Strong metal-support interaction in size-controlled monodisperse palladium-hematite nano-heterostructures during a liquid-solid heterogeneous catalysis

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Metal-semiconductor nanoheterostructure (NHS) exhibits fascinating catalytic performance due to the strong metal-support interaction (SMSI). SMSI in liquid-solid heterogeneous catalysis based on NHS was rarely investigated as compared to the gas-solid counterpart. Two issues, namely, the wet-chemical preparation of monodisperse model catalyst and *in-situ* characterization on the electronic structure, are challenging and studied here. The size of the metal catalyst was finely tuned in a Pd-Fe₂O₃ NHS and electrochemical test revealed that the electronic states differ significantly in liquid environment from in vacuum. The combined amendments resulted in a more reliable conclusion on the SMSI in Suzuki coupling. This study might give some clues on the illusive in-liquid structure-property relationships.

INTRODUCTION

In heterogeneous catalysis, nanoheterostructure (NHS) is an emerging material where the support and the metal unit are integrated as one nanosystem [1–3]. The electron/atom transfer between the two segments would improve the performance, selectivity and stability of the metal catalyst, which is denoted as strong metal-support interaction (SMSI) [4–7]. While gas-solid heterogeneous catalysis sets the basis of chemical industry [8], the liquid-solid counterpart is also quite crucial, especially in fine chemicals [9]. However, most of the studies on SMSI were limited to gas-solid catalysis but very few were on liquid-solid ones. There are two challenges presented ahead.

The first issue is the preparation of monodisperse metal nanoparticles (NPs) on a support, which is crucial to the reliable acquisition on the size dependence in SMSI [10] and also will help to realize the goal, that is, the lowest consumption of noble metal for the highest efficiency in future practice. With the progress in the synthesis of mono-

disperse metal nanocrystals (NCs) [11,12], it is convenient to prepare these metal NCs first and then sinter them with the oxide support, as demonstrated by Cargnello *et al.* [13]. However, the post-annealing might deteriorate the narrow size distribution and the metal-oxide interface is not natively formed. To gain a native metal-support interface, vapor phase methods, such as atomic layer deposition [14] and laser ablation [15], were recently developed to grow size-controllable metal NPs onto semiconductor nanowires (NWs). However, these vapor-phase methods were expensive and non-scalable. Furthermore the resultant catalyst is not dispersible in liquid phase for direct use. While non-uniform supported NPs would come from traditional deposition or impregnation methods [16], scalable wet-chemical methods to directly grow size-tunable monodisperse metal NCs on oxide support are still underdeveloped.

Besides the precise size control of the catalyst, the *in-situ* interrogation on the electronic structure of the catalyst is also vital to obtain a real view on the structure-activity relationship [17]. In operando conditions, the adsorption of reactant molecules, either gaseous [18] or liquid ones [19] to the solid phase, would alter the electronic structure of the catalysts to a certain extent. Hence, the traditional and routinely used vacuum characterizations might be misleading. Gas-phase *in-situ* techniques have been developed in recent years to examine the gas-solid reactions [20], while their liquid-phase counterparts remain retarded [21]. Appropriate methods to characterize the electronic structure of the supported catalyst in liquid still remain scarce. Conventional electronic spectra, such as X-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectroscopy (UPS) are not compatible in liquid phase, while only the expensive scanning tunneling microscopy (STM) [17] or X-ray absorption spectra (XAS) [21] met this demand.

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The combination of size regulated model catalyst and *in-situ* characterization is highly desirable for the study of SMSI, but rarely achieved in a liquid-solid case. To solve the above-mentioned issues, we report here the direct, size-controllable and wet-chemical synthesis of mono-disperse Pd NPs supported on hematite nanorods (NRs) and the investigation on the SMSI via liquid-phase characterizations. The famous Suzuki-Miyaura reaction catalyzed by Pd was chosen as the model reaction. Hematite, as a useful and earth-abundant semiconducting oxide, was chosen as the support material. We found that after adsorption of either the solvent or the reactant, the electrochemical and chemical properties, associated with electronic structures of NHSs, pronouncedly changed, not always the same as those in vacuum. Intuitively, the view from the *in-situ* study brings us closer to the truth and this study will inspire the more reliable understanding on the size- and reaction environment-dependence in the liquid-phase SMSI.

EXPERIMENTAL METHODS

Synthesis

Chemicals

All the reagents were purchased from SCRC or Alfa. De-ionized water was used.

Synthesis of hematite (Fe_2O_3) NRs

0.60 mL of FeCl_3 (1.0 M) and 1.08 mL of $\text{NH}_4\text{H}_2\text{PO}_4$ (0.02 M) was added to 28 mL water, sealed in a 50-mL teflon-lined autoclave and heated at 220°C for 2 h. After the reaction, the product was washed with water and ethanol, centrifuged and re-dispersed in 6.0 mL of water for further use. For electrochemical test, to the Fe_2O_3 product in 6 mL of water was added 24 mL formamide, 0.24 g polyvinylpyrrolidone (PVP) ($M_w = 8,000$) and heated at 85°C for 1.5 h. The PVP-treated Fe_2O_3 NRs were confirmed by XPS that their surface was capped with PVP (see Supplementary Information, part 4-1).

Synthesis of 7 nm Pd- Fe_2O_3 NHSs (Sample 1)

To the as prepared Fe_2O_3 NRs (0.6 mmol Fe, in 6.0 mL water) was added 24 mL formamide, 0.24 g PVP ($M_w = 8,000$) and 0.036 mmol K_2PdCl_4 (0.36 mL $\times$ 0.10 M) and heated at 85°C for 1.5 h. After that, the product was washed and redispersed in 6 mL ethanol. 1 mol% (Sample 1-2) and 3 mol% (Sample 1-3) Pd-to-Fe loading could be obtained via changing the amount of K_2PdCl_4 to 0.006 mmol and 0.018 mmol, respectively.

Synthesis of 10 nm Pd- Fe_2O_3 NHSs (Sample 2)

To the as prepared Fe_2O_3 NRs (0.6 mmol Fe, in 4.0 mL water) was added 16 mL formamide, 0.24 g PVP ($M_w = 8,000$)

and 0.036 mmol K_2PdCl_4 (0.36 mL $\times$ 0.10 M) and heated at 85°C for 1.5 h. The product was washed and redispersed in 6 mL ethanol.

Synthesis of Br-capped 7 nm Pd- Fe_2O_3 NHSs (Sample 3)

It was similar with Sample 2 except for addition of 44 mg KBr.

Synthesis of 4 nm Pd- Fe_2O_3 NHSs (Sample 4)

It was similar with Sample 1 except for addition of 200 mg KBr.

Synthesis of 1.8 nm Pd- Fe_2O_3 NHSs (Sample 5)

It was similar with Sample 1 except for addition of 440 mg KBr.

Synthesis of 7 nm Pd NPs (Sample 6)

25 mg PVP ($M_w = 88,000$) was dissolved in 3.3 mL formamide and heated to 150°C. 5.0 mg PdCl_2 was dissolved in 1.6 mL formamide and injected to the above solution and it was kept at 150°C for 30 min. Acetone was added and the product was centrifuged and redispersed in ethanol.

Synthesis of 10 nm Pd NPs (Sample 7)

25 mg PVP ($M_w = 88,000$) was dissolved in 4 mL formamide and heated to 150°C. To this solution 0.30 mL K_2PdCl_4 (0.10 M in water) was injected and it was kept at 150°C for 10 min. The final products could be obtained by adding acetone and centrifuge.

Synthesis of non-uniform 4 nm Pd- Fe_2O_3 NPs (Sample 8)

To the as prepared Fe_2O_3 NRs (0.6 mmol Fe, in 2 mL water) was added 8 mL formamide, 0.24 g PVP ($M_w = 80,000$) and 0.036 mmol K_2PdCl_4 (0.36 mL $\times$ 0.10 M) and heated at 85°C for 1.5 h.

Catalysis

After optimizations, we chose the following condition for catalysis tests: temperature: 300 K, time: 0–18 h, the amount of phenyl bromide: 0.50 mmol, the amount of phenylboronic acid: 0.65 mmol, the amount of K_2CO_3 : 1.00 mmol, solvent: 1.5 mL water and 1.5 mL ethanol, and the amount of catalyst: 0.5 mol%.

We found that 300 K is enough to activate the coupling reaction. The optimized molar ratio of phenylboronic acid to phenyl bromide is around 1 to 1.5. When this ratio is larger than 2, self-coupling of phenylboronic acid leading to by-product is accelerated. The amount of K_2CO_3 is around 2 to 4 equivalent amounts to phenyl bromide. The solvent was chosen as a 1:1 (v/v) water-ethanol mixture, because both the organic compound and the base (K_2CO_3) would be dissolved and activated. We have also tested the

amount of catalyst and found that 0.5 mol% is the best considering the reaction rate and the dosage.

Characterizations

Electron microscopy and elemental mapping were performed on a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) at 200 kV. C_s -corrected HRTEM were carried out on a Tecnai Titan 80-300 TEM.

Powder X-ray diffraction (PXRD) profiles were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). XPS were recorded on a PHI Quantera SXM spectrometer using monochromatic Al K α X-ray sources (1,486.6 eV) at 2.0 kV and 20 mA, and all the peak values were calibrated according to C_{1s} peak (284.6 eV). Inductively coupled plasma atomic emission spectroscopy (ICP-OES) technique was taken on a 2RIS Intrepid II XSP ICP-OES. ATR-IR was carried out on a Perkin Elmer Spectrum GX FTIR system.

Mott-Schottky Plot was measured on a CHI 650D electrochemical work station using an impedance-capacitance technique. Saturated calomel electrode (SCE) and platinum flag were used as reference and counter electrode, respectively. The working electrode was made by drop-casting 50 μL of the hematite or Pd-hematite dispersion (0.60 mmol Fe in 6.0 mL) onto a 2 cm $\times$ 2 cm fluorine-doped Tin oxide coated glass slide and then calcined at 450°C in Ar for 1 h. The measurement was performed in a 30 mL water/ethanol (v/v = 1:1) solution containing 0.01 mol K_2CO_3 (pH 12). The parameters were as following: voltage scan: -1.0 to 0 V vs. SCE, disturbing amplitude: 0.01 V, frequency: 1 kHz. Before the test, the working electrode was immersed in the solution to achieve equilibrium for 6 h. During the test, Ar was bubbled into the solution and the temperature was maintained at 300 K in a water bath.

RESULTS AND DISCUSSION

Formamide was chosen as both the solvent and reducing agent for its efficiency in synthesizing monodisperse metal NPs [22]. We extended this system to the synthesis of Pd- Fe_2O_3 NHSs from hydrothermally prepared α - Fe_2O_3 NRs [23]. The NRs were dispersed in formamide with palladium precursor (K_2PdCl_4), surfactant PVP, salts (KCl or KBr) and heated to initiate the reduction of Pd(II). (7.0 $\pm$ 1.0)-nm-Pd NPs on α - Fe_2O_3 NRs with a loading amount (confirmed by ICP-OES) of 6 mol% Pd-to-Fe (Sample 1) could be obtained (Fig. 1a). The size of Pd NPs could also be tuned to 10.0 $\pm$ 1.4 nm (Sample 2, Fig. S1a). The temperature and the concentration of Pd should be carefully regulated to controllably initiate the heterogeneous nucleation and inhibit the homogeneous nucleation of the Pd NCs. Different crystal planes were observed in HRTEM

Figure 1 TEM images of (a) Sample 1, (b) HRTEM of Sample 1, (c) Sample 4, (d) HAADF-STEM and elemental mapping of Sample 4, (e) Cs-corrected HRTEM of Sample 5, (f) TEM image of Sample 7.

and assigned to Pd (JCPDS 46-1043) and α - Fe_2O_3 (JCPDS 33-0664) (Figs 1b and e). (012) plane of hematite was present at the interface parallel to (220) plane of Pd (Fig. 1e). It is known that bromide ion is efficient in tuning the metal nanostructures, influencing their nucleation and growth [24]. So we could also obtain heterostructures with 7.0 $\pm$ 0.7 nm Pd (Sample 3, Fig. S1b, Pd/Fe = 6 mol%), 4.0 $\pm$ 0.3 nm Pd (Sample 4, Figs 1c and S1c, Pd/Fe = 6 mol%) and 1.8 $\pm$ 0.2 nm Pd clusters (Sample 5, Figs 1e and S1e, Pd/Fe = 6 mol%) through adding different amount of KBr. HAADF-STEM image confirmed the heterostructure via Z-contrast (Fig. 1d). EDX elemental mapping (Fig. 1d) indicated that Fe and O were uniformly distributed and Pd was scattered as small dots. The phase of α - Fe_2O_3 was verified by PXRD and Pd phase appeared as weak and broadened peaks at 40.0° (111) and 46.6° (200) (Fig. S2) due to its fine grain size.

Based on the finely-tuned NHSs, we assayed the catalytic performance in a Suzuki-Miyaura reaction [25]. The Suzuki-Miyaura reaction involves the coupling of a halo-benzene and aromatic boronic acid, catalyzed by homogeneous [26] or heterogeneous [27] Pd (0) species. Usually, iodobenzene is the most active substrate, bromobenzene is

weaker and chlorobenzene is the most inert [26]. A few reports have dealt with room temperature (RT) reaction between bromobenzene and benzene-boronic acid [28]. For the convenience of further in-solution characterization, we chose phenyl bromide and RT to perform our catalysis. In 18 h, at 300 K, elegant conversion and yield from 70% to >99% were obtained for different substrates at a catalyst-to-substrate molar ratio (C/S) of 0.5 mol% (Table S1). All the products were purified by column chromatography and verified by ^1H NMR (see Supplementary Information, part 3-3).

The relatively inert 4-methoxyl bromobenzene and benzene boronic acid were chosen to calibrate the activity of different NHSs (Table S2). The Turnover Frequency (TOF) was calculated (based on the total mole of Pd) and is listed in Table S2 and plotted as Fig. 2. Among chloride-directing synthesized NHSs, the 7-nm one (Sample 1) was more efficient than the 10-nm one (Sample 2). For bromide-assisted synthesized NHSs, 7 nm-one (Sample 3) is worse than the same-size Cl-capped NHSs (Sample 1), while 4 nm one (Sample 4) showed comparable TOF as Sample 1, chloride-directed one. The 1.8-nm clusters-on-hematite (Sample 5) exhibited the best performance, and the TOF value is the best among those of the reported heterogeneous Pd catalyst, under RT. We also prepared the identical-sized Pd NPs in the same system. In the same system, 7.0 ± 0.9 nm (Sample 6, Fig. S1f) and 10.0 ± 0.7 nm (Sample 7, Fig. 1f) Pd NPs could be synthesized, exhibiting the yield of 33% and 20%, respectively. Their TOF values were significantly lower than those of the same-sized Pd- Fe_2O_3 NHSs, as an indication of the SMSI. A non-uniform Pd- Fe_2O_3 NHS (4.0 ± 2.0 nm, Sample 8, Fig. S1g) was also tested, for comparison with the uniform counterpart, emphasizing the importance of monodisperse model catalyst. Then the reaction was proven to be heterogeneous by filtration experiment, which is also consistent with the literature on the catalysis of Suzuki coupling by PVP-capped Pd NPs [29]. Finally

we measured the kinetic curves of different samples and fit them to obtain the initial reaction rate according to a Langmuir surface single molecule mechanism (part 3-2, in the Supplementary Information).

According to the above results, we adopted an atomistic model (Fig. S5) to explain the reactivity of the different-sized NHSs (see Supplementary Information, part 5) [13]. For bare Pd NPs, only surface atoms were dominated, while if the support (Fe_2O_3 here) was connected, considerable perimeter and corner atoms should be considered. The reactivities of different-sized Pd NPs and NHSs corresponded well with this model (see Supplementary Information, part 5) quantitatively, indicating that the perimeter and corner sites were more active than the surface sites due to lower coordinated numbers and positive responses from the SMSI (e.g., charge transfer).

It is well known that in heterogeneous catalysis, the electronic structure governs the catalytic performance. XPS is a routinely used technique to investigate the charge transfer in supported catalysts. Pd NPs and Pd- Fe_2O_3 NHSs were subjected for XPS (Figs 3a and b) in vacuum. In general, the band bending model was proposed in metal-semiconductor junctions to give a phenomenological description or explanation for the charge transfer of NHSs [30]. In this case, electron was transferred to hematite because the Fermi energy (E_F) of hematite was lower than that of Pd (Scheme 1a, see Supplementary Information, part 4-1) [30]. Similar XPS spectra were observed for 10 nm Pd NPs and 10 nm Pd- Fe_2O_3 NHSs (Fig. S4-1). In terms of SMSI, other possibility than electron transfer, such as encapsulation, alloying and inter-diffusion could be excluded [6] (See Supplementary Information, part 4-1).

To elucidate the nature and effect of the SMSI of Pd- Fe_2O_3 NHSs in vacuum, we performed theoretical investigations using density functional theory (DFT). First of all, we found that the Pd atoms of the Pd_8 cluster-like NP as much as possible bind to the 3-fold coordinated oxygen atoms (O_{3c}) of (012) surface of Fe_2O_3 (Fig. S6a), resembling

Figure 2 TOF values of different samples in Suzuki coupling.

Scheme 1 Band alignment of Pd- Fe_2O_3 NHSs in different environments. Atom denotation: oxygen-blue, carbon-light grey, hydrogen-white, bromine-red, palladium-black, iron-orange. CBM: conduction-band minimum; VBM: valence-band maximum.

Figure 3 Pd 3d XPS spectra of (a) Pd NPs, (b) Pd-Fe₂O₃ NHSs, Mott-Schottky Plot (c) without, (d) with addition of phenyl bromide, (e) ATR-IR spectra.

the case of Pt-ceria system [31]. However, only part of O_{3c} atoms were saturated ultimately, due to the lattice mismatch between the two segments of the NHSs (Fig. S6b). Even so, the bonding model can also result in a well-defined Pd-Fe₂O₃ interface, as shown in Fig. S6. Bader charge analysis indicated that every bound Pd atom donated 0.21–0.4 electrons to Fe₂O₃ support through the Pd-O bonds, while other Pd atoms even at the interface had no contribution to the process, as shown in the electron density difference plot

(Fig. 4a). This result was not only consistent with our XPS measurements in vacuum, but also implied a unique SMSI in such type of partially bonded NHSs (electron transfer only occurring through Pd-O bonds). In contrast to the Pd₈ NP, the accepted electrons were delocalized at undercoordinated 5-fold Fe atoms (Fe_{5c}) of the (012) surface of Fe₂O₃ support and some sub-surface ones, thereby resulting in most of Fe_{5c} atoms, whether bonded or not, to be reduced to Fe²⁺ (Fig. 4b). This would facilitate the catalytic reactions

Figure 4 (a) Isosurface plot of the electron density difference between $\text{Pd}_8\text{-Fe}_2\text{O}_3$ NHS and Fe_2O_3 (012) surface plus Pd_8 cluster-like NP at the isovalue of $0.015 \text{ e}/\text{\AA}^3$. The silver, red and green balls correspond to the Pd, O and Fe atoms, respectively. The yellow areas indicate electron gain, whereas the blue areas indicate electron loss. (b) Charge transfer from Pd_8 to Fe_2O_3 and distribution of reduced $\text{Fe}^{2+}/\text{Fe}^{3+}$ in Fe_2O_3 . The yellow, pale yellow and blue balls correspond to Fe^{2+} , Fe^{3+} ($\delta = 2\text{--}3$), Fe^{3+} , respectively.

that the Fe_2O_3 support involves, such as low temperature CO oxidation [32].

After primary investigation on the electronic structures by in-vacuum XPS route, we turned to a liquid one. Mott-Schottky plot, as a capacitance-voltage scan, was widely used to characterize the flat band potential of a semiconductor [33]. Flat band condition is met at the intercept of Mott-Schottky plot at the x axis (voltage) and this intercept stands for the E_f level of the semiconductor. The equation for Mott-Schottky plot is depicted in Supplementary Information, part 4-3. The positive slope of the Mott-Schottky plot for Fe_2O_3 NRs indicates its n-type nature [28] (Fig. 3c). The flat band potential (V_{fb}) value in ethanol/water/ K_2CO_3 solution of the Fe_2O_3 NRs and $\text{Pd-Fe}_2\text{O}_3$ NHSs were measured to be -0.61 V and -0.58 V vs. SCE (pH 12, $+0.11 \text{ V}$ and $+0.14 \text{ V}$ vs. reversible hydrogen electrode (RHE), or $+4.61 \text{ V}$ and $+4.64 \text{ V}$ vs. vacuum), respectively (the deviations were less than $\pm 0.01 \text{ V}$, see Fig. S4-3). An observable decrease of 0.03 eV for the E_f is found after Pd loading, indicating that the E_f was pulled down by Pd and the electrons transferred from Fe_2O_3 to Pd (Scheme 1b) [30]. This result was also similar with $n\text{-TiO}_2\text{-Pd}$ Schottky junction [34]. In previous literature, the adsorption of water [35,36], ethanol [37,38], OH^- [19] and CO_3^{2-} [39] on hematite or Pd had been studied. Here, E_f of Fe_2O_3 upshifted from -4.85 eV in vacuum [40] to around -4.61 eV ($V_{fb} = +4.61 \text{ V}$ vs. vacuum) in solution, due to the adsorption of liquid species. In metal-semiconductor heterostructures, because the electron density of the metal largely surpasses the semiconductor, the E_f is pinned at the metal level [30]. In our case, the $\text{Pd-Fe}_2\text{O}_3$ holds an E_f at about -4.64 eV and this approximately stands for E_f of Pd. The E_f of Pd might not change much in liquid as compared to vacuum, so it became lower than that of hematite and charge transfer from Fe_2O_3 to Pd occurred.

Moreover, we also studied the effect of selected reactants on the properties of NHSs. After adding bromoanisole, the V_{fb} value of the bare Fe_2O_3 NRs (-0.61 V) remained the same while the $\text{Pd-Fe}_2\text{O}_3$ NHSs shifted to -0.63 V by -0.05 V (Fig. 3d). In heterogeneous Suzuki coupling reaction [41–43], the initial step involves oxidative addition of MeOPhBr to Pd (0), forming a MeOPh-Pd-Br complex that is bond to the surface of Pd (0) NCs [42]. The significant change in V_{fb} of the $\text{Pd-Fe}_2\text{O}_3$ NHSs might stem from the strong adsorption of 4-bromoanisole onto Pd and the upshift of the E_f of Pd (nearly the same as E_f of $\text{Pd-Fe}_2\text{O}_3$) to about -4.58 eV (-0.63 V vs. SCE here). In this case the electrons would flow from Pd to Fe_2O_3 again (Scheme 1c). Then the total E_f of the $\text{Pd-Fe}_2\text{O}_3$ NHSs ascended. Similar results were found for 10 nm $\text{Pd-Fe}_2\text{O}_3$ NHSs (Supplementary Information, part 4-3). In contrast, in bromide capped $\text{Pd-Fe}_2\text{O}_3$ NHSs, the flatband potentials were complex and different due to the smaller size of Pd NCs, as shown in Table S5, part 4-3. The adsorption of MeOPhBr on $\text{Pd-Fe}_2\text{O}_3$ was further confirmed by surface-sensitive ATR-IR (Fig. 3e). The Fe_2O_3 NRs and the $\text{Pd-Fe}_2\text{O}_3$ NHS samples were all equilibrated with a bromoanisole- K_2CO_3 solution in ethanol/water before ATR-IR tests. In Fig. 3e, the peaks around 1000 cm^{-1} are presented for both samples and assigned as carbonate species. The peaks located in the range from 1600 to 1000 cm^{-1} and the fingerprint peak at $\sim 800 \text{ cm}^{-1}$ were found for $\text{Pd-Fe}_2\text{O}_3$ NHSs but absent for Fe_2O_3 NRs (The detailed assignments for the peaks are listed in Supplementary Information, part 4-4). This provided firm evidence that the bromoanisole adsorbed on the Pd surfaces but not onto the Fe_2O_3 .

In the previous studies on liquid-phase SMSI, the authors usually characterize the electronic structure of the NHS catalyst in vacuum, using XPS [44] or XAS [45]. They conclude that electrons flow to or are extracted from the metal NPs to the support, through these in-vacuum observations. In our case, we would conclude that electron extraction from Pd to Fe_2O_3 would lead to better performance of the Pd catalyst, from the vacuum XPS (scheme 1a). However, totally different views would be obtained through *in-situ* examinations (scheme 1b and c). It is clearly demonstrated here that the in-liquid characterization would be closer to the truth and the in-vacuum observation might lead to an illusion.

The favored activation of bromoanisole on Pd in the NHSs might originate from the electron communication across the $\text{Pd-Fe}_2\text{O}_3$ interface. The electronic charge of metallic NCs exerts a major effect on their catalytic reactivity [46]. The electron transfer usually accompanies the partially charged species, such as $\text{Pd}^{\delta+}$, $\text{Pd}^{\delta-}$ or Fe^{2+} . In Suzuki coupling, the rate-determining step involved oxidative insertion of Pd into bromoanisole. Here under the reaction

condition, the Fe_2O_3 withdraws electrons from Pd and the partially positively charged Pd might be more vulnerable to the oxidative addition by bromoanisole.

As we also demonstrated the size-dependence of SMSI in Pd- Fe_2O_3 NHSs, we conclude that by simultaneously tuning the geometric (structural) parameter of NHSs and the reaction environment around them, the properties of these NHSs could be modulated. The current work presents a direct evidence for the connection of the geometrical and environment-dependent electronic effects in the catalytic study.

CONCLUSION

In summary, we synthesized size-controlled Pd NPs and Pd- Fe_2O_3 NHSs and tested their performances in Suzuki coupling. Then we studied the electronic structure of Pd- Fe_2O_3 NHSs in vacuum, in K_2CO_3 solution and with the addition of chemio-adsorptive bromoanisole. It was found that in the three cases, the electronic structures of the NHSs were totally different. We suggest that in the study of SMSI, characterization of the electronic structure in vacuum is not enough and sometimes misleading. We hope that our results would shed light on the study of SMSI in other liquid-solid catalysis.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary data and more discussion are available in the online version of the paper.

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中文摘要 金属-氧化物型纳米异质结构可能存在界面间的电子和物质传输, 因而导致性能的提升, 目前得到广泛的关注. 对于这类金属-氧化物型纳米异质结构在催化反应中的结构-效能关系, 以往的研究存在以下不足之处: 一方面对于尺寸的控制还有欠缺, 不能合成尺寸可控的单分散样品; 另一方面, 对催化剂电子结构的表征主要停留在真空或气相环境, 而液相原位表征方法亟待发展. 本研究发展了一种甲酰胺溶剂合成体系, 可以尺寸连续可调地合成一系列钌-氧化铁纳米异质结构和单独的钌纳米晶. 利用这些模型催化剂, 结合液相电化学测试方法, 我们原位研究了它们的电子结构, 并发现在真空和液相环境中, 这些催化剂的电子结构有明显差异. 这表明传统的真空表征方法可能会造成与真实构效关系的偏离. 研究表明, 高质量的模型催化剂和原位表征方法对于研究构效关系都是至关重要的. 这对于发展高效的金属-氧化物型液-固异相催化剂具有一定的启示意义.