Controlling Reaction Selectivity over Hybrid Plasmonic Nanocatalysts

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Supporting Information

ABSTRACT: The localized surface plasmon resonance (LSPR) excitation in plasmonic nanoparticles has been used to accelerate several catalytic transformations under visible-light irradiation. In order to fully harness the potential of plasmonic catalysis, multimetallic nanoparticles containing a plasmonic and a catalytic component, where LSPR-excited energetic charge carriers and the intrinsic catalytic active sites work synergistically, have raised increased attention. Despite several exciting studies observing rate enhancements, controlling reaction selectivity remains very challenging. Here, by employing multimetallic nanoparticles combining Au, Ag, and Pt in an Au@Ag@Pt core-shell and an Au@AgPt nanorattle architectures, we demonstrate that reaction selectivity of a sequential reaction can be controlled under visible light illumination. The control of the reaction selectivity in plasmonic catalysis was demonstrated for the hydrogenation of phenylacetylene as a model transformation. We have found that the localized interaction between the triple bond in phenylacetylene and the Pt nanoparticle surface enables selective hydrogenation of the triple bond (relative to the double bond in styrene) under visible light illumination. Atomistic calculations show that the enhanced selectivity toward the partial hydrogenation product is driven by distinct absorption configurations and charge delocalization of the reactant and the reaction intermediate at the catalyst surface. We believe these results will contribute to the use of plasmonic catalysis to drive and control a wealth of selective molecular transformations under ecofriendly conditions and visible light illumination.

KEYWORDS: Plasmonic catalysis, nanorattles, platinum, selectivity, visible light, hydrogenation

Plasmonic nanoparticles have emerged as attractive systems to efficiently harvest solar energy in order to drive and control chemical transformations. In plasmonic nanoparticles, incident photons resonantly interact with the collective motion of electrons, a phenomenon known as localized surface plasmon resonance (LSPR). It has been shown the LSPR excitation of nanocatalysts can enhance the rates of several chemical transformations, a phenomena referred to as plasmonic nanocatalysis. Studies on plasmonic nanocatalysis generally focus on nanoparticles supporting LSPR excitation in the visible and near-infrared ranges, such as gold (Au), silver (Ag), and copper (Cu). However, the catalytic properties of these systems are limited. Conversely, several metals that are important for nanocatalysis do not display LSPR excitation in the visible or near-infrared ranges. In this context, multimetallic nanoparticles containing a plasmonic and a catalytic component represent a remarkable opportunity to marry plasmonic and catalytic properties.

The LSPR excitation involves generation of strong electromagnetic fields localized around plasmonic nanoparticles that decay either via the radiative scattering of photons or nonradiatively by the formation of energetic charge carriers (hot electrons and holes). These hot carriers can flow to the surface of the nanoparticle, where they can be injected into the molecular orbitals of adsorbates or metal–adsorbate complexes, activating these species and enabling increased...
reaction rates. In addition, this opens the possibility for controlling the reaction selectivity as the injection of these hot carriers to specific molecular orbitals of adsorbates or metal–adsorbate complex can be maneuvered. Nonetheless, despite several studies of rate enhancements and mechanisms, achieving control over reaction selectivity in plasmonic nanocatalysis remains challenging.

In order to provide insights into reaction selectivity in plasmonic nanocatalysis, we engineered multimetallic plasmonic–catalytic architectures composed of Au, Ag, and Pt. In these systems, we investigated the effect of distinct surface interactions between the substrate and the metal surface, which enable different bond activation pathways for tunable product formation under LSPR excitation. We employed the catalytic hydrogenation of phenylacetylene as a model transformation and multimetallic core–shell and nanorattle architectures as plasmonic catalysts to selectively produce styrene, an important precursor for polystyrene and several copolymers. Our results demonstrated that the preferential bond interaction between the C–C triple bond and Pt at the surface of our catalysts enabled control of reaction selectivity, in which an increase toward the formation of styrene, the semihydrogenation product, was observed under visible light.

The proper choice of nanomaterials compositions and architectures that enables one to combine plasmonic and catalytic properties is fundamental for producing versatile plasmonic nanocatalysts with high activity and the potential for the understanding and control of reaction selectivity. It has been recently postulated that core–shell nanoparticles containing a plasmonic core surrounded by a very thin shell of a catalytic nanoparticle provides an interesting scenario toward enabling the intensification of plasmon-driven catalytic reactions in catalytic metals that do not support SPR excitation in the visible and near-infrared ranges. In addition to these core–shell systems, our group recently demonstrated that plasmon hybridization in multimetallic and plasmonic nanorattles (comprised of an Au sphere inside a AgAu shell, for example) can achieve superior plasmonic catalytic activities relative to nanosphere and nanoshell counterparts. This was observed as a result of plasmon hybridization that leads to higher E-field enhancements relative to individual nanostructures as a result of LSPR excitation, indicating that the nanorattle morphology may be promising in terms of activity enhancements and possibly selectivity assessment in plasmonic nanocatalysis. Therefore, here we focus on multimetallic nanorattles as a target architecture. For our elements of interest, we chose to exploit the well-known plasmonic properties of Au and Ag to enhance and control catalytic transformations at the surface of Pt, an excellent catalytic metal with widespread application.

We first modeled the optical properties of plasmonic nanorattles comprised of a Au nanosphere inside a Pt shell. Figure S1 depicts the electric field enhancement contours calculated by the discrete dipole approximation (DDA) method for Au@Pt nanorattles (Figure S1A,B), as well as the Au nanospheres (Figure S1C) and Pt shells (Figure S1D) counterparts. The Au@Pt nanorattles were 63 nm in outer diameter, 5 nm in shell thickness, and contained a 37 nm Au nanosphere inside its core. The Au nanospheres were 37 nm in diameter, and the Pt nanoshells were 63 nm in outer diameter and 5 nm in shell thickness. Considering a light excitation wavelength matching the maximum in the calculated LSPR extinction spectra (Figure S2), the electric field enhancements were significantly higher for the nanorattles relative to the Au nanosphere when the nanorattle was excited at 713 nm. This can be assigned to the hybridization between the core and shell components that is in agreement with the observation that the calculated extinction spectrum for the Au@Pt nanorattles displayed two bands centered at 481 and 713 nm. Figure S3 shows the contributions from absorption and scattering to the extinction in the Au@Pt nanorattles. These simulations indicate that the presence of a Pt shell in the nanorattles leads to strong absorption as opposed to scattering. This indicates that absorption represents the dominant LSPR decay pathway in the nanorattles. This partitioning of energy between absorption and scattering is beneficial in the context of plasmonic nanocatalysis, as absorption is directly responsible for the generation of hot carriers. Thus, stronger absorption would result in the efficient formation of LSPR-excited charge carriers that can be transferred at the metal–molecule interface and contribute to plasmonic–catalytic performances.

For experimental verification of the modeling results, we wanted to investigate both multimetallic nanorattles and their equivalent multimetallic core–shell nanoparticles. Both architectures comprise a plasmonic core and a shell containing the catalytic material (Pt), allowing us to systematically investigate the role of the nanorattle relative to the core–shell morphology. To achieve this, we designed a synthetic approach that allowed us to obtain both plasmonic nanorattles containing a Au core and a Pt-based shell, and core–shell analogues in which a thin Pt shell is present at the surface of a plasmonic core. Our strategy was based on a combination of seeded growth followed by galvanic replacement as illustrated in Figure 1A (see Supporting Information for details). First, Au nanoparticles 30 nm in diameter were employed as physical templates for the Ag deposition at their surface, leading to Au@Ag core–shell nanoparticles. Then, the Au@Ag core–shell nanoparticles were employed as chemical templates in a galvanic replacement reaction with PtCl6−. In this case, simply by changing the concentration of PtCl6− employed in the synthesis, the final morphology of the material can be precisely maneuvered. When 0.1 mM PtCl6− was employed, the deposition of a thin Pt shell at the Au@Ag surface takes place, generating Au@Ag@Pt core–shell nanoparticles. Conversely, if 0.2 mM PtCl6− is employed, Au@AgPt nanorattles are obtained. Figure 1B–E shows high-resolution electron microscopy (HRTEM) and scanning transmission electron microscope (STEM) high-angle annular dark-field (HAADF) images for multimetallic Au@Ag@Pt core–shell nanoparticles (Figure 1B,C) and Au@AgPt nanoparticles (Figure 1D,E). The STEM-HAADF image of the Au@Ag@Pt (Figure 1C) clearly shows the difference in atomic number contrast between the Au core and the Ag shell. In this case, the Au nanoparticles (NPs) were 32 nm in diameter, and the Ag shell thickness corresponded to 35 nm. The presence of an ultrathin Pt shell <3 nm in thickness is suggested from atomic resolution imaging of the surface of the particle. The lattice fringes we observe in Figure S4 are assigned to the face-centered cubic (111) lattice spacings for Ag and Pt (corresponding to 0.23 nm). For the Au@AgPt nanorattles (Figure 1D,E), the presence of hollow interiors as well as the formation of ultrathin Pt-based shells (<3 nm in thickness) can be also visualized.

To confirm the elemental distributions in the NPs we have employed STEM-energy dispersive X-ray spectroscopy (EDS) elemental mappings and line profiles analysis to the multi-
Interestingly, the Ag elemental maps (Figure 2I) and the line scan of a Pt-based ultrathin shell around 3 nm in thickness. This enabled the preparation of Au@Ag@Pt core−shell NPs and Au@AgPt nanorattles by controlling the concentration of the PtCl$_6^{−2}$ precursor employed during the synthesis (0.1, 0.2 mM, respectively). HRTEM (B−D) and STEM HAADF (C−E) images for Au@Ag@Pt (B,C), Au@AgPt (D,E), nanostructures.

Figure 1. (A) Synthesis of the plasmonic catalysts via the galvanic replacement reaction between PtCl$_6^{−2}$ and Ag in Au@Ag core−shell NPs. This enabled the preparation of Au@Ag@Pt core−shell NPs and Au@AgPt nanorattles. The elemental distribution for Au, Ag, and Pt are depicted in blue (Figure 2B,H), green (Figure 2C,I), and red (Figure 2D,J), respectively. For the Au@Ag@Pt sample, the combined Au (blue), Ag (green), and Pt (red) maps (Figure 2E) clearly show the presence of the three elements in a core−shell architecture in which Pt is present as a thin layer at the surface of Au@Ag NPs. The Pt shell thickness corresponded to <3 nm from STEM-EDS images while the thickness of the Ag shell corresponded to 35 nm, which is in agreement with the STEM-HAADF results. The EDS elemental line scan across the I−II region from Figure 2E confirmed that the core and shell regions were mainly composed of Au and Ag, and that an ultrathin Pt shell covers the Ag layer (Figure 2F). The STEM-EDX results for the Au@AgPt sample (Figure 2G−L) clearly support the formation of the nanorattle architecture displaying a Au core, a hollow interior layer from the partial dissolution of Ag during the galvanic replacement reaction with PtCl$_6^{−2}$, and a Pt-based ultrathin shell around 3 nm in thickness. Interestingly, the Ag elemental maps (Figure 2F) and the line scan profiles (Figure 2L) across regions III−IV in Figure 2K indicate that the ultrathin surface shell may be composed of both Ag and Pt, which was confirmed by XPS results (discussed later).

The ultrathin Pt shells have similar sizes in both Au@Ag@Pt and Au@AgPt nanoparticles making them ideal for comparing their Pt catalytic properties. Together with the plasmonic interiors, these systems are very attractive in terms of marrying plasmonic and catalytic properties. In fact, the LSPR extinction spectra for both Au@Ag@Pt and Au@AgPt revealed the presence of LSPR bands in the visible range (Figure S5). The peak from the dipolar LSPR resonance in Au NPs is shifted to shorter wavelengths (from 530 to 450 nm) upon the formation of the Au@Ag@Pt core−shell architecture. This shift is assigned to the deposition of both Ag and Pt at the Au surface. As the nanorattles were formed and partial dissolution of the Ag interior took place, a slight red-shift of the LSPR to 490 nm occurred. Interestingly, this LSPR band seems to be comprised of two overlapping signals, which could be expected as resulting from the presence of the Au core, a partial Ag shell, and the nanorattle morphology (hybridization between the Au core and the AgPt shell). This behavior agrees with the calculated spectra shown in Figure S2.

In addition to the controlled synthesis of catalytic−plasmonic nanostructures, a critical challenge required to fulfill the potential use of these materials is the synthesis of nanocatalysts at the gram-scale. The immobilization of nanoparticles on solid supports provides an interesting approach to address this challenge. Our synthesis of Au@Ag@Pt and Au@AgPt could be scaled-up, and the resulting nanoparticle suspensions could be immobilized onto commercial SiO$_2$ by an incipient wetness impregnation approach to generate supported nanocatalysts at the gram-scale (Au@Ag@Pt/SiO$_2$ and Au@AgPt/SiO$_2$ respectively) (see Supporting Information for details). Figure S6 depicts scanning electron microscope (SEM) images of the Au@Ag@Pt/SiO$_2$ and Au@AgPt/SiO$_2$ materials (Figure S6A,B, respectively). The SEM images indicate that our approach enables the generation of supported catalysts in which the Au@Ag@Pt and Au@AgPt are well dispersed and uniformly distributed over the support with no significant agglomeration, which is highly desirable in catalytic applications to maximize surface area. Wide-angle powder X-ray diffraction patterns of the supported nanocatalysts indicate that our immobilization approach did not lead to the incorporation of any crystalline impurities, and only peaks assigned to Au and Ag from the multimetallic core−shell and nanorattle nanoparticles could be observed (Figure S7).

Figure 3 presents the XPS spectra for Au@Ag@Pt/SiO$_2$ and Au@AgPt/SiO$_2$ nanoparticles in the Ag 3d and Pt 4f regions (Figure 3A,B, respectively). The binding energy (BE) values and calculated Pt/Ag ratios are shown in Table S1. The Ag 3d region (Figure 3A) showed two photoelectron peaks with maxima at BEs of 374 and 368 eV, ascribed to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ core-levels characteristic of Ag in the metallic state. Noticeably, the BE of the Ag 3d core-level was slightly shifted toward higher BE (positive shift) as the morphology changed from the core−shell structure to the nanorattles. This shift can be assigned to different degrees of electronic interaction between Ag and Pt in the shell.

For instance, our approach could involve the electron transfer from Ag 3d to Pt 4f bands according with the electronegativity values, 1.93 and 2.28, respectively. Regarding the Pt 4f region, the XPS spectra revealed the presence of two peaks at around 70 and 74 eV (Figure 3B) corresponding to the Pt 4f$_{3/2}$ and Pt 4f$_{5/2}$ in the metallic state. Remarkably, the Pt 4f shifted slightly toward lower BE (negative shift) for the Au@Ag@Pt/SiO$_2$ material as compared to the Au@Ag@Pt/SiO$_2$. This negative BE shift in
the Pt 4f core-level agrees with the positive shift observed in the Ag 3d region, suggesting electronic transfer between Ag and Pt in the nanorattles and the formation of a bimetallic shell. These results are also supported by the XANES spectra (Figure S8). This observation agrees with the formation of Au@Ag@Pt core-shell and Au@AgPt nanorattle
multimetallic architectures in which alloying between Ag and Pt takes place in the nanorattles. Finally, the Pt/Ag ratio calculated from the XPS spectra (Table S1) suggests an increase in the Pt content at the surface when the morphology changed from the Au@Ag@Pt core–shell NPs to the Au@AgPt nanorattles. This can be related to the increased amount of PtCl₆²⁻ employed during the synthesis of the multimetallic nanorattles relative to the core–shell nanoparticles. In this case, the Pt/Ag ratio almost doubled as the amount of PtCl₆²⁻ precursor employed during the synthesis doubled. Regarding the Au 4f region (Figure S9), the spectra show only an increase in the background signal as a result of the presence of a metal shell. Overall, our results indicate that the obtained nanostructures present an effective combination of plasmonic and catalytic properties (morphology characterized by plasmonic core and ultrathin catalytic shells) as well as efficient dispersion of nanoparticles over the support, which make them very attractive as plasmonic nanocatalysts.

We anticipate that the partial exposure of the Pt surface to the higher electric field enhancements promoted by the nanorattle morphology makes it an ideal candidate enabling both plasmonic and high catalytic performances. In nanoparticle architectures comprised of a plasmonic core and a nonplasmonic shell, such as Au–Pt and Ag–Pt systems, it has been shown that the nonplasmonic metal can work as a LSPR dissipation channel. For example, this may occur as a result of available direct, vertical electronic transitions (d to s or sp) in Pt as a result of its significantly larger imaginary part of the dielectric function relative that of Ag and Au. This leads to efficient LSPR excitation driven energy transfer from the plasmonic to the nonplasmonic metal. More precisely, the addition of Pt introduces as additional plasmon decay channel via Pt absorption and/or charge transfer of LSPR excited hot electrons. Consequently, this LSPR energy dissipation channel via Pt can be put to work toward enhancing and controlling molecular transformations at its surface.

To assess the potential for controlling plasmonic–catalytic performance using different particle architectures (core–shell vs nanorattles), the activity and selectivity of these were evaluated toward the liquid-phase semihydrogenation of phenylacetylene as a model transformation (Figure 4A). Figure 4B shows the phenylacetylene conversion percent for different supported nanoparticles as catalysts. In addition to the Au@Ag@Pt/SiO₂ core–shell and Au@AgPt/SiO₂ nanorattles, we also included the supported Au and Au@Ag core–shell nanoparticles (Au/SiO₂ and AgAu/SiO₂, respectively) that were employed as starting materials for the synthesis of the Au@Ag@Pt and Au@AgPt materials. In Figure 4B, the reported conversion percent were measured after 8 h of reaction under dark (black bar, no LSPR excitation) and under light irradiation (red bar, LSPR excitation) conditions. Low phenylacetylene conversions (<10%) were detected for both Au/SiO₂ and AgAu/SiO₂, either on dark or under light irradiation. This indicates that both Au and Ag do not display high activities in terms of conversion percent under the employed conditions. Considering the Au@Ag@Pt/SiO₂ and Au@AgPt/SiO₂ catalysts, the phenylacetylene conversion in the dark corresponded to 8 and 44%, respectively. Here, it is plausible that the higher catalytic activity for the Au@AgPt/SiO₂ nanorattles can be assigned to the presence of the hollow interiors, which is expected to increase the available Pt-based active sites relative to the core–shell Au@Ag@Pt/SiO₂. It is important to note that the Pt loading in the Au@Ag@Pt/SiO₂ and Au@AgPt/SiO₂ catalysts corresponded to 0.1 wt %, respectively, as determined by flame atomic absorption spectroscopy (FAAS).

Under light irradiation (LSPR excitation), only a slight increase in the phenylacetylene conversion was observed for the core–shell Au@Ag@Pt/SiO₂ nanoparticles (corresponding to 11%). In contrast, a remarkable increase was observed for the Au@AgPt/SiO₂ nanorattles from 44 to 98%. This result suggests that, despite core–shell systems being the most employed plasmonic–catalytic material in plasmonic nanocatalysis, the nanorattle architecture is capable of enabling a much higher relative enhancement in catalytic activity under LSPR excitation relative to core–shell systems. This higher relative enhancement can be assigned to the plasmon hybridization between the Au nanoparticle core and the AgPt shell. The plasmon hybridization enables the generation of more intense electric field enhancements (Figure S1), which may further contribute to the acceleration of the reaction rates.

It has been demonstrated, both theoretically and experimentally, that the intensity of the electric fields generated as a result of LSPR excitation is an important factor influencing the rate at which the charge carrier is transferred from the plasmonic nanoparticle. The energy of these elevated fields is dissipated through either radiative scattering of photons or nonradiative excitation of energetic charge carriers (i.e., absorption) in the metal nanoparticle. In this case, larger electric field intensities lead to increased rates of energy transfer. More specifically, in both the core–shell and nanorattle multimetallic architectures, the energy concentrated via LSPR excitation can be dissipated through absorption process in the Pt-based shells, increasing the extraction probability of the energetic charge carriers. In our system, this is manifested by the increased rates at which LSPR excited hot electrons and holes can be transferred from the plasmonic component to the nonplasmonic metal. As much higher electric field enhancement (and thus larger energy concentrations) is generated for the nanorattles as opposed to the
reaches 40% after 8 h of reaction. Under light excitation, ethylbenzene increases steadily as a function of time until it decreases to 60% after 8 h. Simultaneously, the formation of becomes close to 100% (after 7 h of reaction) and then increases up to 70% until the phenylacetylene conversion conditions, respectively. In the dark, the formation of styrene reached 100% after 7 or 6 h of reaction time in dark and light selectivity to styrene (Figure S11A,B, respectively). For the conversions were observed; it reached 10% (dark) and 25% Au@AgPt/SiO2 nanorattles (Figure S11C,D), the conversion increased as a function of time for both materials.

The selectivity toward the formation of styrene under dark and light irradiation conditions is shown in Figures S5A,B, respectively (also obtained after 8 h of reaction). In the dark (Figure 5A), Au/SiO2 and Au@Ag/SiO2 not only exhibit low conversion but also poor selectivity for styrene of 58 and 38%, respectively. Au@Ag@Pt/SiO2 core–shell and Au@Ag@Pt/SiO2 nanorattles favored the formation of styrene with selectivity that corresponded to 64 and 87%, respectively. Therefore, the nanorattles were not only more active toward the phenylacetylene conversion under dark conditions but also displayed a higher selectivity for the semihydrogenation reaction relative to the core–shell architecture. Amazingly, under LSPR excitation, the selectivity toward styrene increased for all materials, corresponding to 90, 100, 87, and 84% for Au/SiO2, Au@Ag/SiO2, Au@Ag@Pt/SiO2, and Au@AgPt/SiO2, respectively. These results indicate that plasmonic nanocatalysis can lead not only to improvements in reaction rates but also in reaction selectivity.

Note that the comparison above was made with different conversions at the same reaction time. In order to gain further insights into the reaction selectivity under LSPR excitation, we monitored the conversion percent and selectivity percent as a function of reaction time for Au@Ag@Pt/SiO2 and Au@AgPt/SiO2 nanocatalysts (Figure S11). The phenylacetylene conversion increased as a function of time for both materials. For the Au@Ag@Pt/SiO2 core–shell nanocatalyst, poor conversions were observed; it reached 10% (dark) and 25% (under light illumination) after 8 h of reaction with total selectivity to styrene (Figure S11A,B, respectively). For the Au@AgPt/SiO2 nanocatalysts (Figure S11C,D), the conversion reached 100% after 7 or 6 h of reaction in dark and light conditions, respectively. In the dark, the formation of styrene increases up to 70% until the phenylacetylene conversion becomes close to 100% (after 7 h of reaction) and then decreases to 60% after 8 h. Simultaneously, the formation of ethylbenzene increases steadily as a function of time until it reaches 40% after 8 h of reaction. Under light excitation, a similar profile was observed. However, the formation of styrene increased up to 80% until the phenylacetylene conversion becomes close to 100% (5 h) and then slightly decreased. In this case, the formation of ethylbenzene was up to 6% until 4 h of reaction and then started to increase, reaching 26% after 8 h. Therefore, it becomes clear that over a very broad range of conversion, the selectivity increases under LSPR excitation in the nanorattles. Figure 5C summarizes the styrene selectivity as a function of the phenylacetylene conversion when the reaction was performed under dark and under visible light illumination conditions (red and black traces, respectively). It can be observed that the styrene selectivity was higher under LSPR excitation for all conversion % values. A slight decrease in the styrene selectivity was detected under both conditions as the conversion increased and started to decrease more sharply as

Figure 5. Styrene and ethylbenzene selectivity for the phenylacetylene hydrogenation performed in the dark and under visible light excitation (A,B, respectively) employing supported Au nanospheres, Au@Ag nanoparticles, Au@Ag@Pt nanoparticles, and Au@AgPt nanorattles as catalysts. (C) Styrene selectivity as a function of conversion percentages for Au@AgPt nanorattles under dark (black trace) and visible light excitation conditions (red trace).
the conversion reached 100% (from 80 to 60% in the dark and
from 90 to 74% under LSPR excitation). This sharp decrease
in styrene selectivity after full conversion of phenylacetylene
(Figure 65C) is evidence of the preferential adsorption of
carbon−carbon triple bond on the catalysts surface. Only in
the absence of the alkyne moiety, styrene approaches the
surface and is hydrogenated to ethylbenzene, in a sequential
step.

To gain further insight into reaction selectivity toward
styrene, DFT calculations were performed to understand the
electronic structure of phenylacetylene (Figure 6A,B) and
styrene (Figure 6C,D) adsorbed on Pt layers. Pt(111) was
chosen to represent the energetically most stable facet. Figure
6A shows the density of states (DOS) of phenylacetylene on Pt
(black solid trace) as compared to the molecule in the gas
phase (black dotted trace). It can be observed that the
HOMO−LUMO gap reduces because of a strong hybrid-
ization at the interface. Moreover, phenylacetylene prefers to
adsorb in a tilted con
figuration to maximize the d−π
interaction between the triple bond and the metal d electrons.

Figure 6B shows the charge analysis on total DOS within the
range from the Fermi level (0 eV) to 2 eV. It can be
observed that the energy states within this energy window are
localized at the metal and the C−C triple bond. Figure 6C
shows the styrene adsorption on Pt for comparison. Similarly,
there is strong d−π interaction, however, we find that styrene
adsorbs on Pt in a flat configuration to maintain the
conjugation and to maximize the d−π interaction. In this
case, the integration of energy states between 0 and 2 eV
(Figure 6D) shows that the states are delocalized in the
molecule (both the double bond and the ring due to the
resonance) and the metal. These results indicate that although
there is a localized interaction between the triple bond and the
surface in phenylacetylene, the interaction and the interfacial
charge transfer are more delocalized for styrene. We expect
that with the same amount of energetic charge carriers, more
charges will be localized at the triple bond of phenylacetylene
than the double bond in styrene.

In this context, we would like to propose that this localized
interaction between the triple bond and the surface facilitates
the selective activation of the triple bond under LSPR
excitation via the injection of hot electrons. This would
explain the preferential hydrogenation of the triple bond in
phenylacetylene relative to the double bonds in styrene,
leading to increased selectivity under LSPR excitation for all
the materials. In this case, LSPR-excited hot electrons would
flow from Au or Ag to Pt or be directly generated at the Pt via
absorption under LSPR excitation. This hypothesis is further
supported by control experiments in which the hydrogenation
of styrene as the starting material was evaluated. In this case,
the conversion of styrene after 8 h of reaction (similar
conditions as described in Figure 4) corresponded to 13 (dark)
and 48% (under light excitation), whereas conversion of
phenylacetylene under similar reaction conditions reaches
98% (under light excitation).

By a combination of designer multimetallic nanoparticle
architectures, modeling, and experimental investigations, we
have demonstrated that plasmonic nanocatalysts marrying
plasmonic and catalytic components can lead to not only
enhancement of catalytic activities but also control of reaction
selectivity under visible light excitation. This was demonstrated
toward the liquid phase catalytic semihydrogenation of
phenylacetylene as a proof-of-concept catalytic transformation and using multimetallic Au@Ag@Pt core–shell and Au@AgPt nanorattle architectures as model plasmonic nanocatalysts. We have found that the localized interaction between the triple bond in phenylacetylene and the Pt nanoparticle surface enables the selective activation of the triple bond (relative to the double bond in styrene) under visible light illumination. This was demonstrated by the increased selectivity of the catalytic semihydrogenation reaction of the carbon–carbon triple bond under visible light illumination. Both nanoparticle architectures were comprised of ultrathin Pt-based catalytic shells and allowed the effective combination of plasmonic and catalytic properties, that is, the harvesting of Au or Au@Ag plasmonic properties to enhance catalytic transformation at the surface of the catalytic active but nonplasmonic metal (Pt). In these systems, the addition of Pt enables a new pathway for plasmon decay via direct absorption and/or charge transfer from the plasmonic to the catalytic metal. However, the nanorattles enabled much higher activities because of the plasmon hybridization between the Au nanoparticles cores and the plasmonic–catalytic AgPt shell (that enabling higher electric field enhancements as a result of LSPR excitation). These results indicate that the plasmonic–catalytic nanorattle architecture represents a unique system that combines plasmonic–catalytic properties, provides high active surface area due to the ultrathin catalytic-based shells, and can concentrate high electric field intensities at the surface. They also enable efficient energy transfer to the nonplasmonic metal (Pt), where the LSPR-excited hot carriers lead to the enhancement of activity and selectivity in liquid phase transformations under visible light. We believe the results present herein provide novel insights into the control of selectivity in plasmonic nanocatalysis and may serve as a foundation to allow this field to move beyond plasmonic enhancements of reaction rates, toward the control of reaction selectivity under visible and solar light illumination.

**ASSOCIATED CONTENT**

2 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b03499.

Materials and methods, details on DFT and DDA calculations, figures showing electric field enhancement contours, calculated absorption, scattering, and extinction spectra, experimental extinction spectra, STEM-HAADF, SEM, and HRTEM images, XRD diffraction patterns, XPS spectra, kinetic studies for phenylacetylene conversion, FAAS results (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by FAPESP (Grants 2015/21366-9, 2015/26308-7, and 2016/16738-7), the Serrapilheira Institute (Grant Serra-1709-16900), and CNPq (Grant 422467/2016-0). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) – Finance Code 001. P.H.C.C. and L.M.R. thank the CNPq for the research fellowships. J.Q., T.P.A., and E.C.M.B. thank FAPESP for the fellowships (Grants 2016/17866-9, 2017/07564-8, and 2015/11452-5, respectively). J.L.F thanks CAPES for the fellowship. T.M. and B.W. appreciate support from a NASA EPSCoR Grant (NNX16A-Q97A) as well as computational resources at the OU Supercomputing Center for Education & Research (OSCER) at the University of Oklahoma. S.J.H., Y.-C. W., and Y.Z. thank the Engineering and Physical Sciences (U.K.) (Grants EP/M010619/1, EP/P009050/1) and the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant ERC-2016-STG-EVolvUTEM-715502). We also thank the Brazilian Synchrotron Light Laboratory (LNLS, CNPEM) for XANES (XAFS2) and XPS analysis.

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