Surface Modification on Pd-TiO2 Hybrid Nanostructures toward Highly Efficient H2 Production from Catalytic Formic Acid Decomposition

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Dedication ((optional))

Abstract: Metallic nanocrystals with well-designed surface structures represent a class of model systems for revealing the fundamental physical and chemical processes involved in heterogeneous catalysis. Herein, we show that surface modification can be utilized as an efficient strategy for controlling the surface electronic state of catalysts and thus a knob for tuning their catalytic activity. As model catalysts, the surface-modified Pd tetrahedrons-TiO_2 nanostructures modified with different foreign atoms show the varied activity in the catalytic decomposition of formic acid toward H_2 production. The catalytic activity increases with a reduction in the work function of modified atoms, which can be well explained by surface polarization mechanism. In this hybrid system, the difference in the work functions of Pd and modified atoms results in surface polarization on Pd surface, tuning its charge state. Together with the Schottky junction between TiO_2 and metals, the tuned charge state enables the promotion of catalytic efficiency in the catalytic decomposition of formic acid to H_2 and CO_2.

Development of new carbon cycles has attracted widespread interest owing to the energy and environmental demands.[1-2] Formic acid (HCOOH) is one of the most preferable choices for carbon cycle with tremendous potential.[3] HCOOH can be produced by solar- or electricity-driven carbon dioxide (CO_2) conversion, simultaneously achieving the energy storage into relatively stable liquid chemicals.[4-5] As a release of energy, HCOOH can be catalytic decomposed to CO_2/H_2 or CO/H_2O via two possible pathways:[6]

Dehydrogenation: $HCOOH \rightarrow CO_2 + H_2$ (1)

Dehydration: $HCOOH \rightarrow CO + H_2O$ (2)

It is worth mentioning that Reaction (1) makes HCOOH a promising hydrogen carrier for hydrogen cycle or hydrogen-based energy applications.[2] For this reason, the high stability, low cost and low toxicity of formic acid designate it as one of the most preferable choices for both carbon and hydrogen cycles. In the catalytic decomposition of formic acid, palladium (Pd)-based nanostructures have been commonly used as catalysts.[3, 7] For example, it has been reported that the Pd nanocrystals with increased electric density showed enhanced activity through a Mott-Schottky junction, whose spherical morphology is enclosed by Pd{111} facets.[3] The progress highlights the opportunity that the control of Pd surface electronic density may maneuver the activity of catalytic HCOOH decomposition. According to our recent work, the hybrid nanostructure formed between TiO_2 nanosheets and tetrahedron-shaped Pd nanocrystals shows higher performance than those with other shaped Pd nanocrystals, benefiting from an increased proportion of surface atoms and a reduced steric effect.[8] We thus specifically select the well-defined Pd tetrahedrons covered with {111} facets as a model system for further investigation.

Heterogeneous metallic nanocrystals with well-designed surface structures have been widely developed to meet the increasing energy and environmental demands.[9-11] For instance, various foreign atoms have been introduced into metallic heterogeneous catalysts toward an increase of selectivity in catalytic reactions.[12-14] This new strategy for catalyst design – surface poisoning works through tuning the chemisorption state of reaction molecules. In a typical case, Pd-Pb alloy nanocrystals and Pd-Au alloy nanocubes showed the improved selectivity in semihydrogenation reactions;[12, 15] the reaction selectivity for the aerobic oxidation of styrene was enhanced by modifying Pd concave nanocrystals with Au.[16] These research advances provide useful information for the further design of catalysts. Other than the chemisorption state of reaction molecules, the electronic state of reaction centers is also influenced by foreign atoms due to their difference work functions. For this reason, the systematic studies based on surface modification will provide the opportunity for rationally designing highly active catalysts from the angle of electronic state control.

In this communication, a well-designed surface modification system is developed for tuning the electronic state of catalytic sites based on surface polarization mechanism. In our proposed system, the Pd tetrahedrons covered by {111} facets provide suitable supports with well-defined surface structures for hosting catalytic sites. Furthermore, the Pd nanocrystals are combined with TiO_2 semiconductor, which forms a Mott-Schottky structure to promote the catalytic activity of HCOOH dehydrogenation under light illumination. Based on the Mott–Schottky junctions, foreign atoms are deposited on Pd tetrahedron-TiO_2 hybrid

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nanostructures. Alloying Pd atoms with the foreign atoms at different work functions can significantly alter the electronic state of Pd atoms. Since the electronic state of Pd sites is a critical factor for the HCOOH dehydrogenation reaction,[3] this surface modification manipulates the catalytic activity of HCOOH dehydrogenation reaction. As a proof of concept, the Pd@Ag$_{5\%}$ tetrahedron-TiO$_2$ hybrid nanostructures achieve 98.4% conversion for HCOOH dehydrogenation to H_2 in 1 hour, 5.3 times higher than bare Pd-TiO$_2$ nanostructures under the same conditions.

The Pd tetrahedrons are *in-situ* grown on commercial TiO$_2$ particles through an aqueous-solution synthesis, forming Pd-TiO$_2$ hybrid structures. As the loading amount of 18% Pd on TiO$_2$ turns out to exhibit the best catalytic performance (Figure S1), the weight percentage of Pd nanocrystals deposited on the commercial TiO$_2$ is 18% in all the samples. Transmission electron microscopy (TEM) images (Figure 1a) indicate that the Pd nanocrystals in Pd-TiO$_2$ hybrid nanostructures possess a tetrahedral shape and are supported on TiO$_2$ particles. The average length of tetrahedrons is determined to 6.3 nm as shown in size distribution diagram (Figure S2). As indicated by high-resolution TEM (HRTEM, Figure 1b), the Pd tetrahedral nanocrystals are covered by {111} facets.

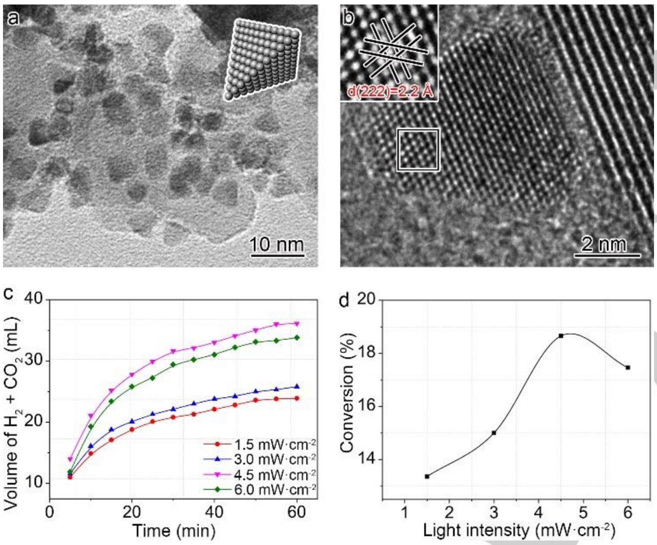

Figure 1. a) TEM and b) HRTEM images of Pd tetrahedron-TiO$_2$ hybrid nanostructures. c) The decomposition of HCOOH to produce H_2, catalyzed by Pd tetrahedron-TiO$_2$ hybrid nanostructures at different light intensities. d) The dependence of catalytic conversion on light intensity. Conditions: 0.5-M aqueous HCOOH solution (5 mL), Pd tetrahedron-TiO$_2$ (Pd: 7.74 mg), 363 K.

Based on the growth of Pd tetrahedrons on TiO$_2$, we evaluate the catalytic activity of Pd-TiO$_2$ hybrid nanostructures in the decomposition of HCOOH in water under different light intensities. The obtained gases are collected by a gas burette filled with water and determined by gas chromatograph (Figure S3). Figure 1c and 1d show the catalytic activity of Pd tetrahedron-TiO$_2$ nanostructures at various light intensities under the same reaction conditions. The volcano-shaped curve shows the maximum activity of Pd tetrahedron-TiO$_2$ nanostructure at 4.5 mW·cm^{-2} with HCOOH conversion of 18.6%. The enhanced activity for the generation of H_2 gas at higher light intensity (below 4.5 mW·cm^{-2}) can be attributed to the increased electron density of Pd by the Mott–Schottky effect, in which the photoexcited electrons in TiO$_2$ are transferred to Pd and become trapped on Pd due to the Schottky barrier.[17] This improvement of catalytic activity also agrees with the previous report in which the increased electron density of Pd{111} by C$_3$N$_4$-Pd Schottky junction could promote the decomposition of HCOOH to H_2 and CO$_2$.[3] As a matter of fact, plasmonic hot electrons can be simultaneously generated in Pd, whose energy is sufficiently high to overcome the Schottky barrier and make them be injected into the conduction band of TiO$_2$.[17] This injection of plasmonic hot electrons into TiO$_2$ conduction band follows an opposite direction against the transfer of photoexcitation electrons from TiO$_2$ to Pd. As Pd is a metal with a low plasmonic coefficient, the photoexcitation of TiO$_2$ together with the trapping of photoexcited electrons on Pd dominates the process over the injection of plasmonic hot electrons at low light intensities. As the light intensity is further increased beyond 4.5 mW·cm^{-2}, however, the photoexcitation in TiO$_2$ is saturated while the generation of plasmonic hot electrons can be continuously promoted.[17] As a result, the injection of plasmonic hot electrons into the conduction band of TiO$_2$ becomes more predominant, reducing the electron density of Pd. This phenomenon has been observed for the TiO$_2$-Pd system previously by our research group.[17] The reduction in the electron density of Pd surface leads to the lower catalytic activity for HCOOH dehydrogenation. It is worth mentioning that the morphology of Pd tetrahdron-TiO$_2$ hybrid nanostructures is well maintained after the catalytic reaction (see Figure S4).

The Pd tetrahedrons on TiO$_2$ supports are further deposited with various metals to form Pd@M (M= Ag, Cu, Au or Pt) tetrahedron-TiO$_2$ nanostructures as illustrated in Figure 2a. The deposition of other metallic atoms is achieved through tightly controlling the reduction of Ag$^+$, Cu^{2+}, Au^{3+} or Pt^{4+} on the surface of Pd tetrahedrons. Given the average edge length of tetrahedrons at 6.3 nm, the surface atoms of a Pd tetrahedral nanocrystal should account for about 35% of the total atoms (see Figure S5). By precisely adjusting the amount of metal precursors below the nucleation concentration, the metallic atoms with less than one atomic layer can be loaded onto the surface of Pd tetrahedrons, instead of undergoing self-nucleation and growth into metallic clusters or particles.[18] It has been reported that the diffusion of metallic atoms is relatively slow at a low temperature (<160 ºC).[19] In this case, the resulted nanostructures should be Pd tetrahedrons with their near-surface region modified by foreign metallic atoms (namely, Pd@M tetrahedron-TiO$_2$). Upon the surface modification, the tetrahedral shape of nanocrystals is well maintained on TiO$_2$ supports (Figure 2b-e). The lattice fringes in HRTEM images (Figure S6) can be assigned to Pd(222), revealing that the nanocrystals are still bounded by Pd{111} facets. Meanwhile, the average length of produced Pd@M tetrahedrons is 6.3-6.4 nm after loading a trace mount of foreign atoms (see the histograms of size distribution in Figure S2).

The presence of foreign metallic atoms (M) in Pd tetrahedrons is confirmed by measuring their chemical compositions with

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inductively coupled plasma-mass spectrometry (ICP-MS). The ICP-MS data (Table S1) show the content of M at 2-8 mol% in the formed Pd@M nanostructures by varying the amount of M^{x+} precursor, which is quite less than the 35% content required for a full atomic layer. Thus the foreign metallic atoms in the resulted nanostructures cannot fully cover the surface of Pd tetrahedrons. In this case, the nanostructures should be the Pd tetrahedrons covered with one layer of PdM (M= Ag, Cu, Au or Pt) alloy surface. To prove this feature, depth-dependent X-ray photoelectron spectroscopy (XPS) has been performed using a synchrotron radiation-based technique at incident photon energies of 450, 500, 600, and 750 eV, providing information for vertical elemental distribution. Taking Pd@Ag tetrahedron-TiO_2 hybrid nanostructures as an example (see Figure S7), the average Ag atomic fractions in our Pd@Ag tetrahedrons decrease from 23% to 10% as the depths are extended from ~0.8 nm (hv = 450 eV) to ~1.0 nm (hv = 750 eV).[20-21] We can thus conclude that the Ag atoms are mostly distributed in the near-surface region of tetrahedrons.

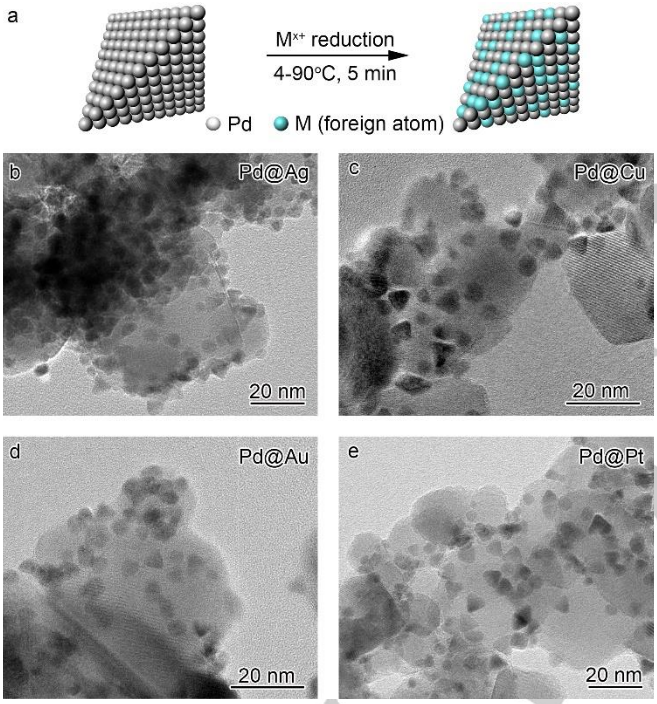

Figure 2. a) Schematic illustration for the deposition of foreign atoms on Pd tetrahedrons. TEM images of b) Pd@$Ag_{5\%}$-TiO_2, c) Pd@$Cu_{5\%}$-TiO_2, d) Pd@$Au_{5\%}$-TiO_2 and e) Pd@$Pt_{5\%}$-TiO_2 hybrid nanostructures.

We are now in a position to evaluate the catalytic performance of Pd@M tetrahedron-TiO_2 nanostructures in HCOOH decomposition. To assess the catalytic activity by each type of modified Pd sites, the decomposition reactions are performed on various catalysts including Pd@$Ag_{2\text{-}8\%}$ tetrahedron-TiO_2, Pd@$Cu_{2\text{-}8\%}$ tetrahedron-TiO_2, Pd@$Au_{2\text{-}6\%}$ tetrahedron-TiO_2 and Pd@$Pt_{2\text{-}7\%}$ tetrahedron-TiO_2 with the same Pd molar amount (0.07 mmol) and light intensity (4.5 $mW \cdot cm^{-2}$). By modifying the Pd tetrahedrons with foreign atoms, the conversion of HCOOH catalyzed by hybrid nanostructures is dramatically enhanced to 98.7% or reduced to 4.2% at the reaction time of 1 hour. Among the catalysts, Pd@$Ag_{5\%}$ tetrahedron-TiO_2 achieves the highest performance with a conversion of 98.7% (Figure 3a). Meanwhile, the Cu- and Au-modified Pd tetrahedron-TiO_2 nanostructures show the enhancement of catalytic conversion from 18.6% (bare Pd-TiO_2) to 63.2% and 35.5%, respectively (Figure 3b and 3c). However, Pd@Pt tetrahedron-TiO_2 exhibit a reduced catalytic activity regardless of the molar ratio of Pt (Figure 3d). Note that bare TiO_2, bare Pd tetrahedrons or M-TiO_2 (M= Ag, Cu, Au or Pt) in the absence of Pd exhibits only a very limited catalytic activity in HCOOH decomposition under the same conditions (Table S2).

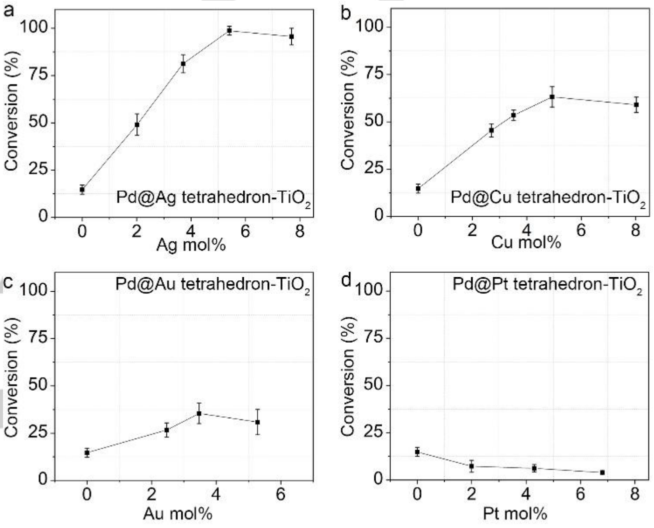

Figure 3. The conversion of HCOOH decomposition to produce H_2, catalyzed by a) Pd@Ag tetrahedron-TiO_2, b) Pd@Cu tetrahedron-TiO_2, c) Pd@Au tetrahedron-TiO_2 and d) Pd@Pt tetrahedron-TiO_2 hybrid nanostructures.

Upon evaluating the catalytic performance of Pd@M tetrahedron-TiO_2 hybrid nanostructures, a question naturally arises: what factor is responsible for the variation in catalytic activity? The side reaction for HCOOH decomposition – HCOOH dehydration produces CO, which may poison Pd surface although it is not a dominating pathway for the HCOOH decomposition on Pd. The poisoning effect of molecular CO on Pd surface is one of the most important issues for Pd catalyst deactivation.[22] For this reason, it is necessary to investigate whether the addition of foreign atoms on surface can tune the adsorption state of molecular CO and thus prevent such a poisoning effect to promote catalytic activity. To explore this possibility, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) has been employed to examine the chemisorption of molecular CO on Pd and Pd@M tetrahedron-TiO_2 nanostructures. Since most samples with ~5 mol% foreign atoms show maximal activity, Pd@$M_{5\%}$ tetrahedron-TiO_2 nanostructures are chosen for further analysis. Typically, we first collect the spectra of samples before CO treatment at room temperature, which can be used as a background. Subsequently, the samples are exposed to pure CO gas for 30 min to enable a CO adsorption equilibrium. Then the samples are treated at room temperature with a N_2 flow to remove the physically adsorbed CO molecules. As shown in the collected spectra (Figure 4a), the peaks located at 1850-1980 cm^{-1} and 2000-2100 cm^{-1} result from the bridge- and top-site occupied CO molecules, respectively.[23] The comparison clearly shows that Pd@Ag$_{5\%}$ tetrahedron-TiO$_2$ nanostructures offer lower CO coverage for the bridge sites according to the reduced wavenumber (1911 cm^{-1} *versus* 1938 cm^{-1} for bare Pd). Although Pd@Pt$_{5\%}$ tetrahedron-TiO$_2$ shows a slight reduced CO coverage, an obvious peak for top-site occupied CO arises. In comparison, the slightly increased wavenumbers of bridge-sites-CO indicate a higher coverage of CO on Pd@Au$_{5\%}$ tetrahedron-TiO$_2$ and Pd@Cu$_{5\%}$ tetrahedron-TiO$_2$. However, the Au- and Cu-modified samples exhibit the improved catalytic performance in HCOOH decomposition against bare Pd. Based on the DRIFTS observations, we can exclude that the poisoning effect of CO is the crucial factor to catalytic performance tuned by the addition of foreign metallic atoms.

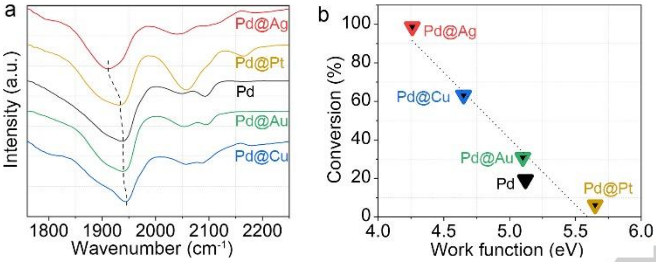

Figure 4. a) DRIFTS spectra of molecular O_2 on Pd and Pd@M tetrahedron-TiO$_2$ nanostructures. b) Plot of the conversion of HCOOH decomposition *versus* the work function of modified M, where M = Ag, Cu, Au and Pt.

As indicated by Table S2 and previous reports, the initial rates of HCOOH decomposition by bare Ag, Cu, Au and Pt are comparably low. However, the Ag-modified Pd tetrahedron-TiO$_2$ nanostructures show the obviously increased activity in catalytic HCOOH decomposition. The promotion effect of Ag, Cu and Au on catalytic HCOOH decomposition follows the order of Ag > Cu > Au, while the Pt-modified sample shows a reduced activity. Thus we assume that the effect of foreign metallic atoms on catalysis should originate from the interaction between different metals. From the viewpoint of electronic structures, various metals possess different work functions, which drives the charge redistribution between the metal atoms (i.e., charge polarization effect).[24] As a matter of fact, the work function of Ag {111}, Cu {111}, Au {111}, Pd {111} and Pt {111} are 4.74, 4.94, 5.31, 5.6 and 5.93 eV, respectively.[21] In order to equilibrate the electron Fermi distribution between metal atoms, electrons prefer to be accumulated from a metal with low work function to that with high work function.[24] Thus the electron density of Pd sites tuned by charge polarization should follow the order of Pd@Ag > Pd@Cu > Pd@Au > bare Pd > Pd@Pt, which agrees with the trend for catalytic activity in HCOOH decomposition (Figure 4b). This reasonable finding again illustrates that the increased electron density of Pd sites can promote HCOOH decomposition.

Another possible effect from foreign metallic atoms reported in literature is surface poisoning,[12, 15] which happens to the metal atoms with large radii. To confirm that this effect of foreign metallic atoms on catalysis does not originate from surface poisoning, we prepare another reference sample by depositing Pb on Pd tetrahedron-TiO$_2$ hybrid nanostructures (Figure 5a). Pb possesses a large atomic radius but a low work function. Thus the Pd@Pb tetrahedron-TiO$_2$ sample should exhibit both surface poisoning and charge polarization effects. As shown in Figure 5b, the Pd@Pb tetrahedron-TiO$_2$ nanostructures offer quite low catalytic activity in HCOOH decomposition. We thus can conclude that HCOOH decomposition is actually suppressed by surface poisoning.

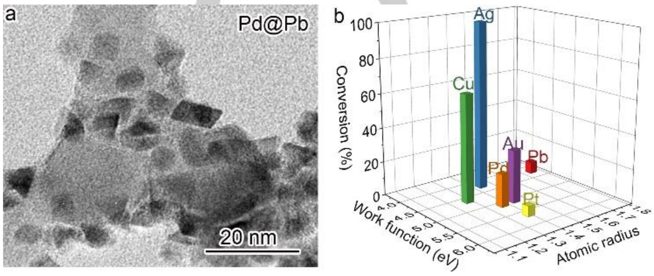

Figure 5. a) TEM image of Pd@Pb tetrahedron-TiO$_2$ hybrid nanostructures. b) The relationship between the conversion of HCOOH decomposition and the work function or atomic radius of modified M for various Pd@M tetrahedron-TiO$_2$ hybrid nanostructures, where M = Ag, Cu, Au, Pt and Pb.

In summary, Pd@M tetrahedron-TiO$_2$ hybrid nanostructures have been developed by controllably depositing foreign metallic atoms on the surface of Pd tetrahedrons. This feature makes it possible to precisely control surface structures without changing the morphology and chemical environment of nanostructures, which sets up a platform for manipulating the electronic state of surface Pd atoms. As such, the catalytic conversion of HCOOH dehydrogenation to produce H_2 can be altered by simply differing the type and concentration of surface-modified foreign atoms. Taken together with Mott-Schottky junction, the nanostructures modified with well-selective metallic atoms achieve the dramatically enhanced HCOOH dehydrogenation under light irradiation. The concept demonstrated here calls for future efforts on the control of surface electronic state toward rational catalyst design.

Experimental Section

HCOOH decomposition reaction. In a typical reaction, the catalyst containing 7.74 mg of Pd was dispersed in 4.9 mL of water with constant magnetic stirring in a home-made quartz reactor, followed by the addition of 0.1 mL of HCOOH. The reaction temperature was kept at 363 K using an oil bath. The dispersion was then subjected to the UV treatment provided by a Xenon-lamp (Solaredge 700, China) parallel light source system under stirring for 1 hour. The volume of produced gases (CO_2+H_2) during the catalytic reaction was monitored by a gas burette system and gas chromatography (GC, 7890 A, thermal conductivity detector, TCD, Ar carrier, Agilent). The content of CO (if any) was analyzed by a GC equipped with a methanation reactor and then detected by using the flame ionization detector (FID) whose detection limit for CO is 1 ppm. No signals for CO were observed for all the samples.

DRIFTS spectroscopic characterizations. The DRIFTS measurement for molecular CO chemisorption was performed using a Bruker IFS 66v Fourier transformation spectrometer with a Harrick diffuse reflectance accessory at room temperature. The usage of Pd and Pd@M-TiO_2 nanostructures was determined by the molar content of Pd atoms (10 mmol).

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Keywords: surface modification • palladium • work function • formic acid • hydrogen production

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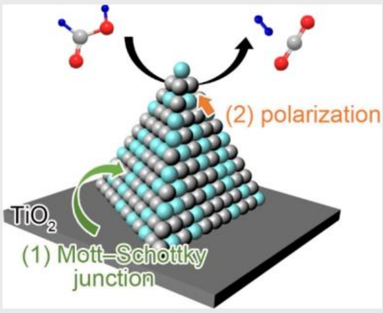
COMMUNICATION

A model system in which Mott-Schottky junction and surface polarization effects are combined has been developed to manipulate the surface electronic state of catalysts. The surface modification of Pd tetrahedron-TiO_2 hybrid nanostructures can effectively alter the electronic state of Pd sites, thereby tuning the catalytic activity of formic acid decomposition toward H_2 production.



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