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PII: S2352-4928(26)01698-3

DOI: <https://doi.org/10.1016/j.mtcomm.2026.116309>

Reference: MTCOMM116309

To appear in: *Materials Today Communications*

Received date: 1 September 2026

Revised date: 27 September 2026

Accepted date: 3 October 2026

Please cite this article as: Filippo Pieretti, Leonardo Agnolon, Arthur Reymond, IbrahiM Abdelsalam, Almudena Marti, Nikolaos Dimitratos, Pedro H.C. Camargo and Robert Wojcieszak, Spectral-architectural tuning of Au–Pd nanocatalysts for on-demand photocatalytic HMF oxidation, *Materials Today Communications*, (2026) doi:<https://doi.org/10.1016/j.mtcomm.2026.116309>

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Spectral-architectural tuning of Au–Pd nanocatalysts for on-demand photocatalytic HMF oxidation

Filippo Pieretti,^{1,2} Leonardo Agnolon,^{1,3} Arthur Reymond,¹ Ibrahim Abdelsalam,⁴ Almudena Marti,¹ Nikolaos Dimitratos,² Pedro H. C. Camargo,⁴ Robert Wojcieszak^{1*}

¹ L2CM UMR 7053, Université de Lorraine, CNRS, Faculté des Sciences et Technologies, Vandœuvre-lès-Nancy, 54506, France

² Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna, Via Piero Gobetti 85, Bologna 40129, Italy

³ Dipartimento di Ingegneria Industriale, Università di Padova, Via Gradenigo 6/a, 35131 Padova, Italy

⁴ Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, PO Box 55, FIN-0014, Helsinki, Finland

Corresponding author: robert.wojcieszak@cnrs.fr

Abstract:

The selective oxidation of biomass-derived 5-hydroxymethylfurfural (HMF) into high-value intermediates and 2,5-furandicarboxylic acid (FDCA) is a key process in sustainable polymer manufacturing. However, conventional thermal processes often require harsh conditions that promote non-selective degradation or high-energy demand. Herein, we establish a comprehensive structure-light-reactivity relationship for the photo-assisted oxidation of HMF in water by systematically comparing zirconia-supported Au–Pd alloy and core–shell nanoarchitectures under thermal and photocatalytic conditions. Monochromatic irradiation at 365, 450, and 523 nm was employed to decouple the contributions of UV photolysis, visible-light activation, and localized surface plasmon resonance (LSPR) of gold. We identify the surface Pd density as the primary structural descriptor governing oxidation depth, while the nanoarchitecture dictates the light-harvesting mechanism. Under thermal conditions, the alloy configuration dominates through synergistic electronic and geometric ensemble effects. Intriguingly, this catalytic ranking undergoes a fundamental reversal under 450 nm irradiation, with the Pd-rich core–shell architecture (AuPd₅₀₀@ZrO₂) outperforming the alloy and achieving near-complete HMF conversion (99.1%), together with significant selectivity toward FDCA (24.9%) and FFCA (25.9%). At 523 nm, close to the Au LSPR maximum, the ranking reverses again in favor of the alloy configuration. This double reversal demonstrated a wavelength-gated reaction steering mechanism where, for a fixed Au-Pd composition, nanoarchitecture alone determines the activity and selectivity. Crucially, the wavelength-dependent response enables precise, external control over product distributions without altering the baseline reaction parameters. Operating in an aqueous medium under mild conditions with low precious-metal loadings, this work demonstrates that combining rational nanostructure design with targeted spectral inputs offers a powerful tool for overcoming conventional thermal Sabatier limitations in renewable carbon upgrading.

Keywords: Au, Pd, nanoparticles, core-shell nanostructures, bimetallic alloys, plasmonic photocatalysis, HMF oxidation, spectral tuning

1. Introduction

Bimetallic nanoparticles exhibit unique properties that enable their widespread application across diverse fields, including electronics, catalysis, and nanomedicine.^{1–6} Their functionalities can be precisely engineered by controlling their composition and atomic arrangement,⁷ a concept that has recently been extended to dynamic surface restructuring under reactive conditions.⁸ This versatility arises from the additional degrees of freedom compared to monometallic counterparts, whereby variations in composition, chemical ordering, and the relative positions of different constituent metal atoms allow for substantially greater tunability of the material properties.⁹ However, this increasing complexity makes atomic-level characterization of bimetallic nanomaterials challenging, as the experimental techniques often lack the spatial resolution and sensitivity required for precise characterization of surface sites.^{10,11} While electronic-structure calculations provide invaluable atomic-level insights, their application has largely been restricted to small heterometallic clusters, which may not accurately replicate the physical and catalytic properties of the larger nanoparticles typically employed in experimental applications.¹² Bridging this gap is crucial, particularly for optimizing catalytic processes such as the sustainable valorization of biomass, as transitioning from a fossil-fuel based economy towards a circular and biomass-derived economy is an urgent priority,¹³ contributing to mitigate anthropogenic CO₂ emissions.¹⁴ A prime example is the selective oxidation of 5-hydroxymethylfurfural (HMF),^{15,16} a key biomass derived platform molecule.^{13,17} As illustrated in Figure 1, HMF oxidation proceeds through competitive pathways, initially yielding either 2,5-di-formylfuran (DFF) or 5-hydroxymethyl-2-furancarboxylic acid (HMFCa). These intermediates are subsequently oxidized to 5-formyl-2-furancarboxylic acid (FFCA), before ultimately yielding the target monomer, 2,5-furandicarboxylic acid (FDCA).

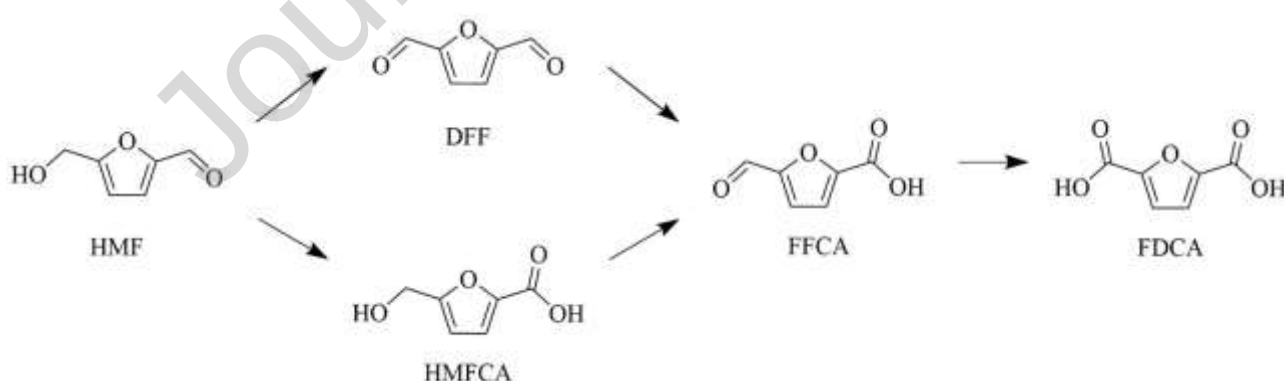


Figure 1. Reaction pathway for 5-hydroxymethylfurfural oxidation

As a key building block for bio-based polymers, FDCA can replace petroleum-derived terephthalic acid (PTA) in the manufacture of polyesters, polyamides, and polyurethanes.¹⁸ The predominant reaction pathways and resulting product selectivity are strongly influenced by reaction conditions, such as pH, which can stabilize specific intermediates.^{19,20} For instance, under alkaline conditions, HMFCa is preferentially formed over DFF, as hydroxide

ions (OH^-) promote the oxidation of the aldehyde group over the hydroxymethyl group.²¹ While the selective oxidation of HMF to FDCA frequently employs noble-metal catalysts, such as gold (Au),²² under pure oxygen or elevated air pressure, these systems typically also require elevated temperatures (80-150°C). Such harsh operating conditions present significant drawbacks, including high energy consumption and the thermal degradation of HMF and its intermediates, posing considerable challenges to industrial-scale production.^{23,24} Therefore, there is a need to develop more environmentally sustainable processes for HMF valorization, particularly towards FDCA as a high-value chemical building block.²⁵ The recent development of the industrial FDCA production process for PEF commercialization further highlights the industrial interest in replacing PET with PEF, a new bio-based polymer, which offers enhanced sustainability and distinctive material properties.^{25,26}

To mitigate these challenges, the choice of catalytic metal phase is crucial, as distinct electronic and surface properties fundamentally govern the reaction network. Recently, a direct comparison of the most widely studied noble metals (Au, Pt, and Pd) under identical aqueous-phase conditions established a clear structural hierarchy: Au (100) and Au (111) crystal facets exhibit superior catalytic activity towards complete oxidation to FDCA, whereas the Au (110) facet selectively yields the HMFC intermediate.²⁷ These differences in activity and selectivity are closely correlated with facet-dependent adsorption energies, revealing that HMF oxidation is dictated not by the bulk properties of the metal, but by the atomic-scale coordination geometry of surface sites.²⁸

In general, gold catalysts preferentially target the aldehyde ($-\text{CHO}$) group of HMF to form HMFC, owing to their ability to activate molecular oxygen and facilitate aldehyde oxidation while preserving the primary hydroxyl functionality under mild conditions.²⁷ This behavior is consistent with the preferential formation of HMFC under alkaline conditions. In addition, OH^- ions promote dehydrogenation, while gold (Au) NPs mediate electron transfer to molecular oxygen, together contributing to the high selectivity toward aldehyde oxidation. In contrast, palladium-based catalysts are highly active for the simultaneous oxidation of both the alcohol and aldehyde groups.²⁹ The divergent selectivities of Au and Pd originate from their distinct binding affinities towards oxygen species and reaction intermediates.³⁰

The existing literature has largely focused on the individual characterization of these catalyst architectures, with limited systematic comparative evaluation under identical experimental conditions. Recently, *Peng and co-workers*³¹ investigated whether the geometric arrangement of bimetallic Pd-Au active sites governs catalytic performance more strongly than their overall chemical composition in thermal catalysis. By comparing three distinct configurations, a physical mixture of monometallic particles, a core-shell architecture, and an alloy, the authors demonstrated an inverse correlation between the degree of alloying and catalytic efficiency. Interestingly, the physical mixture of Pd/C and Au/C outperformed the integrated bimetallic systems. This superior performance was attributed to the preservation of the distinct catalytic identities of the monometallic particles, which could operate synergistically while effectively bypassing the Cannizzaro disproportionation side reaction. However, this enhanced activity proved to be transient, as operando characterization revealed that Pd leaches from the support and redeposits onto Au/C particles, ultimately forming a core-shell structure that alters the catalytic landscape.

Despite these insights, a comprehensive side-by-side evaluation of different Au-Pd nanoarchitectures under both thermal and photocatalytic conditions, spanning UV, visible light, and plasmonic excitation, remains lacking. The absence of such comparative studies hinders a clear delineation of the relative advantages and limitations of each structural motif, thereby restricting the rational optimization of catalyst design for HMF oxidation. In particular, the complex interplay between nanoparticle composition, structural configuration, optical response, and light-induced charge-carrier dynamics has yet to be systematically elucidated.

In this work, we address these critical knowledge gaps through a systematic comparison of zirconia-supported Au-Pd core-shell and alloy nanoarchitectures for the selective thermal and photo-assisted oxidation of HMF toward FDCA. All catalysts were evaluated under strictly identical reaction conditions across both thermal and photocatalytic regimes, employing monochromatic irradiation at 365, 450, and 523 nm to probe UV, visible, and localized surface plasmon resonance (LSPR) excitation pathways, respectively. This systematic approach enables a direct assessment of how catalyst architecture and excitation wavelength modes govern catalytic activity, product selectivity, and structural stability. By decoupling structural and photophysical contributions to reactivity, this study provides mechanistic insights into the role of nanoarchitecture in thermally and light-driven HMF oxidation. These findings establish clear structure-function correlations and position nanoarchitecture as a design principle for controlling the outcome of light-driven catalysis, and developing efficient, robust, and economically viable Au-Pd catalytic systems for biomass valorization.

2. Results and discussion

2.1. Blank experiments

A series of control experiments was conducted to decouple photochemical, dark thermal, and base-driven contributions to HMF oxidation. Initial control reactions were conducted in the absence of both catalyst and NaOH (Table 1, entries 1-4), followed by the absence of catalyst and presence of NaOH (Table 1, entries 5-8), under monochromatic irradiation at 365, 450, and 523 nm establishing the non-catalytic baseline. To systematically decouple photothermal heating from photochemical conditions in the presence of catalysts, control reactions were performed under dark conditions at 40°C (Table 1, entries 9-16) serving as a dual purpose: quantifying the intrinsic thermocatalytic activity while providing a temperature-matched control corresponding to the steady-state photothermal heating of 39°C, generated by 10 W LED irradiation. Additionally, ZrO₂ was chosen as a support for its wide bandgap, ensuring photo-inactivity across all tested wavelengths (365, 450, and 523 nm) and thereby unambiguously correlate the observed photoactivity with the Au-Pd compositions. A fixed reaction duration of 4 h was intentionally selected to establish a standardized kinetic regime across all wavelengths (365, 450, and 523 nm) and nanoarchitectures (alloy and core-shell). This timeframe represents an optimal operational window that provides a sufficient dynamic range to discriminate product distribution and intrinsic catalytic activity under both UV and visible-light excitations, while avoiding kinetic saturation of intermediates.

Table 1. Decoupling Photolytic Over-Oxidation from Base-Mediated Deprotonation Kinetics

Entry	Light (nm)	Catalyst	NaOH (mol equiv.)	Temp (°C)	Conv. (%)	Selectivity (%)				C.B. (%)
						DF	HMFC	FFC	FDC	
						F	A	A	A	
1	365	-	-	-	62.5	0.0	0.1	0.1	0.0	37.7
2	450	-	-	-	1.3	7.3	4.8	0.0	0.0	98.9
3	523	-	-	-	0.0	0.0	0.0	0.0	0.0	99.7
4	-	-	-	40	4.8	0.0	0.2	1.1	0.0	95.5
5	365	-	2:1	-	45.9	0.3	4.3	4.8	0.0	58.4
6	450	-	2:1	-	33.5	0.0	4.3	0.4	0.0	68.1
7	523	-	2:1	-	15.3	0.0	4.4	0.0	0.0	85.4
8	-	-	2:1	40	11.1	0.0	5.7	0.5	0.0	89.6
9	-	Au/ZrO ₂	2:1	40	90.7	0.0	96.2	1.8	0.3	95.4
10	-	Pd/ZrO ₂	2:1	40	62.3	0.0	46.8	42.3	4.8	96.1
11	-	ZrO ₂	2:1	40	14.8	0.0	11.6	0.9	0.0	87.0
12	-	AuPd ₁₀ @ZrO ₂	2:1	40	31.4	0.0	50.5	1.2	0.0	84.8
13	-	AuPd ₅₀₀ @ZrO ₂	2:1	40	70.3	0.5	42.5	38.5	3.2	89.3
14	-	Au ₃ Pd ₁ /ZrO ₂	2:1	40	99.5	0.0	88.9	6.1	1.6	96.6
15	-	Au ₁ Pd ₁ /ZrO ₂	2:1	40	77.5	0.0	86.2	10.1	0.6	97.9
16	-	Au ₁ Pd ₂ /ZrO ₂	2:1	40	96.2	0.0	69.8	31.4	12.1	96.0

Under these catalyst- and base-free conditions (Table 1, entries 1–4), HMF conversion remained negligible under visible light irradiation at 450 and 523 nm, confirming that direct photolysis in the visible region does not significantly promote HMF oxidation. In contrast, substantial HMF conversion (62%) was observed under UV irradiation at 365 nm (Table 1, entry 1), which can be attributed to higher energy UV photons. However, this conversion was accompanied by a pronounced decrease in carbon balance (38%), suggesting the occurrence of non-selective degradation pathways, potentially including the over-oxidation to CO₂ and/or the formation of insoluble humins.³² In these baseline experiments, HMFC and DFF were the only detected products, while FFCA and FDCA were not observed. These results indicate that, in the absence of both catalyst and base, oxidation of the aldehyde group to HMFC is kinetically favored over oxidation of the hydroxymethyl functionality.¹¹

Control reactions were subsequently performed in the absence of catalyst but in the presence of base (entries 5–8) to evaluate the base-driven oxidation pathways. The introduction of hydroxide ions markedly enhanced HMF conversion at all irradiation wavelengths, confirming the important mechanistic role of OH⁻ in promoting deprotonation and facilitating oxidative pathways.^{27,33} Under these conditions, the reaction temperature increased from ambient to 39 °C as a result of radiant heating from the LED source, thereby introducing a modest thermal contribution. Although the presence of base substantially enhanced HMF conversion, it also promoted undesired side reactions, including humin formation and base-induced degradation pathways, resulting in a noticeable loss of carbon balance.^{27,34} This effect was particularly pronounced at higher irradiation energies, where the carbon balance decreased despite the higher conversion rates. Notably, the product

distribution exhibited a strong wavelength dependence. Under 450 nm irradiation, the selectivity shifted toward FFCA formation, whereas in the absence of base, DFF was the predominant intermediate. These findings demonstrate that both irradiation wavelength and the base concentration strongly influence the reaction network, altering the competition between the aldehyde-first and alcohol-first oxidation pathways.

The observed decrease in the carbon balance may be associated with partial mineralization of HMF to CO₂ and/or the formation of undetected degradation products. This hypothesis could be further supported by quantifying dissolved inorganic carbon species in the aqueous phase through changes in HCO₃⁻/H₂CO₃ concentrations before and after reaction.³⁵ While HMFCa selectivity remained generally high under most of the evaluated conditions, a notable exception observed under 450 nm irradiation, where FFCA formation became favored. Taken together, these results clearly demonstrate that the excitation wavelength plays a decisive role in determining product distribution, in agreement with recent findings by *Reymond et al.*¹⁶ who identified irradiation wavelength as a key selectivity-determining parameter alongside shell thickness. Following these control experiments, thermal catalytic tests were conducted using Au_xPd_y catalysts supported on ZrO₂ featuring either core-shell (Au_xPd_y@ZrO₂) or alloy (Au_xPd_y/ZrO₂) architectures to elucidate the influence of nanoarchitecture on catalytic performance.

2.2. Thermal catalysis: core-shell vs alloy architectures

A direct comparison between the core-shell AuPd₁₀@ZrO₂, AuPd₅₀₀@ZrO₂ catalysts with supported Pd/ZrO₂ under thermal conditions (Table 1, entries 10, 12 and 13) reveals a clear dependence of HMF conversion on Pd content. Increasing the Pd loading enhances HMF conversion and is accompanied by an improvement in the carbon balance, from 84.8% for AuPd₁₀@ZrO₂ to 89.3% for AuPd₅₀₀@ZrO₂ and 96.1% for Pd/ZrO₂. However, selectivity toward FDCA remains negligible for AuPd₁₀@ZrO₂ (0.0%) and increases only marginally for AuPd₅₀₀@ZrO₂ (3.2%) and Pd/ZrO₂ (4.8%). These results indicate that the core-shell architecture, even at high Pd content, promotes HMF conversion but does not efficiently direct the reaction toward the deeper oxidation steps required for FDCA formation.

In contrast, the Au_xPd_y/ZrO₂ catalysts featuring an alloy architecture exhibit distinct behavior. As the Pd content increases (Table 1, entries 14, 15, and 16), HMF conversion increases, following a trend similar to that observed for the core-shell systems. Crucially, however, the alloy catalysts maintain a relatively high carbon balance, while FDCA selectivity increases with increasing Pd fraction, from 1.6% to 12.1%. This trend suggests that Pd plays an important role in promoting deeper oxidation, while alloying in an intimate atomic-scale mixing with Au modifies the electronic environment and adsorption properties of the active sites, lowering the activation barriers for consecutive oxidation steps more effectively than isolated core-shell interfaces under thermal activation, thereby facilitating the sequential oxidation of HMF-derived intermediates.³⁶ These observations are consistent with previous reports highlighting the enhanced performance of integrated Au–Pd alloy catalysts for HMF oxidation.³⁷ Overall, these results demonstrate that, under thermal conditions, the alloy architecture is more effective than the core-shell architectures in driving the reaction network toward complete HMF oxidation. In particular, the highest FDCA selectivity obtained for the alloy system (12.1%) is substantially higher than that observed for the corresponding core–

shell catalyst with comparable Pd enrichment (3.2%). This contrast highlights the importance of atomic-scale metal arrangement, rather than Pd content alone, in determining the product distribution.

2.3. Photocatalytic performance of core-shell $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts

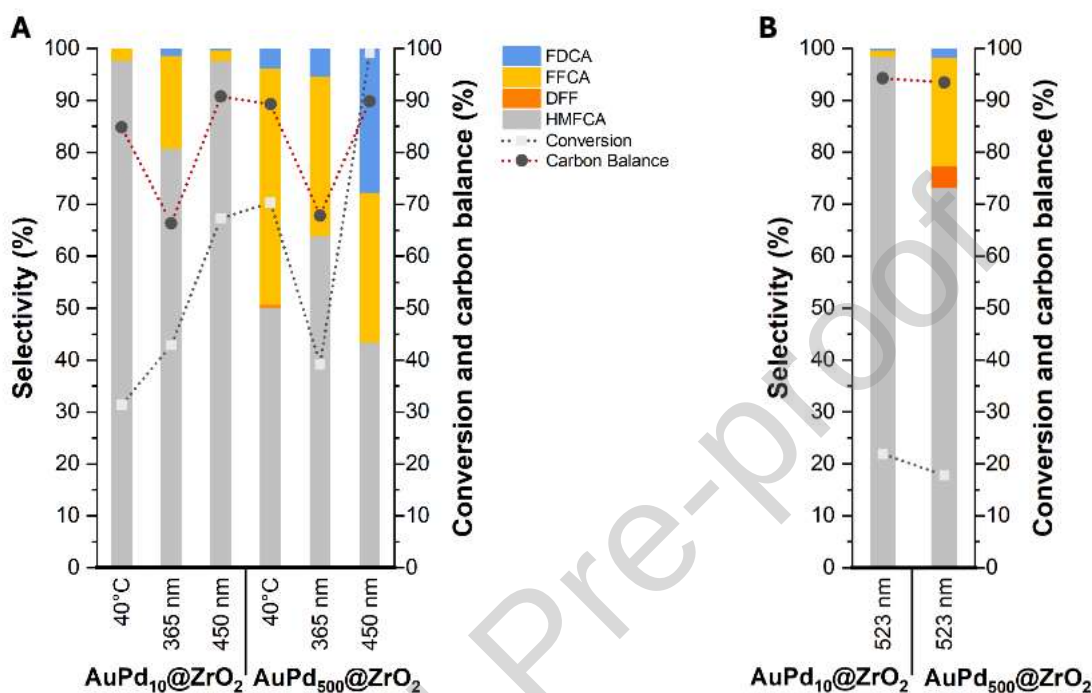


Figure 2. Photocatalytic performance of $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts with core-shell architecture

Figure 2 compares the performance of two core-shell $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts with distinct Pd loadings (AuPd_{10} and AuPd_{500}), enabling a direct evaluation of the effect of surface Pd enrichment under monochromatic irradiation. In addition to these, two intermediate compositions, $\text{AuPd}_{100}/\text{ZrO}_2$ and $\text{AuPd}_{200}/\text{ZrO}_2$, were also synthesized and characterized (Figures S4-S8, and S9); and their photocatalytic performances are reported in the Supporting Information (Figures S10-S12). The photocatalytic behavior of the unsupported Au–Pd core–shell nanoparticles is also provided in the Supporting Information and reveals a detrimental effect on catalytic activity in the absence of the ZrO_2 support (Figures S11-S12). Specifically, ZrO_2 support was selected to its wide bandgap, which prevents direct photoexcitation across the entire irradiation range employed (365–523 nm), thereby ensuring that the observed activity originates from the Au–Pd nanoparticles. However, it plays a crucial role as a high surface area dispersant and provides metal-support interactions (SMSI) that enable to modulate interfacial electronic state and stabilize active sites.^{38,39} Here, we focus on the two extreme compositions to highlight the effect of Pd surface enrichment more clearly. A clear, Pd-dependent photocatalytic behavior is observed across the evaluated conditions. For the $\text{AuPd}_{10}/\text{ZrO}_2$ system, irradiation at 450 nm provides the highest photocatalytic performance, increasing HMF conversion from 31.4% under dark thermal conditions to 67.3% under catalysis. Despite this substantial enhancement in activity, product formation remains strongly biased toward HMFCa, with a

selectivity of 84.2%. This result indicates that while visible-light excitation accelerates the initial oxidation of the aldehyde group, it cannot efficiently promote the subsequent oxidation steps required for FDCA formation. Thus, at low Pd loading, photocatalysis enhances overall HMF conversion but does not substantially increase the oxidation depth. In contrast, the Pd-rich AuPd₅₀₀@ZrO₂ catalyst exhibits a markedly different catalytic behavior. Under thermal conditions, it achieves 70% conversion with good carbon balance (89%), but a marginal FDCA selectivity (~3%), yielding HMFCa and FFCA in nearly equimolar proportions. Under higher-energy UV irradiation at 365 nm, HMF conversion decreases to 39% and is accompanied by a lower carbon balance, indicating that competitive, non-selective photodegradation pathways become prominent at higher photon energies. This behavior is consistent with the control experiments discussed above (Table 1, Entry 1). Remarkably, shifting the excitation wavelength to 450 nm allows AuPd₅₀₀@ZrO₂ catalyst to reach near-complete HMF conversion (99.1%) while maintaining an excellent carbon balance (89.9%). More importantly, FDCA selectivity reaches 24.9%, accompanied by 25.9% selectivity toward FFCA. This result demonstrates that visible-light excitation, combined with a high surface concentration of Pd, can efficiently promote deeper oxidation along the consecutive HMF → HMFCa/DFF → FFCA → FDCA reaction pathway. The simultaneous formation of FFCA and FDCA further suggests that the reaction proceeds beyond the primary oxidation products rather than being limited by the accumulation of HMFCa or DFF. Taken together, these results indicate that Pd surface enrichment plays a central role in determining both HMF conversion and oxidation depth, while the presence and arrangement of Au influence the electronic and optical properties of the bimetallic nanoparticles.^{36,40,41} Increasing the Pd surface concentration therefore enhances the accessibility of sites capable of promoting the consecutive oxidation steps, whereas the specific nanoarchitecture determines how these surface sites interact with the incident light.

To systematically assess the potential contribution of the LSPR of Au, catalytic tests were also conducted at 523 nm, a wavelength typically associated with plasmonic excitation of Au nanoparticles. However, in the AuPd₅₀₀@ZrO₂ core-shell structure, the Au core is encapsulated by multiple Pd shells, rendering the outer catalytic surface predominantly Pd-terminated (Figures 7 and S8). Consistent with this structural arrangement, the catalytic activity at 523 nm is significantly lower than at 450 nm for both core-shell catalysts. The lower photon energy, combined with the limited accessibility of the Au core, is expected to strongly attenuate any direct contribution from Au-centered LSPR to the observed photocatalytic activity. The HMF conversion values obtained for AuPd₁₀@ZrO₂ and AuPd₅₀₀@ZrO₂ at 523 nm are also relatively similar, further suggesting that increasing the Au core size or Pd shell thickness does not provide a significant photocatalytic advantage under these conditions. Nevertheless, AuPd₅₀₀@ZrO₂ catalyst generates higher fractions of FFCA and DFF compared to AuPd₁₀@ZrO₂ under 523 nm irradiation, further highlighting the influence of surface Pd on the reaction pathway. In particular, the enhanced formation of DFF over the Pd-rich catalyst suggests that a higher Pd surface density facilitates oxidation of the primary alcohol (hydroxymethyl) group, thereby enabling the reaction network to proceed through alternative or parallel oxidation pathways. Overall, these results highlight the strong dependence of light-driven catalytic behavior on nanoparticle nanoarchitecture. In core-shell configurations where Au is not directly exposed at the surface, the outer Pd

shell acts as a plasmonic-damping layer, attenuating direct Au-centered plasmonic excitation, and photocatalytic performance is governed predominantly by the surface chemistry of the outer Pd shell. More importantly, the comparison between 450 and 523 nm demonstrates that the photocatalytic response cannot be attributed solely to the presence of Au or to plasmonic excitation, but instead results from the interplay between excitation wavelength, nanoparticle architecture, and surface Pd composition.

2.4. Photocatalytic performance of alloyed $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts

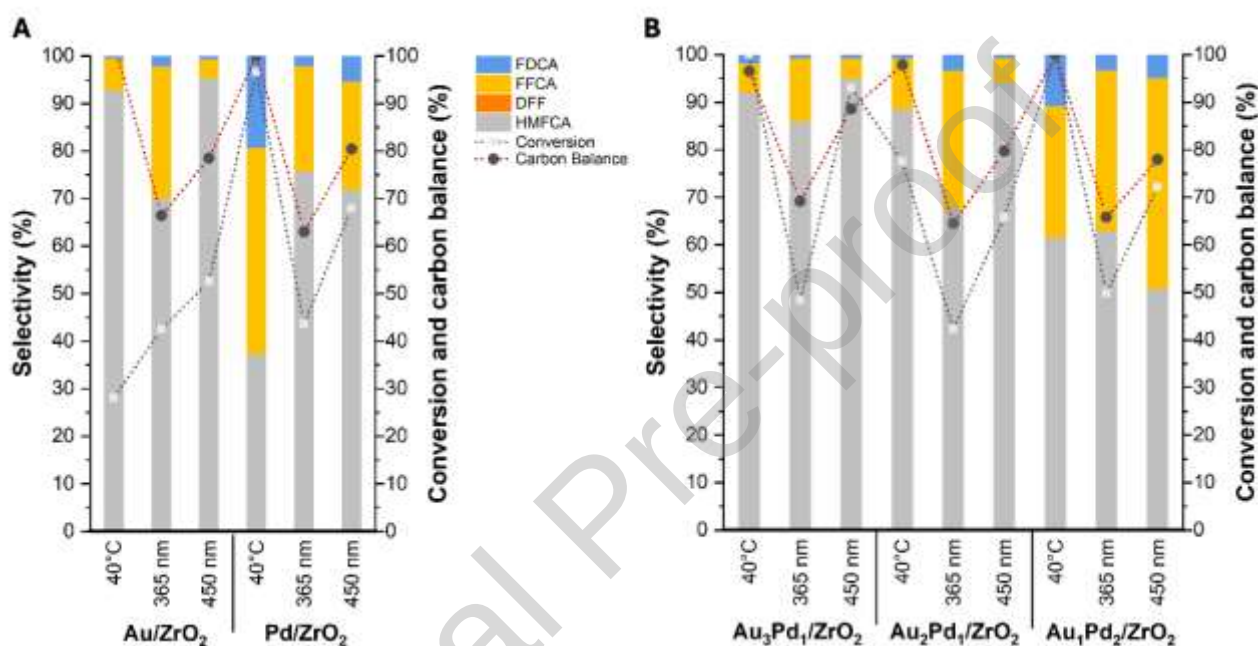


Figure 3. Photocatalytic performance of $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts with different Au molar ratios

Figure 3 compares the photocatalytic performance of $\text{Au}_x\text{Pd}_y/\text{ZrO}_2$ catalysts featuring an alloy architecture with different Au molar ratios. A distinct, wavelength-dependent trend is observed across all alloy compositions. Monochromatic irradiation at 450 nm consistently provides the highest catalytic activity, whereas UV excitation at 365 nm results in the lowest conversion and a substantially reduced carbon balance, which may be associated with the formation of humins, soluble oligomers, and/or other unidentified degradation products.^{32,42} Dark thermal catalysis generally exhibits an intermediate performance profile, with the notable exception of $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$ catalyst. Under thermal conditions, $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$ alloy achieves complete HMF conversion (100%) with a FDCA selectivity of 12.1% while maintaining a high carbon balance of 96%. The high activity of this particular composition may be related to the high density of exposed Au–Pd interfacial sites, which have been widely reported to promote oxidation reactions through synergistic geometric and electronic effects.⁴³ Under 365 nm irradiation, the alloy catalysts behave similarly to core–shell systems, exhibiting substantially lower carbon balances and reduced product selectivities, consistent with the occurrence of non-selective over-oxidation and degradation pathways. In contrast, irradiation at 450 nm provides a more favorable balance between activity and product selectivity. Under these conditions, $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$ displays high HMF conversion and

a relatively stable carbon balance, with selectivities of 3.3% toward FDCA and 30.7% toward FFCA. Importantly, a clear compositional trend emerges under visible-light irradiation. As the composition shifts from $\text{Au}_3\text{Pd}_1/\text{ZrO}_2$ to $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$, the product distribution is progressively shifted away from HMFCa and toward the more deeply oxidized products FFCA and FDCA. This evolution indicates that increasing the surface Pd fraction facilitates the sequential oxidation of HMF-derived intermediates. The progressive decrease in HMFCa accumulation, accompanied by an increase in FFCA and FDCA formation, suggests that Pd-rich alloy surfaces favor the further transformation of primary oxidation products rather than their accumulation.

Mechanistically, the enhanced performance of the alloy catalysts can be rationalized by the intimate atomic-level mixing of Au and Pd inherent to the alloy architecture, in contrast to the spatially segregated metal domains present in the core-shell architectures. Such bimetallic integration can modify the local electronic environment of Pd and Au and thereby influence the adsorption and activation of oxygen-containing furan intermediates.^{36,41} This fine electronic and geometric tuning interplay may effectively facilitate the sequential oxidation steps required to reach FFCA and FDCA. The higher performance of Pd-rich compositions is therefore consistent with a greater contribution from Pd-containing active sites to the deeper oxidation pathway. Furthermore, under 450 nm irradiation, the additional light input further enhances the catalytic response of the alloy systems. The pronounced improvement relative to the corresponding dark thermal conditions suggests that the incident light contributes to the observed reactivity through a combination of photothermal and/or photoinduced electronic excitation within the metallic alloy nanoparticles. Importantly, the moderate photon energy at 450 nm provides substantially higher conversion while avoiding the severe carbon losses observed under 365 nm irradiation. This wavelength-dependent behavior highlights the ability of the Au-Pd alloy architecture to couple compositional tuning with spectral control of HMF oxidation.

2.5. Direct comparison: Alloy vs. core-shell architectures

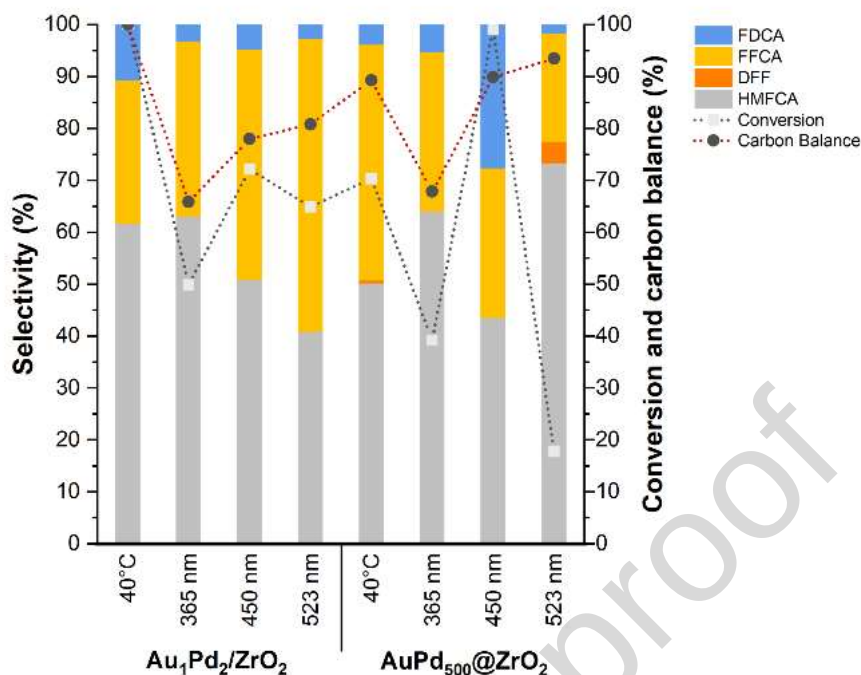


Figure 4. Comparison of alloyed $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$ and core-shell $\text{AuPd}_{500}@\text{ZrO}_2$ catalysts

Figure 4 directly contrasts the catalytic profiles of the alloyed $\text{Au}_1\text{Pd}_2/\text{ZrO}_2$ and the core-shell $\text{AuPd}_{500}@\text{ZrO}_2$ systems, highlighting the decisive role of metallic nanoarchitecture under different excitation conditions. Under thermal catalysis, the alloy configuration clearly outperforms the core-shell counterpart in terms of FDCA selectivity. This behavior is consistent with the enhanced synergistic interaction and geometric ensemble effects characteristic of intimate, atomic scale mixing of Au and Pd. This trend aligns seamlessly with established literature demonstrating that active sites situated at Au-Pd interfaces dramatically lower the activation barriers of oxygenated intermediates and thereby facilitate consecutive oxidation steps.⁴¹ Conversely, under high-energy irradiation at 365 nm, both catalysts exhibit substantially reduced carbon balances and compromised product selectivities.⁴⁴ This deterioration is consistent with the occurrence of non-selective photodegradation and radical driven over-oxidation pathways induced under high-energy irradiation.⁴⁵ Importantly, the similarity of this behavior for the two nanoarchitectures indicates that the beneficial effect of structural control is strongly dependent on the excitation regime.

The structural characteristics of the monometallic reference catalysts were first evaluated by electron microscopy. As shown in Figure 5A–F, the HAADF-STEM images reveal well-dispersed Au/ZrO_2 and Pd/ZrO_2 nanoparticles with relatively uniform particle distributions.

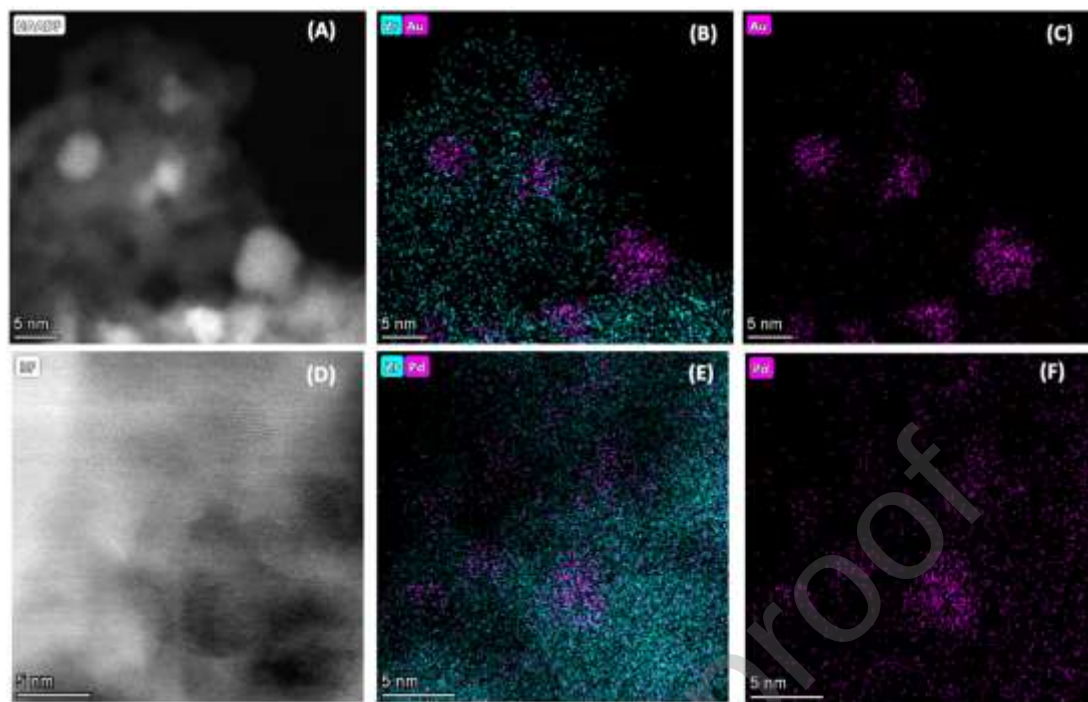


Figure 5. HAADF-STEM images of the Au/ZrO₂ and Pd/ZrO₂ catalysts

The structural integrity and elemental distribution of the bimetallic alloy system were subsequently investigated using high-resolution electron microscopy. The HR-TEM and HAADF-STEM images (Figure 6A–D) provide evidence for the alloyed architecture, with Au and Pd distributed throughout the nanoparticles. The corresponding STEM-EDS elemental maps (Figure 6B–D) further confirm the spatial distribution and intimate mixing of Au and Pd within the analyzed particles.

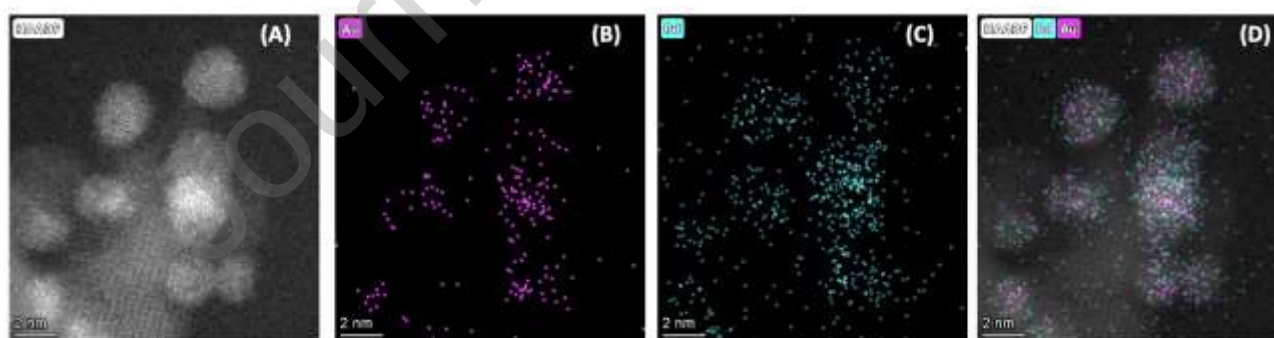


Figure 6. Structural and compositional characterization of Au₃Pd₁/ZrO₂. (A) HAADF-STEM image. Corresponding STEM-EDS elemental maps of the region in: (B) Au, (C) Pd, and (D) the Au₃Pd₁/ZrO₂ overlay

The same characterization methodology was applied to the core-shell AuPd₅₀₀@ZrO₂ catalyst (Figure 7A–D and Figure S8 A–F). In this case, the elemental maps clearly reveal an Au-rich core surrounded by a Pd-rich shell, confirming the intended core-shell nanoarchitecture. The spatial segregation of Au and Pd is particularly relevant to the photocatalytic behavior because the outer surface is predominantly Pd-terminated, whereas the Au component is located beneath the shell.

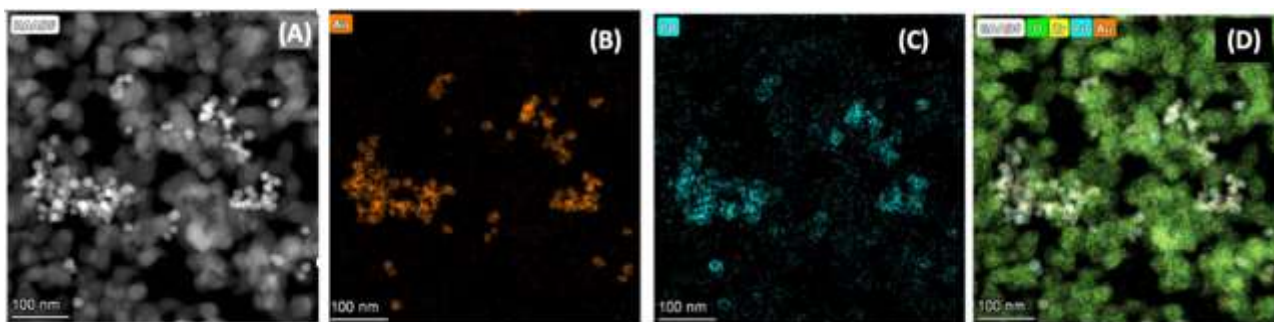


Figure 7. Structural and compositional characterization of $\text{AuPd}_{500}@\text{ZrO}_2$. (A) HAADF-STEM image. Corresponding STEM-EDS elemental maps of the region in: (B) Au, (C) Pd, and (D) the $\text{AuPd}_{500}@\text{ZrO}_2$ overlay

The transition from purely thermally driven to light-assisted reactivity further highlights the importance of the Au–Pd nanoarchitecture. UV-Vis spectroscopy (Figure 8) shows that, despite the substantial Pd shell thickness in AuPd_{500} , a broad optical feature remains in the vicinity of 520 nm. This persistent optical feature indicates that the Au core retains a residual localized surface plasmon resonance (LSPR) feature near 520 nm, although its intensity is progressively attenuated as the Pd shell thickness increases. This observation provides evidence that the optical properties of the Au core remain electronically active, with the near-field electromagnetic enhancement effectively extends into the surface Pd layers to modulate localized electronic states despite shell attenuation. Interestingly, moving to the visible light regime, irradiation at 450 nm induces a striking reversal in catalytic ranking. While the alloy structure exhibits superior performance under purely thermal conditions, the Pd-rich core–shell catalyst ($\text{AuPd}_{500}@\text{ZrO}_2$) becomes the most selective system for deep oxidation, yielding 24.9% of FDCA and 25.9% of FFCA. The preferential activation under 450 nm monochromatic excitation wavelength is consistent with the residual optical absorption of the core–shell nanoparticles, suggesting that the Au core may contribute to the enhanced photocatalytic response through plasmon-mediated effects, although the precise contribution of near-field enhancement and/or hot-carrier processes cannot be distinguished solely from the steady-state catalytic and UV–Vis measurements, as illustrated in Figure 8.

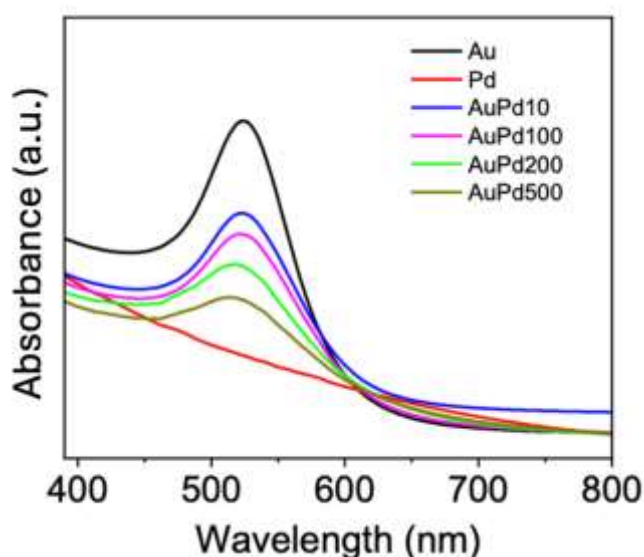


Figure 8. UV-Vis absorption spectra of the $Au_xPd_y@ZrO_2$ catalysts

The different catalytic responses of the alloy and core–shell systems therefore reveal a pronounced architecture-dependent reversal of the structure–activity relationship. Under purely thermal conditions, the intimate mixing of Au and Pd in the alloy provides a high density and statistical distribution of chemically coupled bimetallic sites, which favors the consecutive oxidation of HMF-derived intermediates. However, under 450 nm irradiation, the spatial separation of the light-absorbing Au core from the Pd-rich catalytic surface appears to become advantageous. In this context, the $AuPd_{500}@ZrO_2$ architecture can be rationalized through an antenna-reactor framework, where the Au core acts as an optical antenna concentrating photon energy while the outer Pd shell serve as the catalytic reactor driving surface oxidation. Therefore, this architecture potentially decouples light harvesting from surface catalysis, allowing the Au core to contribute to the photophysical response while the crystalline Pd shell provides an optimized surface-dominated chemical environment, creating a synergistic effect that drives deep oxidation pathways more efficiently than random alloyed configurations. The progressive attenuation of the plasmon band with increasing Pd shell thickness nevertheless does not completely eliminate the optical response of $AuPd_{500}@ZrO_2$. One possible interpretation is that the electromagnetic field generated by the Au core extends into the surrounding Pd shell and influences the electronic environment of the surface Pd sites. However, this near-field contribution should be regarded as a plausible mechanism rather than a direct demonstration based solely on the UV–vis data. Additional time-resolved spectroscopic measurements would be required to distinguish unequivocally between near-field enhancement, hot-carrier transfer, and photothermal contributions. The architectural divergence between the alloy and core–shell systems under visible-light irradiation can therefore be rationalized in terms of their different photon-harvesting and charge-transfer environments. In the core–shell $AuPd_{500}@ZrO_2$ catalyst, the resulting spatial separation of light absorption and surface reaction sites may favor a plasmon-mediated enhancement of the Pd-catalyzed oxidation pathway.⁴⁶ Conversely, the Au–Pd alloy provides intimate electronic coupling between the two metals throughout the nanoparticle, potentially facilitating light-induced electronic excitation and charge redistribution at catalytically accessible bimetallic sites.⁴³ This distinction becomes particularly evident at 523 nm, where the alloy architecture exhibits substantially higher HMF conversion than the core–shell system (64.9% versus 21.9%). At this wavelength, the stronger response of the alloy may reflect more efficient coupling between the optical excitation and the catalytically accessible bimetallic surface, whereas the thicker Pd shell in the core–shell architecture substantially attenuates the optical response of the buried Au core. Thus, the relative performance of the two architectures depends strongly on the excitation wavelength. Taken together, these results demonstrate that Au–Pd nanoarchitecture provides an additional degree of control over light-driven HMF oxidation. The alloy and core–shell structures do not simply differ in their intrinsic catalytic activity; they respond differently to the spectral input, resulting in a wavelength-dependent reversal of their catalytic ranking. One possible interpretation is that the electromagnetic field generated by the Au core extends into the surrounding Pd shell and influences the electronic environment of the surface Pd sites. However, this near-field contribution should be

regarded as a plausible mechanism rather than a direct demonstration based solely on the UV–Vis data. Additional time-resolved spectroscopic measurements would be required to distinguish unequivocally between near-field enhancement, hot-carrier transfer, and photothermal contributions.

3. Conclusion

This study establishes a comprehensive structure–light–reactivity relationship for the photo-assisted oxidation of HMF over zirconia-supported Au–Pd nanoarchitectures. By systematically comparing alloy and core–shell configurations under identical thermal and monochromatic irradiation conditions, we demonstrate that catalytic performance is governed by a delicate interplay between surface Pd availability, interfacial electronic coupling, and the energy of the incident photons. The results reveal a pronounced spectral–architectural switch in the catalytic behavior. Under 450 nm irradiation, the Pd-rich core–shell AuPd₅₀₀@ZrO₂ catalyst exhibits the highest activity and enhanced selectivity toward the deeper oxidation products, reaching 99.1% HMF conversion with 24.9% FDCA and 25.9% FFCA selectivity. The persistence of a plasmonic absorption feature near 520 nm suggests that the buried Au core serves as a remote light-harvesting antenna of the core–shell nanoparticles. The enhanced activity observed at 450 nm is therefore consistent with a plasmon-mediated contribution, potentially involving near-field electromagnetic enhancement and/or photoinduced electronic effects to activate the surface Pd sites. In contrast, the Au₁Pd₂/ZrO₂ alloy exhibits superior performance under thermal conditions and a markedly higher conversion than the core–shell catalyst at 523 nm via direct hot-carrier generation across unquenched bimetallic interfaces. The intimate atomic mixing of Au and Pd facilitates hot-carrier generation at the bimetallic interface, which, coupled with the absence of a plasmonic-quenching shell, allows for a more effective energy harvesting. These results demonstrate that the spatial arrangement of Au and Pd determines not only the intrinsic catalytic properties of the nanoparticles but also their response to external spectral excitation. Across both nanoarchitectures, the surface Pd density emerges as an important structural descriptor governing oxidation depth. Increasing the Pd fraction promotes the conversion of primary oxidation products toward FFCA and FDCA, whereas the specific nanoarchitecture acts as the spectral filter that determines which light-harvesting mechanism dominates. High-energy UV irradiation at 365 nm promotes non-selective degradation pathways and substantial carbon loss, highlighting the importance of excitation wavelength in maintaining catalytic selectivity. The use of 450 nm and 523 nm excitation, in contrast, provides a sustainable pathway to control the reaction network without requiring toxic additives or severe thermal conditions.

Overall, this work demonstrates that nanoarchitecture and excitation wavelength can be considered complementary design parameters for controlling photocatalytic HMF oxidation. By dynamically altering interfacial charge distribution via targeted spectral excitation, this photon-steered approach offers a rational strategy to bypass traditional Sabatier scaling constraints that intrinsically limit thermal biomass oxidation. The catalytic response can be modulated through the combined control of surface composition, metal arrangement, such as core-shell for near-field deep oxidation or alloy for hot-carrier-driven

kinetics, and catalytic pathways can be programmed with external light input, by dynamically altering interfacial charge distribution via targeted spectral excitation. This work provides a versatile blueprint for the design of next-generation photocatalysts, offering a robust strategy for the sustainable, energy efficient upgrading of renewable carbon resources.

4. Methods

4.1. Chemicals and materials

All chemicals were obtained from commercial suppliers and used without further purification. 5-(Hydroxymethyl)furfural (HMF, $\geq 99\%$), 2,5-furandicarboxylic acid (FDCA, 97%), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA, 97%), 5-formyl-2-furancarboxylic acid (FFCA, 98%), 2,5-diformylfuran (DFF, 97%), sodium borohydride (NaBH_4 , 99%), polyvinyl alcohol (PVA, MW 9,000–10,000 g mol⁻¹, 80% hydrolyzed), ascorbic acid ($\geq 99\%$), potassium hydroxide (KOH, $\geq 85\%$), sodium citrate tribasic dihydrate ($\geq 99\%$), tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), potassium palladium(II) chloride (K_2PdCl_4 , 99%), and zirconium dioxide (ZrO_2) were obtained from Sigma-Aldrich. Sodium hydroxide (NaOH, 97%) was purchased from Fisher Scientific. Ethanol (99.5%) and 2-propanol (99.9%) were from Ajax Finechem and Sigma-Aldrich, respectively. Deionized water (18.2 M Ω ·cm) was used throughout. All glassware was cleaned with freshly prepared aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$, v/v) prior to use.

4.2. Synthesis of alloyed AuPd nanoparticles

Au-based alloy nanoparticles were synthesized by the sol-immobilization method (Figure S1).⁴⁷

Aqueous solutions of the metal precursors (HAuCl_4 and K_2PdCl_4) were prepared at a total metal concentration of 0.13 mmol L⁻¹. Polyvinyl alcohol (PVA, M.W. 9,000–10,000 g mol⁻¹) was added as a stabilizing agent (PVA:metal weight ratio = 1.2:1) and the mixture was stirred for 3 min. A freshly prepared aqueous solution of NaBH_4 was then added (NaBH_4 : metal molar ratio = 5:1) to reduce the metal precursors; the immediate color change of the solution confirmed nanoparticle formation via plasmon resonance. After 30 min, ZrO_2 support powder was added and the suspension acidified below the isoelectric point of ZrO_2 to promote electrostatic adsorption of the nanoparticles onto the support. The slurry was stirred for 1 h, filtered over a Büchner funnel, washed with distilled water (~ 1 L) until neutral pH was achieved. The recovered solid was dried overnight at room temperature and subsequently at 80 °C for 4 h.

4.3. Synthesis of core-shell AuPd nanoparticles

AuPd core-shell nanoparticles were synthesized by a seeded-growth approach based on the Turkevich method.⁴⁸ Au seeds were prepared by adding $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (2 mL, 25 mM) to a boiling aqueous solution of sodium citrate (5 mg mL⁻¹, 95 mL) at 100 °C for 8 min. The Pd shell was deposited by stepwise reduction of Pd^{2+} onto the citrate-stabilized Au seeds: in each cycle, KOH (150 μL , 0.1 M), ascorbic acid (120 μL , 0.1 M), and PdCl_2 (30 μL , 0.1 M) were added sequentially to 10 mL of Au seed suspension at room temperature and

stirred for 30 min. One deposition cycle yielded Au@Pd-1L; three consecutive cycles yielded Au@Pd-3L. The resulting core-shell colloids were immobilized onto ZrO₂ following the same acidification and filtration procedure described for the alloy catalysts.

4.4. Catalyst characterization

The metal loadings were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) analysis, performed using Agilent 720-ES ICP-OES equipment combined with Vulcan 42S automated digestion system. Transmission Electron Microscopy (TEM) images were recorded by placing a drop of the particles dispersion in isopropanol onto a carbon film supported on a copper grid. FEI Tecnai microscope was used to record the images. More than 600 particles were used for the particle-size distribution analysis. It was performed using Image J software. For the analysis of individual nanoparticles, high resolution Scanning Transmission Electron Microscopy (STEM) was performed on a TITAN Themis 300 S/TEM microscope equipped with (1) a probe aberration corrector and monochromator, allowing spatial resolution of 70 pm and energy resolution of 150 meV; (2) a super-X windowless 4 quadrant SDD (silicon drift detector) detection system for STEM-EDX mapping and several annular dark field detectors; (3) a high-resolution post column GIF, the GATAN's Quantum ERS/966 with 2kx2k Ultrascan camera with 994G sensor, for the acquisition of electron energy loss spectra. To investigate the elemental distribution within bimetallic particles, high-angle annular dark field (HAADF) imaging and high-resolution electron energy loss spectroscopy (HR- EELS) were carried out in the STEM mode. Measurements were performed with a spot size of about 500 pm, a semi-convergence angle between 16 and 21 mrad, and a probe current of approximately 100 pA. For HAADF images, collection angles between 50 and 200 mrad were chosen. Dual EELS acquisition was performed in the spectral imaging mode with a collection angle of 49 mrad, a 0.25 eV/ch dispersion, a step between 150 and 700 pm, and a dwell time between 50 and 200 ms. Alignment of the energy drift was done on the zero-loss peak. When possible, noise reduction by PCA was performed on the spectrum images using HyperSpy. The LSPR band of nanoparticles was measured by absorption spectroscopy using the PerkinElmer Lambda 900 UV-Vis-NIR spectrometer. The samples were diluted in ultrapure water and measured against water as the reference.

4.5. Photocatalytic and thermal catalytic activity tests

Photocatalytic oxidation reactions were carried out using two Illumin 8 batch reactors (Asynt), each accommodating eight parallel reaction tubes under identical conditions (Figure S2). One reactor was equipped with a 365 nm LED array (8 × 10 W), the second with a 450 nm LED array (8 × 10 W); the operating temperature under irradiation stabilized at 39 °C. Reactions at 523 nm were performed in a sealed F-reactor (Asynt, internal radius 1.8 cm, 8 mL volume), operated in batch mode and equipped with a glass window secured by screw fittings, allowing irradiation from a 523 nm LED source positioned directly above the reactor. In a typical experiment, 5.0 mg of catalyst was suspended in 3.0 mL of an aqueous HMF solution (25 mM). For base-assisted conditions, 3 equiv. of NaOH were added (pH 13, verified by pH indicator). Reactions were conducted at atmospheric pressure for 4 h under

magnetic stirring (600 rpm). Thermal control experiments were performed under identical conditions with the light source disabled and temperature set to 40 °C. After reaction, the catalyst was removed by filtration through a PTFE membrane, and the filtrate was analyzed by HPLC. Concentrations of HMF, intermediates (HMFCA, DFF, FFCA), and FDCA were quantified against external calibration curves (Figure S3).

4.6. Analytical methods and calculations

Quantitative determination of liquid-phase reactants and products was performed by high-performance liquid chromatography (HPLC) using a Thermo Scientific Vanquish system equipped with a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) and a variable-wavelength UV/Vis detector set at $\lambda = 265$ nm. Isocratic elution was conducted using an aqueous 5 mM H₂SO₄ mobile phase (0.005 mol L⁻¹) at a constant flow rate of 0.6 mL min⁻¹. The autosampler injection volume was set to 10 μ L and the column compartment was thermostatted at 40 °C. Total run time per sample was 65 min. Chromatographic peaks corresponding to HMF and the reaction products (HMFCA, DFF, FFCA, and FDCA) were unambiguously identified via multipoint external calibration curves constructed using analytical-grade standards.

Given that HMF and all corresponding intermediates retain the six-carbon (C₆) furanic core, molar concentrations directly reflect carbon-molar equivalence. Substrate conversion, product yields, product selectivities, and overall carbon balance were calculated according to equations (1)-(4):

$$\text{HMF Conversion (\%)} = \frac{C_{\text{HMF},0} - C_{\text{HMF}}}{C_{\text{HMF},0}} \cdot 100 \quad (1)$$

$$\text{FDCA Yield (\%)} = \frac{C_{\text{FDCA}}}{C_{\text{HMF},0}} \cdot 100 \quad (2)$$

$$\text{Relative FDCA Selectivity (\%)} = \frac{C_{\text{FDCA}}}{(C_{\text{HMFCA}} + C_{\text{DFF}} + C_{\text{FFCA}} + C_{\text{FDCA}})} \cdot 100 \quad (3)$$

$$\text{Carbon Balance (\%)} = \frac{C_{\text{HMF}} + C_{\text{HMFCA}} + C_{\text{DFF}} + C_{\text{FFCA}} + C_{\text{FDCA}}}{C_{\text{HMF},0}} \cdot 100 \quad (4)$$

Where $C_{\text{HMF},0}$ is the initial concentration of HMF, and C_{HMF} , C_{HMFCA} , C_{FFCA} , C_{DFF} and C_{FDCA} are the molar concentrations of the respective compounds after the reaction.

5. Data Availability Statement

All data supporting the findings of this study are available within the article and its Supplementary Information. Additional raw data are available from the corresponding author upon reasonable request

6. Conflicts of Interest

The authors declare no conflicts of interest.

7. Acknowledgements

This work was supported by “Lorraine Université d’Excellence”, as part of the France 2030 Program, under reference ANR-15-IDEX-04-LUE. This work was partly done in the Pôle de compétences en chimie analytique environnementale, ANATELo, LIEC laboratory, UMR 7360 CNRS – Université de Lorraine. The authors specifically thank Maximilien Beuret for his contribution in ICP analysis.

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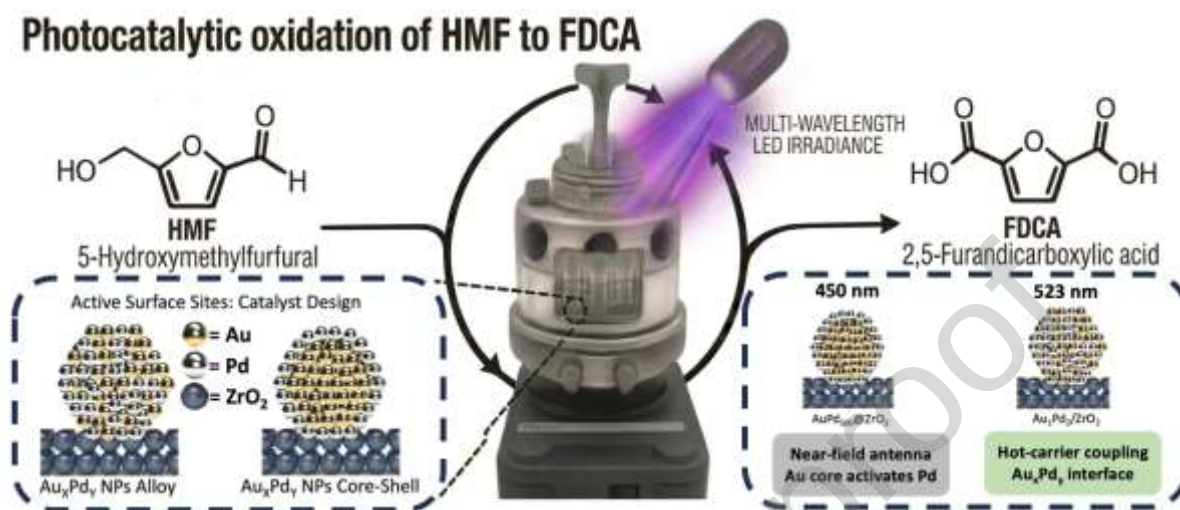
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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



Highlights:

- Wavelength-gated reaction steering enables precise, external control of aqueous HMF oxidation pathways without changing thermal parameters.
- Double catalytic ranking reversal occurs between Au–Pd alloy and core–shell architectures across dark, 450 nm, and 523 nm regimes.
- Core–shell $\text{AuPd}_{500}@\text{ZrO}_2$ achieves 99.1% HMF conversion with high FDCA and FFCA selectivity under mild 450 nm visible-light irradiation.
- Surface Pd density governs oxidation depth, while the nanoarchitecture dictates the decoupling of UV, visible, and LSPR light-harvesting modes.