalytic processes.

Controlling the size and shape of metal nanoparticles also allows us to control the optical properties of these materials. For example, noble metals nanoparticles (Au, Ag, Cu) interact with UV–vis light through an excitation of localized surface plasmon resonance (LSPR), which is highly sensitive to the size and shape of the nanostructures. This excitation is accompanied by the creation of short-lived energetic electrons on the surface of the nanostructure. We showed recently that these energetic electrons could drive photocatalytic transformations on these nanostructures. The photocatalytic, electron-driven processes on metal nanoparticles represent a new family of chemical transformations exhibiting fundamentally different behavior compared with phonon-driven thermal processes, potentially allowing selective bond activation. In this Account, we discuss both the impact of the shape of metal nanoparticles on the outcome of heterogeneous catalytic reactions and the direct, electron-driven photocatalysis on plasmonic metal nanostructures of noble metals. These two phenomena are important examples of taking advantage of physical properties of metal materials that are controlled at nanoscales to affect chemical transformations.

## Introduction

In this Account, we discuss recent discoveries relating various physical characteristics of metallic nanostructures

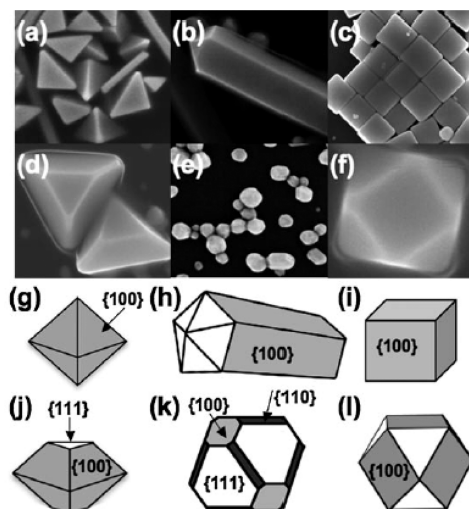
of controlled size and shape to heterogeneous catalysis. We recognize that nanoscience has always played a critical role in heterogeneous catalysts.<sup>1–4</sup> The intersections of

catalysis and nanoscience have mainly centered on robust and scalable synthesis of catalytic materials with high surface to volume ratio. While making active materials with high surface areas is crucial, this will not be the central issue of this Account. Multiple excellent reviews have been written describing various approaches to the design of high surface area solid state materials.<sup>5,6</sup> We will focus on two additional, recently reported phenomena crossing the interface of nanoscience and heterogeneous catalysis: (I) the impact of the shape of metal nanoparticles on the outcome of heterogeneous catalytic reactions and (II) direct photocatalysis on plasmonic metal nanostructures of noble metals. We focus on these two phenomena not because they are fundamentally related to each other but rather since we consider them to be important examples of taking advantage of physical properties of metal materials that are controlled at nanoscales to affect chemical transformations.

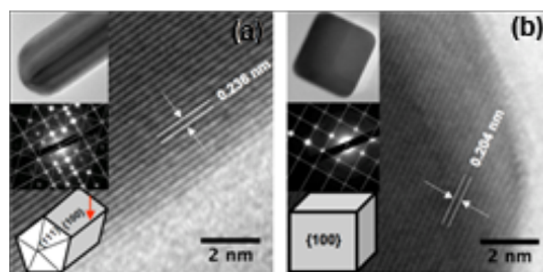
### Control of the Surface Sites through the Synthesis of Metal Nanoparticles of Targeted Shape

The active site in heterogeneous catalytic reactions is a collection of surface atoms that adsorb reactants and facilitate transformations of chemical bonds. Experimental surface science studies and quantum chemical calculations on well-defined metal surfaces have shown that the arrangement of atoms at the surface often affects dramatically the rates of chemical reactions and the distribution of products (i.e., selectivity).<sup>7</sup> It has been an open question whether it is possible to take the advantage of the different surface chemistry exhibited by different surface facets to fine-tune the outcome of catalytic reactions by designing active materials (i.e., metal nanoparticles) that are terminated with the surface facet that is optimal for a particular reaction.

Conventional strategies for the synthesis of metallic heterogeneous catalysts have primarily relied on impregnation of metal salts on high surface area support materials. Subsequent heat treatment results in the nucleation and growth of metal particles on the support. Particle size can be manipulated by varying the concentration of the metal salt deposited on the support or the extent of the heat treatment. The process usually yields quasi-spherical particles terminated by low-energy surface facets, such as the (111) surface for fcc crystals and a small fraction of under-coordinated surface sites. While this synthesis procedure is scalable and robust, the major drawback is the lack of control over the nature of the surface sites, making it almost impossible to tailor the structure of the active site and potentially fine-tune the reaction outcome.



**FIGURE 1.** SEM images and structural models of Ag metal particles: (a, g) right bipyramids; (b, h) pentagonal nanowires; (c, i) cubes; (d, j) truncated right bipyramids; (e, k) quasi-spherical; (f, l) truncated cubes. Reproduced from ref 12. Copyright 2010 Wiley-VCH.



**FIGURE 2.** HRTEM of (a) nanowire and (b) nanocube. Insets show zoomed out TEM images of the nanostructures, electron diffraction patterns, and model structures. Reproduced from ref 13. Copyright 2010 Wiley-VCH.

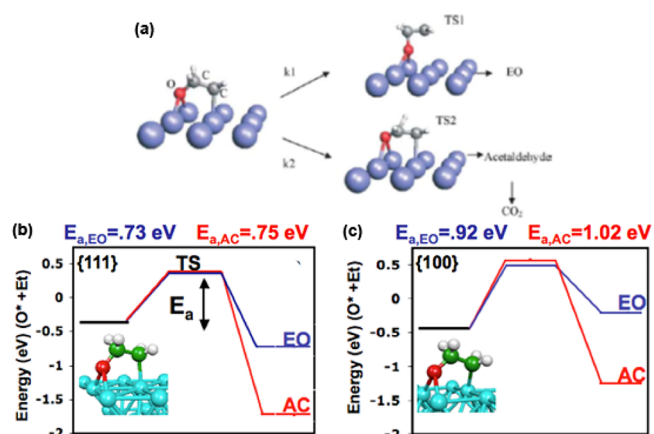
An alternative approach to the synthesis of metal nanoparticles is based on using growth-controlling reagents to kinetically direct the growth process away from the most thermodynamically stable surface facets.<sup>8–11</sup> Oxidizing metal etchants such as Cl anions and O<sub>2</sub> are used to control the shape of metal seed particles.<sup>9,11</sup> Organic stabilizer molecules are then employed to direct the growth of the seed into a nanostructure of a particular shape. Metal nanoparticle geometry is controlled by the geometry of the seed particles and the concentrations of metal precursors and stabilizer molecules.<sup>11</sup> Figure 1 shows Ag nanocubes, nanowires, and bipyramids, synthesized using the growth-directed approach.<sup>12</sup> A critical feature of these nanostructures is that they are not terminated by the most stable surface facets, which in the case of Ag is the (111) surface. For example, the shapes in Figure 2 are characterized by high concentration of the (100) surface facet as corroborated by

high-resolution transmission electron micrographs (HRTEM) and selected area electron diffraction (SAED) patterns of representative Ag nanocubes and nanowires.<sup>13</sup>

## Relationship between the Shape of Metal Nanoparticles and the Outcome of Catalytic Reactions

The ability to control the shape of metal nanoparticles and more importantly the surface facets that terminate the particle potentially opens avenue for the design of optimized heterogeneous catalysts. By controlling the surface facet exposed to reactants, we can start affecting the chemical transformations taking place on the metal particles and changing the outcome of a catalytic process. Some of the first reports of shape-specific catalytic performance of metal particles centered on the analysis of cubic, tetrahedral, and spherical Pt nanoparticles in a solution phase electron transfer reaction involving hexacyanoferrate (III) and thio-sulfate ions.<sup>14</sup> Indications that the shape of metal nanoparticles affects the outcome of catalytic reactions were further supported by the reports that in partial oxidation of styrene,<sup>15</sup> catalysts containing Ag nanowires exhibited significantly higher selectivity for styrene oxide compared with catalysts containing Ag spheres. Xu et al. compared the activity of Ag nanoplates, nanospheres, and nanocubes in the oxidation of styrene by *tert*-butylhydroperoxide showing that nanocubes were the most active.<sup>16</sup> They postulated that high concentration of the (100) surface facet on nanocubes compared with the two other shapes was responsible for the high activity of these materials. Bratlie et al. examined benzene hydrogenation over cubic and cuboctahedral Pt nanoparticles.<sup>17</sup> They found that both cyclohexane and cyclohexene were formed over cuboctahedral Pt particles, mainly terminated by the (111) surface facet, whereas only cyclohexane was formed over cubic Pt particles, largely terminated by the (100) facet. The authors attributed the difference in the product selectivity to the difference in the concentration of the (100) and (111) surface facets on the particles of different shapes. Other similar results of particle shape specific hydrogenation of unsaturated hydrocarbons were reported.<sup>18–20</sup>

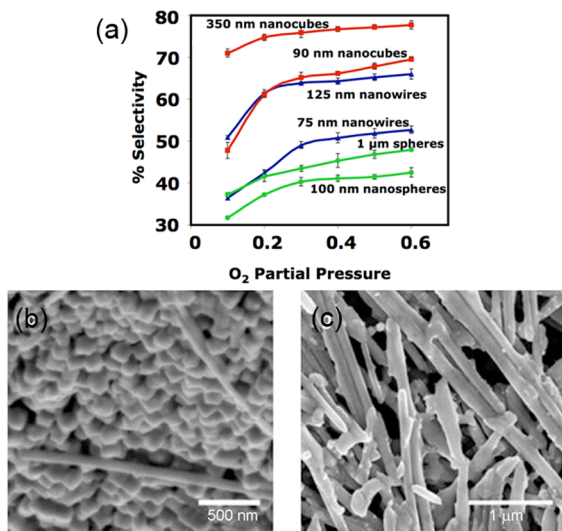
During this time, we were attempting to develop a molecular mechanism for ethylene epoxidation on silver surfaces. Based on DFT calculations, surface science experiments on well-defined single-crystal surfaces, and kinetic isotope labeling studies, it was suggested that the selectivity for EO is controlled by the chemistry of the surface oxametallacycle (OMC) intermediate, which is formed on Ag in the



**FIGURE 3.** (a) Schematic for competing OMC pathways. Reproduced from ref 24. Copyright 2004 Elsevier Inc. (b, c) Potential energy surfaces for transformation of OMC to AC and EO on Ag(111) and Ag(100). Energies are referenced to O(ads) and ethylene(g). Reproduced from ref 25. Copyright 2008 American Chemical Society.

reaction of ethylene and oxygen.<sup>21–24</sup> It was proposed that this intermediate undergoes competing isomerization reactions on Ag to form either the selective EO product or unselective acetaldehyde (AC) product. AC subsequently reacts to form combustion byproducts. The potential energy surfaces for oxametallacycle conversion to EO and AC on the Ag(111) and Ag(100) surfaces calculated using quantum chemical DFT calculations are depicted in Figure 3.<sup>24</sup> The results in Figure 3 show that on the Ag(111) surface, the activation barriers for the selective and unselective elementary steps are comparable to each other. On the other hand, on the Ag(100) surface, the activation barrier for the formation of AC is larger than the activation barrier for the formation of EO.<sup>25</sup> These DFT results led us to postulate that if Ag materials terminated by the (100) surface facet could be synthesized then these materials should perform the reaction with higher EO selectivity than the catalysts synthesized using standard wet impregnations strategies, mainly terminated by the (111) facet.

Motivated by the molecular insights about the reaction mechanism of ethylene epoxidation and advances in the synthesis of metal nanoparticles of different shapes and surface terminations, we decided to study the impact of Ag nanoparticle shape on product selectivity in the epoxidation reaction. Our hypothesis was that nanoparticles that are rich in the Ag(100) surface facet should exhibit higher selectivity. We were reluctant to engage in these studies since we had anticipated that the high mobility of silver atoms at reaction temperatures would rapidly erase any trace of the initial structure and the initial surface sites. It turned out that we were at least partially wrong in this assumption. Some of our



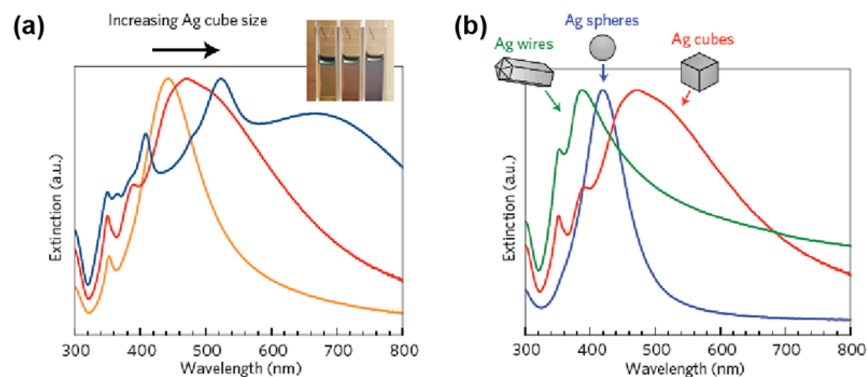
**FIGURE 4.** (a) Selectivity for EO for nanocubes, nanowires, and nanospheres of different diameters, as a function of oxygen partial pressure, at  $T = 510$  K. SEM images of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-supported cube (b) and wire (c) catalysts after 48 h on stream. Reproduced from ref 13. Copyright 2010 Wiley-VCH.

results are shown in Figure 4 where the intrinsic steady-state EO selectivity is plotted as a function of the particle size and shape and the O<sub>2</sub> partial pressure for six different catalysts measured at ethylene conversions between 4% and 5% at 510 K.<sup>13</sup> All catalysts contained Ag nanoparticles, prepared using the above-described directed growth methods. The catalysts were pretreated before the reaction using an identical procedure. The figure shows that nanocube and nanowire catalysts are more selective than the nanosphere catalysts for all particle sizes with Ag nanocubes showing better performance than Ag nanowires. The enhanced selectivity of nanocubes and nanowires, mainly terminated by the (100) surface facet, compared with nanospheres, which are dominated by the (111) surface termination, is consistent with the results of DFT calculations. Figure 4a also shows that for a given particle shape, higher EO selectivity was obtained on larger particles. We postulated that the higher selectivity of larger compared with smaller particles can be explained by a lower concentration of under-coordinated Ag surface sites in larger particles. We hypothesized that the under-coordinated surface sites activate unselective sequential and parallel chemical pathways leading to full oxidation of ethylene. Figure 4a shows that an increase in the EO selectivity is also achieved if the reaction is operated at excess of O<sub>2</sub> (i.e., high O<sub>2</sub>/ethylene ratio). We proposed, based on the analysis of the product distribution as a function of incremental changes in the partial pressure of O<sub>2</sub>, that in an excess of O<sub>2</sub> the impact of the under-coordinated Ag sites is

diminished since oxygen atoms preferentially adsorb on the under-coordinated Ag sites, effectively saturating these sites. The saturation of these sites moves the main reaction channels to well-coordinated surface sites, which are intrinsically more selective.

Our studies of the relationship between the shape of Ag nanoparticles and the product distribution in ethylene epoxidation, along with numerous other reports of particle shape-specific outcomes of heterogeneous catalytic reactions stimulate a number of questions. The synthesis of metal nanoparticles of different shape is fairly complex, and it involves oxidizing etchant molecules, reducing agents, and organic growth-directing molecules. There is a possibility that some of these "impurity" compounds end up attached to the particle affecting the catalytic process. Significant efforts are usually made to remove these compounds from the particles. These efforts involve pretreatment of the material before it is used in a catalytic study in ozone or oxygen at moderate temperatures, with the intent of removing organic stabilizer molecules through their combustion. For example, in our ethylene epoxidation studies, Ag particles were pretreated in O<sub>2</sub> at ~500 K for three hours. Subsequent elemental mapping of catalysts, using X-ray photoelectron spectroscopy (XPS) and energy dispersion spectroscopy (EDS), showed that there were no detectable impurities that could account for the observed particle shape-specific selectivity.<sup>13</sup> It is important to state that even with this extensive pretreatment procedure and catalyst characterization efforts, it is impossible to be completely confident that some of the impurities do not affect the outcome of the reactions.

While the issue of sample purity is very important in establishing rigorous structure–performance relationships, it is less relevant for practical applications in commercial heterogeneous catalysis. Questions that are much more critical to potential commercialization are centered on the long-term stability of these materials under operating conditions. The unique chemical activity of shaped metal nanoparticles is derived from their quasi-stable geometry, and there is a thermodynamic driving force for metal nanocubes or nanowires to collapse to the lowest energy quasi-spherical shapes. On atomic scales, this change in particle morphology might manifest itself in a restructuring of the (100) surface facets into the more stable (111) surface facet. While we were positively surprised by the robustness of our Ag-shaped nanoparticles under reaction conditions, we found that the selectivity of shaped Ag nanoparticles exhibited a small drop of ~1–2% for each 24 h on stream. SEM images of nanowire and nanocube samples used on stream for 48 h



**FIGURE 5.** (a) Normalized UV–vis extinction spectra in solution for Ag nanocubes of  $56 \pm 8$ ,  $79 \pm 13$ , and  $129 \pm 7$  nm edge lengths (b) for Ag cubes, spheres, and wires of similar sizes,  $\sim 75$  nm effective diameter. Reproduced from ref 27. Copyright 2011 Macmillan Publishers Limited.

are shown in Figure 4b,c. The image shows that there are changes in the morphology of nanoparticles. We believe that these morphological changes are the main reason for the observed drop in EO selectivity as a function of time of stream.

It is imperative to identify approaches to preserve the targeted shape and size of catalytic particles in reactive environments on commercial time scales. One way to accomplish this is to introduce “stabilizers” on the surface with the function to “freeze” the shape of the nanoparticle under reaction conditions. For example, it has been shown that the shape of nanoparticles can be stabilized by encasing them in thin, porous  $\text{SiO}_2$  shells.<sup>26</sup> A potential problem with this strategy is that the active surface area accessible to reactants will be lowered by the introduction of the stabilizers. Also, the introduction of solid inorganic materials results in a large number of sites at the interface of the metal particles and the inorganic stabilizers. These sites often have unpredictable chemical activity, which could further influence the reaction outcome. In general, we would expect these interfacial sites to be particularly problematic in processes where the selectivity is the figure of merit, since these sites might open up additional unselective reaction channels. Alternatively, it has been suggested that the stability can be enhanced if organic stabilizer molecules, used to direct the growth of the nanostructure, are not removed in the process of catalyst pretreatment. Again, the issues of the surface area loss, unpredictable chemical activity of the surface sites to which the organic stabilizer is attached, and the long-term stability of the organic stabilizers under reaction conditions should be considered.

## Direct Photocatalytic Reactions on Plasmonic Metal Nanoparticles

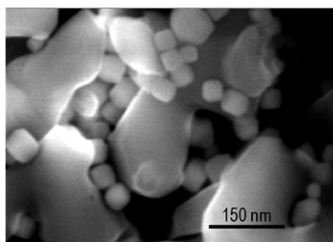
As discussed above, our work on ethylene epoxidation on shaped Ag nanoparticles made us keenly aware of the

potential long-term stability problems. These problems are particularly relevant at elevated temperature where thermal restructuring leading to changes in the particle size and shape is accelerated. We also understood that the Ag nanoparticles, as well as the nanoparticles of other noble metals, exhibit remarkable physical properties when illuminated with UV–vis photons. In Figure 5,<sup>27</sup> we show UV–vis extinction spectra for various Ag nanostructures. The measured extinction of light is due to the resonant excitation of localized surface plasmons (LSPR). LSPR is characterized by spatially nonhomogeneous, oscillating electric fields in the neighborhood of the nanostructures.<sup>28–32</sup> These fields are orders of magnitude more intense than the electric field of photons impinging on the nanoparticles; that is, the field is amplified in the regions localized at the surface of the nanostructure. In an inert environment, surface plasmons relax by either re-emitting resonant photons (scattering) or forming energetic charge carriers (energetic electrons and holes) at the surface of nanostructures. In the presence of adsorbates on the surface, the surface plasmons can also relax by transferring electron density directly to the adsorbate in the mechanism referred to as chemical interface damping (CID).<sup>33</sup> As shown in Figure 5, the resonant wavelength is controlled by the size and shape of the nanoparticles.

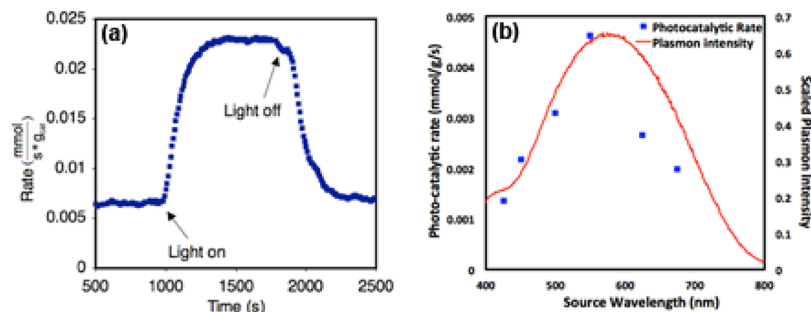
We hypothesized that the transient transfer of electrons from an excited plasmonic metal to adsorbates, directly via CID or indirectly by the adsorbate capturing energetic electrons formed through the relaxation of surface plasmons, might result in an electron-driven catalytic chemistry on plasmonic nanostructures. These light-driven, electron-mediated reactions would require lower operating temperatures compared with their purely thermal counterparts. For example, the rate of ethylene epoxidation is governed by the rate of dissociation of  $\text{O}_2$  on Ag.<sup>34</sup> If the process of oxygen dissociation can be activated by energetic electrons

on Ag nanoparticles illuminated with resonant light, then the operating temperature of the catalytic processes can be lowered without sacrificing the reaction rate. This would in principle lead to an extended lifetime of our shaped Ag particles that achieve very high selectivity such as Ag nanocubes. Over the past few years,<sup>27,35–37</sup> we have not only shown that illuminated plasmonic metals can activate electron-driven photochemical transformation, but also for the first time demonstrated that these electron-driven reactions on plasmonic metals exhibit fundamentally different behavior than thermal phonon-mediated processes, providing us with additional levers to optimize the long-term stability, activity, or selectivity of heterogeneous catalytic reactions. It is exciting that these reports of plasmon-stimulated, electron-mediated photochemistry on metal nanoparticles of noble metals under relatively low-intensity were reaffirmed by others,<sup>38–51</sup> resulting in a very vibrant new field of photochemistry and photocatalysis by plasmonic metals.

Our original experiments, testing the hypothesis of electron-mediated chemical transformations on plasmonic metals, included measuring the rates of catalytic epoxidation of ethylene to form ethylene oxide on Ag nanostructures with and without low intensity visible light illumination at temperatures between 400 and 500 K and atmospheric pressure. Figure 6<sup>36</sup> shows a scanning electron micrograph of the



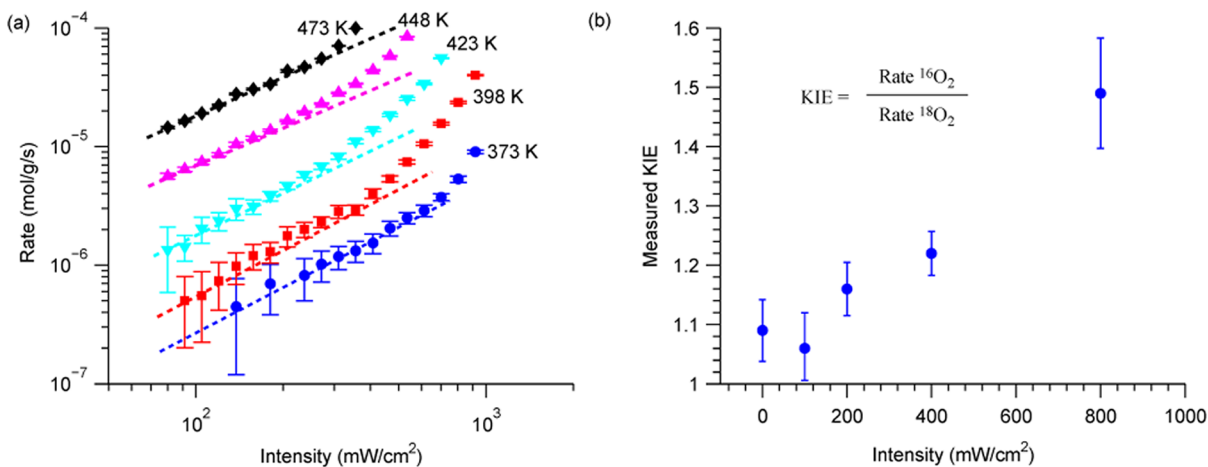
**FIGURE 6.** Scanning electron micrograph of Ag nanocubes supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Reproduced from ref 36.



**FIGURE 7.** (a) The rate of ethylene epoxidation at 450 K in dark and with visible illumination on Ag nanocubes supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Reproduced from ref 35. Copyright 2011 Macmillan Publishers Limited. (b) Photocatalytic rate as a function of the source wavelength at 470 K. Overlaid is the plasmon intensity spectrum. Reproduced from ref 36.

photocatalyst, which contained isolated and clustered Ag nanocubes, supported on larger, inert  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles. Under these operating conditions steady-state reaction rate is controlled by the rate of O<sub>2</sub> dissociation.<sup>34</sup> Therefore, we essentially measured the steady-state rate of O<sub>2</sub> dissociation on plasmonic Ag nanostructures. The photocatalytic reaction rate was obtained by subtracting the rate of the pure thermal process (light off) from the rate of the photothermal process (light on) obtained for an otherwise constant set of external conditions.

We observed that the steady-state reaction rate at 450 K and atmospheric pressure was  $\sim 4$  times higher when the visible light source of  $\sim 250$  mW/cm<sup>2</sup> intensity (approximately twice the intensity of sunlight) was illuminating the catalyst compared with the rate for the thermal process (light off), see Figure 7a. With this light intensity, identical reaction rates were obtained at 40 K lower temperature compared with the thermal process (light off). The rate was fully reversible responding instantaneously to the introduction and removal of the light flux. We also found that there was a one-to-one mapping between the wavelength-dependent rate of plasmon excitation and the wavelength-dependent photocatalytic rate, indicating that surface plasmons were driving the photocatalysis, see Figure 7b. The photocatalytic rate exhibited a linear dependence on source intensity up to  $\sim 300$  mW/cm<sup>2</sup> and a superlinear power-law dependence above  $\sim 300$  mW/cm<sup>2</sup> (i.e., rate  $\propto$  (intensity)<sup>*n*</sup>, with *n* > 1), see Figure 8a. The linear dependence of photo-induced reaction rate on source intensity at the limit of low intensity and the intensity-dependent transition from the linear to superlinear regime are signatures of electron-driven chemical reactions on metals.<sup>52</sup> We note that these transitions to the superlinear rate have been observed on metal single crystals only at many orders of magnitude higher source intensities.<sup>52</sup>



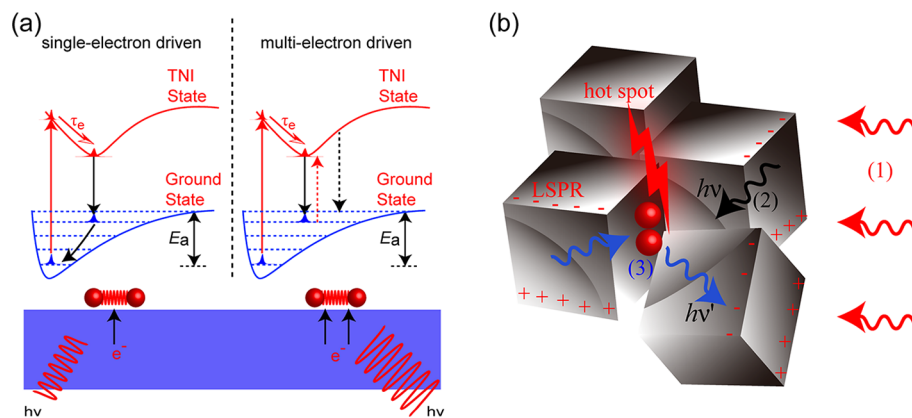
**FIGURE 8.** (a) Photocatalytic rate as a function of source intensity at various temperatures.<sup>36</sup> (b) Measured kinetic isotope effect, at constant reaction rate, as a function of source intensity. Reproduced from ref 36.

Further evidence that the observed photocatalytic activity was driven by energetic electrons came from kinetic isotope labeling studies, which involved exchanging <sup>16</sup>O<sub>2</sub> and its <sup>18</sup>O<sub>2</sub> isotopes and monitoring the reaction rate as a function of this exchange. It has been shown previously that the kinetic isotope effect (KIE) is larger for electron-driven reactions compared with thermal, phonon-mediated, chemical reactions on surfaces.<sup>53</sup> Figure 8b shows the KIE, the ratio of steady-state rate of the photocatalytic process for <sup>16</sup>O<sub>2</sub> and its <sup>18</sup>O<sub>2</sub> isotopes, measured at constant reaction rates as a function of light intensity. At zero intensity (light off), the KIE (at *T* = 498 K) was 1.09 ± 0.04, consistent with the O<sub>2</sub> dissociation controlling the rate of the reaction.<sup>54</sup> In the linear rate-intensity regime (light intensity below 300 mW/cm<sup>2</sup>), the KIE increased to ~1.16 ± 0.04, reaching 1.49 ± 0.09 in the superlinear regime at the intensity of 800 mW/cm<sup>2</sup>. The enhanced KIE is a distinct signature of electron-driven photocatalytic reactions on metals.<sup>53</sup> The observed high KIE could not be accounted for if a thermal phonon-mediated process is assumed.

We had postulated that Ag surface plasmons relax, transferring electron density to O<sub>2</sub> and thereby inducing electron-driven O<sub>2</sub> dissociation on Ag. It was important to demonstrate that this mechanism and the experimental observables discussed in the previous paragraphs could be supported by molecular models for electron-driven reactions on metals. Some classical models for electron-driven surface chemistry, mainly DIET (desorption induced by electronic transition) and DIMET (desorption induced by multiple electronic transitions), were developed to describe molecular desorption reactions on metal single crystals illuminated by high intensity short laser pulses.<sup>55,56</sup> We adopted these

models to describe the process of electron-induced O<sub>2</sub> dissociation on Ag. In our model, energetic electrons populate unoccupied adsorbate orbitals (in this case the 2π\* antibonding O–O orbital), creating a transient negative ion (TNI) O<sub>2</sub><sup>-</sup> species.<sup>57–59</sup> The evolution of the TNI on its potential energy surface (PES) results in the elongation of the O–O bond due to a longer equilibrium bond distance for the TNI compared with neutral O<sub>2</sub> molecule. The electronic relaxation of TNI results in the return of O<sub>2</sub> to the neutral PES, albeit in an excited vibrational state. In this process, the adsorbate acquires vibrational energy. The chemical reaction takes place when the vibrational energy is sufficient to overcome the activation barrier. In the efforts to model the electron-driven reactions on metals, we employed the PESs for ground O<sub>2</sub> state and the TNI state calculated using DFT calculations. We note that an almost identical mechanism was proposed subsequently for the electron-driven activation of H<sub>2</sub> on plasmonic Au nanoparticles.<sup>41</sup> We showed that this mechanism can account for all experimental observations including the intensity-dependent KIE and an observed exponential relationship between the rate of the photocatalytic process and operating temperature, see Figure 9.

We postulated that the active centers are clusters of multiple Ag nanoparticles that meet two criteria. The first criterion is that the product of the cluster optical cross-section and the local intensity of resonant photons interacting with the cluster (this product is effectively the rate of plasmon formation) is sufficiently high to support the required rate of plasmon excitation. The optical cross-section is a function of the cluster size and the geometric arrangement of the nanostructures in the cluster. It has been shown that for plasmonic Ag nanoparticles with diameters of a few



**FIGURE 9.** (a) Molecular mechanism of electron-driven processes in the linear (left panel) and superlinear regime (right panel). In the linear regime, a single electron excitation deposits vibrational energy into the adsorbate by accelerating the molecule along the TNI PES for the lifetime,  $\tau_e$ . If vibrational energy is not sufficient to overcome the activation barrier,  $E_a$ , the adsorbate returns to the thermally equilibrated state. In the superlinear regime, multiple excitations of the adsorbate occur within the vibrational lifetime. (b) A schematic of the proposed active complex of plasmonic Ag particles that can support superlinear rate. Photons interacting with the active complex are from the source (1), elastically scattered from other nanoparticles (2), or inelastically scattered from the adsorbates (3). Reproduced from ref 36.

tens of nanometers, the optical cross-section can be up to 20–50 times larger than the geometric cross-section.<sup>60</sup> The local intensity of resonant photons can be enhanced compared with the source intensity at some spots by elastic and inelastic scattering of resonant and Stokes-shifted photons by Ag nanoparticles in the reactor, Figure 9b. This is particularly the case for the 3-D, dense packing of Ag nanocubes used in our studies. The second criterion for the active complex is that there has to be an efficient focusing of electromagnetic energy on some regions of the complex where plasmons decay transferring electron density to  $O_2$ . Most likely, these active regions, as shown in Figure 9b, are junctions between two particles, characterized by very large electric fields, and the capacitive coupling of the oscillating electron cloud in one Ag particle to the oscillating electron cloud of the neighboring particle focuses the flux of charge carriers.<sup>61</sup>

While the above-discussed mechanism based on surface plasmon-mediated, electron-driven photocatalytic reactions at the hot spots of an active cluster of Ag nanoparticles can explain all our experimental results, it is important to state that alternative explanations are possible. For example, a slow thermalization of energetic electrons resulting in a nonlinear response of nonthermalized electron density distribution to photon intensity would yield a nonlinear photoyield even if the photoreactions were driven by a single vibronic excitation.<sup>59,62</sup> Another possible mechanism assumes direct inelastic collisions of  $O_2$  with the local electron density, which is due to plasmons characterized by high spatial and temporal gradients, where  $O_2$  gains energy and moves to a higher energy (more reactive) state.<sup>63</sup>

A very appealing feature of these systems is that it appears that due to the electron-driven nature of chemical transformations on illuminated plasmonic metal nanostructures, it is possible to efficiently funnel energy in a reaction coordinate without dissipating it throughout the entire material. In this particular case, energetic electrons from Ag selectively deposit energy in the O–O vibrational mode, heating this mode and enhancing the rate of  $O_2$  dissociation. This selective activation of chemical bonds on the surface of the catalysts is fundamentally different than the chemical bond activation in conventional thermocatalytic processes on metals where a phonon bath of the metal substrate randomly distributes energy in all reaction coordinates and where the selectivity toward the activation of a particular bond is governed only by the free energy barrier to activate the bond. For the electron-driven processes, the selectivity is governed not only by the energy barriers on the ground state PES but also by coupling of electronically excited state (the TNI state) with the reaction coordinates, which depends on the ground and TNI PESs. These light-driven, electron-mediated chemical processes provide us with an additional lever to affect the outcome of chemical transformation on solid metal surfaces and possibly design systems with improved outcomes as we showed recently by designing Cu-based plasmonic catalysts that exhibit significantly improved selectivity in epoxidation of propylene when illuminated with resonant light.<sup>37</sup>

## Outlook

Although the findings discussed above appear promising, there are a number of questions that still need to be



addressed. Strategies for the synthesis of metal nanostructures with targeted size and shape are inherently complex and do not lend themselves to convenient scale-up. Synthesis of particles of targeted shapes and sizes directly on high surface area supports is currently not possible. Potential presence of surface impurities makes the establishment of rigorous structure–performance relationships very challenging. In addition, it is imperative to identify approaches to preserve the targeted shape and size of catalytic particles in reactive environments on commercial time scales. It is also critical to develop a deeper understanding of photocatalytic transformations on plasmonic metal nanostructures, which at this point is in embryonic stage.

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