

# Boosting Catalytic Selectivity through a Precise Spatial Control of Catalysts at Pickering Droplet Interfaces

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**ABSTRACT:** Exploration of new methodologies to tune catalytic selectivity is a long-sought goal in catalytic community. In this work, oil-water interfaces of Pickering emulsions are developed to effectively regulate catalytic selectivity of hydrogenation reactions, which was achieved via a precise control of the spatial distribution of metal nanoparticles at the droplet interfaces. It was found that Pd nanoparticles located in the inner interfacial layer of Pickering droplets exhibited a significantly enhanced selectivity for *p*-chloronilline (up to 99.6%) in the hydrogenation of *p*-chloronitrobenzene in comparison to those in the outer interfacial layer (63.6%) in pure water (68.5%) or in pure organic solvents (46.8%). Experimental and theoretical investigations indicated that such a remarkable interfacial microregion-dependent catalytic selectivity was attributed to the



microenvironments of the coexistence of water and organic solvent at the droplet interfaces, which could provide unique interfacial hydrogen-bonding interactions and solvation effects so as to alter the adsorption patterns of p-chloronitrobenzene and p-chloroniline on the Pd nanoparticles, thereby avoiding the unwanted contact of C–Cl bonds with the metal surfaces. Our strategy of precise spatial control of catalysts at liquid–liquid interfaces and the unprecedented interfacial effect reported here not only provide new insights into the liquid–liquid interfacial reactions but also open an avenue to boost catalytic selectivity.

## INTRODUCTION

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Chemical reactions at organic-water interfaces are increasingly recognized to be substantially different from those occurring in bulk water or organic phase because of their unique interfacial properties.<sup>1-9</sup> Particularly, some important reactions such as the formation of hydrogen peroxide<sup>10,11</sup> and the reduction of ketone<sup>12</sup> have been reported to spontaneously occur on water microdroplets. Recently, several experimental and theoretical studies have revealed that organic-water interfaces had intriguing features, such as ordered molecular orientation,<sup>13–15</sup> interfacial acidity/basicity,<sup>16–18</sup> and spontaneous electric field.<sup>19,20</sup> These interfacial features provide vast opportunities to tune the surrounding environments of catalytic reactions and then to further improve the performance of catalysts. For instance, homogeneous proline and other organocatalysts have been reported to exhibit enhanced reactivity and stereoselectivity on the water surface due to the specific interfacial interaction.<sup>21-23</sup> However, it still remains a formidable challenge for organic-water interfaces to rationally regulate catalytic reactions proceeding on solid catalysts because it is extremely difficult to precisely control their spatial location at organic-water interfaces at the nanoscale.

Pickering emulsions that are stabilized by solid particles have been documented to be an ideal platform for the assembly of catalysts at oil–water interfaces because of the extremely high stability of the formed droplets.<sup>24–29</sup> Up to date, various solid catalysts, including differently shaped SiO<sub>2</sub>,  $^{30,31}$  zeolites,  $^{32,33}$ TiO<sub>2</sub>,  $^{34}$  and g-C<sub>3</sub>N<sub>4</sub>,  $^{35,36}$  have been reported to be assembled at droplet interfaces for biphasic catalysis. Although enhanced reaction activity has been achieved, these solid catalysts were distributed randomly around the oil-water interfaces, with the one part of active components protruding into the oil phase and the other part into the water phase. Janus particles with a shape of dumbbell or surfactant-like were also designed for biphasic catalysis.<sup>37,38</sup> Nevertheless, their submicron-scale (≥200 nm) particle sizes guided most of the surface-loaded active sites far away from the oil-water interfaces too much. Consequently, these methods are still incapable of precisely controlling the interfacial reaction locus, so that the catalytic reactions simultaneously proceed in both the inner and outer interfacial layers of Pickering emulsion droplets. However, the inner and outer interfacial layers of the droplets have a different microenvironment in terms of interfacial hydrogen bonds, solvent environments, polar gradients, etc. These

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Scheme 1. Schematic Diagrams Illustrating the Catalytic Reactions Occurring at Different Interfacial Microregions of Pickering Droplets<sup>a</sup>



a'(a) Schematic illustration for different reaction loci at oil-water interfaces of water droplets by controlling the interfacial location of metal NPs: reaction occurring in the outer interfacial layer (left) and reaction occurring in the inner interfacial layer (right). (b) Schematic illustration for the interfacial assembly strategy for controlling the spatial location of metal NPs at droplet interfaces and then the interfacial reaction locus.

differences possibly imposed a remarkable impact on the diffusion process, molecular adsorption, and surface reactions (Scheme 1a), leading to different reaction outcomes. Very recently, our group implemented a spatial control of solid catalysts at droplet interfaces via an interfacial coordination interaction enabled by a phosphorus ligand, and enhanced catalytic selectivity was obtained in cinnamaldehyde hydrogenation.<sup>39</sup> However, because of the ligand modification and the relative complexity of the constructed system, this method for tuning catalytic selectivity is difficult to be generalized, and importantly, the intrinsic role of oil-water interfaces in improving catalytic selectivity has yet to be revealed. Accordingly, an in-depth understanding of the liquid-liquid interfacial catalysis effects and further development of efficient methods for rationally regulating catalytic selectivity are still highly desired.

Herein, we developed a simple and straightforward interfacial assembly strategy to precisely control the spatial location of metal NPs at the oil–water interfaces of Pickering emulsions for unveiling the nature of droplet interfaces in regulating metal-catalyzed hydrogenation reactions. Janus nanosheets with an asymmetric surface property were superior solid emulsifiers for constructing Pickering emulsions; more importantly, they often had a flat interfacial assembly behavior at the droplet interfaces.<sup>40–42</sup> By regioselectively loading metal

NPs on the hydrophilic or hydrophobic surface of Janus mesoporous silica nanosheets (JMSNs) with a nanoscale thickness, the metal NPs were directly positioned in the inner or outer interfacial layer of as-forming Pickering droplets solely, respectively. Interestingly, we found a novel phenomenon of interfacial reaction locus-dependent catalytic selectivity in the hydrogenation of *p*-chloronitrobenzene. The metal NPs located in the inner interfacial layer displayed a significantly enhanced selectivity (up to 99.6%) for pchloroaniline yet without the expense of catalytic activity compared with those in the outer interfacial layer (63.6%) and in other solvents (46.8-68.5%). Experimental investigation along with theoretical calculation revealed that a hitherto unreported interfacial effect, stemmed from the hydrogenbonding interactions and the solvation effect in the interface regions, was responsible for the significantly boosted catalytic selectivity.

# RESULTS AND DISCUSSION

**Controlling the Spatial Location of Metal NPs at Oil– Water Interfaces.** JMSNs with one surface being hydrophilic and the other being hydrophobic were chosen as special solid emulsifiers to precisely control the spatial location of metal NPs at oil–water interfaces due to their unique interfacial assembly behavior of two-dimensional materials. As illustrated

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**Figure 1.** Characterization of the spatial distribution of Pd NPs at Pickering droplet interfaces. (a, b) SEM images, (c) HAADF-STEM image, and (d) EDX element mappings of Pd-phi/JMSNs. (e) Optical microscopy image of Pickering emulsions stabilized by Pd-phi/JMSNs. (f) CLSM image of the Pickering emulsions stabilized by Pd-phi/JMSNs with the Pd NPs labeled with Rhodamine B and JMSNs labeled with FITC-I. (g, h) Z-stacked three-dimensional (3D) CLSM images of the inner surface (g) and the outer surface (h) of the Pickering emulsions stabilized by Pd-phi/JMSNs with the Pd NPs labeled with FITC-I. (i, j, k) Cryo-TEM images and (l) Cryo-STEM image of Pd-phi/JMSNs stabilized Pickering emulsions.

in Scheme 1b, hydrophilic PVP-capped Pd NPs were first selectively supported on the hydrophilic surface of JMSNs by a simple adsorption process. Subsequently, the obtained catalyst (Pd-phi/JMSNs) was assembled at oil-water interfaces by emulsifying a mixture of organic solvent (i.e., toluene) and water to form Pickering emulsions. Because JMSNs preferred to be parallelly flat at droplet interfaces (such an interfacial assembly behavior was theoretically supported in attachment energy<sup>43,44</sup>), the Pd NPs loaded on the hydrophilic side of JMSNs were exactly positioned in the inner interfacial layer of Pickering droplets. Similarly, hydrophobic oleylamine-capped Pd NPs, obtained via a simple ligand exchange process (Figure S1), were solely supported on the hydrophobic surface of JMSNs (the obtained catalyst denoted as Pd-pho/JMSNs). After a process of interfacial assembly, the same Pd NPs were just rightly placed in the outer interfacial layer of Pickering droplets. Consequently, the metal-catalyzed reaction was desirably controlled to occur solely in the inner interfacial layer or in the outer interfacial layer, and the very thin thickness and mesochannels of JMSNs enabled the metal sites to be still highly accessible to reactants.

To firmly and regioselectively load PVP/Pd NPs, JMSNs with aminopropyl groups  $(-NH_2)$  modified on both sides and hydrophobic octyl groups  $(-C_8H_{18})$  modified exclusively on one side were prepared via crushing the corresponding Janus hollow microspheres<sup>41</sup> (Figure S2a). Ultrasonication-assisted crushing in the liquid phase was performed with a homogenizer to avoid the stacking of nanosheets. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the as-obtained JMSNs had a morphology of discrete nanosheets and the nanosheets contained both a smooth surface and a rough one (Figure S2d-g). The cross-sectional TEM images display that the ordered mesochannels of JMSNs were perpendicular to the nanosheet, and the thickness was nearly 30 nm (Figure S1h,i). Au-NPs labeling experiment combined with Fourier transform infrared (FTIR) spectra and thermogravimetry (TG) analysis further confirm that the smooth side (Si-OH/NH<sub>2</sub>) was hydrophilic, while the rough side  $(Si-C_8H_{18}/NH_2)$  was hydrophobic (Figure S3). Although the  $-NH_2$  groups (serving as sites for anchoring metal NPs) were present at both sides of JMSNs, PVP/Pd NPs could still be selectively loaded on their hydrophilic side because of the hydrophilic interactions. Low-



**Figure 2.** Catalytic performance evaluation. (a) Schematic illustration of different catalytic reaction systems, including Pd-phi/JMSNs-O, Pd-phi/JMSNs-W, Pd/C<sub>8</sub>-SiO<sub>2</sub>-PE, Pd-pho/JMSNs-PE, and Pd-phi/JMSNs-PE. (b) Possible reaction pathways for the selective hydrogenation of *p*-CNB over Pd-based catalysts. (c) Conversion and product distribution of different catalytic reaction systems within a 7.5 h reaction period. (d) Conversion and product distribution of Pd-phi/JMSNs in the PE systems constructed using different organic solvents as the oil phase within the 7.5 h reaction period. (e) Kinetic plots of selective hydrogenation of *p*-CNB over Pd-phi/JMSNs in the PE system. (f) Kinetic plots of selective hydrogenation of *p*-CNB over Pd-phi/JMSNs and Pd-pho/JMSNs in the PE system or in the water phase for selective hydrogenation of *p*-CAN within a 15.0 h reaction period. Reaction conditions: 2 mL of toluene, 2 mL of water, 0.2 mmol of *p*-CNB, 20 mg of catalyst (Pd: 0.5 mol %), 2.0 MPa H<sub>2</sub>, 25 °C.

magnification SEM and TEM images exhibit that the obtained catalyst (Pd-phi/JMSNs) still remained a morphology of discrete nanosheets (Figures 1a and S4). From the highmagnification SEM image (Figure 1b), we can clearly see several Pd NPs with a strong contrast (marked by yellow circles) being positioned on the smooth surface of JMSNs, while there are almost no similar Pd NPs observed on their rough surface, revealing that most of the Pd NPs have regioselectively been loaded on the hydrophilic surface of JMSNs. This statement could be further validated by the highangle annular dark-field scanning TEM (HAADF-STEM) image, in which the Pd NPs are dominantly distributed in the hydrophilic smooth surface (Figure 1c). Energy-dispersive Xray (EDX) elemental mapping shows the presence of Si, C, and Pd elements on the nanosheets (Figure 1d). According to the ICP-MS (inductively coupled plasma mass spectrometry)

analysis, the Pd loading amount was estimated to be about 0.5 wt %. Nitrogen sorption analysis confirmed the high BET surface area and uniform pore size (2.4 nm) of Pd-phi/JMSNs (Figure S5), and its BET surface area was slightly lower than that of JMSNs owing to the introduction of Pd NPs.

Due to the asymmetric surface wettability of JMSNs, Pdphi/JMSNs had a superior interfacial activity to emulsify different biphasic oil-water systems for producing thermodynamically stable Pickering emulsions. Using toluene as the oil phase, Pickering emulsions were obtained by shaking vigorously. The optical microscopy image shows that the droplets distributed in size in the range of 50–150  $\mu$ m (Figure 1e). The emulsion type was identified as water-in-oil through fluorescence dyeing of the water and oil phase (Figure S6a-c). Then, the Pd NPs and JMSNs were separately labeled with Rhodamine B and fluorescein isothiocyanate I (FITC-I) to

examine the spatial location of the catalyst at the oil-water interfaces by fluorescence imaging. As shown in the confocal laser scanning microscopy (CLSM) image, both red and green fluorescent rings were around the droplet (Figure 1f). The Zstacked 3D CLSM images further display that the red fluorescence appeared on the inner surface of the droplet (Figure 1g), while the green fluorescence was on the outer surface (Figure 1h), indicating that the Pd NPs were facing the inner water phase of the droplet. Furthermore, cryo-TEM was carried out to provide direct evidence of the spatial distribution of the Pd NPs at the droplet interfaces. As depicted in Figure 1i, a micron-sized sphere could be observed and its particle size  $(\sim 100 \ \mu m)$  remained highly consistent with that of Pickering emulsions after the water droplets were frozen. Interestingly, the nanosheets were observed to vertically arrange at the border of the microsphere in the magnified TEM images (Figure 1j), and their rough surface was outward yet the smooth surface was inward (Figure 1k). In sharp contrast, the nanosheets parallelly laid in the central regions of the microsphere (Figure S6f). These observations directly demonstrated that the catalyst, as expected, was organized at the droplet interfaces in a parallelly flatting manner. More importantly, as evidenced by the cryo-STEM image in Figure 1l, almost all of the Pd NPs were localized on the internal surface of the frozen water droplet. Clearly, the Pd NPs of Pdphi/JMSNs have been precisely placed in the inner interfacial layer of water droplets.

On the basis of this interfacial assembly strategy, the Pd NPs could also be arranged in the outer interfacial layer of Pickering droplets. SEM and HAADF-STEM images support that the Pd NPs of Pd-pho/JMSNs have been selectively loaded on the hydrophobic surface of JMSNs (Figure S7a-c). The Z-stacked 3D CLSM images confirmed that the Pd NPs have been exactly placed in the outer interfacial layer of Pickering droplets (Figure S7d-i). If the Pd NPs were loaded on both sides of JMSNs in an arbitrary way (Pd/JMSNs, which was prepared via an impregnation method<sup>41</sup>), they would randomly distribute around the droplet interfaces. Likewise, if using conventional interface-active silica nanospheres  $(C_8$ -SiO<sub>2</sub>) as a solid emulsifier for constructing Pickering emulsions, the surface-loaded Pd NPs would also randomly distribute near the droplet interfaces (Figure S8). Taken together, we have successfully achieved the precise control of the interfacial location of Pd NPs and then the interfacial reaction locus via an interfacial assembly strategy. Such an exquisite control allowed us to investigate the intrinsic effect of oil-water interfaces on catalytic reactions.

Oil-Water Interfaces Boosting Catalytic Selectivity. Catalytic hydrogenation of halonitrobenzenes is widely recognized as an alternative process for producing functionalized arylamines that are important intermediates for the synthesis of fine chemicals, including medicines, dyes, and pigments.<sup>45-48</sup> However, undesired carbon-halogen (C-X) bond scission is often accompanied by the reduction of the nitro group (Figure 2b), resulting in low selectivity for the desired product haloanilines. In this regard, avoiding dehalogenation of both halonitrobenzenes and haloanilines is crucial to the implementation of high selectivity for haloanilines. We notice that the halogen group of halonitrobenzenes and haloanilines is less polar while the nitro or amino group is polar, which makes it possible for both molecules to orient at oil-water interfaces.<sup>49,50</sup> With such a preferential molecular orientation, oil-water interfaces may regulate molecular

adsorption patterns on the surfaces of metal NPs located in the inner interfacial layer. Thereupon, selective hydrogenation of p-chloronitrobenzene (p-CNB) was selected as a model reaction to investigate the impact of oil-water interfaces on the catalytic performances of metal NPs. First, we examined the catalytic behavior of Pd-phi/JMSNs, Pd-pho/JMSNs, and Pd/JMSNs in ethanol, which was viewed as a good solvent for nitroarene hydrogenation.<sup>51,52</sup> It was found that these catalysts showed a similar reaction kinetic with a selectivity of 50~60% for *p*-chloroaniline (*p*-CAN) at a conversion of  $\geq$ 90% (Figure \$9) within 9.0 h. The conventional interface-active catalyst  $(Pd/C_8-SiO_2)$  also exhibited a similar catalytic activity and p-CAN selectivity (58.8%). Nitrobenzene (NB), a product of p-CNB dechlorination, was not detected during all of these reaction progresses (Figure S9). These results indicate that these Pd-based catalysts with different metal locations had a nearly identical intrinsic activity and selectivity for p-CNB hydrogenation.

Subsequently, these catalysts were separately served as the solid emulsifier to construct Pickering emulsion (PE) systems and then position the Pd NPs in different microregions of droplet interfaces for *p*-CNB hydrogenation (Figure 2a). Optical microscopy images show that the obtained emulsions had a similar droplet size of 50–150  $\mu$ m (Figure S10). The catalytic results are displayed in Figure 2c. It was observed that Pd-phi/JMSNs, Pd/JMSNs, and Pd/C $_8\text{-}\mathrm{SiO}_2$  exhibited a nearly full conversion ( $\geq$ 99%) within 7.5 h in the PE system under the same conditions as the reaction in ethanol, while Pd-pho/ JMSNs gave a lower conversion of 81.7%. Interestingly, Pdphi/IMSNs presented a superior selectivity of 89.2% for the target product (p-CAN), which was significantly higher than that of Pd-pho/JMSNs (63.6%), Pd/JMSNs (64.9%), and Pd/  $C_8$ -SiO<sub>2</sub> (56.7%). Such a high selectivity achieved over Pd-phi/ JMSNs in the PE system was also much higher than those obtained in the pure water phase (68.5%) and pure oil phase (63.4%) as well as in ethanol (46.8%).

The reaction kinetic was then studied to further check the enhanced catalytic performance of Pd-phi/JMSNs in the PE system. As shown in Figure 2e,f, Pd-phi/JMSNs presented a faster reaction rate with an increase of catalytic efficiency (defined as the moles of converted reactants per mole of Pd per h) from 31 to 44.9  $h^{-1}$  in comparison to Pd-pho/JMSNs. This activity enhancement stemmed from the different interfacial microenvironments should be mainly attributed to the promoting effect of water (for example, H-shuttling effect),<sup>53-57</sup> which could be supported by the remarkable activity difference of Pd-phi/JMSNs in water and toluene phase (Figure S11a). The catalytic efficiency of Pd-phi/JMSNs in the PE system was also higher than that obtained in ethanol  $(25.8 \text{ h}^{-1})$  and in pure water  $(25.7 \text{ h}^{-1})$ . Importantly, we found that the p-CAN selectivity over Pd-phi/JMSNs in the PE system was always higher than that obtained over Pd-pho/ JMSNs and that obtained in pure water during the whole reaction process (Figure S11c,d). After largely extending the reaction time to 24 h, Pd-phi/JMSNs did not display any loss in p-CAN selectivity, while the p-CAN selectivity of Pd-pho/ JMSNs was significantly decreased from 63.6 to 35.8%. This observation revealed that positioning the Pd NPs in the inner interfacial layer prevented the target product of p-CAN from further hydrogenation to the byproduct aniline (AN). To confirm this validation, we performed the hydrogenation reaction of p-CAN in the PE system under the same conditions. It was found that Pd-phi/JMSNs gave a conversion

Table 1. Selective Hydrogenation of Various Chloronitrobenzenes over Pd-phi/JMSNs<sup>a</sup> and Pd/C<sub>8</sub>-SiO<sub>2</sub><sup>b</sup> in the PE System

Product		NH <sub>2</sub>	CI NH <sub>2</sub>	
<b>Controlled</b> inner interfacial reaction <sup>a</sup>	99.9% ( <b>89.2%</b> )	99.9% ( <b>93.2%</b> )	99.9% ( <b>97.8%</b> )	99.9% ( <b>89.7%</b> )
<b>Uncontrolled</b> interfacial reaction <sup>b</sup>	99.9% (56.7%)	99.9% (81.7%)	99.4% (77.1%)	99.9% (80.7%)
Product				сі—
<b>Controlled</b> inner interfacial reaction <sup>a</sup>	99.9% ( <b>99.6%</b> )	99.9% ( <b>88.9%</b> )	99.9% ( <b>93.8%</b> )	99.9% ( <b>99.2%</b> )
<b>Uncontrolled</b> interfacial reaction <sup>b</sup>	99.8% (87.0%)	97.8% (81.0%)	91.8% (85.4%)	99.9% (51.2%)

"Numbers in brackets refer to the chloroaniline selectivity obtained over Pd-phi/JMSNs in the PE system. <sup>b</sup>Numbers in brackets refer to the chloroaniline selectivity obtained over Pd/ $C_8$ -SiO<sub>2</sub> in the PE system. Reaction conditions: 0.2 mmol of chloronitrobenzene, 2 mL of toluene, 2 mL of water, 20 mg of catalyst (Pd: 0.5 mol %), 2.0 MPa H<sub>2</sub>, 25 °C.



**Figure 3.** Impact of oil-water interfacial microenvironments on catalytic performances. (a) Schematic illustration for the interfacial proximity between the Pd NPs of Pd-phi/JMSNs and the oil-water interfaces. (b) Catalytic efficiency and *p*-CAN selectivity of Pd-phi/JMSNs with different JMSN thicknesses (30–100 nm) in the PE system. (c) Schematic illustration for different interfacial interactions between *p*-CNB and interfacial H<sub>2</sub>O molecules at the oil-water interfaces with different interfacial properties. (d) Conversion and *p*-CAN selectivity of Pd-phi/JMSNs in different PE systems within the 7.5 h reaction period.

of only 15.2% within an extended reaction time of 15.0 h (Figures 2g and S12), which was 3.4 times lower than that obtained over Pd-pho/JMSNs (52.0%). The hydrogenation rate of *p*-CAN over Pd-phi/JMSNs in the PE system was also 3.1-fold lower than that obtained in the water phase. Combining all of the above results, we could conclude that the oil—water interface of Pickering droplet plays a critical role in boosting both catalytic activity and product selectivity of Pd NPs in the *p*-CNB hydrogenation.

Furthermore, we inspected the catalytic performances of Pdphi/JMSNs in other PE systems constructed using different organic solvents, including benzene, ethyl acetate, cyclohexane, and octane as the oil phase. Similar water-in-oil Pickering emulsions were obtained in all of the cases (Figure S13) and all of them gave a conversion of >80% under the same conditions (Figure 2d). Importantly, these investigated PE systems presented a superior *p*-CAN selectivity ( $\geq$ 90%), which was substantially higher than that obtained in pure water. The octane-based PE system even exhibited a remarkable *p*-CAN selectivity of 99.6%. These results point to the fact that the outstanding catalytic selectivity of the Pd NPs in the inner interfacial layer of Pickering droplets was a general phenomenon.

Chloronitrobenzenes substituted with various groups were examined to further confirm the generality of oil-water interfaces in regulating catalytic selectivity. The results are presented in Table 1. Pd-phi/JMSNs displayed an excellent selectivity of 93.2-97.8% at a full conversion in the hydrogenation of chloronitrobenzenes with different substituent positions under the same conditions for *p*-CNB. For other chloronitrobenzenes with different substituent groups, including -CH<sub>3</sub>, -OCH<sub>3</sub>, -Cl, -NH<sub>2</sub>, and -OH, Pd-phi/JMSNs also presented a superior selectivity of 88.9-99.6% for haloanilines in the PE system. Notably, these results were all higher than those obtained over  $Pd/C_8$ -SiO<sub>2</sub> in the PE system (Pd NPs randomly distributed near the droplet interfaces). Interestingly, it was found that chloronitrobenzenes with hydrophilic groups substituting at the ortho-position of the  $-NO_2$  group exhibited a higher selectivity. A similar phenomenon was also observed in the hydrogenation of chloronitrobenzenes with hydrophobic substituent groups at the ortho-position of the -Cl group. These results are indicative of a substituent effect, which is likely because these special substituent groups promoted the molecular orientation of chloronitrobenzene and chloroaniline at the oil-water interfaces.

We also examined the recyclability of Pd-phi/JMSNs in the PE system. The catalyst was separated via high-speed centrifugation and washed with ethanol several times at the end of the reaction. The recovered catalyst was directly used for the next reaction cycle. As displayed in Figure S14a, the conversions obtained within the 3.0 h reaction period hardly declined (67.6-69.4%) after three successive reaction cycles, and the conversion obtained for the fifth reaction cycle decreased from the initial 69.4-56.2%. The obtained p-CAN selectivity always remained at a high level (95.5-98.5%). This result suggested a good recyclability, which could be further confirmed by the hot filtration test (Figure S14b). Moreover, we found that Pd-phi/JMSNs still remained a superior interfacial activity after the fifth reaction cycle (Figure S14c) owing to the unique Janus structure of JMSNs. By analyzing the residual filtrate using ICP-MS, ppm Pd species could be detected, indicating that the metal NPs have leached out slightly from the catalyst.

Impact of Oil-Water Interfacial Microenvironments on Catalytic Selectivity. To confirm the impactful role of oil-water interfaces in boosting reaction selectivity, we further investigated the influence of the distance of the Pd NPs away from the droplet interfaces on the catalytic performances, which was achieved by tuning the thickness of JMSNs. By altering the dosage of tetraethyl orthosilicate (TEOS) in the synthetic process, JMSNs with a controllable thickness of 50-100 nm were obtained (Figure S15a-c). After loading the Pd NPs and forming Pickering emulsions (Figure S15d-f), the proximity between Pd NPs and the oil-water interfaces of droplets was controlled (Figure 3a). We could see from the reaction kinetics that the activity of Pd-phi/JMSNs in the PE system was largely declined when adjusting the thickness of JMSNs from 30 to 100 nm (Figure S16a), with the catalytic efficiency significantly reducing from 44.9 to 4.0 h<sup>-1</sup> (Figure 3b). Interestingly, the selectivity was first improved from 89.2 to 94.5% and then dramatically decreased to 69.6% (Figure 3b). Since the thickness of JMSNs had no influence on the activity and selectivity of Pd-phi/JMSNs in ethanol (Figure

S16d), the remarkable correlation between the catalytic performance of Pd-phi/JMSNs and the JMSN thickness in the PE system should be stemmed from the variation in the reaction microenvironment. A thicker nanosheet implied that the Pd NPs had a farther distance to the oil-water interfaces. In this case, it would be more difficult for the p-CNB molecules to contact with the Pd NPs, resulting in the decreased catalytic activity. Meanwhile, the product molecules also had a lower possibility to approach the Pd NPs, leading to the enhanced catalytic selectivity. However, if the Pd NPs were too far from the oil-water interfaces, their surrounding environments would contain only water molecules, with the reaction microenvironment consistent with that in the bulk water phase (Figure 3a). Therefore, a similar catalytic selectivity was presented to that obtained in the pure water phase. These results highlight the importance of the interfacial reaction microenvironment in achieving a high catalytic selectivity.

Furthermore, several additives were separately introduced into the PE system to alter the oil-water interfacial properties (Figure 3c), and then their impact on the catalytic behavior of the Pd NPs was investigated. As shown in Figure 3d, when ethanol with a volume ratio of 10% was added to the typical PE system of Pd-phi/JMSNs, a similar activity was achieved but the p-CAN selectivity was distinctly decreased from 89.2 to 77.1% under the same conditions. A more pronounced decline in the p-CAN selectivity (58.4%) was presented when introducing triethylamine into the PE system. It was even observed that the *p*-CAN selectivity was sharply declined from 84.4 to 44.2% along with the volume ratio of triethylamine gradually increasing from 5 to 15% (Figure S17a). Because triethylamine exhibited little influence on the p-CAN selectivity in ethanol (Figure S17b), the sharp selectivity decline induced by the addition of triethylamine into the PE system must be originated from the modification of the oilwater interfacial properties. When ethanol or triethylamine molecules were introduced into Pickering droplets, they would also enrich at the oil-water interfaces and then substantially perturb the interfacial interaction between p-CNB and interfacial water molecules (which was suggested by the dynamic interfacial tension analysis in Figure S18), thereby resulting in the sharp decline in the *p*-CAN selectivity. On the other hand, water was replaced with deuterated water  $(D_2O)$ that could serve as a stronger hydrogen donor to construct the PE system for *p*-CNB hydrogenation (Figure S19a). Under the same conditions, a remarkable p-CAN selectivity of 98.3% accompanied by a similar activity was achieved (Figures 3d and S19b). Mass spectrum of the product indicated that water did not directly participate in the reaction process as a reactive molecule (Figure S20). Because of their stronger capacity for hydrogen donation,<sup>58</sup> the interfacial  $D_2O$  molecules might have a stronger interaction with p-CNB than interfacial H<sub>2</sub>O molecules, making p-CNB more prone to enrich at the oil-D<sub>2</sub>O interfaces (supported by the dynamic interfacial tension analysis in Figure S21). Such a reinforced interfacial interaction contributed to the remarkable p-CAN selectivity. Saline water was also used to construct the PE system for p-CNB hydrogenation, and a slightly enhanced selectivity (91.2%) was observed. This was possibly caused by the salting-out effect, preventing p-CNB and p-CAN from diffusing into the bulk water phase and ensuring that the reactants were directly hydrogenated at the oil-water interfaces.

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**Figure 4.** Liquid–liquid interfacial catalysis effect. (a–f) MD simulations for the molecular behavior of *p*-CNB and *p*-CAN at the toluene–water interface. (a, d) Density profiles of toluene, water, and the N and Cl atoms of *p*-CNB (a) and *p*-CAN (d) across the toluene–water interface. (b, e) Typical snapshots showing the hydrogen-bonding interactions between *p*-CNB (b) or *p*-CAN (c) and the interfacial water molecules. (c, f) Hydrogen bond density of *p*-CNB in the system of *p*-CNB/toluene–water (c) and *p*-CAN in the system of *p*-CAN/toluene–water (f). (g) Density functional theory (DFT) calculations for the adsorption modes of *p*-CNB and *p*-CAN on the clean Pd(111) surface and on the water-covered Pd(111) surface; DFT calculations for the coadsorption pattern of toluene and *p*-CAN on the water-covered Pd(111) surface; DFT calculations for the inner interfacial layer of Pickering droplets. IHB was referred to as the interfacial hydrogen-bonding interaction.

Additionally, we found that the reaction temperature had a prominent impact on the catalytic selectivity of Pd-phi/JMSNs in the PE system. With an increase of reaction temperature from 25 to 60 °C, the activity of Pd-phi/JMSNs in the PE system was improved while the *p*-CAN selectivity was gradually decreased from 89.2 to 62.7% (Figure S22). This was likely due to the fact that high temperatures weakened the interactions between *p*-CNB or *p*-CAN and the interfacial water molecules, thus presenting a declined *p*-CAN selectivity. All of these interfacial property–catalytic performance associations pointed to the general fact that the interaction between reactants/products and interfacial water molecules

was the decisive factor for boosting the catalytic selectivity of the Pd NPs in the inner interfacial layer of droplets.

**Origin of the Enhanced Catalytic Selectivity.** Molecular dynamics (MD) simulation was then employed to investigate the interfacial behavior of *p*-CNB and *p*-CAN at oil–water interfaces (Figure 4a–f). In accordance with the reactant concentration in the hydrogenation reaction, water and toluene containing *p*-CNB or *p*-CAN with a concentration of 0.1 mol/L were randomly mixed at a molecular level to conduct the demixing simulations. After the MD relaxation, an equilibrated interfacial structure of toluene–water with a thickness of ~12 Å was clearly observed (Figure S23). Notably, such an interface was far from being flat, with a

spot of water molecules protruding into the toluene phase. These protrusions and fluctuations were typical characteristics of oil-water interfaces, which has been theoretically reported to facilitate molecular transport across oil-water interfaces.<sup>51</sup> Interestingly, p-CNB and p-CAN tended to enrich around the toluene-water interfaces. To further inspect their interfacial behavior, the distributions for the N and Cl atoms of all of the p-CNB or p-CAN molecules in the system were counted. As displayed in the density profile (Figure 4a), the N atoms of p-CNB molecules mainly appeared in the interfacial regions while their Cl atoms were in the toluene phase. This observation suggested a preferential molecular orientation, with the  $-NO_2$  group pointing toward the water phase and the C-Cl group toward the toluene phase. For the p-CAN molecules, a more pronounced distribution for the N and Cl atoms was observed in the density profile (Figure 4d), elucidating that p-CAN had a more ordered molecular orientation at the toluene-water interfaces. With such an orientation, the toluene-water interfacial tension would be lowered. As depicted in Figure S24, the measured dynamic toluene-water interfacial tension gradually decreased along with the increase in the concentration of p-CNB or p-CAN, and the decrement caused by p-CAN was more pronounced. These results supported the results of MD simulations.

To disclose the origin of the molecular orientation, we carefully screened and analyzed the simulation snapshots from 200 to 300 ns (an equilibrium state has been reached during this period). We discovered that hydrogen-bonding interactions were ubiquitous between the  $-NO_2$  groups of p-CNB and the water molecules in the interfacial regions. As shown in a typical snapshot (Figure 4b), a strong hydrogen bond with a bond length of 2.15 Å was formed between the O atom of p-CNB and the H atom of interfacial water molecules. We then counted the number of hydrogen bonds appeared in all of the p-CNB molecules during this period. Figure 4c displays the profile of hydrogen bond density along with time. It could be observed that the hydrogen bond number was timeindependent. There was, on average, 1.8 hydrogen bonds presenting in the p-CNB molecules during this period. Likewise, there were strong hydrogen-bonding interactions between *p*-CAN and the interfacial water molecules, and the bond length of the hydrogen bond (2.07 Å) was slightly shorter in comparison to p-CNB (Figure 4e). The average hydrogen bond numbers were even as high as 5.2 (Figure 4f), suggesting that the interfacial water molecules have a stronger hydrogen-bonding interaction with *p*-CAN than with *p*-CNB. In addition, we also inspected the hydrogen bond profile of the system containing 0.05 mol/L p-CNB and 0.05 mol/L p-CAN by the same method. It was found that the hydrogen bond density appeared in the p-CNB molecules was stronger than that obtained in the system containing only p-CNB (Figure S25d). This result revealed that the p-CAN molecules orientated at the interfaces could promote the interfacial orientation of p-CNB molecules, which could be further evidenced by the distributions of the N and Cl atoms (Figure S25b) and the formation of p-CNB/p-CAN dimers (Figures S26 and S27). Collectively, due to the strong hydrogenbonding interactions in the interfacial region (which was very different from that in the bulk water phase<sup>16,60</sup>), *p*-CNB and *p*-CAN had a tendency to enrich at the oil-water interfaces, with the polar  $-NO_2$  or  $-NH_2$  groups pointing toward the water phase but the less polar C-Cl groups toward the oil phase. With such a preferential molecular orientation, the C-Cl

groups of *p*-CNB and *p*-CAN would be far away from the oil—water interfaces, which was conducive to avoiding contact of C-Cl groups with the metal NPs located in the inner interfacial layer of Pickering droplets.

Density functional theory (DFT) calculations were further used to investigate how the oil-water interface regulated the adsorption behavior of reactant and product molecules on the surface of Pd NPs. According to the high-resolution TEM (HRTEM) images, the Pd(111) plane was employed as a model for the calculations (Figure S28). After screening all of the possible adsorption sites and adsorption conformations (Figure S29), it was found that *p*-CNB preferentially adsorbed on the clean Pd(111) surface via the aromatic ring with an adsorption energy of -2.28 eV (Figure 4g), which was much higher than those via the  $-NO_2$  group (-1.01 eV). Such an adsorption conformation implied that both the C-Cl group and the  $-NO_2$  group have access to the metal surfaces. For the p-CAN molecule, an identical adsorption pattern was observed (Figures 4g and S30). The adsorption energy of p-CAN binding with the Pd(111) surface via the aromatic ring (-2.57)eV) was significantly higher than those via the  $-NH_2$  group (-1.29 eV). The parallel adsorption configurations of *p*-CNB and *p*-CAN together with the stronger binding interaction of *p*-CAN in comparison to p-CNB increased the possibility of dechlorination on the Pd NPs and lead to a low selectivity in the hydrogenation of p-CNB, remaining fully consistent with the catalytic result of Pd-phi/JMSNs in ethanol. Subsequently, the adsorption modes of *p*-CNB and *p*-CAN were examined on the Pd(111) surface covered with monolayer adsorption of water molecules (Figure S28b). As shown in Figure 4g, the most stable adsorption configuration of both p-CNB and p-CAN on the water-covered Pd(111) surface was still one with the aromatic ring lying parallel to the surface (Figures S31 and S32). Nevertheless, the adsorption energy of p-CNB (-2.66 eV) was higher than that of p-CAN (-2.12 eV), which was caused by their different interactions with water molecules. A weak adsorption of product molecules was beneficial to their desorption from the metal surface, thus improving the catalytic selectivity. This calculation result was further confirmed by the experimental phenomenon, namely, Pd-phi/JMSNs exhibited a higher *p*-CAN selectivity at a full conversion in water (68.5%) than in ethanol (46.8%).

To further rationally introduce the solvation effect of toluene into the calculation models, we first inspected the binding interaction of toluene with the clean Pd(111) surface and the water-covered Pd(111) surface. It was found that toluene displayed a strong adsorption on the clean Pd(111) surface (Figure S33) and the water-covered Pd(111) surface (Figure \$34) but the optimized adsorption energies on both models (-2.15 or -1.76 eV) were largely lower than that of *p*-CNB and p-CAN. This result suggested that p-CNB and p-CAN adsorbed at the surfaces would not be replaced by toluene via competitive adsorption. Meanwhile, toluene had a very weak interaction with the water adlayer (Figure S35), giving an adsorption energy of only -0.17 eV. Therefore, typical coadsorption of toluene and *p*-CNB or *p*-CAN was performed on the water-covered Pd(111) surface to rationally simplify the toluene-water interfaces on the Pd(111) plane for evaluating their effect on the molecular adsorption behavior. After comprehensively checking all of the possible coadsorption patterns (Figure S36), p-CNB was observed to preferentially bind with the water-covered Pd(111) surface still via the aromatic ring (Figure 4g). Although the preferential adsorption

configuration was unaltered in this case, we discovered that the C-Cl group of p-CNB was tilted up pronouncedly and the tilted angle was higher than that on the clean Pd(111) surface and the water-covered Pd(111) surface (Figure 4g), making the Cl atom of p-CNB away from the metal surface. More interestingly, the most stable coadsorption configuration of p-CAN and toluene on the water-covered Pd(111) surface was one with the *p*-CAN molecule vertical to the surface (Figures 4g and S37). The coadsorption mode binding via the  $-NH_2$ group showed a higher adsorption strength (-2.58 eV) than that binding via the aromatic ring (-2.47 eV). With such an adsorption pattern, the C-Cl group of p-CAN was thoroughly prevented from approaching the metal surface, which was supported by the catalytic results of p-CAN hydrogenation tests (Figure S12). The difference in the coadsorption patterns was likely due to their different binding interactions with the water adlayer (Figures 4g, S38, and S39).

On the basis of all of the above results and analysis, a liquid-liquid interfacial catalysis effect could rationally elucidate the significantly enhanced catalytic selectivity of Pd NPs located in the inner interfacial layer of Pickering droplets (Figure 4h). For the Pd NPs, the C–Cl group of *p*-CNB and *p*-CAN was accessible to the metal surface due to the parallel adsorption patterns. The adsorption strength of p-CAN was higher than that of *p*-CNB, which was detrimental to the fast desorption of p-CAN from the metal surface. These features gave rise to a low catalytic selectivity of intrinsic Pd NPs in the p-CNB hydrogenation. When the Pd NPs were precisely positioned in the inner interfacial layer of Pickering droplets, they were very close to the oil-water interfaces and were highly accessible to the hydrophobic reactants. Importantly, because of the distinctive microenvironments of the coexistence of water and organic solvent in the interfacial regions, providing concurrently hydrogen-bonding interactions with interfacial water and solvation effects of organic solvent, the oil-water interfaces regulated the adsorption behavior of p-CNB and p-CAN on the surface of Pd NPs, especially for p-CAN. The less polar C-Cl groups were prevented from direct contact with the catalyst surfaces. In addition, due to the unique interfacial microenvironments, the adsorption strength of p-CAN that was stronger on the clean metal surfaces than that of *p*-CNB became weaker on the metal NPs in the inner interfacial layer, thus facilitating the timely desorption of p-CAN. Accordingly, this interfacial effect contributed to the superior reactivity and significantly enhanced selectivity of the controlled inner interfacial reaction. Oil-water interfaces providing a reaction microenvironment with a stronger interfacial interaction can regulate molecular adsorption more efficiently and then present a higher reaction selectivity. Reactants with special substituent groups to reinforce interfacial interactions will also generate a higher reaction selectivity.

Generality of the Interfacial Effect of Pickering Droplets in Regulating Catalytic Selectivity. Since the interfacial effects of Pickering droplets were involved in the unique microenvironment in the inner interfacial layer rather than the surface structure modifications of metal NPs, other metal NPs were then extended for selective hydrogenation of p-CNB in the PE system. By the same interfacial assembly strategy, Rh NPs or Pd nanowires were separately loaded on the hydrophilic surfaces of JMSNs and then introduced into the inner interfacial layer of Pickering droplets (Figure S40). As expected, these catalysts were all catalytically active and selective for producing *p*-CAN from *p*-CNB in the PE system (Figure S41), with a selectivity of 97.0–99.0%. Significantly, the obtained *p*-CAN selectivity was higher than that of the metal NPs distributing randomly near the droplet interfaces (77.3–82.8%) and that obtained in the ethanol phase (60.0–67.0%). These results not only further consolidate the proposed interfacial catalysis effect but also demonstrate the general applicability of our strategy in regulating the reaction selectivity of metal catalysts.

## CONCLUSIONS

In summary, oil-water interfaces of Pickering droplets have been explored to effectively regulate the catalytic behavior of metal NPs in hydrogenation reactions, which was achieved by precisely controlling their spatial distribution at the droplet interfaces. Pd NPs located in the inner interfacial layer of Pickering droplets exhibited a substantially higher catalytic selectivity (up to 99.6%) than those in the outer interfacial layer (63.6%) and in other solvents (46.8-68.5%) in the hydrogenation of halonitrobenzenes. This interfacial microregion-dependent selectivity, only associated with the interfacial properties of Pickering droplets, was found to be a general phenomenon, which was applicable to different metal NPs and various halonitrobenzenes. Experimental investigation and theoretical calculation revealed that the microenvironments of the coexistence of water and organic solvents at the droplet interfaces modulated the adsorption behavior of reactant and product molecules on the metal NPs located in the inner interfacial layer to avoid the direct contact of C-Cl bonds with the metal surface. Such an unprecedented interfacial catalysis effect was responsible for the significantly enhanced catalytic selectivity. This work not only demonstrates the great significance of liquid-liquid interfaces in catalysis but also provides an innovative methodology for regulating catalytic reactions on solid catalysts.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c12120.

Experimental details; supplementary characterization data, including SEM images, TEM images, FTIR, optical microscopy images, and nitrogen sorption analysis; supplementary catalytic data; supplementary MD and DFT results; and MS data for the products (PDF)

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## Notes

The authors declare no competing financial interest.

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