Heterometallic antenna–reactor complexes for photocatalysis

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Metallic nanoparticles with strong optically resonant properties behave as nanoscale optical antennas, and have recently shown extraordinary promise as light-driven catalysts. Traditionally, however, heterogeneous catalysis has relied upon weakly light-absorbing metals such as Pd, Pt, Ru, or Rh to lower the activation energy for chemical reactions. Here we show that coupling a plasmonic nano-antenna directly to catalytic nanoparticles enables the light-induced generation of hot carriers within the catalyst nanoparticles, transforming the entire complex into an efficient light-controlled reactive catalyst. In Pd-decorated Al nanocrystals, photocatalytic hydrogen desorption closely follows the antenna-induced local absorption cross-section of the Pd islands, and a supralinear power dependence strongly suggests that hot-carrier-induced desorption occurs at the Pd island surface. When acetylene is present along with hydrogen, the selectivity for photocatalytic ethylene production relative to ethane is strongly enhanced, approaching 40:1. These observations indicate that a nanocatalyst may greatly expand possibilities for developing designer photocatalytic substrates.

Industrial processes depend extensively on heterogeneous catalysts for chemical production and mitigation of environmental pollutants. These processes often rely on metal nanoparticles dispersed into high surface area support materials to both maximize catalytically active surface area and for the most cost-effective use of expensive catalysts such as Pd, Pt, Ru, or Rh (1, 2). However, catalytic processes utilizing transition metal nanoparticles are often energy-intensive, relying on high temperatures and pressures to maximize catalytic activity. A transition from extreme, high-temperature conditions to low-temperature activation of catalytically active transition metal nanoparticles could have widespread impact, substantially reducing the current energy demands of heterogeneous catalysis. Light-driven chemical transformations offer an attractive and ultimately sustainable alternative to traditional high-temperature catalytic reactions. Metallic plasmonic nanostructures are a new paradigm in photoactive heterogeneous catalysts (3–6). Plasmonic nanoparticles uniquely couple electron density with electromagnetic radiation, leading to a collective oscillation of the conduction electrons in resonance with the frequency of incident light, known as a localized surface plasmon resonance (LSPR). These resonances lead to enhanced light absorption in an area much larger than the physical cross-section of the nanoparticle, and such optical antenna effects result in strongly enhanced electromagnetic fields near the nanoparticle surface. An LSPR can be damped through radiative reemission of a photon, or nonradiative Landau damping with the creation of energetic “hot” carriers: electrons above the Fermi energy of the metal and/or holes below the Fermi energy. In this context, “hot” refers to carriers of an energy that is a significant fraction of the plasmon energy that would not be generated thermally at ambient temperature. Plasmonic metal nanoparticles have been shown to induce chemical transformations directly on their surfaces, through either phonon-driven or charge-carrier-driven mechanisms in Au (7–10), Ag (11, 12), Cu (13, 14), and, recently, Al (15) nanoparticles. Although these “good” plasmonic metals show initial promise for plasmon-induced photocatalytic chemistry, in general they are not universally good catalytic materials despite finding niche applications in a few industrial processes.

In comparison, noncovalent transition metals have historical precedence as excellent catalysts, yet are generally considered poor plasmonic metals, because they suffer from large nonradiative damping, which results in broad spectral features and weak absorption across the visible region of the spectrum (16–18). Many catalytic transition metal nanoparticles (Pt, Pd, Rh, Ru, etc.) possess LSPRs in the UV, but this is disadvantageous for photocatalysis because of poor overlap with conventional laser sources or, alternatively, with the solar spectrum. Increasing transition metal nanoparticle size redshifts optical absorption, but it increases cost and reduces surface area, and therefore catalytic activity. Recently, it has been shown that plasmonic nanoparticles can be used to increase optical absorption in adjacent nanoparticles (19–22), for instance, enabling hydrogen detection (23, 24).

Previous reports of photocatalytic transformation in plasmonic metal nanoparticle systems rely on the metal to double as both the antenna and catalyst. We demonstrate this antenna–reactor concept by showing that plasmonic aluminum nanocrystal antennas decorated with small catalytic palladium reactor particles exhibit dramatically increased photocatalytic activity over their individual components. The modularity of this approach provides for independent control of chemical and light-harvesting properties and paves the way for the rational, predictive design of efficient plasmonic photocatalysts.

Significance

Plasmon-enhanced photocatalysis holds significant promise for controlling chemical reaction rates and outcomes. Unfortunately, traditional plasmonic metals have limited surface chemistry, while conventional catalysts are poor optical absorbers. By placing a catalytic reactor particle adjacent to a plasmonic antenna, the highly efficient and tunable light-harvesting capacities of plasmonic nanoparticles can be exploited to drastically increase absorption and hot-carrier generation in the reactor nanoparticles. We demonstrate this antenna–reactor concept by showing that plasmonic aluminum nanocrystal antennas decorated with small catalytic palladium reactor particles exhibit dramatically increased photocatalytic activity over their individual components. The authors declare no conflict of interest.


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light-harvesting antenna and the catalytic surface. Here we show that the optical antenna effects of plasmonic metal nanoparticles can be used to directly enhance light absorption and modify the catalytic activity of directly adjacent reactive metal nanoparticle surfaces. This “antenna–reactor” complex, with the antenna and reactor composed of two distinct materials, is illustrated schematically in Fig. 1A. We note that the experimental antenna–reactor complexes designed for this work are separated by 2- to 4-nm dielectric aluminum oxide interfacial layers rather than complete separation as illustrated in Fig. 1A. Here we show that antenna–reactor complexes, focusing on Al as the antenna and Pd as the reactor, can be used to photoactively drive catalytic reactions under mild, ambient temperature and pressure conditions. Such modular, heterometallic complexes offer greatly increased degrees of freedom in the design of photocatalytic complexes, expanding the possible materials that can be used as light-driven catalysts. Manipulating the materials used for both the plasmonic antenna and catalytic reactor can theoretically lead to numerous possibilities for controlling plasmon-assisted absorption enhancements and specific reactivities (SI Appendix, Figs. S1 and S2).

**Results**

We synthesized heterometallic nanoparticle complexes consisting of aluminum nanocrystals (AlNC) (25) decorated with multiple smaller Pd islands as an embodiment of the antenna–reactor concept. Pd nanoparticles function as the optically lossy catalytic material coupled to the plasmonic AlNC “antenna.” The AlNC core is surrounded by an intrinsic 2- to 4-nm self-limiting oxide (26), separating it from Pd islands grown directly onto the outside of the Al$_2$O$_3$ shell using a weak-capping growth approach (27) (SI Appendix, Fig. S3). This antenna–reactor geometry leads to internal field enhancements and increased optical absorption in the Pd islands decorating the surface. We show, via calculated near-field enhancements in a 10-nm Pd island at the surface of a 110-nm AlNC (Fig. 1B and C) and, for comparison, a 110-nm Al$_2$O$_3$ nanosphere (Fig. 1D and E), the effect of coupling a plasmonic antenna to an optically lossy transition metal. The local field enhancement in the Pd island for the antenna–reactor geometry is over one order of magnitude higher than for the Al$_2$O$_3$ nanosphere case, due to the plasmon-enhanced near fields at the AlNC surface. This effect leads to a drastic increase in hot-carrier production in the reactive Pd islands decorating the surface, because hot-carrier generation is proportional to internal field intensity enhancement rather than bulk material absorption (28).

The wavelength-dependent absorption in Pd for the AlNC–Pd antenna–reactor and the Al$_2$O$_3$–Pd control case was calculated using the finite difference time domain (FDTD) method and is shown in Fig. 1F. The AlNC–Pd antenna–reactor geometry (solid red curve) shows an increased absorption at ~500 nm corresponding to plasmon-assisted absorption enhancements from the dipolar resonance of the AlNC (SI Appendix, Fig. S4). In contrast, the Al$_2$O$_3$–Pd geometry (black curve) shows only a broad, weak absorption across the visible region of the spectrum, with slight increase in the UV (<400 nm).

We also show that the absorption enhancements in such heterometalic systems can be calculated directly as the product of absorption in the reactor metal (Fig. 1F, black curve) and the near-field enhancements (blue curve) to yield the calculated absorption (dashed red curve) without the use of extensive FDTD simulations. Interestingly, if the original Pd absorption in an isolated geometry (black curve) is multiplied by the electric field enhancement (blue curve) on the antenna particle alone at the position where the Pd island would be situated, this calculated absorption (dashed red curve) closely matches the Pd absorption in the coupled geometry. This provides further evidence for the antenna-induced absorption enhancement mechanism and suggests that the optical response of the antenna–reactor system can be determined by modeling separate responses from the individual catalytic reactor and the plasmonic antenna. This insight provides a path for straightforward optimization of antenna–reactor structures, where the antenna response can be tuned independently to provide the best spectral overlap with reactor photocatalytic activity.

Experimental evidence for coupling between the Al plasmonic nanocrystal and the Pd islands shows distinct modes corresponding to the individual antenna and reactor constituents as well as the coupled system (Fig. 2). Using electron energy loss spectroscopy
(EELS) performed in a monochromatic, probe-corrected scanning transmission electron microscope (STEM), distinct modes corresponding to Al, Pd, and the coupled Al–Pd complex are observed. Nonnegative matrix factorization was used to separate the information encrypted in the EELS spectrum image into spectral components (Fig. 2A) and a set of coefficients corresponding to the nanometer-scale resolution spatial distribution of the plasmon excitation probability, herein referred to as plasmon maps (Fig. 2B–E) (29, 30). The two Al modes show a maximum electron loss probability at 6 eV and 7 eV (Fig. 2A), both with a secondary shoulder at ∼2.5 eV corresponding to the dipolar resonances of AlNC–Pd (confirmed with UV-visible spectroscopy, SI Appendix, Fig. S4). In the plasmon maps shown in Fig. 2B–E, an outline of the nanoparticle structure [also shown as the high-angle annular dark-field STEM (HAADF-STEM) in Fig. 2A, Inset] has been overlaid to assist in visualization relative to the specific components of the complex. One can see from the Al LSPR maps that prominent excitation from Al is found at the Al–Al₂O₃ interface, with highest intensity in regions of the Al nanoparticle surface without Pd decoration (Fig. 2B and C). This can be attributed to local damping of the Al LSPR through interactions and coupling with Pd interband transitions (31). The plasmon excitation probability is damped where smaller nanoparticle aggregation is found, but is nearly completely eliminated in and around larger (>10 nm) Pd islands. Of the two modes attributed to Pd, only one exhibits coupling to the Al core. This mode corresponds to plasmon-assisted enhancements in Pd directly on the surface of the AlNC, and will be referred to as the “antenna mode” (Fig. 2D). The second mode can be attributed to Pd interband transitions (Fig. 2E) (18). The antenna mode reveals intensity across a broad range of energies (1.5–6 eV) that overlay the dipolar resonance contribution from Al. The two modes contributed from Pd show how the proximity of a lossy catalytic metal to a plasmonic metal core can influence the electronic properties of the decorating catalytic metal. The antenna mode (red) shows clear enhancements on the surface of the Pd islands in areas with high coverage and large islands (Fig. 2D). Chemically synthesized AlNCs can exhibit small protrusions of excess Al₂O₃ extending from their surfaces. In this specific antenna–reactor nanoparticle, a larger protrusion of Al₂O₃ decorated with Pd, indicated with a white arrow in the HAADF-STEM in Fig. 2A, Inset, is observed at the base of the nanoparticle. For the antenna mode of the composite nanoparticle, this region shows no enhancement (Fig. 2D). However, when the Pd interband transitions are excited (Fig. 2E), a strong excitation is observed across the entire nanoparticle, including the Pd found on the Al₂O₃ protrusion (a secondary example and experimental description of EELS plasmon mapping is provided in SI Appendix, Figs. S5 and S6).

For the AlNC–Pd complex, the wavelength dependence of HD production (Fig. 3A, red) closely follows the calculated absorption cross-section (black) supporting a hot-carrier mechanism (34). When qualitatively compared with pristine AlNCs, the wavelength dependence of HD production is dramatically different (green), with the maximum HD production occurring at a photoexcitation wavelength of 800 nm, corresponding to the interband transition of Al (15). Quantitative consumption of H₂ on Au (7, 8) and Al (15)—is the interaction of the generated hot carriers with adsorbed H and D atoms on Pd, inducing desorption of HD. The plasmon-induced dissociation, recombination, and desorption processes are all charge-neutral. As the chemical reaction is completed, the hot electrons recombine with the holes. For the AlNC–Pd complex, the wavelength dependence of HD production (Fig. 3A, red) closely follows the calculated absorption cross-section (black) supporting a hot-carrier mechanism (34). When qualitatively compared with pristine AlNCs, the wavelength dependence of HD production is dramatically different (green), with the maximum HD production occurring at a photoexcitation wavelength of 800 nm, corresponding to the interband transition of Al (15). Quantitative consumption of H₂ on Au (7, 8) and Al (15)—is the interaction of the generated hot carriers with adsorbed H and D atoms on Pd, inducing desorption of HD. The plasmon-induced dissociation, recombination, and desorption processes are all charge-neutral. As the chemical reaction is completed, the hot electrons recombine with the holes.

Temperature dependence measurements between 300 K and 400 K without external illumination show an increase in HD generation with increasing temperature; however, the calculated wavelength-dependent local maximum temperature increase expected on the nanoparticle surface is only between 2 K and 16 K for Al and Pd surfaces, respectively, within the experimental range of excitation laser power densities (SI Appendix, Fig. S9). Such small local temperature increases under illumination suggest that, although photothermal heating of the Pd lattice may contribute slightly to H₂ desorption, the primary cause can be attributed to
the excitation of photoexcited hot carriers in the antenna–reactor complex. To estimate the importance of hot electrons versus holes for the desorption process, we calculated densities of states and analyzed the contributions of Pd–H bonding and antibonding interactions, from DFT (SI Appendix, Figs. S10–S13). The bonding Pd–H orbitals lie very low in energy (~6 eV below the Fermi level), so a hot-hole-initiated process seems less likely from these initial results. In contrast, the Pd–H antibonding interactions manifest just above the Fermi level and thus can be expected to be easily populated by hot electrons. From these DFT results, a hot-electron-initiated destabilization of the Pd–H bonds leading to desorption seems more likely. However, we caution that the band structure obtained from DFT does not necessarily reflect (or quantitatively capture) the correct physics of excited carriers on the surface. Therefore, embedded correlated wave function calculations are underway that remedy the too-facile charge transfer of DFT (35), to identify the exact mechanism of hot-carrier-mediated hydrogen desorption from Pd surfaces.

Additional contributing reaction mechanisms include H$_2$ migration through the oxide to the AlINC surface and hot-electron transfer across the oxide into Pd. Migration of H$_2$ followed by dissociation by plasmon- and interband-transition–induced hot carriers was found to be the primary mechanism in pristine AlINC (15) and certainly also contributes in the antenna–reactor complex. However, it is a small effect because, as shown in SI Appendix, Fig. S8, the overall rate of HD production on AlINC–Pd antenna–reactors is nearly two orders of magnitude higher than in pristine AlINCs. By comparing the wavelength dependence of HD production on pristine AlINCs and AlINC–Pd, specifically the drastic increase in the HD yield at the Al dipolar plasmon, we can conclude that electron transfer effects also play only a minor role for the overall reactivity. Thus, we conclude that the plasmon-assisted absorption enhancements in Pd at 500 nm (Fig. 1F) are the major effect responsible for the increase in reactivity.

The photocatalytic properties of the AlINC–Pd antenna–reactor complex are translatable to other chemical reactions, such as hydrogenation. One important and industrially relevant reaction is the selective reduction of acetylene (36). Ethylene is a commodity chemical precursor used in the production of polyethylene-based materials with widespread commercial use; however, under traditional thermal conditions, ethane is also produced in a side reaction during hydrogenation of acetylene. With AlINC–Pd antenna–reactor complexes, we have found a drastic increase in the selective reduction of acetylene to ethylene under white-light illumination compared to traditional thermal reduction (Fig. 4). This selectivity also shows a large increase with increased laser power density (red); representative gas chromatograms for both thermal and photohydrogenations are shown in SI Appendix, Fig. S14. An increase in ethylene:ethane product ratio from ~7 to ~37 is observed for the photohydrogenation case (red). In contrast, traditional thermal heating of the AlINC–Pd complexes showed that ethylene:ethane selectivity leveled off at a maximum of ~10:1 before showing a drop to ~6:1 at 360 K (black).

This selectivity enhancement seen in photohydrogenation, yet not seen in traditional thermal hydrogenation, is likely due to the availability of dissociated H$_2$. In both photohydrogenation and thermal hydrogenation cases, acetylene adsorbs on the surface and undergoes the first and second hydrogenations to produce ethylene (37–39). At this point, two forward reaction pathways are possible: ethylene desorption or subsequent hydrogenation of ethylene to deuterium (HD) production (a.u.).

Fig. 3. AINC–Pd photocatalytic reactivity for the hydrogen–deuterium exchange reaction. (A) Wavelength dependence of H$_2$ desorption on AINC–Pd (red) and pristine AlINC (green) and the calculated absorption cross-section of AlINC–Pd (black). The sample was irradiated with a power density of 5 W/cm$^2$ at all wavelengths. (B) Power dependence measurements of HD production at the dipolar plasmon resonance (492 nm, 2.52 eV) and the Al interband transition (800 nm, 1.55 eV).

Fig. 4. AINC–Pd photocatalytic reactivity toward selective acetylene hydrogenation. Selectivity of ethylene:ethane production by acetylene hydrogenation under illuminated (red) and thermal (black) conditions.
produce ethane. Both desorption and hydrogenation of ethylene from Pd(111) have similar activation barriers within the margin of error of previous DFT calculations (37). Therefore, the availability of dissociated H₂ dictates the branching ratio between these two reaction pathways. In photocatalytic hydrogenations, plasmon-induced hot carriers lead to rapid desorption of H₂, biasing the equilibrium toward desorption and thus limiting the availability of hydrogen on the surface for additional hydrogenation of ethylene. The hypothesis of hot-carrier-induced H-starved surfaces leading to increased selectivity is also backed up by reduced yields of ethylene in the photocatalytic hydrogenation case (SI Appendix, Fig. SI4). With illumination, there is less surface-activated H, which also reduces the likelihood of the first and second hydrogenations of acetylene needed to produce ethylene. In thermal hydrogenations, ethylene yields are higher (T > 360 K) at the expense of reduced selectivity, most likely due to minimal changes in dissociated H₂ surface coverage, and enough kinetic energy in the system to overcome the activation energies and favor subsequent hydrogenations of ethylene. The selectivity increase observed for the photocatalysis of ethylene could open doors for developing more selective hot-carrier-driven chemistry.

Conclusions
The direct coupling of plasmonic nanoantennas with catalytic nanoparticles into a single heterometallic complex allows for absorption enhancements in poorly light-absorbing catalytic metals. With antenna–reactor complexes, hot-carrier production and photothermal heating can be dramatically increased near catalytically active surfaces. This concept is a highly modular one; for example, tuning the composition or size of the plasmonic antenna allows for light-induced photocatalysis at specific wavelengths of the electromagnetic spectrum, enabling optimization of such complexes for specific chemical reactions and reaction pathways. Likewise, by changing the “reactor” to different metals, alloys, semiconductors, or insulators, the surface chemistry and photocatalytic activity can be highly tuned. The plasmon-induced hydrogen desorption reported here shows that the antenna–reactor geometry increases hot-carrier production, thereby allowing for new, light-driven reaction pathways on the catalytic metal. Developing this antenna–reactor concept to favor specific hot-carrier-driven photocatalytic processes where control over reaction specificities is highly desirable opens a new door for the development of precise, highly predictive control of catalytic chemistry using light.

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