

Facile One-Pot Synthesis of Au–Pd Core–Shell Nanoparticles with Enhanced Catalytic Performance

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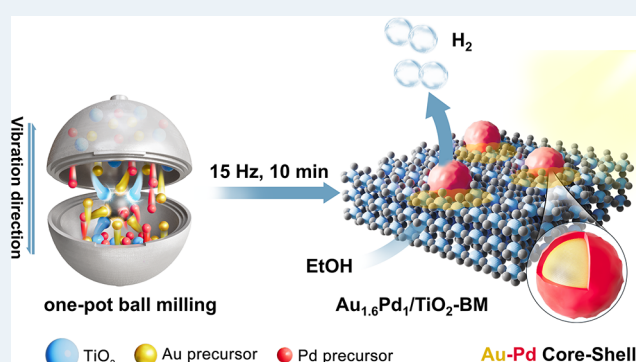
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ABSTRACT: Bimetallic nanoparticles offer catalytic properties arising from electronic exchange between their constituent metals, which is highly sensitive to structural configuration. In particular, this electronic interplay modulates the metal-support interaction, a key factor controlling catalytic performance. Core–shell architectures provide an effective platform to tailor these effects with atomic precision. Here, we demonstrate that Au(core)–Pd(shell) nanoparticles supported on TiO₂, synthesized through a simple one-pot ball-milling approach, exhibit markedly enhanced photocatalytic hydrogen evolution compared with both AuPd-alloy and a physical mixture of monometallic counterparts. Density functional theory calculations reveal that the core–shell structure weakens metal-support interactions relative to the alloy, thereby promoting higher surface reactivity. These findings demonstrate how mechanochemistry can attain precise structural control in supported bimetallic systems, optimize electronic coupling, and boost photocatalytic activity for hydrogen production.

KEYWORDS: mechanochemistry, core–shell, bimetallic cocatalysts, photocatalysis, metal-support interactions



1. INTRODUCTION

Bimetallic nanoparticles-supported catalysts have attracted growing attention owing to their distinctive properties with respect to their monometallic counterparts.^{1–5} In particular, bimetallic cocatalyst systems are regarded as promising candidates for photocatalytic hydrogen evolution, as they can overcome the intrinsic limitations of the single-metal catalysts by, for instance, tuning the work function (Schottky barrier),^{6,7} modulating the electronic structure of the active metal,⁸ promoting hydrogen spillover or inverse spillover,⁹ stabilizing metallic nanoparticles,¹⁰ and modifying the physicochemical properties of the support.^{11,12} To achieve visible-light-responsive photocatalysts, plasmonic metals, typically Au, Ag and Cu, have been widely incorporated into bimetallic systems due to their localized surface plasmon resonance (LSPR) effects.^{13–15} Depending on the combination of plasmonic and non-plasmonic components, the optical response of these systems can be precisely tuned across the UV-vis-NIR region by controlling particle size, morphology, and metal composition.¹⁶ However, the Fermi level of plasmonic metals lies within the s-band, resulting in poorer catalytic activity compared with d-band metals such as Pt and Pd.¹⁷ The enhanced molecular binding affinity of d-band metals arises from the stronger hybridization between their d-orbitals and the lowest unoccupied molecular orbitals of adsorbates. Consequently, integrating

plasmonic and catalytically active metals within a single nanostructure offers a compelling strategy to synergistically optimize photocatalytic efficiency, selectivity, and stability.^{18–20}

The structure and electronic configuration of bimetallic systems critically determine the interactions at both the metal-metal and metal-semiconductor interfaces, thereby governing their catalytic performance.²¹ Among various architectures, core-shell Au–Pd nanoparticles have shown particular promise by combining the plasmonic properties of Au (core) with the catalytic functionality of Pd (shell),^{22–24} with surface Pd sites facilitating the associative desorption of H₂ and/or inhibiting the reverse transfer of trapped electrons back to TiO₂.^{25,26} Although wet-chemical methods have been extensively explored for synthesizing Au–Pd core-shell nanoparticles,^{27–30} these approaches often require multiple steps and are sensitive to the choice of precursors, capping agents, and reducing agents, complicating structural control.^{31,32} Here, we report a simple

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mechanochemical one-pot ball-milling (BM) approach to synthesize Au(core)–Pd(shell) nanoparticles supported on TiO₂. Mechanochemical synthesis has emerged as an environmentally benign and scalable alternative to conventional solution-based methods, overcoming limitations related to solubility, multi-step processing, and the use of hazardous organic reagents.^{33–35} This technique has recently enabled the preparation of metal clusters, alloys, and supported single-atom catalysts (SACs),^{36–40} but, to our knowledge, has not yet been applied to the formation of core-shell bimetallic nanostructures. The resulting Au(core)–Pd(shell)/TiO₂ catalysts exhibit exceptional activity for photocatalytic hydrogen generation under both UV and simulated solar illumination, outperforming AuPd-alloy and monometallic systems. Density functional theory (DFT) calculations reveal that the core-shell structure undergoes significantly less structural distortion upon adsorption on TiO₂ than the alloy counterpart, resulting in a weaker metal-support interaction and higher intrinsic reactivity. These findings introduce a general design concept for enhancing the catalytic performance of bimetallic nanoparticles: constructing core-shell architectures with high-electronegativity core atoms to modulate metal-support interactions and optimize surface reactivity.

2. RESULTS AND DISCUSSION

2.1. Photocatalytic Performance

The photocatalytic H₂ evolution reaction was first evaluated on a series of AuPd/TiO₂-BM samples with varying Au/Pd ratios under both UV-vis and UV illumination (Figure 1a,b). A total metal loading of 1 wt % was selected based on our previous studies.^{38,41} Accordingly, the photocatalysts denoted as Au/TiO₂-BM,

Au_{1.6}Pd₁/TiO₂-BM, Au_{0.5}Pd₁/TiO₂-BM, Au_{0.2}Pd₁/TiO₂-BM, and Pd/TiO₂-BM in Figure 1 correspond to Au_{1wt%}Pd_{0wt%}, Au_{0.75wt%}Pd_{0.25wt%}, Au_{0.5wt%}Pd_{0.5wt%}, Au_{0.25wt%}Pd_{0.75wt%}, and Au_{0wt%}Pd_{1wt%}, respectively. The actual metal loadings of the samples, both before and after the photoreaction, are summarized in Table S1. Good agreement was found between the nominal and measured compositions, and no metal loss or compositional changes were observed after the photoreaction.

Under UV light illumination, the H₂ evolution rate was enhanced under increasing Pd content. However, the observed trend was not linear (see dashed line in Figure 1b), revealing a pronounced synergistic interaction between Au and Pd that enhances photocatalytic activity. The maximum synergy was achieved at an atomic Au/Pd ratio of 1.6, corresponding to an H₂ evolution rate of 26.2 mmol h^{−1} g_{cat}^{−1} and an apparent quantum yield (AQY) of 4.6%. It is important to mention that when the photoreactions were conducted under UV-vis illumination, the temperature of the photoreactor increased notably (to ca. 60 °C), compared with the temperature recorded under dark (ca. 25 °C) and UV-only (ca. 30 °C) conditions. Because elevated temperature can enhance photocatalytic activity,^{41–43} additional experiments were performed under UV illumination at 60 °C (using an external hot-air blower, denoted as UV+heating) to decouple the thermal contribution from visible-light irradiation. The H₂ evolution rates under UV+visible, UV+heating, and the corresponding net visible-light contribution are displayed in Figure 1a. Notably, under visible-light excitation, Au_{1.6}Pd₁/TiO₂-BM exhibited markedly higher photoactivity than the other samples, suggesting that Pd species promote the surface plasmon resonance effect of Au at specific Au/Pd ratios. To further confirm this synergistic effect, the photocatalytic H₂ evolution was examined on monometallic samples containing equivalent

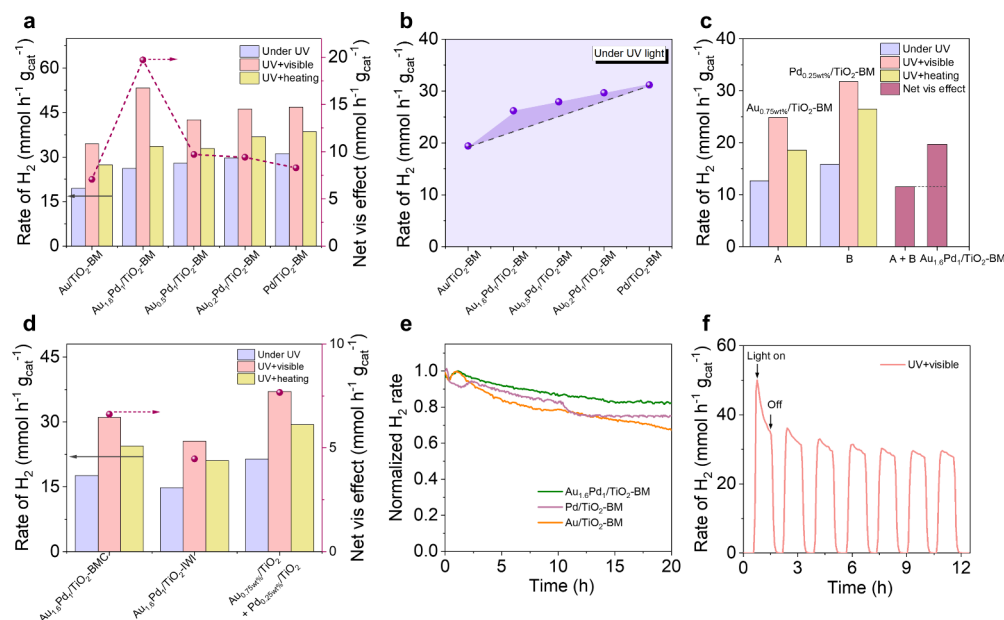


Figure 1. H₂ photoproduction rates of different photocatalysts. (a) AuPd/TiO₂-BM samples with different molar ratio of Au and Pd obtained by ball milling under UV light, UV+visible light, and UV+heating conditions. The corresponding net visible effect was calculated by subtracting the heating effect induced by the visible light source (right Y axis). (b) AuPd/TiO₂-BM samples under UV light. (c) Au_{0.75wt%}/TiO₂-BM (A) and Pd_{0.25wt%}/TiO₂-BM (B) under UV light, UV+visible light and UV+heating conditions. A+B refers to the arithmetic sum of the net visible effect for H₂ production rate of Au_{0.75wt%}/TiO₂-BM and Pd_{0.25wt%}/TiO₂-BM. The H₂ rate of Au_{1.6}Pd₁/TiO₂-BM sample is shown for comparison. (d) Au_{1.6}Pd₁/TiO₂ photocatalysts prepared by different methods. (e) 20-h stability tests under UV light irradiation of selected photocatalysts. (f) Recyclability test under UV+visible light irradiation of Au_{1.6}Pd₁/TiO₂-BM.

metal loadings ($\text{Au}_{0.75\text{wt\%}}/\text{TiO}_2\text{-BM}$ and $\text{Pd}_{0.25\text{wt\%}}/\text{TiO}_2\text{-BM}$; Figure 1c). The arithmetic sum of their individual net visible-light contributions ($11.5 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$) was significantly lower than that of the bimetallic $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ catalyst ($19.6 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$), further demonstrating the existence of a strong synergistic interaction between Au and Pd that amplifies photocatalytic efficiency.

The influence of the precursor milling order on photocatalytic H_2 production was also investigated. As shown in Figure S1, the photocatalysts prepared through sequential milling ($\text{Au}_{1.6}\text{-Pd}_1\text{TiO}_2\text{-BM}$ and $\text{Pd}_1\text{-Au}_{1.6}\text{TiO}_2\text{-BM}$) displayed lower H_2 evolution rates than the one-pot milled $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ sample under both UV and visible-light irradiation. Interestingly, the sequentially milled samples exhibited nearly identical activity under UV illumination ($\sim 20 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$), closely following the dashed trend line in Figure 1b. This indicates the absence of synergistic interaction between Au and Pd when introduced sequentially. Therefore, the one-pot ball-milling route is essential to create the local environment necessary for Au and Pd to interact and form the unique active structures responsible for enhanced H_2 evolution. This finding underscores mechanochemistry as a powerful and effective approach for the synthesis of bimetallic catalysts with superior performance.

Additionally, H_2 evolution was tested on a sample prepared by physically mixing the monometallic catalysts ($\text{Au}_{0.75\text{wt\%}}/\text{TiO}_2 + \text{Pd}_{0.25\text{wt\%}}/\text{TiO}_2$; Figure 1d). The resulting photocatalyst exhibited considerably lower photoactivity than $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ (Figure 1a), with a net visible-light contribution of only $7.7 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, compared with $19.6 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ catalyst. Together, these results provide compelling evidence that the unique synergistic effect between TiO_2 , Au and Pd arises exclusively from the simultaneous one-pot milling of metals and support. For comparison, reference catalysts $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$, which were prepared by conventional incipient wet impregnation (IWI) and ball milling followed by calcination at 300°C (BMC), respectively, were also tested (Figure 1d). The ball-milled sample clearly outperformed both references under UV and UV-vis irradiation. Notably, the synergistic enhancement induced by mechanochemical treatment disappeared after calcination (BMC sample), prompting a detailed investigation into how thermal treatment disrupts the unique Au–Pd– TiO_2 interaction, as discussed below. The photocatalytic hydrogen production achieved over the most active photocatalyst, $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$, is compared with those reported in the literature for AuPd/TiO_2 photocatalysts in Table S2. Although direct comparison is not straightforward due to significant differences in catalyst composition and photocatalytic reaction conditions among studies, the available data suggest that the mechanochemically prepared $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ photocatalyst exhibits superior hydrogen photoproduction performance compared with the AuPd/TiO_2 systems reported to date.

Photocatalyst stability is a critical factor for practical applications. It is well established that metal clusters and atoms, especially Au species, tend to agglomerate during prolonged illumination due to their high surface free energy.^{44,45} Whereas $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ showed comparable stability to $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ (Figure S2a,b), it was markedly more stable than the corresponding monometallic catalysts $\text{Pd}/\text{TiO}_2\text{-BM}$ and $\text{Au}/\text{TiO}_2\text{-BM}$ (Figures 1e

and S2c). Altogether, these findings demonstrate that the bimetallic photocatalyst synthesized by one-pot ball milling exhibits not only outstanding photoactivity but also excellent stability under photocatalytic conditions. To further evaluate the operational durability of the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ photocatalyst under simulated solar irradiation (UV+visible), real-time hydrogen production was monitored over seven consecutive light-on/light-off cycles spanning a total of 12.5 h (Figure 1f). Following an equilibration period during the first three cycles, the catalyst reached a stable hydrogen production rate of $\sim 30 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, which was consistently maintained throughout cycles 4–7.

2.2. Characterization of $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ Photocatalyst

To elucidate the unique metal-support interactions generated during the milling process, the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ photocatalysts prepared by BM, IWI, and BMC were comprehensively characterized. X-ray diffraction (XRD) patterns were collected to identify the crystalline phases of the as-prepared photocatalysts and the TiO_2 support (Figure S3a,b). All samples exhibited nearly identical diffraction features, confirming that the TiO_2 crystal structure remained intact after both ball milling and calcination treatments. The reflections at 2θ values of 25.3° , 37.9° , 48.1° , 54.2° , 55.1° and 75.2° correspond to the (101), (004), (200), (105), (211) and (215) planes of the anatase phase (JCPDS No. 21-1272), respectively. The peaks at 27.5° , 36.1° , 41.4° , 62.8° , 69.0° and 70.3° are assigned to the (110), (101), (111), (002), (301) and (112) planes of rutile (JCPDS No. 21-1276). No diffraction signals attributable to Au or Pd were detected, owing to their low overall loading ($<1 \text{ wt\%}$) and high dispersion. Raman spectroscopy further confirmed the structural integrity of TiO_2 (Figure S3c). All samples exhibited characteristic anatase phonon modes at $143.8 (E_g)$, $196.3 (E_g)$, $396.6 (B_{1g})$, $516.5 (A_{1g} + B_{1g})$ and $638.1 (E_g) \text{ cm}^{-1}$, consistent with the dominant anatase phase observed in XRD. Notably, the main E_g mode of the ball-milled samples showed neither significant peak broadening nor frequency shift compared with pristine TiO_2 , indicating that the mild milling process did not introduce detectable structural defects into the TiO_2 lattice. UV-vis absorption spectra and corresponding Tauc plots were recorded for $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ (BM, IWI and BMC) as well as for the $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$ series (Figure S3d–f). The estimated bandgap values of the bimetallic $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ photocatalysts were consistently smaller than those of the monometallic counterparts ($\text{Au}/\text{TiO}_2\text{-BM}$ and $\text{Pd}/\text{TiO}_2\text{-BM}$) and pristine TiO_2 , with values of 3.02–3.07 eV compared to 3.13, 3.08, and 3.20 eV, respectively. This bandgap narrowing suggests that strong electronic interactions between TiO_2 , Au and Pd modify the band structure of TiO_2 , thereby facilitating photocatalytic activity. Interestingly, no distinct surface plasmon resonance bands were detected in the UV-vis spectra of $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$ samples, while both $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ exhibited the characteristic plasmonic absorption associated with Au nanoparticles (Figure S3d). The bandgap energies of the IWI and BMC samples were determined to be 3.03 and 3.07 eV, respectively (Figure S3e), comparable to those of the $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$ series (Figure S3f). These results collectively indicate that the one-pot ball-milling process leads to a distinct electronic configuration of Au and Pd species intimately interacting with TiO_2 , distinct from that obtained by conventional impregnation routes or after calcination.

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) combined with energy-dispersive X-ray spectroscopy (EDX) mapping was employed to directly examine the morphology and structure of the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ photocatalysts. As shown in Figures 2a and S4a, the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BM sample features uniformly distributed nanoparticles with an average size of 3.2 ± 0.8 nm homogeneously dispersed over the TiO_2 surface. The EDX elemental maps clearly reveal a core-shell configuration, with Au concentrated in the core and Pd preferentially located at the periphery. Lattice fringes with an interplanar spacing of $2.4 \text{ \AA}$ are observed in the core of the nanoparticles, in good agreement with the (111) crystallographic plane of Au. This Au(core)–Pd(shell) structure indicates that the ball-milling process promotes the migration of Pd atoms onto the Au surface, leading to the formation of intimate Au–Pd interfaces. Such an architecture enhances charge transfer efficiency and modulates the surface electronic properties, thereby rationalizing the superior photocatalytic activity observed for the ball-milled sample. Importantly, both the core-shell configuration and the nanoparticle size (3.3 ± 1.1 nm) remain unchanged after photocatalytic operation (Figures 2b and S4b), accounting for the remarkable stability of the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BM sample. The lattice fringe analysis of the particle shown in Figure 2b reveals an interplanar spacing of $2.4 \text{ \AA}$ in the core of the nanoparticle,

consistent with the (111) plane of Au, and an interplanar spacing of $2.2 \text{ \AA}$ in the shell, corresponding to the (111) crystallographic plane of Pd, thus confirming the core-shell structure. In contrast, the EDX elemental maps of the reference catalyst prepared by incipient wetness impregnation ($\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -IWI; Figures 2c and S4c) show distinct segregation of Au and Pd domains (1.2 ± 0.6 nm) rather than a core-shell configuration, reflecting weaker interaction between Au and Pd and limited atomic-level mixing. After the photocatalytic reaction, the nanoparticles in this sample exhibited slight growth, reaching an average size of 2.4 ± 0.8 nm (Figures 2d and S4d). Likewise, HAADF-STEM-EDX analysis of the calcined sample ($\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BMC; Figures 2e and S4e) reveals the collapse of the core-shell structure, leading to the formation of AuPd alloy nanoparticles, while maintaining a similar particle size to that of the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BM sample (3.3 ± 1.0). In this case, most of the lattice spacings across the nanoparticles are approximately $2.3 \text{ \AA}$, consistent with the formation of an AuPd alloy (Figure 2d), although in some particles distinct Au and Pd domains can be distinguished (Figure S4d). These results collectively demonstrate that the atomic-scale mixing induced by the one-pot mechanochemical synthesis is essential to generate and preserve the Au(core)–Pd(shell) architecture. From a thermodynamic point of view, Au is expected to dominate the surface of AuPd nanoparticles under vacuum conditions because

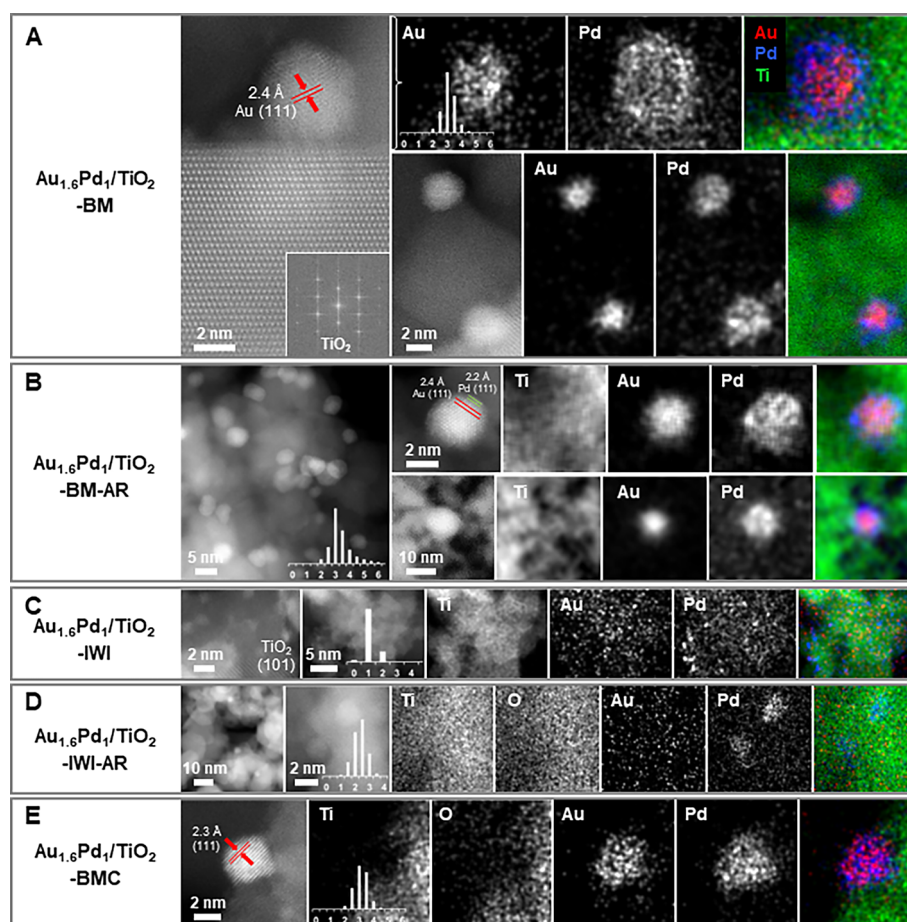


Figure 2. AC-HAADF-STEM-EDX characterization. Images and elemental mappings of fresh and after reaction $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BM (A,B) and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -IWI (C,D) samples. AR refers to samples after reaction. (E) Fresh $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2$ -BMC. The panels containing scale bars are HAADF-STEM images.

Au possesses a lower surface energy than Pd. Accordingly, Au surface segregation has been widely reported after thermal treatments under vacuum or reducing atmospheres.^{46,47} In contrast, under oxidizing conditions, Pd can segregate to the surface through the formation of an oxidized palladium layer, which lowers the surface energy of Pd atoms.^{48,49} DFT studies have also confirmed the stabilization of Pd at the nanoparticle surface in the presence of O₂.⁵⁰ Considering that the mechanochemical synthesis is performed in air and under highly energy conditions involving atomic rearrangement events, the formation of a Pd-enriched shell surrounding an Au-rich core is thermodynamically plausible. The lower photocatalytic activity of the BMC sample compared with the BM counterpart is attributed to the calcination step at 300 °C, which, consistent with the findings of Wilson et al., disrupts the unique synergistic core-shell configuration created by ball milling and creates alloyed nanoparticles.⁴⁷

The identification of an Au(core)–Pd(shell) nanostructure in the ball-milled sample strongly suggests a distinctive electronic environment at the metal-metal and metal-support interfaces. To further substantiate this configuration and probe the electronic state and local coordination of Au and Pd species, X-ray photoelectron spectroscopy (XPS) was carried out (Figures 3, S5, and S6). The Au 4f XP spectra of the fresh photocatalysts (Au_{1.6}Pd₁/TiO₂-BM, Au_{1.6}Pd₁/TiO₂-IWI, and Au_{1.6}Pd₁/TiO₂-BMC) reveal the coexistence of three oxidation

states, Au⁰ (4f_{7/2} at 83.4 eV), Au⁺ (84.5 eV), and Au³⁺ (85.8 eV), as shown in Figure 3a–c. Notably, the fraction of oxidized Au species (Au^{δ+}, the sum of Au⁺ and Au³⁺) is markedly higher in Au_{1.6}Pd₁/TiO₂-BM (83.6%) compared to Au_{1.6}Pd₁/TiO₂-IWI (46.7%) and Au_{1.6}Pd₁/TiO₂-BMC (58.5%) (Figure S5a–c). After the photocatalytic reaction, the oxidized Au species in Au_{1.6}Pd₁/TiO₂-BM were fully reduced to metallic Au⁰ (Figure 3a), whereas in the IWI and BMC samples they remained largely unchanged (Figures 3b,c and S5a–c).

In the Pd 3d region, all samples display characteristic signals at around 334.9 and 340.2 eV, corresponding to the 3d_{5/2} and 3d_{3/2} levels of metallic Pd, together with higher binding energy components at around 336.0 and 337.0 eV assigned to Pd²⁺ and Pd⁴⁺, respectively (Figure 3d–f). The proportion of metallic Pd⁰ species in the fresh catalysts follows the order Au_{1.6}Pd₁/TiO₂-BM (56.8%) > Au_{1.6}Pd₁/TiO₂-IWI (29.2%) > Au_{1.6}Pd₁/TiO₂-BMC (22.3%). After photoreaction, the Pd⁰ fraction in Au_{1.6}Pd₁/TiO₂-BM significantly increased to 82.6%, while negligible changes were observed for the IWI and BMC counterparts (Figure S5d–f). Interestingly, when Pd clusters were directly deposited on TiO₂ by ball milling (Pd/TiO₂-BM), previous studies reported oxidation of Pd during photocatalysis, leading to decreased stability.³⁸ In contrast, in the present Au_{1.6}Pd₁/TiO₂-BM system, Pd becomes more reduced after UV irradiation. This remarkable stabilization and reduction behavior can be attributed to the strong Au–Pd interaction

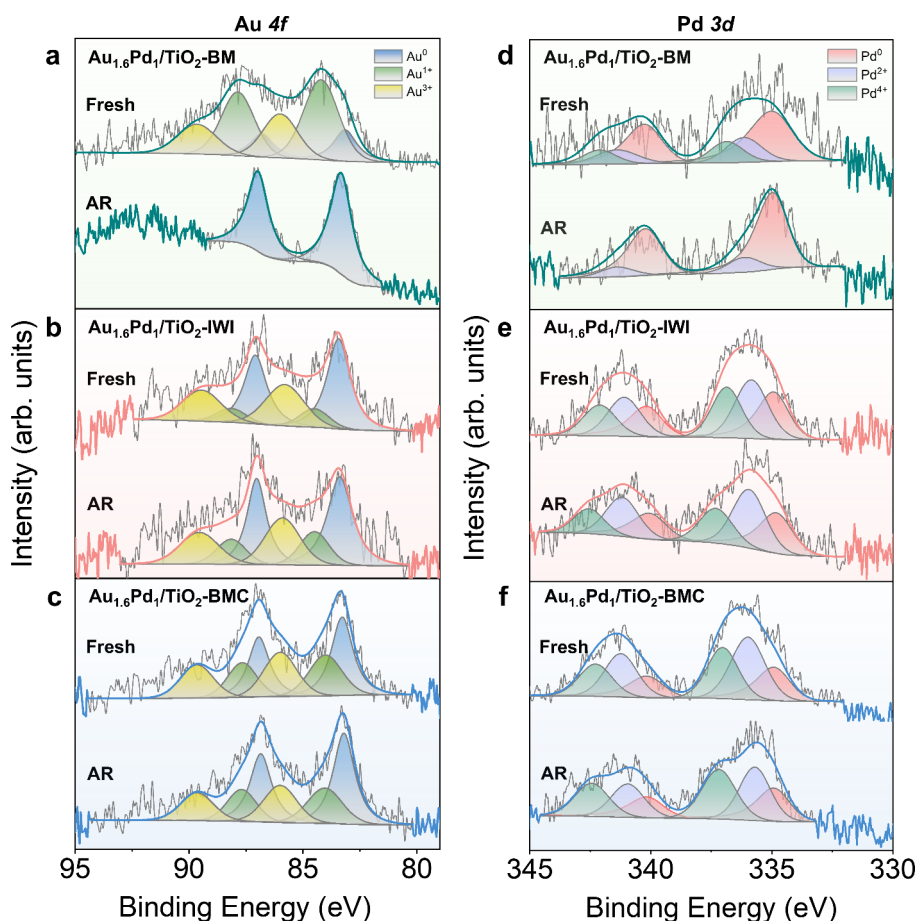


Figure 3. XPS analysis of Au_{1.6}Pd₁/TiO₂ photocatalysts. (a–c) Au 4f spectra of fresh and after reaction Au_{1.6}Pd₁/TiO₂-BM, Au_{1.6}Pd₁/TiO₂-IWI, and Au_{1.6}Pd₁/TiO₂-BMC. (d–f) Pd 3d spectra of fresh and after reaction Au_{1.6}Pd₁/TiO₂-BM, Au_{1.6}Pd₁/TiO₂-IWI, and Au_{1.6}Pd₁/TiO₂-BMC. AR refers to samples after reaction.

within the core-shell structure. On the other hand, a slight shift is observed towards lower binding energies in the Au^0 peak for the reacted $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ sample calcined at 300°C , which contains AuPd alloy nanoparticles, compared with the reacted $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ sample, which exhibits a core-shell structure (83.4 vs. 83.2 eV for $\text{Au } 4f_{7/2}$). Since Au is more electronegative than Pd, this shift is consistent with electronic donation from Pd to Au as a consequence of alloy formation. In the alloyed nanoparticles, most Au atoms are expected to be in direct contact with Pd atoms, promoting electronic charge redistribution between the two metals. In contrast, in the core-shell nanoparticles, Au atoms are predominantly located in the core and only a small fraction is directly exposed to Pd. Therefore, the observed binding-energy shift provides further evidence for the proposed AuPd alloy structure.

The Ti 2p spectra (Figure S6a–c) exhibit two peaks at 458.5 and 464.2 eV in all catalysts, characteristic of the Ti^{4+} state of TiO_2 .^{51,52} The O 1s spectra (Figure S6d–f) show bands at 529.7 and 531.4 eV, corresponding to lattice oxygen and surface hydroxyl groups (O–H), respectively. After the photocatalytic reaction, an additional low-binding-energy O signal (527.3 eV) appears exclusively in $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$, consistent with previous observations for Pd/ $\text{TiO}_2\text{-BM}$.³⁸

The Au L_3 -edge X-ray absorption near-edge structure (XANES) spectra of $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ (Figure S7a) exhibit a subtle but consistent increase in the white-line intensity at $\sim 11,921$ eV and in the resonance feature at $\sim 11,934$ eV relative to the Au foil reference. These features are sensitive to the occupancy of Au 5d states and are attributed not to charge redistribution arising from Au–Pd interactions, but rather to charge redistribution with the TiO_2 support.^{53,54} The Fourier-transformed Pd K-edge extended X-ray absorption fine structure (EXAFS) spectra (R-space, Figure S7b) of both $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ and $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ display two main contributions at ~ 1.5 and ~ 2.0 Å, which can be assigned to Pd–O scattering paths and are consistent with the presence of oxidized Pd species, in agreement with the XPS results. The $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$ sample exhibits higher amplitudes for both Pd–O contributions than $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$, suggesting a more ordered and/or higher-coordinated Pd–O environment in the impregnated sample.⁵⁵ In contrast, the $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$ sample exhibits an additional contribution at ~ 2.5 Å that is absent in $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$. This feature can be associated to Pd–Pd and/or Pd–Au scattering paths, indicating the presence of direct metal-metal interactions. This observation is fully consistent with the close spatial association between Au and Pd revealed by HAADF-STEM-EDX for $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$, in contrast to the higher dispersion and segregation of both metals observed in $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$. These results provide further evidence that the ball-milling synthesis promotes intimate Au–Pd contact and the formation of bimetallic interfaces that are not achieved by conventional impregnation.

Steady-state photoluminescence (PL) spectra were recorded to probe the separation and recombination dynamics of photoexcited charge carriers in the bimetallic AuPd-supported TiO_2 photocatalysts. As shown in Figure S8a, all samples exhibit an emission band centered at 420–450 nm. Upon decoration with AuPd nanoparticles, the PL intensity decreases progressively in the order $\text{TiO}_2 > \text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI} > \text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC} > \text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$. The markedly lower PL intensity of $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ indicates a reduced recombination rate of

photogenerated electron-hole pairs and a longer carrier lifetime under light irradiation, which correlates with its superior photocatalytic performance.⁵⁶ Electrochemical impedance spectroscopy (EIS, Nyquist plots) was further employed under simulated solar illumination to gain insight into the charge-transfer behavior at the semiconductor-electrolyte interface. Typically, the arc radius in the Nyquist plots reflects the charge-transfer resistance of the photocatalyst, providing information on electron-transport kinetics at the working electrode interface.⁵⁷ A smaller arc radius corresponds to more efficient electron transfer. As shown in Figure S8b, the introduction of AuPd nanoparticles reduced the arc radius compared to pristine TiO_2 P90, with $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ exhibiting the smallest radius, consistent with the PL results. Moreover, the transient photocurrent responses (Figure S8c) further confirm that $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ exhibits the most efficient generation and transport of photoexcited carriers, in agreement with both PL and EIS analyses. Collectively, these findings demonstrate that the Au–Pd core-shell nanostructure on the TiO_2 surface effectively suppresses electron-hole recombination and promotes charge migration, thereby accounting for its enhanced photocatalytic hydrogen evolution activity.

2.3. First-Principles DFT Calculations

We performed first-principles calculations based on density functional theory (DFT, see Methods for technical details) to investigate the energetic, structural, and electronic properties of monometallic (Au_{55} , Pd_{55}) and bimetallic (AuPd-alloy, Au–Pd core-shell) clusters supported on the anatase TiO_2 (001) surface (Figure 4a). The (001) facet was chosen for these calculations owing to its single, well-defined 5c-Ti adsorption environment, which enables unambiguous resolution of the photoinduced metal-to-support charge-transfer mechanism; based on the results reported in our previous work,⁴⁴ extension of this analysis to the more heterogeneous and predominant (101) surface is reasonable. As an initial step, we assessed the stability of these metal- TiO_2 systems under photoexcitation conditions. To this end, the cluster adsorption energy (E_{abs}) was calculated as a function of the photoinduced electronic density populating the TiO_2 conduction band (n , Figure 4b).

We found that, with increasing light irradiation, or equivalently, increasing n , the magnitude of E_{abs} increases for all systems ($E_{\text{abs}} < 0$ denotes thermodynamically favorable adsorption). The interaction between the metallic clusters and the TiO_2 substrate is strongest for Pd_{55} and the bimetallic clusters, followed by Au_{55} , consistent with the experimentally observed photocatalytic activity trend (Figure 1f). This correlation becomes more pronounced with increasing n . These results indicate that photoexcitation generally strengthens the metal-support interaction, thereby stabilizing the clusters under illumination. Hence, the differences in photocatalytic performance among the various clusters cannot, in principle, be attributed to a light-induced tendency towards cluster coalescence.

Subsequently, we computed the total and projected densities of states (pDOS; Figure 4c,d) to elucidate the electronic interactions governing the distinct catalytic behaviors of the clusters. The Au_{55} cluster exhibits a compact Au d -band centered well below the Fermi energy (E_{F}), with negligible intensity at E_{F} and limited overlap with O p -states (Figure 4c), consistent with weak metal-oxygen coupling and low intrinsic reactivity. In contrast, Pd_{55} displays a broad d -manifold crossing E_{F} accompanied by strong Pd $d/\text{O } p$ hybridization (Figure 4c), indicative of a

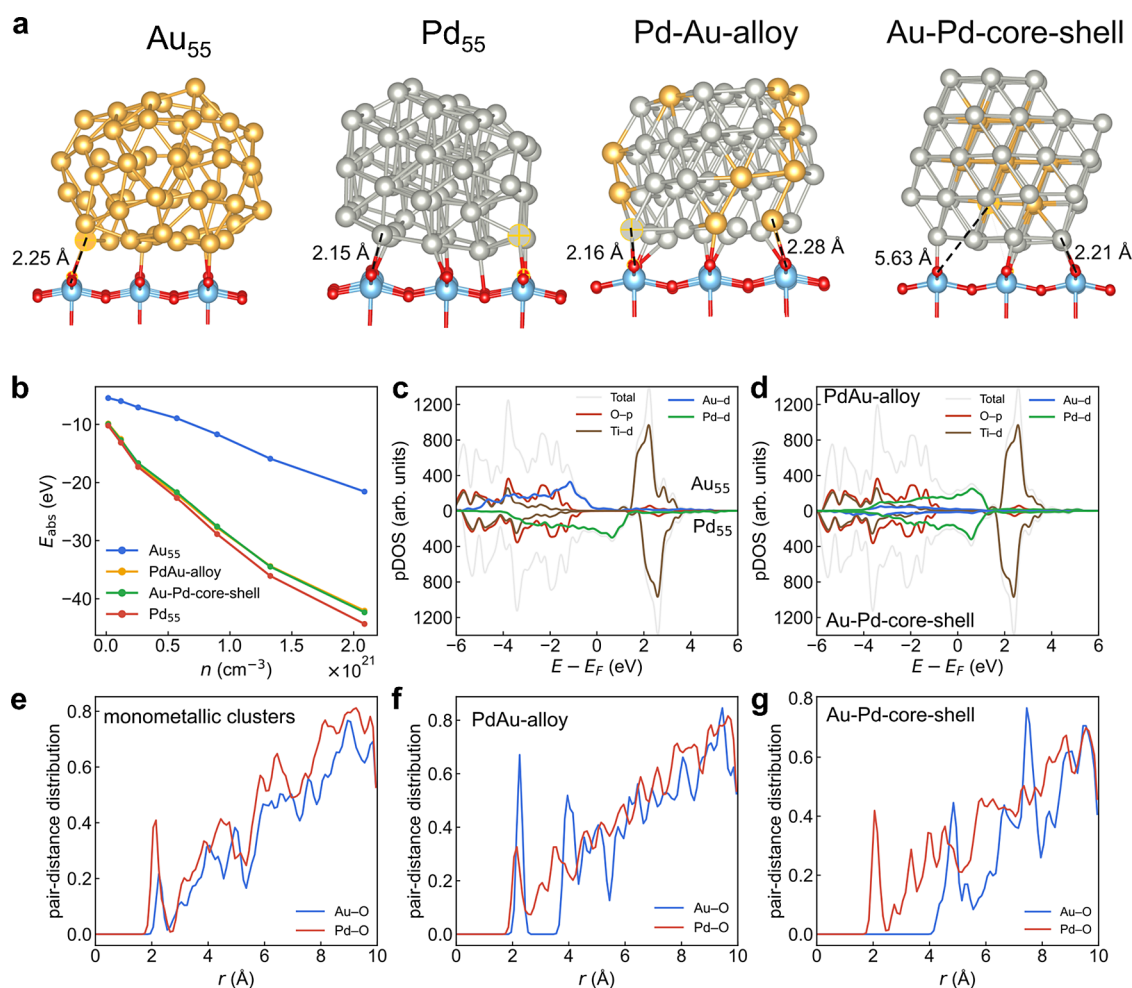


Figure 4. First-principles simulations of metallic clusters absorbed on the anatase TiO_2 (001) surface. (a) Relaxed geometries obtained from DFT calculations for monometallic (Au_{55} , Pd_{55}) and bimetallic (AuPd-alloy, Au–Pd core-shell) clusters. The shortest distance between metallic (cluster) and oxygen (substrate) atoms are highlighted. Au, Pd, Ti and O atoms are represented by yellow, gray, blue and red spheres, respectively. (b) Cluster absorption energy as a function of light-excited electronic density in the conduction band, n . Total and projected density of electronic states for (c) monometallic and (d) bimetallic clusters. The Fermi energy level, E_F , has been shifted to zero in all cases. (e–g) Pair-distance distribution functions calculated for metallic (cluster) and oxygen (TiO_2) atoms.

more reactive metal-support interface capable of facilitating charge transfer and performing redox reactions. For the AuPd-alloy and Au–Pd core-shell cluster, the Au and Pd d -states are redistributed across the valence band, with Au states shifting upward and Pd states shifting downward toward E_F , resulting in intermediate near-Fermi intensity and enhanced O p -state coupling (Figure 4d). This feature reflects strong metal-oxygen hybridization and high intrinsic reactivity, comparable to that observed of Pd_{55} . These pDOS results help rationalize the experimentally observed photocatalytic trends. The Au_{55} cluster exhibits the lowest activity owing to its negligible d -orbital occupation at E_F . The AuPd-alloy cluster also shows lower activity than Pd_{55} and Au–Pd core-shell clusters, as many of its surface sites are occupied by Au atoms (Figure 4e–g), which are less effective than Pd atoms in releasing photoexcited electrons for catalysis and promoting photoactivity.²²

To rationalize the photocatalytic differences observed between the Pd_{55} and Au–Pd core-shell clusters, we examined their structural features (Figure 4a,e–g) and adsorption energies (Figure 4b). The Pd_{55} cluster exhibits the strongest binding to

the TiO_2 surface; as a result, the number of free Pd active sites, those not involved in charge exchange with the substrate, is smaller than in the Au–Pd core-shell cluster (Figure 4a,e,g). In contrast, the Au–Pd core-shell cluster retains approximately 5% more free Pd surface sites, which enhances its capacity for molecular adsorption and catalytic transformation. The weaker surface binding of Au–Pd core-shell compared with Pd_{55} arises from the higher electronegativity of the Au atoms in the core, which partially diverts the interaction between the outer Pd atoms and the TiO_2 surface. Accordingly, the structural distortions experienced by Au–Pd core-shell upon adsorption are far less pronounced than those of Pd_{55} (Figure 4a). These observations, therefore, unveil a potential design principle for optimizing Pd-based bimetallic photocatalysts: incorporating a high-electronegativity core can mitigate excessive metal-support coupling, preserve a greater number of active Pd surface sites, and thereby enhance overall catalytic performance.

Overall, our results allow us to propose that under UV+visible irradiation, the Au core in $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ generates hot electrons, which can contribute to the reduction of Au during

photocatalysis, consistent with the changes observed in Figure 3a. Simultaneously, the Schottky junction formed at the TiO_2 -AuPd interface, arising from the difference in work functions between TiO_2 (4.6–4.7 eV), Au (5.10–5.47 eV), and Pd (5.22–5.60 eV), promotes charge separation by enabling electron transfer from the bimetallic cocatalyst to the TiO_2 semiconductor during the photocatalytic reaction.⁵ This process is expected to be further enhanced by the high intrinsic reactivity of the Pd-rich shell produced by ball milling, while photo-generated holes preferentially accumulate on the Pd shell. The combined effect of hot-electron generation, efficient interfacial charge separation, and the reactive Pd-rich shell suppresses electron-hole recombination and prolongs the lifetime of the photogenerated charge carriers, in agreement with the photoluminescence results (Figure S8a).

3. CONCLUSIONS

One-pot mechanochemical synthesis enables the formation of Au(core)-Pd(shell) nanoparticles on TiO_2 with outstanding photocatalytic performance and stability for hydrogen evolution. The simultaneous co-milling of metals and support is essential to induce atomic-level mixing and create the unique Au-Pd- TiO_2 interfacial environment responsible for the observed synergistic enhancement, an effect absent in conventionally prepared or thermally treated samples. Experimental and theoretical analyses converge to show that the Au core electronically modulates the Pd shell, weakening its interaction with TiO_2 and preserving a greater number of reactive Pd sites. This configuration enhances charge separation, accelerates interfacial charge transfer, and maximizes catalytic efficiency. Beyond this specific system, the principles established here offer a promising route for the rational design of advanced bimetallic photocatalysts. By engineering core-shell architectures that combine high-electronegativity cores with catalytically active shells, new avenues are opened for the development of next-generation photocatalysts for solar-to-fuel conversion.

4. METHODS

4.1. Materials

All reagents were used directly as provided commercially without any further purification. Palladium (II) acetate (Acros Organics, 47.5% Pd), gold (III) acetate (Alfa Aesar, 99.9%), commercial TiO_2 P90 (Degussa) were used. Absolute ethanol and acetone were purchased from Scharlau. Milli-Q water (H_2O) was routinely used.

4.2. Preparation of $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$

For the bimetallic photocatalysts, varying amounts of gold (III) acetate (0.0057–0.0000 g) and palladium (II) acetate (0.0000–0.0063 g) were mixed with TiO_2 P90 in a 10 mL stainless-steel jar to achieve a nominal total noble metal loading of 1 wt%. Milling was performed at 15 Hz for 10 min with a ball-to-powder ratio (BPR) of 45 using a single 15 mm stainless-steel ball, following previously optimized conditions,^{38,41} unless otherwise specified. The obtained photocatalysts were labeled as $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$, where *n* refer to the molar content with respect to Pd.

4.3. Preparation of $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$

According to the photocatalytic performance of the $\text{Au}_n\text{Pd}_1/\text{TiO}_2\text{-BM}$ photocatalysts, the highest H_2 production was observed at an Au/Pd molar ratio of 1.6. Consequently, the same amount of Au acetate (0.0043 g) and Pd acetate (0.0016 g) were decorated on the surface

of TiO_2 (0.2941 g) by the incipient wetness impregnation method. Pd (II) acetate and Au (III) acetate powders were dissolved in 5 mL of acetone and glacial acetic acid, respectively. The obtained solutions were dropped simultaneously on TiO_2 P90 powders. The resulting slurry was dried in air at 50 °C for 3 h, followed by a calcination treatment at 300 °C for 3 h (denoted as $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-IWI}$).

4.4. Other Reference Photocatalysts

To investigate the influence of milling sequence on the catalytic activity of photocatalysts, Au, Pd and TiO_2 were added into the milling jar in different orders with the same milling parameters. For instance, a mixture of Au acetate and TiO_2 P90 was first milled for 10 min at 15 Hz, then Pd acetate was added for a further 10 min milling to obtain the $\text{Pd}_1\text{-Au}_{1.6}\text{TiO}_2\text{-BM}$. Likewise, the sample $\text{Au}_{1.6}\text{-Pd}_1\text{TiO}_2\text{-BM}$ was also prepared by two independent milling steps of 10 min each by exchanging the Au and Pd orders. The sample $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BM}$ was calcined at the same temperature as the IWI sample (300 °C for 3 h), denoted as $\text{Au}_{1.6}\text{Pd}_1/\text{TiO}_2\text{-BMC}$. A BPR value of 45 was used for the preparation of all reference photocatalysts.

4.5. Photocatalyst Characterization

X-ray diffraction (XRD) was collected on a Bruker D8 diffractometer using a Cu K α radiation source ($\lambda = 1.541 \text{ \AA}$). In a typical experiment, the 2 θ diffraction (Bragg) angles were measured by scanning the goniometer from 20° to 80° with a step size of 0.02° and dwell time of 1 s. Ultraviolet-visible diffuse reflectance spectra were collected using a UV-VIS-NIR spectrometer (Shimadzu UV-3600). The measurement was performed at room temperature by using BaSO_4 as a reference standard. The obtained diffuse reflectance data in a wavelength range of 200–800 nm was converted to absorbance spectra through Kubelka-Munk function. Tauc plots were used to estimate the band gap energy (E_g) of photocatalysts from UV-vis spectra based on $[F(R_\infty) E]^{1/2}$ versus photo energy *E*, where $R_\infty = R_{\text{sample}}/R_{\text{BaSO}_4}$. Raman spectroscopy was collected with a Renishaw's inVia Qontor Raman microscope (Leica DM2700 M) over the range of 50–800 cm^{-1} . A laser excitation source of 532 nm, grating of 2400 lines mm^{-1} and laser power of 1 mW cm^{-2} were kept for all measurements. Scanning electron microscopy (SEM) was performed using a Zeiss Neon40 Crossbeam Station operated at 5 kV. The steady-state photoluminescence (PL) spectra were recorded under an excitation of 290 nm through a Fluorolog Horiba Jobin Yvon spectrofluorometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a SPECS system equipped with a PHOIBOS 150 EP hemispherical energy analyzer, an MCD-9 detector and an XR-50 X-ray source operating at 150 W. C 1s signal at 284.8 eV was used as the reference to calibrate the binding energy (BE). The fitting procedure was based on the binding-energy positions of the peaks, the spin-orbit splitting values, the full width at half maximum (FWHM), and the relative separations between the signals associated with the different oxidation states of the same element. Table S3 summarizes the parameters used for the deconvolution of the Au 4f and Pd 3d spectra. High angle annular dark field images (HAADF-STEM) were acquired using a double-corrected Scanning Transmission electron microscope (ThermoFisher SPECTRA 300) located in the ALBA synchrotron, which was operated at 200 kV. The HAADF images were obtained using a convergence semi-angle of around 20 mrad and collection angles of around 67–200 mrad. EDX maps were obtained using a 4-quadrant windowless SuperX detector. Au L_{3-} and Pd K-edge X-ray absorption spectroscopy (XAS) measurements were carried out at the NOTOS beamline (BL16) at the ALBA Synchrotron Light Facility. The synchrotron radiation emitted by a bending magnet was monochromatized using a double crystal Si(111) monochromator, and the rejection of higher harmonics was performed by choosing appropriate angles and coatings of the collimating and focusing mirrors. The catalysts were pressed into pellets and all spectra were recorded in fluorescence mode using a 13-channel silicon drift detector. The slit gap in front of the I_0 ionization chamber was adjusted for each sample to ensure correct deadtime

values. Energy calibration was carried out using Au and Pd foils at the Au L₃- and Pd K-edges, respectively. XANES and EXAFS data reduction and normalization were performed using the Athena software package, by removing the atomic absorption background using a cubic spline and normalizing to the edge height. The k^2 -weighted χ spectra were Fourier-transformed into R-space using a k -range of 3.0–14.9 Å^{−1}. The actual metal loadings of the photocatalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 3200RL).

4.6. Photoelectrochemical Measurements

The photoelectrochemical (PEC) measurements were carried out on a Bio-Logic VMP3 multichannel potentiostat with a three-electrode configuration at room temperature. A Pt mesh (1 cm²), an Ag/AgCl (3.0 M) electrode (+0.205 V vs. NHE at 25 °C) and a fluorine doped tin oxide (FTO, $R = 7 \Omega$) glass loaded photocatalyst (10 mg) were employed as counter electrode, reference electrode and working electrode, respectively. An aqueous solution of Na₂SO₄ (0.5 M, 30 mL, pH = 7) was used as electrolyte. The FTO glasses were washed with acetone and absolute ethanol under ultrasonic bath three times alternately. The system was stabilized for at least 30 min at open circuit potential (OCP) prior to each measurement. Electrochemical impedance spectroscopy (EIS) was collected at 10 mV amplitude relative to OCP conditions at frequencies from 1 MHz to 10 mHz under a solar simulator (LCS-100 94011A, Newport). Transient photocurrent measurements were carried out under on/off cyclic light irradiation by manual chopping the light source at 30 s intervals.

4.7. Photocatalytic Tests

The photocatalytic hydrogen evolution reaction was carried out at room temperature and atmospheric pressure under dynamic conditions. An argon gas (Ar) stream (20 mL min^{−1}) was passed through a saturator, which contained a liquid mixture of water (H₂O, 150 g) and ethanol (EtOH, 17 g). The resulting gaseous mixture of H₂O, EtOH and Ar was directly introduced into the photoreactor. 9.4 mg of each photocatalyst was dispersed in 0.5 mL absolute ethanol and treated by ultrasonication for 10 min to form a homogeneous suspension. Afterward, the slurry was dropped onto a circular cellulose paper (from Albet, thickness 0.18 mm, area of 11.94 cm²) and dried at 50 °C for 1 h to achieve a homogeneous dispersion of the photocatalyst. This amount of photocatalyst corresponds to the optimized photocatalyst loading required to maximize photon transfer, in agreement with previous studies (Figure S9).³⁸ The impregnated paper was placed upside down in the middle of the glass photoreactor with two separated tubular sections, along with an O-ring. The light source was positioned at the bottom of the photoreactor. A K-type thermocouple was attached to the top part of the photoreactor in order to measure the temperature directly on the sample during the reaction. The thermocouple was connected to an automatic TC-08 data logger from Pico Technology, which was continuously recording data during the experiment. The gas hourly space velocity (GHSV) was 5583 h^{−1}. Prior to the photoreaction, the system was purged with Ar gas (20 mL min^{−1}) for 30 min. The products evolving from the outlet of the photoreactor were analyzed online every 4 min using a micro-gas chromatograph (Agilent 490) equipped with MS 5 Å, Plot U, and Stabilwax columns, enabling the comprehensive detection of products potentially generated through ethanol dehydrogenation, ethanol decomposition, and ethanol reforming reactions. Under light irradiation, only hydrogen and acetaldehyde were detected, in equimolar amounts, according to the reaction $C_2H_5OH \rightarrow H_2 + CH_3CHO$, demonstrating that ethanol dehydrogenation was the exclusive source of hydrogen production (Figure S10). No ethanol conversion was observed over any of the photocatalysts under dark conditions within the experimental conditions investigated, confirming that the reaction is purely photocatalytic. To assess long-term photostability, continuous reaction runs were conducted under UV irradiation for 20 h. Additionally, catalyst recyclability and operational dynamics under simulated solar irradiation

were further examined through seven consecutive light-on/light-off cycles, each consisting of 1 h of UV+visible illumination using a Hamamatsu LC8 solar simulator, followed by a 40-min dark purge. The apparent quantum yield (AQY) was evaluated using the equation:

$$AQY (\%) = \frac{2N_{H_2}}{N_P} \times 100 = \frac{2nN_A}{E_T/E_P} \times 100 = \frac{2nN_A}{(PSt)/(\frac{hc}{\lambda})} \times 100$$

where N_{H_2} and N_P represent the number of generated H₂ molecules and the number of incident photons reaching the sample, respectively. n and N_A refer to the H₂ moles evolved during the light exposure and the Avogadro constant, respectively. E_P and E_T are the energy of a photon and the total energy reaching the catalyst, respectively. P (W m^{−2}), t (s), and S (m²) are the power density of incident monochromatic light, the duration of the incident light exposure and the irradiation area, respectively.

4.8. First-Principles DFT Calculations

We performed first-principles calculations based on density functional theory (DFT) with the VASP software package,⁵⁸ using the PBE exchange-correlation functional and considering the following electrons as valence: Au 5d, 6s; Pd 4d, 5s; Ti 3d, 4s, 3p; O 2s, 2p.^{59–62} A “Hubbard- U ” scheme with $U = 3$ eV was employed for a better treatment of the localized Ti d electronic orbitals.⁶³ Wave functions were represented in a plane-wave basis truncated at 650 eV. For integrations within the Brillouin zone, a Monkhorst-Pack k -point grid was employed with a density equivalent to $16 \times 16 \times 12$ for the anatase unit cell. Geometry relaxations were performed by using a conjugate-gradient algorithm that allowed for cell shape variations and the geometry relaxations were halted when the forces on the atoms fell all below 0.005 eV Å^{−1}. By using these technical parameters, we obtained zero-temperature energies converged to within 0.5 meV per formula unit. The slab supercells contained a total of 384 Ti–O atoms (substrate) and 55 metallic atoms (cluster). A vacuum region of 30 Å thickness was considered in all the slab simulations.

Metallic cluster structures were relaxed on the TiO₂ surface slabs following the same electronic and ionic protocols as described above. A total of 60 different cluster orientations relative to the substrate were sampled in order to determine the lowest-energy configurations. Metallic cluster absorption energies were calculated as: $E_{\text{abs}} = E_{\text{M@anatase}} - E_{\text{anatase}} - E_{\text{M}}$, where $E_{\text{M@anatase}}$ is the energy of the cluster-TiO₂ system, E_{anatase} the energy of the anatase (001) TiO₂ slab, and E_{M} the energy of the isolated metallic cluster.

To simulate photoexcitation effects in cluster@TiO₂ systems, we used an effective DFT approach equivalent to that followed in previous works.^{64–66} This method consists in constraining the partial occupancies of electronic orbitals by adjusting the width of the corresponding Fermi smearing. In particular, a Fermi smearing of σ (eV) in the constrained DFT calculations implies considering the electronic occupation function $f(E, \sigma) = 1/(\exp[(E - E_F)/\sigma] + 1)$ instead of the usual step function $f(E) = 1$ for $E \leq E_F$ and $f(E) = 0$ for $E > E_F$. For a given σ , the corresponding light-excited electronic density in the conduction band, n , was estimated as the ratio of the number of electrons in the conduction band, N_{CB} , and volume of the TiO₂ substrate, namely, $n = N_{\text{CB}}/V_{\text{sub}}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.6c04991>.

Additional photocatalytic performance tests and results; XRD patterns; Raman spectra; UV-vis absorption spectra; SEM images; AC-HAADF-STEM images and corresponding elemental mappings; XPS spectra and results; XAS spectra; ICP-OES analyses; photoluminescence

spectra; and photoelectrochemical measurements (DOCX)

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Author Contributions

Y.C., L.S., and J.L. conceived the idea and analyzed the data. Y.C., A.A., and M.T. conducted the experiments. J.L., B.M., and K.G. performed the HAADF-STEM-EDX measurements. G.M. and C.C. performed the DFT study. M.A. performed the XAS measurements. All authors contributed to the writing and revision of the manuscript.

Notes

The authors declare no competing financial interest.

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