

Structurally Modulated AuPd Alloy Nanorods for Plasmon-Promoted Methanol Electrooxidation

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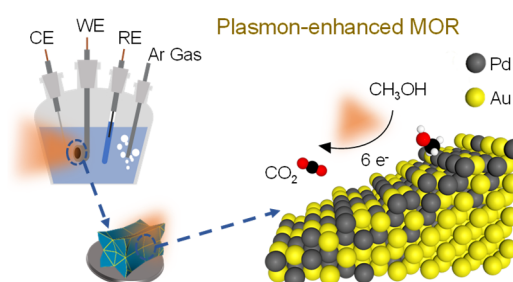
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Abstract: The spatial arrangement of plasmonic metals relative to catalytically active components directly governs the coupling efficiency between hot carriers and the local electromagnetic field at the catalytic interface, thereby profoundly affecting the activity and selectivity of plasmon-enhanced electrocatalytic reactions. However, relying solely on a catalytic metal as the dominant surface species often results in significant plasmon damping. At the same time, synergistically optimizing plasmonic enhancement and intrinsic catalytic activity through precise control of the composition, facets, and thickness of bimetallic alloys remains a major challenge in synthesis and structural design. In this study, Au@Au_xPd_y alloy core-shell nanorods with tunable shell composition and thickness were constructed, achieving a balance between plasmonic enhancement and intrinsic catalytic activity toward the methanol oxidation reaction (MOR). Through a combination of experimental observations, single-particle dark-field scattering spectroscopy, and numerical simulations, the alloy-shell-dependent extinction characteristics and their correlation with the plasmonic enhancement effect were elucidated. Under light irradiation, the optimal Au@Au₅Pd₅ nanorods show a 1.88-fold enhancement in current density for MOR. The as-designed bimetallic nanocatalysts can also be used as active substrates for *in situ* Raman spectroscopic studies of MOR. This work provides important insights for designing bimetallic nanostructures that integrate efficient plasmonic enhancement with high catalytic activity for plasmon-promoted catalysis.



Keywords: plasmonics; bimetallic nanoparticles; Au-Pd alloy; plasmon-enhanced electrocatalysis; methanol oxidation reaction

1. Introduction

Facing the dual pressures of global energy scarcity and environmental degradation, the development of efficient and stable catalytic systems for clean energy conversion has become a critical direction in scientific research [1–3]. Metal-based nanomaterials, owing to their unique physicochemical properties, exhibit broad application prospects in numerous catalytic reactions [4–10]. Through precise regulation of the morphology, facets, and composition of metal nanomaterials, researchers have significantly enhanced their catalytic performance [11–14]. Among these strategies, alloying two or more different metals can effectively integrate the advantages of each component, yielding catalytic behavior superior to that of single metals [15–18]. However, relying solely on compositional and structural optimization still struggles to overcome the intrinsic activity limits of catalysts, prompting researchers to explore strategies that introduce external energy, such as light, to further promote catalytic reactions.



Among various external energy sources, solar energy is highly attractive due to its renewability and abundance [19–22]. Plasmonic metal nanoparticles (NPs), leveraging their localized surface plasmon resonance (LSPR) characteristics, can interact strongly with visible light, thereby converting light energy into chemical energy efficiently [23–29]. Studies have shown that incorporating plasmonic metals into conventional catalytic systems significantly enhances the catalytic efficiency of various reactions, including hydrogen evolution, oxygen evolution, methanol oxidation, and oxygen reduction, under light irradiation [30–34]. The enhancement is primarily attributed to the hot carriers generated upon LSPR excitation, and these high-energy electrons or holes can effectively lower reaction barriers and accelerate reaction kinetics [35–40]. Nevertheless, despite substantial progress in plasmon-assisted catalysis, the full integration of plasmonic functionality and electrocatalytic functionality at the nanoscale design remains a challenge.

To integrate plasmonic and catalytic functions, bimetallic nanostructures represent an important design strategy [11,41]. Forming an alloy between a plasmonic metal like Au and a catalytic metal like Pd offers the prospect of simultaneously introducing light absorption capability and catalytically active sites within a single nanoparticle [42–45]. However, conventional alloy structures face a significant dilemma. If the proportion of the plasmonic metal is too low, the LSPR effect is weak, and light utilization becomes insufficient. Conversely, if the catalytic metal content is too low, the intrinsic catalytic activity fails to meet the requirements [46–49]. Moreover, the atomic arrangement, facet structure, and particle size and thickness of the different metals in the alloy all exert complex influences on both plasmonic properties and catalytic performance [50–52]. Indeed, systematically tuning the composition, facets, and thickness of bimetallic nanostructures, and thereby optimizing the alloy composition and morphology design, holds promise for greatly improving light utilization efficiency and generating a significant synergistic effect between plasmonic and electrocatalytic functions [53]. However, complex heterogeneous alloy structures are not only difficult to synthesize but also challenging to model clearly for studying their plasmonic properties, which poses numerous obstacles to the implementation of the above regulation strategies.

In this work, we demonstrate a synthetic strategy that incorporates plasmonic components into the catalytic shell, substantially alleviating the LSPR damping induced by Pd and overcoming the limitations of existing plasmonic alloy catalysts. Specifically, we synthesized a series of Au@Au_xPd_y alloy core-shell bimetallic nanorods (NRs). By precisely controlling the synthetic parameters, we were able to continuously and controllably tune the AuPd alloy shell from high-index to low-index facets, thus achieving an optimal balance between catalytic performance and plasmonic enhancement. Using the methanol oxidation reaction (MOR) as a model electrochemical reaction, the Au@Au₅Pd₅ NRs exhibited a 1.88-fold increase in peak current under light irradiation. With the appropriate addition of Ag, the plasmon-promoted catalytic performance could be further enhanced. Through combined single-particle spectroscopy, numerical simulations, and *in situ* surface-enhanced Raman spectroscopy (SERS), we show the advantages of the alloy shell in tuning plasmonic characteristics as well as spectroscopically monitoring intermediate species during the MOR. This work creates a framework for designing bimetallic nanostructures that integrate efficient plasmonic enhancement with high MOR catalytic activity.

2. Material and Methods

2.1. Chemicals and Materials

Gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99%), sodium borohydride (NaBH₄, 99%), and L-ascorbic acid (AA, 99.9%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Palladium (II) chloride (PdCl₂, 99%), methanol (CH₃OH, 99.9%), and anhydrous potassium hydroxide (KOH, granular) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Silver nitrate (AgNO₃, 99.9995% metals basis) was obtained from Alfa Aesar (Tewksbury, MA, USA). Cetyltrimethylammonium bromide (CTAB, >98%) and sodium oleate (NaOL, >97%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). HCl (37 wt% in water, 12.1 M) was purchased from Fisher Scientific (Pittsburgh, PA, USA). All reagents were used as received without further purification. Millipore ultrapure water (18.2 MΩ resistivity) was used for all experiments.

2.2. Synthesis of Au NRs

Au NRs were synthesized using a previously published seed-mediated growth protocol with minor modifications (see more details in Supporting Information) [11]. The Au seeds were prepared by reducing HAuCl₄ with NaBH₄ in the presence of CTAB. The seed solution was stirred for 2 min and then left undisturbed for 30 min before use. The growth solution was prepared by reducing HAuCl₄ with AA in the presence of CTAB, NaOL, and AgNO₃, followed by the addition of Au seeds to grow Au NRs. The resulting particles were collected by centrifugation, followed by removal of the supernatant, and finally redispersed in 30 mL of 100 mM CTAB.

2.3. Synthesis of Au@Au_xPd_y and Au@Au_xPd_yAg_n Core-Shell NRs

Au@Au_xPd_y core-shell NRs with different structures were prepared through overgrowth of the Au NRs in the presence of HAuCl₄, PdCl₂, CTAB, and AA, following previously published work with some modifications (see more details in Supporting Information) [11]. The synthesis method for adding Ag to the shell is generally the same, except that the corresponding proportion of AgNO₃ is added to the growth solution. The resulting core-shell NRs were washed twice with water through centrifugation/redispersion cycles and finally redispersed in 200 μL of 20 mM CTAB.

2.4. Characterizations

The optical extinction spectra of the nanoparticles were measured on aqueous colloidal suspensions at room temperature using a Shimadzu UV-2600i spectrophotometer. The morphologies and structures of the nanoparticles were characterized by scanning electron microscopy (SEM) using a Zeiss Merlin Compact and a Zeiss GeminiSEM 500 field emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). The samples for SEM were dispersed in water and drop-dried on silicon wafers. Transmission electron microscopy (TEM) images and EDS elemental maps were obtained using a JEOL JEM-2100 Plus transmission electron microscope (JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 200 kV. All samples for TEM measurements were dispersed in water and drop-dried on 300 mesh Formvar/carbon-coated Cu grids.

2.5. Plasmon-Enhanced MOR Measurements

MOR tests were performed in a highly transparent quartz electrolytic cell with a CHI-760e electrochemical analyzer (Austin, TX, USA) using a three-electrode cell system. The three-electrode cell consisted of a glassy carbon electrode (GCE, 3 mm diameter) with a catalyst, a graphite rod, and a Hg/HgO electrode (in 1 M KOH), which served as the working, counter, and reference electrodes, respectively. The MOR test was carried out in 1 M KOH + 0.5 M methanol solution by applying 0 V to 1.2 V vs. RHE at a scan rate of 50 mV s⁻¹. Plasmon-enhanced tests were performed by illuminating the center of the GCE with an Xe lamp (350 W) from the side of the cell and then starting the CV test. The incident light power density was measured to be 127.39 mW/cm² using a power meter. Thus, the incident photon-to-current conversion efficiency (IPCE) was calculated based on the following equation [54]:

$$IPCE = 1239.8 \times \frac{J_p}{\lambda \cdot P_L} \quad (1)$$

where J_p is the photocurrent density (mA/cm²), λ is the incident light wavelength (nm), and P_L is the light power density at the corresponding wavelength (mW/cm²).

2.6. Single-Particle Dark-field Scattering (DFS) Measurements

Single-particle DFS measurements were conducted on a home-built dark-field microscope based on an inverted microscope body (Zeiss AxioObserver ml, Carl Zeiss AG, Oberkochen, Germany) with a hyperspectral detection system [55]. Light generated from a tungsten-halogen lamp and filtered through a visible band-pass filter (500–800 nm, LBTEK, MEFH10-800SP) was circularly polarized and directed through an oil-immersion dark-field condenser (Carl Zeiss AG, Oberkochen, Germany, numerical aperture (NA) = 1.4) to create annular symmetric excitation with an incident angle of 69°, resulting in a total internal reflection (TIR) excitation condition for NPs deposited onto an indexed ITO glass substrate. The annular symmetric excitation geometry effectively eliminates the effects of extrinsic chirality. The scattered light was collected with a 50× air-spaced objective (Carl Zeiss AG, Oberkochen, Germany, NA = 0.8) and passed to a hyperspectral detection system consisting of an imaging spectrograph with a slit aperture (SpectraPro 2156, Teledyne Princeton Instruments, Acton, MA, USA) coupled to a thermoelectrically cooled back-illuminated CCD camera (Pixis 400BR, Teledyne Princeton Instruments, Acton, MA, USA) and mounted on a computer-controlled translation stage (LTA-HL, Newport Corporation, Irvine, CA, USA).

2.7. Numerical Simulations

Simulations of the far-field and near-field optical properties of Au NRs, Au@AuPd NR, and Au@Pd NRs were performed using the finite-difference time-domain (FDTD) method (Lumerical). The geometric models of Au NRs, Au@AuPd NR, and Au@Pd NRs were constructed based on orientation-dependent SEM and TEM images. The dielectric permittivity tabulated by Johnson and Christy was used for Au and Pd [56], and water was used as a background with a refractive index of 1.33. For the Au-Pd alloys, the composition-dependent dielectric

function reported by Stofela et al. was adopted [57]. The minimum mesh size was set to 1 nm to guarantee the convergence of the calculations.

2.8. In situ Surface-Enhanced Raman Scattering (SERS) Measurements

SERS was measured with an XploRA PLUS spectrometer (HORIBA, Ltd., Kyoto, Japan) with an excitation wavelength of 638 nm. The power of the excitation laser that focused on the samples was adjusted using a 1% neutral density filter. A 50 $\times$ objective lens (N.A. = 0.5) and a holographic grating of 600 grooves/mm with a 5 s acquisition time were used for data collection unless mentioned otherwise. The Raman spectrometer was calibrated using a standard silicon wafer before measurements. For the *in-situ* electrochemical SERS measurements of MOR intermediates, a three-electrode cell system was also employed. The sample was drop-cast onto a custom-made platinum-carbon electrode surface as the work electrode. A platinum wire and a saturated calomel electrode (SCE) were employed as the counter electrode and reference electrode, respectively.

3. Results and Discussions

Au@Au_xPd_y NRs represent a class of bimetallic functional materials that integrate Au with strong LSPR and Pd with excellent electrocatalytic activity at the nanoscale, enabling efficient light harvesting across a broad visible-NIR spectral range while retaining the high intrinsic catalytic activity of Pd for catalytic reactions [58–60]. Since both the plasmonic effect and catalytic performance of the alloy are governed by its composition, we systematically varied the Au/Pd ratio in the shell over a wide range to balance plasmonic enhancement and catalytic activity. In this study, the Au@Au_xPd_y NRs (x and y are used to show the estimated ratio of Au/Pd in the alloy shell) were synthesized via overgrowth on the Au NRs (see Figure S1A in Supporting Information) reported previously [11], and under the same conditions, we also synthesized Pd nanosheets (Pd NSs) without adding Au NRs as a control (Figure S1B). As shown in Figure 1A, when only a small amount of Pd precursor ($[\text{H}_2\text{PdCl}_4]/[\text{HAuCl}_4] = 2:8$) was added during the synthesis, elongated hexoctahedral (ETOH) NRs were formed. As the proportion of Pd precursor increased ($[\text{H}_2\text{PdCl}_4]/[\text{HAuCl}_4] = 5:5$), truncated concave cuboidal (TCCB) NRs were formed. When the $[\text{H}_2\text{PdCl}_4]/[\text{HAuCl}_4]$ ratio was further increased ($[\text{H}_2\text{PdCl}_4]/[\text{HAuCl}_4] = 8:2$), the high-index-faceted TCCB NRs gradually transformed into low-index-faceted quasi-cuboidal (QCB) NRs. The structural evolution of these morphologies has been reported in previous work [11], and the SEM images of Au NRs, Au@Au₈Pd₂ NRs, Au@Au₅Pd₅ NRs, and Au@Au₂Pd₈ NRs in Figure 1B confirm the structural features described above. The HAADF-STEM image in Figure 1C reveals the TCCB morphology of Au@Au₅Pd₅ NRs, and the EDS mappings clearly confirm their core-shell structure with an AuPd alloy shell.

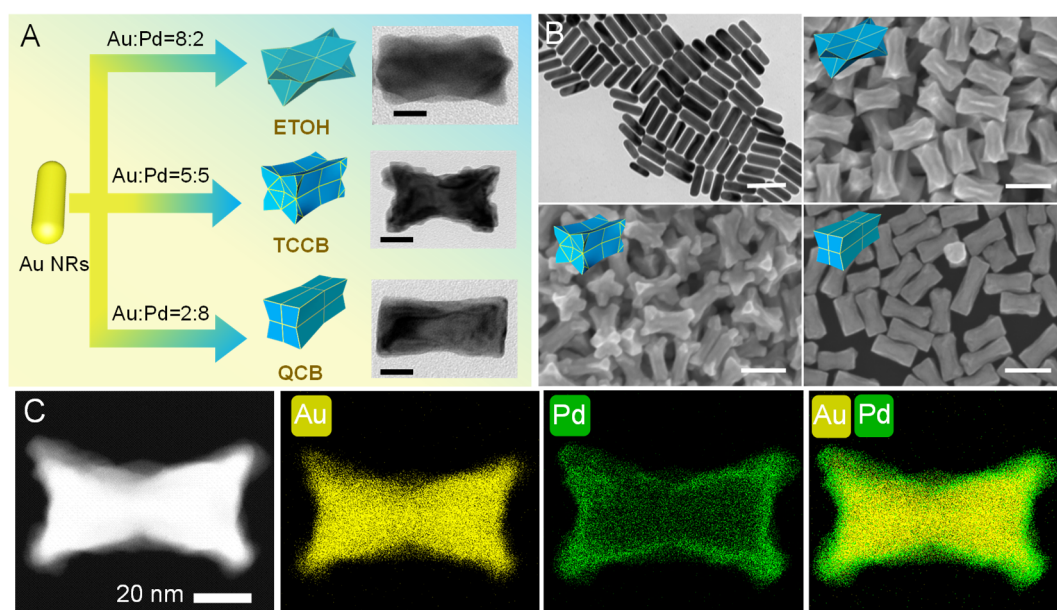


Figure 1. Structurally Modulated AuPd Alloy NRs. (A) Schematic illustration of the geometric and compositional control of AuPd alloy NRs by tuning the ratio between Au and Pd precursors. Insets: corresponding TEM images. Scale bars: 20 nm. (B) SEM images of Au NRs, ETOH NRs, TCCB NRs, and QCB NRs. Scale bars: 100 nm. (C) HAADF-STEM image and EDS elemental mapping of individual Au@Au₅Pd₅ TCCB NRs.

Photoelectrocatalytic measurements were conducted using a typical three-electrode system in a highly transparent quartz electrolytic cell, as shown in Figure 2A. In this system, a power-adjustable xenon lamp illuminated the L-shaped glassy carbon electrode from the side to achieve plasmonic enhancement of methanol electrooxidation. Numerous studies have demonstrated that Au exhibits LSPR under light illumination, generating hot carriers, whereas Pd does not [32]. To verify the plasmonic enhancement effect on MOR, electrochemical tests were performed on Au@Au₅Pd₅ NRs, Pd NSs, and Au NRs before and after light exposure, respectively. As shown in Figure 2B, the oxidation current of Au@Au₅Pd₅ NRs was significantly enhanced after illumination (from 1.71 mA/cm² to 3.23 mA/cm² at 0.79 V vs. RHE). In contrast, the MOR current of Pd NSs was hardly enhanced, and the enhancement of Au NRs was minimal. This can be explained by the fact that Pd exhibits weak LSPR and therefore cannot effectively promote MOR. For Au, the reaction current indicates that it is not an ideal MOR catalyst (only 0.059 mA/cm² at 0.79 V vs. RHE), and thus its contribution to the MOR current is negligible, even though it can generate hot carriers under illumination. The above results demonstrate that combining a plasmonic metal with a catalytically active metal enables effective utilization of LSPR to enhance electrocatalytic performance.

The MOR activities of the three representative nanostructures were evaluated both in darkness and under light illumination (Figure 2C). For Au@Au₈Pd₂ NRs and Au@Au₅Pd₅ NRs, the MOR peak currents (1.64 mA/cm² at 0.81 V vs. RHE and 1.71 mA/cm² at 0.79 V vs. RHE, respectively) are higher than that of Au@Au₂Pd₈ NRs (1.18 mA/cm² at 0.78 V vs. RHE), which can be attributed to the high-index facets of the ETOH and TCCB structures that are believed to provide highly active catalytic sites [11]. Under light illumination, the MOR current of Au@Au₅Pd₅ NRs increased significantly to 3.23 mA/cm², which is higher than that of Au@Au₈Pd₂ NRs (2.55 mA/cm²). For Au@Au₂Pd₈ NRs, the MOR current increased from 1.18 to 1.88 mA/cm². Notably, Au@Au₅Pd₅ NRs exhibit the best enhancement effect for MOR. We also performed MOR enhancement tests on various other catalysts with different AuPd shell compositions (Figure S2). To compare catalytic performance more accurately, we normalized the currents by the real electrochemical surface areas (A_{real}), as the compositions differ. The A_{real} values were calculated from cyclic voltammetry (CV) curves measured in 1 M KOH aqueous solution saturated with Ar (see Figure S3 for details). The PdO reduction peaks for all samples exhibit complete and well-shaped profiles, with stable peak positions and no significant peak distortion or severe deterioration of the signal-to-noise ratio as the Pd content decreases. The normalized currents of each catalyst were summarized in Figure 2D. Overall, the catalytic activities of these catalysts in darkness can be roughly divided into three groups according to their geometric structures, which are related to their compositions. Au@Au₆Pd₄, Au@Au₅Pd₅, and Au@Au₄Pd₆ NRs share a similar TCCB structure and exhibit the best intrinsic MOR activity owing to their high-index facets and appropriate AuPd ratios [11]. By contrast, Au@Au₉Pd₁, Au@Au₈Pd₂, and Au@Au₇Pd₃ NRs, the three catalysts with an ETOH structure, possess even more abundant high-index facets. However, due to their low Pd content, there are insufficient reaction sites, resulting in slightly lower activity. As for the other catalysts with a high Pd content, their MOR performance is the poorest, which may be attributed to their low-index facet structure and the weak electron modulation effect arising from the small amount of Au. Nevertheless, their MOR performance changed markedly after light irradiation.

To directly evaluate the plasmonic enhancement effect of different structures on MOR, we defined the ratio of the peak current after illumination to that before illumination as the enhancement factor (EF). As shown in Figure 2E, the EF values of different catalysts exhibit a volcano-shaped relationship. The closer the Au/Pd ratio, the better the plasmonic enhancement effect on MOR. We attribute this phenomenon to the matching between the hot carrier donor and acceptor. Specifically, when Au is the majority component in the alloy shell, the LSPR is very strong, and abundant hot holes are generated upon illumination. However, owing to the lack of Pd catalytic sites, these hot holes cannot be effectively utilized. Conversely, an excessively high Pd content weakens the LSPR and fails to generate sufficient hot holes to promote the MOR, which is in line with recent observations [52]. A schematic illustration of the methanol oxidation process driven by hot carriers generated via the plasmonic effect is shown in Figure S4. Additionally, in the alkaline MOR system, photogenerated hot electrons are mainly dissipated via external circuit extraction, recombination with hot holes, and the hydrogen evolution reaction (HER). While we proposed that the hot holes were mainly used for the oxidation of methanol, while the hot electrons could be transferred to reduce H₂O to form H₂, the underlying mechanisms could be much more complicated and require further scrutiny. We also quantitatively evaluated the incident photon-to-current conversion efficiency (IPCE) of materials. The calculation was performed on the Au@Au₅Pd₅ sample under 750 nm monochromatic light excitation. The photocurrent density, taken as the difference between the light and dark CV curves at the oxidation peak potential, was ~1.71 mA/cm², and the incident light power density was measured to be 127.39 mW/cm². The IPCE value was determined to be approximately 2.21%. This value falls within a reasonable range for complex multi-electron reaction systems in photoelectrocatalysis, confirming that plasmon-generated hot carriers indeed participate effectively in the MOR.

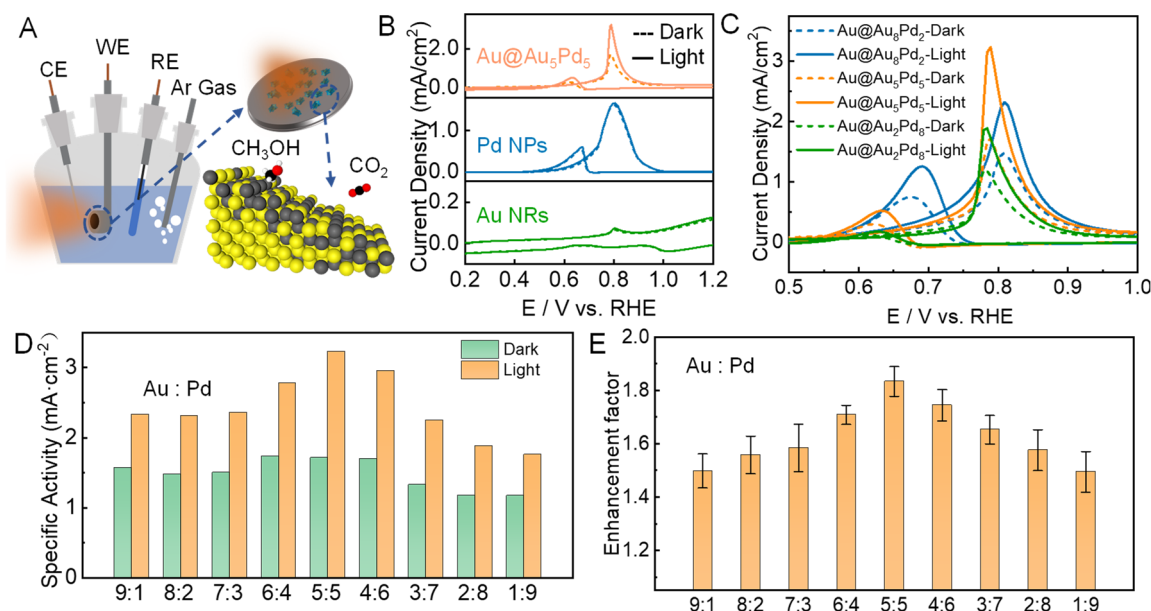


Figure 2. Plasmon-promoted MOR on Au@Au_xPd_y alloy NRs. **(A)** Schematic of the electrochemical reaction cell, atomic model of the catalyst, and MOR reaction diagram. **(B)** MOR curves of Au@Au₅Pd₅ NRs, Pd NSs, and Au NRs obtained in 1 M KOH + 0.5 M methanol at a scan rate of 50 mV s⁻¹ under darkness (dashed lines) and light illumination (solid lines). **(C)** MOR curves of Au@Au₈Pd₂, Au@Au₅Pd₅, and Au@Au₂Pd₈ NRs representing ETOH, TCCB, and QCB structures, respectively. The test was performed in 1 M KOH + 0.5 M methanol at a scan rate of 50 mV s⁻¹ under darkness (dashed lines) and light illumination (solid lines). **(D)** Comparison of the specific activities of catalysts with different Au/Pd ratios before and after illumination. The specific activity was calculated by normalizing the current by the area of each catalyst. **(E)** The plasmonic enhancement factor (EF) of each catalyst as a function of different Au/Pd ratios. The EF was calculated as the ratio of the MOR peak current after light illumination to that before light illumination.

From the above studies, we have identified the optimal conditions for synthesizing Au@Au_xPd_y core-shell NRs with the best plasmonic enhancement effect. However, one issue still exists: variations in the Au/Pd ratio occurred simultaneously with facet transformation, and we have previously discussed how facet evolution affects MOR performance. In addition, it is difficult to evaluate whether different facet structures affect the plasmonic enhancement of electrocatalysis. To investigate this issue, we synthesized a series of Au@Au_xPd_y NRs with the same Au/Pd ratio but different geometric structures by controlling the reaction conditions (Figure 3). As shown in Figure 3A, when the Au/Pd ratio was fixed at 1:1, the catalyst gradually evolves from TCB NRs to quasi-cuboidal (QCB) NRs, and eventually to TCCB NRs (denoted as Au₅Pd₅-1, Au₅Pd₅-2, and Au₅Pd₅-3, respectively) with increasing AA concentration. The extinction spectra of these catalysts are changed, indicating the geometry-dependent LSPR (Figure S5). As shown in Figure 3B, their MOR performance in darkness differs, and this trend is maintained after light illumination. However, the MOR test results in Figure 3C indicate that their EFs are very similar. Although slight differences exist, they are negligible compared to the significant changes observed in Figure 2E. This indicates that different facet structures have little influence on the EF. Meanwhile, the intrinsic activity of the catalyst could be regulated by designing the geometric structure. We further performed controlled experiments with the Au/Pd ratio fixed at 8:2 and 2:8, and similar results were obtained (Figure S6). In addition, by appropriately adjusting the AA and CTAB concentrations, TCB NRs with different Au/Pd ratios can also be obtained (Figure 3D). In this way, we can focus solely on the effect of the Au/Pd alloy composition on plasmonic enhancement. The extinction spectra confirm the continuous and controllable structural evolution of the synthesized TCB shell. In addition, SEM characterization reveals that the as-prepared nanoparticles exhibit uniform morphology and good reproducibility (Figure S5). Figure 3E shows the MOR enhancement ratios of this series of catalysts, and the results still exhibit a volcano-shaped relationship, similar to the trend observed in Figure 2E. Based on the above results, we can draw two conclusions. First, the intrinsic activity of the alloy can be effectively improved by tuning the facets, whereas the effect on plasmonic enhancement is negligible. Second, the proportion of the plasmonic metal in the alloy is the main factor determining the enhancement effect of MOR.

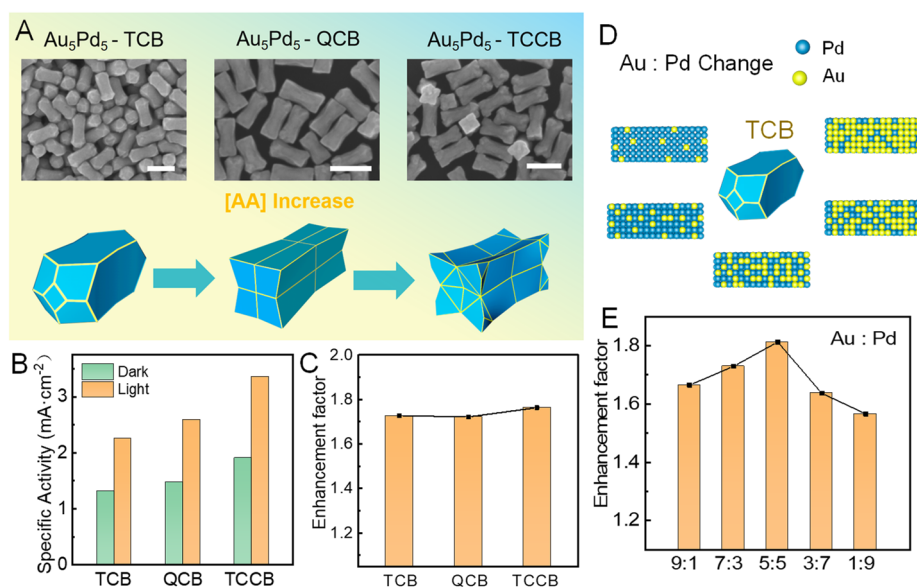


Figure 3. Impact of surface structure and alloy composition of Au@Au_xPd_y NRs on plasmon-promoted MOR. (A) Schematic illustration of the facet transformation and corresponding SEM images of Au@Au₅Pd₅ NRs into TCB, QCB, and TCCB structures with the same Au/Pd compositional ratios. The reactions were carried out in the presence of 40 mM CTAB and increasing concentrations of AA at a [H₂PdCl₄]/[HAuCl₄] molar ratio of 1:1. Scale bar: 100 nm. (B,C) Comparison of the (B) specific activity and (C) EFs of Au@Au₅Pd₅ NRs with TCB, QCB, and TCCB structures before and after light illumination. (D) Schematic illustration of the adjustment of the Au/Pd alloy ratio with a fixed TCB structure. The reactions were carried out in the presence of 20 mM CTAB, 10 mM AA, and various [H₂PdCl₄]/[HAuCl₄] molar ratios with the total concentration of H₂PdCl₄ + HAuCl₄ fixed at 0.4 mM. (E) EFs of TCB NRs with different [H₂PdCl₄]/[HAuCl₄] molar ratios.

Although similar core-shell nanostructures have been reported for plasmonic-enhanced electrocatalysis, their synthesis often requires careful control of the shell thickness, because an increase in shell thickness causes exponential attenuation of the properties of the plasmonic properties of the core metal. Interestingly, when plasmonic metals were incorporated into the shell, the catalysts overcame this limitation to some extent. We speculate that with Au incorporated into the shell, the plasmonic metal in the shell can co-generate LSPR with the internal Au NRs as an integrated whole under illumination. This greatly alleviates the LSPR damping induced by Pd. Meanwhile, alloying Au with Pd induces hybridization of the Au d-band, which activates interband transitions in the near-IR region and thereby generates additional high-energy hot holes. Also, the interplay between interband and intraband excitations can be manipulated by varying the alloy compositions, which could also contribute to the effect of plasmon-enhanced MOR [57,61]. In addition, the Au atoms in the shell are randomly dispersed around the Pd atoms, which can be regarded as forming hot carrier transfer channels. In this way, the hot carriers can efficiently participate in the catalytic reaction. Therefore, plasmon-enhanced MOR, in this case, can be attributed to the balance between plasmonic hot carrier generation and interband/intraband transition contributions. To confirm this hypothesis, we synthesized Au@Au₅Pd₅ NRs with different shell thicknesses by controlling the concentration of the metal precursors. The TEM images in Figure S7A clearly show the variation in shell thickness. In addition, we synthesized Au@Pd NRs with only Pd in the shell as a control. With increasing Pd precursor concentration, Pd grows into a cuboidal shape along the Au NRs (Figure S7C). From the EDS mapping images in Figure S8, the Au NR core can be clearly distinguished from the Pd shell, which is markedly different from the alloyed Au@Au₅Pd₅ NRs (Figure 1C). When tested under the same conditions, the EF values for MOR before and after light illumination were obtained (Figure S7B). It can be seen that the MOR enhancement effect decreases with increasing shell thickness, but the attenuation trend is very gradual. In contrast, the EF of the pure Pd-coated catalyst decreases rapidly with increasing shell thickness (Figure S7D). The shell thickening may alter particle dimensions and LSPR properties, but the aspect-ratio change is modest, and the EF was measured under broadband Xe lamp illumination, where minor LSPR shifts remain within the effective spectral coverage. Therefore, the size effect contributes minimally to EF variation. Furthermore, we fixed the Au/Pd ratio in the shell at 8:2 and 2:8, and investigated the influence of shell thickness on LSPR for these compositions. As expected, the higher the proportion of Au in the shell, the smaller the effect of thickness variation on the MOR enhancement (Figure S9). The above experimental results provide strong evidence for our initial hypothesis that incorporating plasmonic

metals into the shell can help preserve the LSPR effect of the inner Au core. This greatly simplifies the design of core-shell catalysts with LSPR properties.

We further introduced a second plasmonic metal (Ag) into the alloy to improve the plasmonic enhancement of MOR (Figure 4). Again, we continued to use the seed-mediated method, but added AgNO₃ in an appropriate proportion to the synthesis of Au@Au₅Pd₅ NRs. From the SEM image in Figure 4A,B, the Au@Au₅Pd₅Ag₁ structure is close to that of TCB with a highly rough surface. This change is also reflected in their extinction spectra (Figure S10), where three peaks are observed for Au@Au₅Pd₅Ag_{0.5}, located around 780, 540, and 400 nm, respectively. When the Ag content increased, the peak at 780 nm blue-shifted to 730 nm, while the other two peaks showed no significant change. As the Ag content continued to increase, the peaks around 540 and 730 nm disappeared and were replaced by a new peak around 560 nm. This phenomenon is accompanied by the precipitation of small Ag NPs on the catalyst surface, giving rise to complex spectral coupling behavior. When the catalyst composition reached Au@Au₅Pd₅Ag₃, the peak near 400 nm also became weaker, and eventually the coupled peak red-shifted to around 590 nm. The addition of Ag brings substantial changes to the optical properties of the entire system, which inspires us to further investigate their performance in plasmon-promoted MOR. In Figure 4D, we compared the MOR curves of Au@Au₅Pd₅ and Au@Au₅Pd₅Ag₁ in darkness and under light illumination. It was found that the addition of a small amount of Ag slightly affected the intrinsic performance of the catalyst, and the peak current measured in darkness decreased. However, under light illumination, the current of Au@Au₅Pd₅Ag₁ exceeded that of Au@Au₅Pd₅, indicating a stronger plasmonic enhancement effect. By comparing catalysts with different Ag contents, we observed an interesting phenomenon. The enhancement effect improved with the addition of a small amount of Ag, but when the Ag content increased beyond a certain level (beyond 10%), the EF began to decline, showing a volcano curve (Figure 4E). The maximum EF was found to be ~2.02 for Au@Au₅Pd₅Ag₁. [d2.1] We attribute this to the precipitation of excess Ag NPs on the surface, which occupy the catalytic sites. Meanwhile, the excess Ag NPs themselves may undergo oxidation under these conditions, further consuming the photogenerated holes and resulting in a decreased EF. Furthermore, we synthesized Au@Au₈Pd₂Ag_n and Au@Au₂Pd₈Ag_n NRs for comparison and obtained similar results (Figure S11).

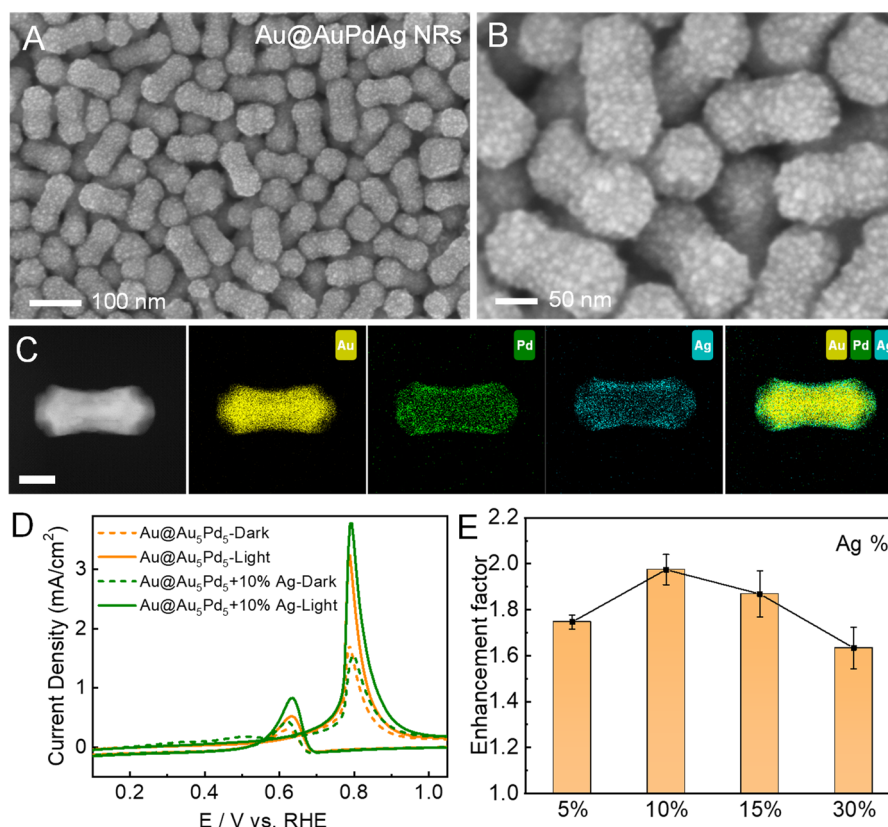


Figure 4. Integration of Ag with Au@Au₅Pd₅ NRs for plasmon-promoted MOR. (A,B) SEM images of Au@AuPdAg alloy NRs. (C) HAADF image and EDS mapping of Au@Au₅Pd₅Ag₁ NRs. Scale bar: 20 nm. (D) MOR curves of Au@Au₅Pd₅ NRs and Au@Au₅Pd₅Ag₁ NRs, obtained in 1 M KOH + 0.5 M methanol at a scan rate of 50 mV s⁻¹ under darkness (dashed lines) and light illumination (solid lines). (E) EFs of Au@Au₅Pd₅Ag_n NRs obtained with different amounts of Ag.

The underlying mechanism for plasmonic-enhanced electrocatalysis is complex, including several different contributions that intertwine with each other, such as hot carrier injection, electromagnetic field enhancement, and local lattice heating. These phenomena are accompanied by plasmon damping, and this process is completed within 5–20 fs. It is difficult to measure it directly in time-resolved experiments with such fast relaxation. Since the linewidth Γ of the LSPR is proportional to its decay rate, the relaxation process can be indirectly inferred by measuring the linewidth. For the homogeneous linewidth of an LSPR, there are four main damping pathways [48,62],

$$\Gamma = \Gamma_b + \Gamma_{rad} + \Gamma_{surf} + \Gamma_{HCT} \quad (2)$$

Here, Γ_b and Γ_{surf} denote bulk damping and electron-surface scattering, respectively. Γ_{rad} denotes radiative damping, while Γ_{HCT} represents plasmon damping, arising from charge transfer at the heterogeneous interface. This refers to the energy attenuation caused by the inability of hot electrons and hot holes to recombine after separation under plasmon excitation. The attenuation mechanisms mentioned above are related to the shape, size, material, and dielectric constant of the nanoparticles. For any synthesis method, it is difficult to obtain perfectly uniform particles. Consequently, the measured ensemble spectra are typically inhomogeneous (Figure 5A). Thus, single-particle scattering measurements are promising to provide optical properties of individual particles that are free from the averaging effect.

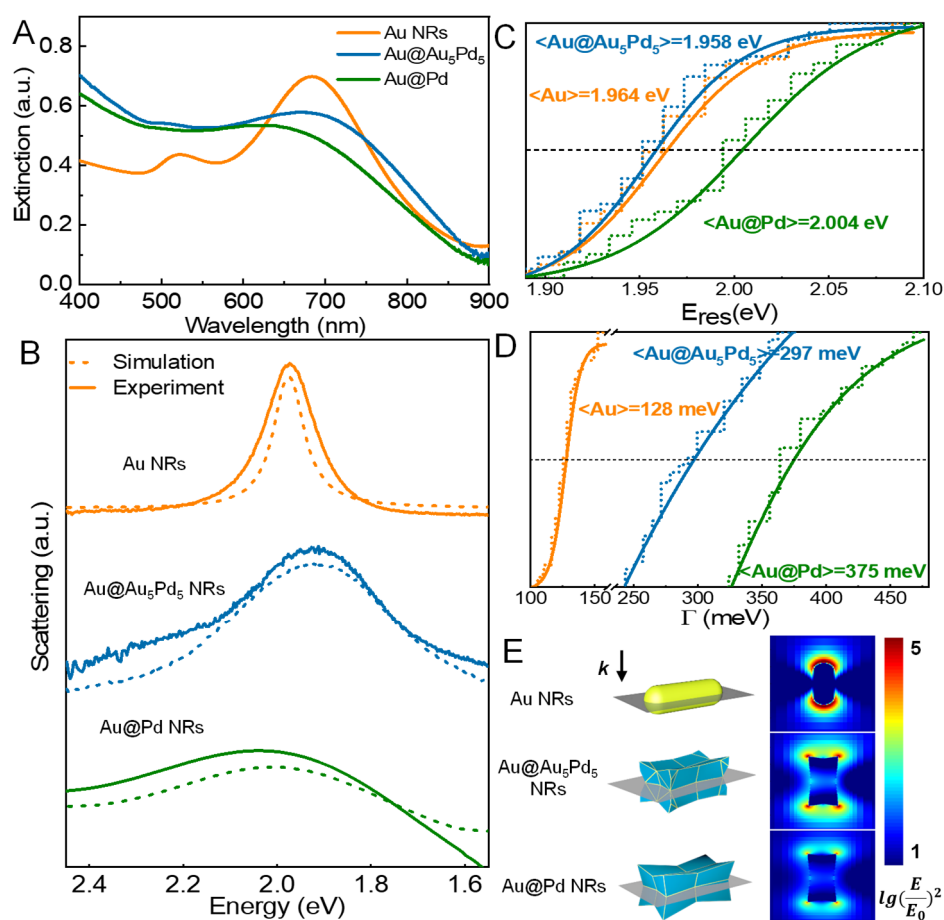


Figure 5. Experimental and simulated optical properties of Au@AuPd alloy NRs. (A) Optical extinction spectra of Au, Au@Au₅Pd₅, and Au@Pd NRs. (B) Single-particle scattering spectra of Au, Au@Au₅Pd₅, and Au@Pd NRs, together with their corresponding simulated scattering spectra. (C,D) Fitted cumulative distribution functions (CDFs) of the resonance energy E_{res} and linewidth Γ extracted from single-particle scattering spectra of Au NRs (orange lines), Au@Au₅Pd₅ NRs (blue lines), and Au@Pd NRs (green lines). Dotted lines represent the experimental CDF values, and solid lines are the fitted CDFs. (E) Simulated electromagnetic field intensity distribution profiles of Au, Au@Au₅Pd₅, and Au@Pd NRs upon the excitation of 680 nm light.

Under dark-field microscopy, the samples were imaged under white-light illumination, allowing true-color images of the particles on the glass substrate to be recorded (Figure S12). We measured three samples, namely Au NRs, Au@Au₅Pd₅ NRs, and Au@Pd NRs, and obtained their representative single-particle scattering spectra (Figures 5B and S12). These spectra conform to a Lorentzian distribution and are in good agreement with the

spectra obtained by FDTD simulation. From the single-particle scattering spectra in Figure 5B, it can be seen that after the AuPd shell grows on the Au NRs, the spectral peak is clearly red-shifted and broadened, indicating that the presence of Pd induces plasmon damping of the Au core. For Au@Pd NRs, the peak position is blue-shifted with more severe peak broadening, and the peak shape no longer conforms to a Lorentzian distribution. This indicates that the Pd shell severely hinders the LSPR of Au, and the spectrum of these particles is closer to that of Pd black. Each uniform bright spot in the dark-field image represents a single particle. With software assistance, the scattering spectrum of each bright spot can be scanned and recorded, allowing statistical data to be collected (Figure S12). All spectral data were compiled as cumulative distribution functions (CDFs) in Figure 5C,D, where Figure 5C shows the resonance energy (E_{res}) and Figure 5D shows the linewidth Γ . As shown in Figure 5C, compared with Au NRs, the AuPd alloy shell induces a relatively small shift in E_{res} , indicating that Au@Au₅Pd₅ NRs largely retain the plasmon resonance of Au NRs. In contrast, the E_{res} of Au@Pd NRs shifted significantly. As mentioned above, the behavior observed here is closer to that of pure Pd. The plasmonic behavior can be more clearly understood from the change in Γ shown in Figure 5D. The Γ of Au@Au₅Pd₅ NRs increases by 297 meV compared with that of Au NRs. Since Au@Au₅Pd₅ NRs still retain the plasmonic characteristics of Au NRs, this portion of the damping can be attributed to the energy loss from hot carrier transfer at the Au-Pd interface, namely, Γ_{HCT} . In contrast, Au@Pd NRs exhibit an obvious increase in Γ , indicating that their hot carrier utilization efficiency is much lower than that of Au@Au₅Pd₅ NRs. The simulated electromagnetic field enhancement profiles of the three particles in Figure 5E further demonstrate their differences in LSPR at 680 nm light excitation. The hot spots of both Au@Au₅Pd₅ NRs and Au@Pd NRs are concentrated at the four corners, but the former are clearly stronger than the latter.

The as-prepared core-shell NPs are also an excellent substrate for surface-enhanced Raman scattering (SERS) measurement, which allows *in situ* SERS characterization of MOR (Figure 6) [63]. Under the plasmonic enhancement effect of the Au core, weak Raman scattering signals can be amplified by a factor of more than 10^6 . Importantly, Raman spectroscopy is highly capable of identifying signals at low wavenumbers ($<800\text{ cm}^{-1}$), which contain information on various oxidizing species, hydroxides, and metal-oxygen bonds [64–69]. This capability is essential for understanding the processes and mechanisms of complex electrocatalytic reactions such as MOR [70], oxygen reduction reaction (ORR) [71–74], and CO₂ reduction reaction (CO₂RR) [75–78]. To compare the enhancement effects of different Au/Pd ratios on SERS signals, we first performed Raman spectroscopy measurements on a series of Au@Au_xPd_y using thiophenol (TP) as the probe molecule (Figure 6A). Owing to the presence of a benzene ring in the TP molecule and the strong binding affinity between sulfur and noble metals, the Raman signal of TP is readily identifiable and can be used to evaluate the SERS effect of the substrate. In Figure 6B, a series of SERS peaks belonging to TP can be observed at approximately 944, 1004, 1025, and 1578 cm^{-1} (Table S1) [35]. The peak at 520 cm^{-1} corresponds to the silicon substrate, and this peak was used to normalize all Raman signals. It can be seen that as the proportion of Au in the shell decreased, the intensity of the TP Raman signal in the SERS spectra also decreased. When the Au/Pd ratio in the shell was reduced to 2:8, the TP signal could hardly be detected, indicating that the plasmonic enhancement effect had been significantly weakened. This demonstrates that the Au in the shell indeed plays a role in extending the plasmonic effect of the core.

Since Au@Au₅Pd₅ NRs exhibited a pronounced SERS enhancement effect and excellent MOR catalytic performance, we further conducted *in situ* SERS tests of MOR using the *in situ* electrochemical cell (Figure 6C). The SERS spectra were recorded from negative to positive potentials to avoid irreversible signal interference caused by oxidation of the catalyst surface and CO poisoning. As shown in Figure 6D, a consistently sharp peak at 1022 cm^{-1} can be attributed to the C-O stretching mode of methanol. At low potentials (below 0.5 V vs. RHE), a SERS band near 471 cm^{-1} can be observed (Table S2) [79]. As the potential was shifted from 0.5 to 0.9 V, this band became less distinct. Upon further increasing the potential, the SERS band near 471 cm^{-1} disappeared and was replaced by a band near 527 cm^{-1} . These two SERS bands correspond to Pd-C stretching of adsorbed CO and Pd-O stretching, respectively [80]. Regarding the possible contribution of Au-CO species, the adsorption of CO on Au is considerably weaker than on Pd, and therefore the Au-CO Raman signal can be reasonably neglected. The disappearance of the Pd-C band and the appearance of the Pd-O band represent a classical CO oxidation process, indicating that CO adsorbed on the Pd surface is oxidized as the potential increases. Correspondingly, a SERS band above 2000 cm^{-1} was observed, and its intensity increased with increasing potential before abruptly disappearing beyond 1.2 V. This SERS band is also attributed to the C-O stretching of adsorbed CO. The increase in its intensity indicates that the MOR process involves the accumulation of CO intermediates. The abrupt disappearance of this signal beyond 1.2 V coincides with the appearance of the Pd-O band, suggesting that the Pd surface becomes largely covered by oxygen species at this stage. This prevents further CO adsorption and its subsequent conversion to CO₂, signaling the termination of methanol oxidation. This also explains the decrease in MOR current at high potentials observed in the CV curves (Figure 2B,C). Admittedly, the potentials obtained from

the *in-situ* SERS measurements do not perfectly match those in the CV curves. This discrepancy may arise from the lag caused by the limited capacity and insufficient diffusion within the *in situ* electrolytic cell. The bands located near 1500 cm^{-1} are more complex. The band observed at 1490 cm^{-1} can be attributed to the stretching vibrations of COO^- and CO_3^{2-} . In the potential range of 0.6 to 1.0 V, the band that appears at 1581 cm^{-1} may belong to the intermediates of surface-adsorbed CO_2 , as its appearance and disappearance are slightly delayed relative to CO adsorption. Although the peak positions differ somewhat from those reported in the literature (Table S2) [79], we assign this band based on the relative positions of the two sets of peaks, and we attribute the observed shift to the presence of Au in the catalyst shell. With the aid of *in situ* SERS spectroscopy, the reaction mechanism of MOR can be elucidated through analysis of the intermediate species.

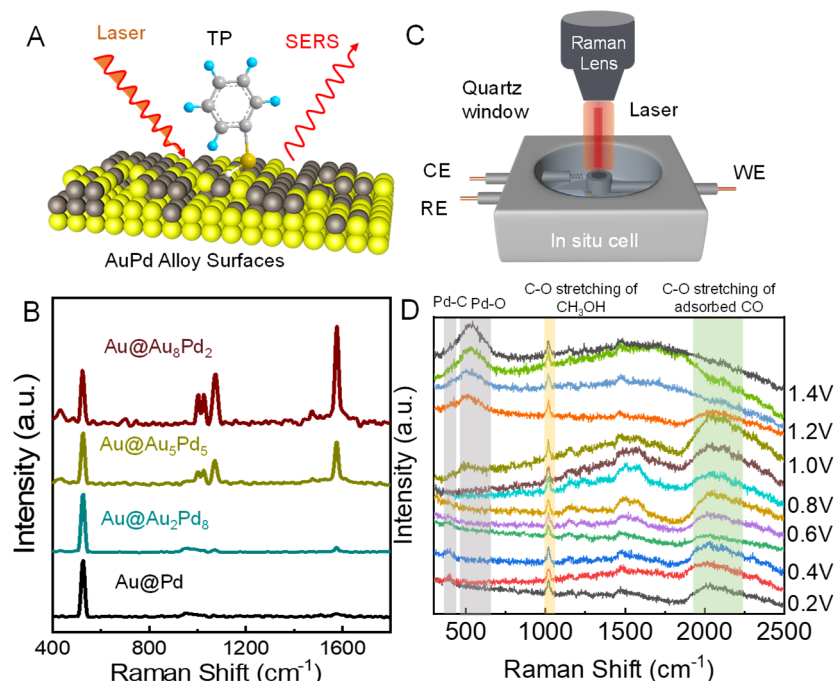


Figure 6. Applications of $\text{Au}@Au_xPd_y$ NRs in SERS measurements of MOR. (A) Schematic diagram of the collection of SERS signals of TP that is adsorbed on the surface of AuPd alloy. TP: thiolphenol. (B) SERS spectra obtained by adsorption of TP molecules on $\text{Au}@Au_xPd_y$ NRs of different compositions, as marked in the panel. (C) Diagram of the *in situ* electrochemical cell integrated with SERS measurements. (D) *In situ* SERS spectra of $\text{Au}@Au_5Pd_5$ NRs obtained by varying the potential under MOR test conditions. The potential was varied from 0.2 to 1.4 V vs. RHE in steps of 0.1 V. The highlighted bars in different colors correspond to the Raman vibration modes as marked on the top of each bar.

4. Conclusions

In summary, we report a strategy for promoting plasmon-enhanced MOR through rational regulation of the structure and composition of the AuPd alloy shell. By balancing the active sites and plasmonic enhancement effects, the as-synthesized $\text{Au}@Au_5Pd_5$ NRs achieved a 1.88-fold enhancement in MOR current under light irradiation. With the addition of an appropriate amount of Ag, this enhancement was further increased to 2.02-fold. Most importantly, this structure, which integrates both plasmonic and catalytic functionalities, is highly suitable for *in situ* electrochemical SERS studies. The proposed synthesis strategy can also be extended to other multimetallic catalytic systems. It holds great potential for applications in plasmon-enhanced electrocatalysis and in mechanistic studies of electrocatalytic reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://media.sciltp.com/articles/others/2609081417086798/MI-26070137-SI.pdf>, with additional experimental details on sample preparation, together with figures and tables including SEM/TEM images, optical extinction spectra, dark-field images, single-particle scattering spectra, EDX mapping, and MOR results, as noted in the text.

Author Contributions: Z.W. and G.C. contributed equally to this work. Q.Z., L.S., Z.W. and G.C. conceived and designed the experiments. Z.W., G.C. and G.Y. performed the synthesis, analysis, simulations, and measurements. Z.W., G.C., L.S., V.B. and Q.Z. co-wrote the paper. Q.Z. and L.S. supervised the entire study. All the authors contributed to the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

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