Journal of Catalysis 397 (2021) 205-211

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Near-field enhancement by plasmonic antennas for photocatalytic Suzuki-Miyaura cross-coupling reactions



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ARTICLE INFO

Article history: Received 28 February 2021 Revised 10 March 2021 Accepted 17 March 2021 Available online 29 March 2021

Keywords: Plasmonic antennas Near-field enhancement "Antenna-reactor" catalysts Cross-coupling reactions Substrates effect

ABSTRACT

It is well documented that placing a plasmonic antenna close to catalytically active nanoparticles can enhance their catalytic activity in chemical reactions via the near-field enhancement effect. Less known is whether and how the near-field enhances the reactivity of the reactant substrates involved in these reactions. Herein, we prepared an "antenna-reactor" catalyst with Au nanoparticles absorbing light as an optical antenna and the adjacent Pd nanoparticles acting as a chemical reactor to study the near-field enhancement effect in Suzuki–Miyaura cross-coupling reaction involving various substrates. The results showed that the activity of Pd nanoparticles were significantly enhanced in the presence of Au antennas. Excessively increasing the density of Au antennas, however, suppressed the reaction due to the interaction between neighboring electromagnetic hot spots. Moreover, the near-field affected different substrates in different extents, enhancing more to reactions that involve substrates with higher electron cloud density at the reactive center. The overall effect of the near-field to the catalytic reactions was proved to be an integrated result of the effect of Au nanoparticle density and reactive center electron cloud density. This study provides enriched understanding for the near-field enhancement effect in photocatalytic reactions with various substrates, and deepened insights for new "antenna-reactor" photocatalyst design.

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1. Introduction

Plasmonic metal nanoparticles (Au, Ag, Cu and Al, *etc.*) can harvest visible photons through the localized surface plasmon resonance (LSPR) effect. As one of the significant characteristics of LSPR effect, the absorption cross-section of the plasmonic nanoparticle is much larger than its physical geometry, resulting in harvesting photons more efficiently. [1–3] The LSPR originates from the light-driven collective oscillation of the conduction electrons. [3–4] Given the moderate adsorption of many organic/inorganic molecules on the surface of plasmonic metals, photo-excited plasmonic nanoparticles can act as good catalysts to drive chemical reactions by generating hot carriers through nonradiative Landau damping or providing localized high temperature through photothermal effect. [5–12] Besides, LSPR also leads to the great enhancement of the electromagnetic fields near the nanoparticle surface. [13–14] The near-fields are initially used to amplify the

signals in Raman spectroscopy, yet it is also reported that it can be used for enhancing the catalytic activity of non-coinage metal nanoparticles. [15–19]

In recent years, many "antenna-reactor" catalytic systems have been reported, in which the plasmonic nanostructures harvest light as an optical antenna while the adjacent transition metal nanoparticles or semiconductors act as the chemically-active sites to drive chemical reactions enhanced by the localized near-field of these plasmonic nanostructures. [16-17,20] Such systems include Ag antenna-enhanced Pt nanoparticles for CO oxidation, Au antenna-enhanced TiO₂ nanostructures for dye decomposition and water splitting, and Al antenna-enhanced Pd, Ir nanoparticles for hydrogenation of acetylene and decomposition of nitrous oxide, etc. [16–17,21–23] However, these works mainly put their focus on the enhancement to active sites, ignored the possible interaction between the near-field and the reactant molecules (Scheme 1a). Since reactant molecules normally interact with active sites either by strong chemisorption or physisorption via their reactive center atoms, the electron cloud densities of the reactive center could play an important role in determining the reaction rate because the behavior of electron cloud is also affected by the near-field







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Scheme 1. (a) Illustration of the "Au antenna-Pd reactor" system under light irradiation. (b) The preparation process and structure of the "antenna-reactor" catalysts.

through electromagnetic force. In this context, how the near-field affect a type of reactions involving different substrates (with different electron cloud densities at their reactive center) is still an open question.

Herein, we designed a "Au antenna-Pd reactor" catalytic system to study the near-field enhancement effect in chemical reactions from a perspective of reaction substrates. As illustrated in Scheme 1b, to eliminate possible hot electron transfer contribution from the support under light illumination, Au nanoparticles were deposited on ZrO₂ that has a large bandgap of around 5-7 eV, and is unable to be excited by light with a wavelength longer than 248 nm. [24] In this scenario, Au nanoparticles act as lightabsorbing antenna to harvest visible photons through LSPR of Au nanoparticles, while catalytically-active Pd nanoparticles work as the reaction sites (reactor) for chemical reactions. Before loading Pd nanoparticles, a 2 nm thick SiO₂ layer was coated onto the Au/ZrO2 nanostructure to encapsulate Au nanoparticles, preventing the Pd and Au nanoparticles from directly contacting with each other but enabling a close spatial distance between them, therefore avoiding the enhancement from the bimetallic synergistic effect or charge redistribution between Au and Pd, and constructing an ideal platform for near-field enhancement study. Suzuki-Miyaura crosscoupling was selected as the model reaction because the electron cloud density at reactive centers of aryl halides can be altered by introducing electron-donating or electron-withdrawing substituent groups to benzene rings at different positions, which is beneficial to evaluate the near-field enhancement to various substrate molecules.

2. Results and discussion

The density of electromagnetic hot spots can be adjusted by controlling the loading amount of "Au antennas". Transmission electron microscopy (TEM) image in Fig. 1a shows the morphology of 3% Au/ZrO₂ before SiO₂ coating. The Au nanoparticles were evenly dispersed at the surface of ZrO₂, having an average diameter of around 5 nm (Figure S1a) and presenting very sharp edges, implying a clean surface of these Au nanoparticles. The particle spacing is centered at 3 nm as revealed by the statistical analysis of 200 nanoparticles based on TEM images (Figure S1b). Then, a layer of SiO₂ was coated on the Au/ZrO₂ nanostructure through hydrolysis of sodium silicate at elevated temperatures. [25] As shown in Fig. 1b, after coating, a clear SiO₂ layer with lower contrast than that of ZrO₂ under TEM can be observed around the

Au/ZrO₂ catalyst. The thickness of the SiO₂ layer is around 2 nm and it is fully covered on Au nanoparticles as shown in the inset in Fig. 1b. The X-ray powder diffraction (XRD) result of the asprepared catalyst (Figure S2) well-matched with the monoclinic ZrO₂ crystal (PDF#65-1025), showing no diffraction peaks for any crystalline SiO₂ species, implying the amorphous nature of the SiO₂ layer. Fig. 1c shows the finished catalyst after Pd deposition. The Pd nanoparticles (as indicated by the red arrows) were dispersed outside the SiO₂ shell and close to the encapsulated Au nanoparticles. The mapping scan shown in Fig. 1d demonstrates the elemental distribution in the as-prepared catalyst, further confirming the existence of SiO₂ shell and Au, Pd nanoparticles. As a reference, the pristine ZrO₂ without Au deposition was also coated by a layer of SiO₂ and further deposited with Pd to give the "standard activity" of the Pd catalysts in the absence of near-fields (Figure S3). The "antenna-reactor" catalysts with 1%, 5%, and 7% Au loading amount were also prepared to study the enhancement resulted from different density of electromagnetic hot spots, and their morphology are shown in Figure S4.

Next, we studied the chemical states of Au and Pd nanoparticles in catalysts using X-ray photoelectron spectroscopy. As $Pd3d_{5/2}$ partially overlaps with $Zr3p_{3/2}$, we determined the chemical state of Pd based on its $3d_{3/2}$ orbit. Fig. 1e shows a singlet of $Pd3d_{3/2}$ at 341.0 eV, corresponding to 335.7 eV for $Pd3d_{5/2}$ (spin-orbit components Δ = 5.3 eV), revealing the metallic nature of Pd nanoparticles. [26–27] The Au4f region (Fig. 1f) shows doublet separated by 3.7 eV, identified as Au4f_{5/2} and Au4f_{7/2}, respectively. The binding energy for Au4f_{7/2} centered at 83.9 eV, indicating the Au nanoparticles are in a metallic state, and therefore able to harvest photons through LSPR effect. [28–29]

The light response of catalysts was studied using Ultravioletvisible (UV-vis) spectroscopy (Fig. 2). The pristine ZrO₂ has no absorption in the visible light (400–800 nm) region but strongly absorbs photons with a wavelength shorter than 250 nm due to interband excitations (Fig. 2a). [24] After Au loading, a new absorption peak appeared at around 530 nm, which can be attributed to the excitation of the LSPR of Au nanoparticles, and the peak gradually intensified and broadened with the increase of Au loading amount. [3–4] Fig. 2b shows the absorption curves of the catalyst sample in different stages of preparation, and the spectrum of 3% Au/ZrO₂ was also plotted here as a reference. After SiO₂ coating (the green line), the LSPR absorption of Au nanoparticles was still clearly observed, although the overall absorption intensity decreased in the range of 250–800 nm, probably owing to the

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Fig. 1. TEM images of (a) 3%Au/ZrO₂; (b) 3%Au/ZrO₂ after SiO₂ coating (denoted as SiO₂/3%Au/ZrO₂); (c) the finished catalyst (after Pd deposition, denoted as 1.5%Pd/SiO₂/3% Au/ZrO₂); (d) Mapping scan of the 1.5%Pd/SiO₂/3%Au/ZrO₂ catalyst. High resolution XPS spectra of (e) Zr3p_{1/2} and Pd3d_{3/2} and (f) Au4f region.



Fig. 2. UV-vis spectra of (a) Au/ZrO2 with different Au loading amount, and (b) the "antenna-reactor" catalyst in different stages of preparation.

reflection or diffusion of the SiO_2 layer to light. With further deposition of Pd nanoparticles on the SiO_2 layer, an absorption tail was generated in the long-wavelength range (>600 nm), as a result of interband excitation of Pd nanoparticles. [30–31] The contribution of Pd nanoparticles to light absorption was also observed in the control sample Pd/SiO₂/ZrO₂, in which the baseline elevated overall, because the light absorption of Pd typically originate from a combination of a free-electron (Drude) response (normally associated with the LSPR), and an interband transition (involving the 5*d* electrons). [32]

The performance of the "antenna-reactor" catalysts was evaluated using the Suzuki–Miyaura cross-coupling as a model reaction (Fig. 3a). Suzuki–Miyaura cross-coupling is one of the most powerful and versatile organic synthetic reactions for building C—C bond



Fig. 3. (a) The Suzuki–Miyaura cross-coupling reaction equation and (b) the conversion of iodobenzene using different catalysts. Reaction conditions: 0.4 mmol iodobenzene (1 equiv.), 0.48 mmol phenylboronic acid (1.2 equiv.), 2 mL of 1,4-dioxane as solvent, 20 mg catalysts, 50 mg Cs₂CO₃, 40 °C, Ar atmosphere, 0.4 W·cm⁻² visible light (400–800 nm), 12 h.

of biaryl compounds, which have many important applications in chemistry and material sciences. [33] The coupling partners are typically a boronic acid and an aryl halide, catalyzed by Pd species, in both homogeneous and heterogeneous systems. [34] In this work, the boronic acid part of the coupling reaction is fixed as phenylboronic acid while various aryl halides are employed as variable substrates for the near-field enhancement study. The oxidative addition step is known as the rate-determining step in the Suzuki-Miyaura cross-coupling reactions, and it is believed that this step involves the electron transfer from the catalytically-active atoms (e.g. Pd) to the halide atoms to initiate the reaction. [35–37] The near-field enhancement of LSPR may enhance such an electron transfer process if the reactive sites are located within the radiation scope of electromagnetic hot spots, thereby promoting the overall catalytic activity.

Firstly, using iodobenzene as the simplest substrate, SiO₂ coated ZrO_2 (SiO₂/ ZrO_2) was tested in a control experiment and the results showed that the insulator SiO₂ shell and ZrO₂ could not initiate the coupling reaction (the first line in Fig. 3b). Similarly, no iodobenzene conversion was observed for SiO₂ coated Au/ZrO₂ catalysts with different Au loading amount, confirming the insulating effect of the SiO₂ layer and the inactivity of Au nanoparticles to the reaction. Then, identical amount of Pd nanoparticles (1.5 wt%) was further deposited to study the near-field enhancement effect of Au nanoparticles. As shown in Fig. 3b, in the absence of Au nanoparticles, 47.8% iodobenzene conversion was achieved, which is regarded as the "standard activity" of the Pd nanoparticle catalyst. When introducing 1 wt% Au nanoparticles, the activity of Pd nanoparticles was enhanced by 4.7% under the same reaction conditions, with the conversion of iodobenzene increased to 52.5%. The conversion further increased to 63.1%, showing a 15.3% enhancement, when 3 wt% Au nanoparticles were deposited. Nevertheless, when further increase the Au loadage to 5 wt% and 7 wt %, the conversion did not increase as expected, but decreased by 13% and 26.6%, respectively, resulting in activity even lower than that without the near-field.

The above results indicate that the LSPR induced electromagnetic field around Au nanoparticles indeed affected the activity of

Pd nanoparticles, but it does not always enhance the photochemical activity, sometimes also depressing the reaction. The final result of the near-field to a reaction depends largely on the density of electromagnetic hot spots. It is reported both experimentally and theoretically that the activity of reactive sites can be enhanced around an isolated plasmonic nanoparticle. [16–17] In this context, when the electromagnetic hot spots are sparse (e.g. 1 wt% and 3 wt % Au loadage), the enhancement effect can be considered as the collective contribution of numerous isolated Au nanoparticles. Therefore, the enhancement is amplified with the increase of nanoparticle number. However, when the density of Au nanoparticles increased exceeding a threshold, where the overlapping of electromagnetic fields happens, a more complicated physical model has to be considered, i.e., one needs to consider the effect of interactions between neighboring electromagnetic hot spots. [38–39] The decreased conversions observed on catalysts with 5 wt% and 7 wt% Au loadage were presumably caused by such a hot spot interaction, which may result in a complex and disordered electromagnetic field that suppressed the activity of Pd nanoparticles. This suppressing phenomenon was also revealed by subsequent experiments and will be further discussed hereinafter.

With an understanding on how different densities of the electromagnetic hot spot affect the catalytic activity of adjacent Pd nanoparticles, we next fixed the hot spot density by using 1.5 wt %Pd/SiO₂/3wt%Au/ZrO₂ as a model catalyst, while manipulating substituent groups of aryl halides to study the role of the reactive center electron cloud density (the iodine atom) in the reaction. Methyl is an electron-donating group and can affect the electron cloud density of iodine atom when substituting H atoms in the molecule. The methyl in *meta*-position has a weak conjugate effect and moderate inductive effect and therefore shows the weakest electron-donating effect to the iodine atom. [40] In comparison, its para-substituted counterpart (4-iodotoluene) has the weakest inductive effect but a moderate conjugate effect, showing a slightly higher electron-donating effect. The methyl at ortho-position contributes the most to iodine electron cloud density, as a result of both the strongest conjugate effect and inductive effect. Thus the electron cloud density of iodine atom in iodotoluene is in the order

of *meta < para < ortho* as illustrated in Fig. 4a. Interestingly, the extent of enhancement was found to be consistent with the electron cloud density of iodine atoms; that is, reactions involving aryl halides with high iodine electron cloud density showed the greatest enhancement (increased by 12% for 2-iodotoluene) in aryl halide conversion, while the enhancement for substrates with relative low iodine electron cloud density was much more moderate (only a 5.8% increase for 3-iodotoluene).

Performing the experiment using electron-withdrawing groups substituted aryl halides gave the same trend. Fluorine is the strongest electron-withdrawing group in halogens due to its high electronegativity. A *para*-substituted fluorine greatly decreased the electron cloud density of iodine. Since the electron-withdrawing ability of halogen substituents decreases in the order of F > Cl > Br, the electron cloud density of iodine is in the order of 1-fluor o-4-iodobenzene < 1-chloro-4-iodobenzene < 1-bromo-4-iodoben zene. As a result, the conversion enhancement for the three substrates is 6.5%, 14.9%, and 18.8%, respectively (Fig. 4b), in line with the conclusion obtained using the electron-donating group substituted aryl halides.

In cross-coupling reactions, I- is a better leaving group than Brand Cl- because of the weak C—I bond resulted from the low electronegativity of iodine. [37,41] In this context, higher electron could density in iodine atom could weaken the C—I bond and therefore be beneficial to the oxidative addition step that is normally believed the rate-determining step in Suzuki-Miyaura cross-coupling reactions. [37] Within the near-field, this trend was amplified because of the interaction between electrons and the intense electromagnetic field. [42] In this case, both the electron transfer from Pd atoms into iodine atom and the activation of the rate-determining step were promoted by the near-field enhancement effect.

Upon further investigation using different aryl halide substrates, we found that the near-field resulted enhancement is not identical to every substrate, but proportional to the "standard activity" of reactions using each substrate. As shown in Fig. 5a, when the near-field was applied to iodobenzene, the absolute conversion was enhanced by 15.3%, from 48% to 63.3%, much higher than that of bromobenzene and chlorobenzene, for which only 1.7% and 1.0% absolute enhancement was observed. The neglectable enhancement in the latter two cases is because of their low "standard activity" that resulted from the low reactivity of the substrates. [37] In other words, the experimental results demonstrated that applying a near-field to a reaction did not change the reaction pathway, unable to initiate a reaction that cannot be triggered in the absence of the field, but only promoting the reaction by an extent proportional to the "standard activity" of the reaction.

When changing the substrate to 4-iodoanisole, the sample 1.5% $Pd/SiO_2/3\%Au/ZrO_2$ showed a decreased conversion (-7.6%, Fig. 5b) in comparison to the "standard activity", similar with the phenomenon observed on iodobenzene substrate catalyzed by 5 wt% and 7 wt% Au deposited samples (Fig. 3b). In the previous discussion, we ascribed the suppression effect to the interactions between neighboring electromagnetic hot spots. However, the hot spot interaction should not be responsible to the decreased conversion for the 4-iodoanisole substrate because 3 wt% is not a very high Au loadage according to the previous result and the electromagnetic hot spot interaction could be very mild in this case. Therefore, we deduce that the reason could be because of the substrate itself. As methoxy is a very strong electron-donating group, the electron cloud density of the iodine atom in 4-iodoanisole could be even higher than that of methyl-substituted substrate and thus more sensitive to the near-field. In this case, even a very mild hot spot interaction can negatively affect the reaction. As a result, the near-field showed an overall suppression effect to this specific substrate. To verify our inference, a catalyst with minimal hot spot interaction (1.5%Pd/SiO₂/1%Au/ZrO₂) was employed for the 4-iodoanisole substrate. As expected, a 4.1% enhancement was achieved, similar to that for the iodobenzene substrate in Fig. 3, confirming that excessive hot spots can suppress the



Fig. 4. Near-field enhancement to the Suzuki–Miyaura cross-coupling reaction using substrates with (a) electron-donating and (b) electron-withdrawing groups. The red balls in molecular structures present the iodine atom in aryl halides, and their brightness corresponds to the electron cloud density of iodine atoms which are affected by the other substituent group on the benzene ring. The 3 wt% Au nanoparticles loaded catalyst was employed as the typical sample to compare with the catalyst without Au nanoparticles. Reaction conditions: 0.4 mmol iodobenzene (1 equiv.), 0.48 mmol phenylboronic acid (1.2 equiv.), 2 mL of 1,4-dioxane as solvent, 20 mg catalysts, 50 mg Cs_2CO_3 , 40 °C, Ar atmosphere, 0.4 W·cm⁻² visible light (400–800 nm), 12 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Near-field enhancement to the Suzuki-Miyaura cross-coupling reaction using (a) different aryl halides and (b) 4-iodoanisole. Reaction conditions: 0.4 mmol iodobenzene (1 equiv.), 1.2 equiv. phenylboronic acid, 2 mL 1,4-dioxane, 20 mg catalysts, 50 mg Cs₂CO₃, 40 °C, Ar atmosphere, 0.4 W·cm⁻² visible light (400–800 nm), 12 h.

reaction by the interaction among them. However, the overall reaction results (enhancement or depression) are decided by the balance between substrate sensitivity and the hot spot density.

The effects of near-fields around an excited Au nanoparticle to the reaction was summarized into two situations in Fig. 6. In the first situation, Pd nanoparticles are in the radiation scope of a single Au nanoparticle that has enough distance with the adjacent ones (Fig. 6a). No hot spot interaction occurs in this scenario, and therefore the electromagnetic field overall enhances the reaction, corresponding to the results observed for samples with 1 wt% and 3 wt% Au loading amount. Based on the statistic results (Figure S1), we employed two 5 nm Au nanoparticles with 3 nm gap between them as a model to simulate the near-field enhancement using an electrostatic eigenvalue method. The detailed simulation method was reported previously. [43] The simulation result showed that the resonance frequency for a single Au nanoparticle with 5 nm diameter is approximately 525 nm (Figure S5a). A significant surface charge distribution of the coupled plasmon mode can be observed on the dimer Au nanoparticle surface (Fig. 6b), suggesting a great interaction potential with their neighboring Pd nanoparticles. The corresponding electromagnetic field intensity simulation at the dimer Au particle's surface (Fig. 6c) shows a ~30 times enhancement in comparison to the incoming photo flux and the electromagnetic field displayed a large radiation scope that is able to act on the adjacent Pd nanoparticles and enhance their catalytic activity.

In contrast, if two Au nanoparticles close enough (situation 2, Fig. 6d), parts of their near-fields could overlap and interact with



Fig. 6. Schematical illustration and simulation of two situations in near-field enhancement. Situation 1: (a) no hot spot interaction occurring around two well-distanced Au nanoparticles; (b) simulated surface charge distribution mapping of the coupled plasmon mode and (c) electric field intensity near two Au nanoparticles (5 nm in diameter) with 3 nm distance between them. Situation 2: (d) hot spot interaction occurring around two Au nanoparticles with short distance; (e) simulated surface charge distribution mapping of the coupled plasmon mode and (f) electric field intensity near two Au nanoparticles (6 nm in diameter) with 1 nm distance between them.

each other, generating an overall suppressing effect to the reaction, as experimentally revealed by the performance of 5% and 7% Au loaded catalysts. Since the average Au nanoparticle size increased with the increase of Au loadage, the simulation in this case was conducted on a model consists of two 6 nm Au nanoparticles with 1 nm gap between them (Figure S6). In comparison to the 5 nm Au nanoparticle, the resonance frequency of a single Au nanoparticle with 6 nm diameter slightly redshifted to 544 nm as shown in Figure S5b. The surface charge distribution of the coupled plasmon mode on the particle surface was also observed (Fig. 6e), but not as significant as that in the situation 1, implying a mild influence to the adjacent Pd nanoparticles. Moreover, although the electromagnetic field in the gap between the two nanoparticles was greatly amplified through the hot spot interaction, the radiation scope shrank obviously compared to that for the situation 1. Therefore, such a near-field around Au nanoparticles may be unable to act on the adjacent Pd nanoparticles due to the space and distance limitations, and even suppress the reaction by negatively affecting the active sites or reactant molecules through its complex and disordered electromagnetic field.

3. Conclusion

In summary, a series of "antenna-reactor" catalysts were prepared and their performance on the Suzuki-Miyaura crosscoupling reaction was evaluated in terms of varied electromagnetic hot spot density and electron cloud density in the halogen atoms. In the catalysts, ZrO₂ supported Au nanoparticles act as antennas which absorb light through LSPR and generate electromagnetic field near their surface, while the subsequently deposited Pd nanoparticles play a role of the real active sites enhanced by the near-field for cross-coupling reactions, with a 2 nm thick SiO₂ layer coated on Au nanoparticles to avoid the direct contact of the two kinds of metal nanoparticles. The as-prepared catalysts showed considerable enhancement under visible light irradiation in the presence of 1% and 3% Au nanoparticles while suppression was observed when excessive Au nanoparticles were deposited, presumably owing to the interaction between adjacent electromagnetic hot spots. Besides, the overall enhancement was also decided by the electron cloud density at the halogen atom which is the reactive center of the reactant aryl halides. In a series of iodobenzene substrates with different substituents, the one with higher electron cloud density in iodine atom was more sensitive to the field, resulting in a greater enhancement to the conversion. It is worth noting that the enhancement resulted from the nearfield is not identical to every substrates, but proportional to the "standard activity" of each substrate in Suzuki-Miyaura crosscoupling reactions, because the near-field does not change the intrinsic reaction pathway, only amplify the reaction results. The new findings in this work regarding the interaction between the reactive center electron cloud density and the near-field enriched the knowledge base of near-field enhancement and may provide creative insights for new "antenna-reactor" catalysts design.

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.

Acknowledgement

J.X. is grateful for the financial support from the Australian Research Council (DP190101607). Q.X. thanks the Japan Society for the Promotion of Science (JSPS) for a JSPS Postdoctoral Fellowship for Research in Japan (P19336). Science and Engineering Faculty and Central Analytical Research Facility (CARF) at QUT are greatly acknowledged for technical assistance.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2021.03.020.

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