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Design of Pd{111}-TiO_2 interface for enhanced catalytic efficiency towards formic acid decomposition

Yang You[†], Hao Huang[†], Song Xia, Zijian Cai, Panyiming Liu, Chengming Wang, Ran Long[*], Li Song & Yujie Xiong[*]

Hefei National Laboratory for Physical Sciences at the Microscale, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, China

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Supports are commonly implemented in the industrial application of heterogeneous catalysts to improve the stability and recyclability of catalysts. The supported catalysts often show the enhanced activity and selectivity in various catalytic reactions. However, the specific contributions of electronic and steric effects to a catalytic system often remain elusive due to the lack of well-defined model systems. In this work, two types of uniform Pd nanocrystals covered by {111} facets in tetrahedral and octahedral shapes, respectively, are synthesized with identical chemical environment and loaded on TiO_2 supports to form hybrid structures (Pd{111}-TiO_2) towards the application of formic acid decomposition. Our observation suggests that the polarization effect at the interface of Pd-TiO_2 enhances its activity in formic acid decomposition. Moreover, the Pd tetrahedrons-TiO_2 hybrid structure whose Pd{111}-TiO_2 interface possesses a larger angle shows higher catalytic activity, owing to the reduced steric effect as compared to Pd octahedrons-TiO_2. This study reveals the nature of interface effects in formic acid decomposition, and provides a guidance for the related catalyst design.

palladium, facet, formic acid decomposition, interface

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The design of highly efficient heterogeneous catalysts is critical to the development of approaches for saving energy in industrial chemical production [1,2]. To this end, fundamental understanding on the working mechanisms in the catalytic reactions becomes a central theme of catalysts design [3,4]. It is well known that the heterogeneous catalytic reaction essentially occurs on the surface of catalyst. Thus catalytic performance relies on the interaction between related molecules and surface structure, including molecular adsorption, molecular activation (e.g., orbital hybridization), bond cleavage and bond formation. As demonstrated in many catalytic reactions, the surface structure of catalysts play crucial roles in tailoring the activity and selectivity in catalytic reactions. For instance, it has been discovered that octahedral Pd nanocrystals exhibit superior catalytic activity to cubic Pd nanocrystals in Heck-type coupling reactions, but cubic Pd nanocrystals show higher catalytic activity than octahedral Pd nanocrystals in Suzuki-type coupling reactions [5].

Based on surface control, catalytic performance can be further boosted by loading catalysts on supports. In the industrial application of heterogeneous catalysts, supports are commonly implemented to improve the stability and recyclability of catalysts. Moreover, the supported catalysts often show the enhanced activity and selectivity in various catalytic reactions [6–8]. Great efforts have been devoted to

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[†] These authors contributed equally to this work.
[*] Corresponding authors (email: longran@ustc.edu.cn; yjxiong@ustc.edu.cn)

elucidate the fundamental mechanisms behind each phenomenon over the past decades [6,9]. For instance, it has been reported that the control over the interface between Ag nanoplates and CuO dramatically enhances the activity in catalyzing CO oxidation [10]. As such, interface control becomes quite important to the development of catalyst design. However, the addition of supports may bring about an electronic effect and/or a steric effect to catalytic processes, which are often entangled together. This forms the obstacle for appreciating the specific contributions of electronic and steric effects in a catalytic system. To clarify the case, one has to controllably form various interface structures as model systems, which firstly relies on the formation of well-defined surface structures on nanocrystals. Taken together, the precise control over interface structures based on specific surface structures should be fundamentally important to mechanism investigation and catalyst design.

In recent years, formic acid (FA) has received broad interests due to its tremendous potential in hydrogen cycle and carbon cycle [11,12]. Carbon recycling can be accomplished through the catalytic conversion of carbon dioxide (CO_2) to FA with solar or electric energy, which simultaneously achieves the storage of energy in liquid chemicals [13–15]. In the meantime, the transformation between CO_2 and FA involves a cycle of hydrogen resource (see Figure 1). As a matter of fact, the decomposition of FA may follow two possible pathways [16]:

Dehydrogenation:

$$\mathrm{HCOOH} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \quad \Delta G = -48.4\ \mathrm{kJ/mol} \tag{1}$$

Dehydration:

$$\mathrm{HCOOH} \leftrightarrow \mathrm{CO} + \mathrm{H_2O} \quad \Delta G = -28.5\ \mathrm{kJ/mol} \tag{2}$$

Apparently, reaction (1) is an ideal pathway for the double cycles of carbon and hydrogen. In the reaction system of FA dehydrogenation, palladium (Pd)-based materials have been identified as the most active catalysts owing to the lowest effective barrier and highest efficiency [6,16–21]. However, the usage of capping agents in the synthesis of different Pd nanocrystals has led to various chemical environment on nanocrystal surface, which would bring challenges for the understanding on active sites in catalytic reactions. Since the nature of active sites in FA decomposition is fundamentally important to catalyst design, the interface structure control based on specific facet structures and identical chemical environment will provide a platform for investigating the relationship between interface structures and catalytic performance.

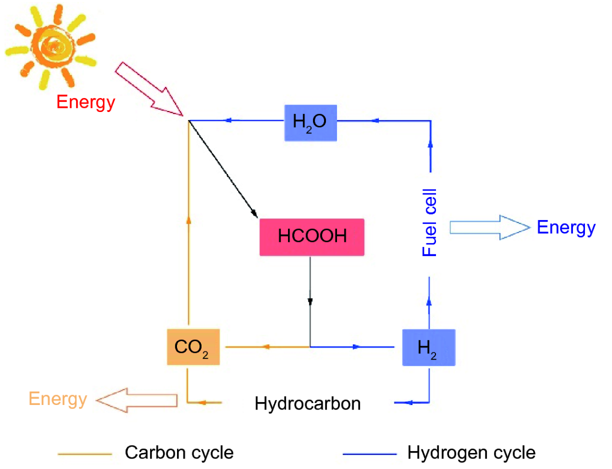

Figure 1 Schematic illustrating the cycles of carbon and hydrogen through HCOOH (color online).

In this communication, we report the synthesis of Pd tetrahedral and octahedral nanocrystals with identical chemical environment, particle size and surface crystal facet through a one-step process in the presence of formaldehyde via kinetics control. This synthesis paves the way to form two Pd{111}-TiO_2 hybrid nanostructures with different interface angles. The identical chemical environment and crystal facet of Pd{111}-TiO_2 hybrid nanostructures allow us to investigate the interface-dependent catalytic effects for the future development of high-efficiency catalytic structure. As a proof-of-concept, we demonstrate that the Pd{111}-TiO_2 hybrid nanostructure with a larger interface angle exhibits higher catalytic activity in FA dehydrogenation, while the polarization effect at the interface of Pd-TiO_2 enhances the catalytic activity of both nanostructures in FA dehydrogenation.

In the synthesis, we employ a simple reaction system which includes Pd precursor (K_2PdCl_4), stabilizer (poly(vinyl pyrrolidong), PVP), reductant (ascorbic acid, AA) and capping agent/co-reductant (formaldehyde) in aqueous media. The slow reduction of Pd^{2+} generates 8-nm single-crystal nano-tetrahedrons covered by {111} facets at a feeding rate of 5–45 mL/h as indicated by transmission electron microscopy (TEM) images (Figure 2(a) and Figure S1(a), Supporting Information online). However, when the feeding rate is controlled up to 90 mL/h, the growth of nanocrystals can be turned into 8-nm single-crystals nano-octahedrons, which is also covered by {111} facets. High-resolution TEM (HRTEM) characterization (Figure 2(c, d)) verifies the majority of {111} facets on surface for both tetrahedrons and octahedrons, although a very small portion of {100} facets can be observed on the corners of truncated octahedrons. Furthermore, a higher feeding rate (360 mL/h) produces cuboctahedron nanocrystals enclosed by a mix of {111} and {100} facets (see Figure S1). This sequence implies that the synthetic process of Pd nanocrystals is under the kinetic control of atomic addition.

To elucidate the formation mechanism of nano-tetrahedrons, we have collected samples from different feeding stages at a feeding rate of 5 mL/h (see Figure S2). TEM images show that the nanocrystals take a tetrahedral shape at the early growth stage when only 25% of Pd precursor is injected into the synthetic system. In addition, the time-

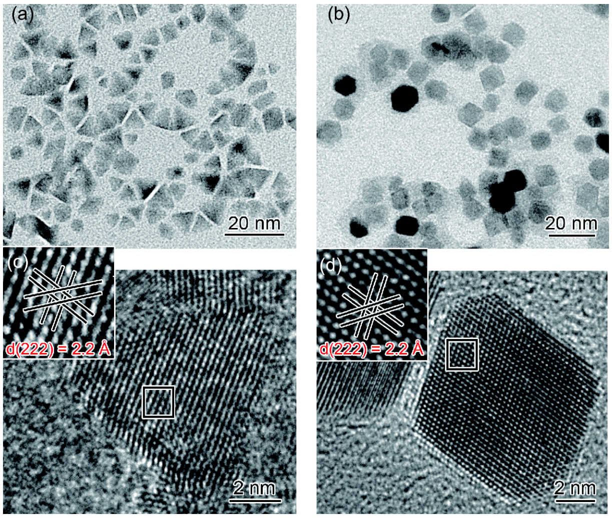

Figure 2 Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of Pd (a, c) tetrahedrons and (b, d) octahedrons used in the investigation. (a, b) TEM; (c, d) HRTEM (color online).

dependent results confirm that the tetrahedral shape of nanocrystals is well maintained and the nano-tetrahedrons slightly grow from 5 to 8 nm. Similar growth patterns have also been observed for the synthesis of Pd nano-octahedrons. The nanocrystals take a cuboctahedral shape and then grow into octahedrons with their corners slightly truncated at a feeding rate of 90 mL/h (see Figure S3).

Based on the surface control, we further synthesize Pd-TiO_2 hybrid structures with exposed Pd {111} facets through a previously developed protocol—*in-situ* growth [22]. This material system provides identical atomic arrangement and chemical environment at their interface. TEM images (Figure 3(a, c)) clearly show that the Pd nanocrystals with an average edge length of 8-nm have a tetrahedral and octahedral profile, respectively. High-resolution TEM (HRTEM) characterization (Figure 3(b, d)) confirms that the tetrahedrons and octahedrons are both enclosed by {111} facets. According to the geometries of tetrahedrons and octahedrons, they possess different interface angles of 109.5° and 70.5°, respectively. As the samples are identical in terms of surface chemical environment, atomic arrangement and particle size, we can safely rule out the possibility that the catalytic activity is affected by facet or size effects in the following FA dehydrogenation reactions.

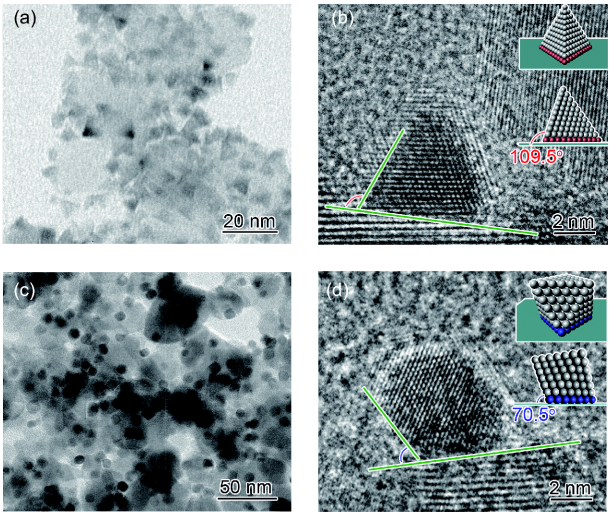

Figure 3 TEM and HRTEM images of (a, b) Pd tetrahedrons-TiO_2 and (c, d) Pd octahedrons-TiO_2 with the same Pd{111} surface facets but different interface angles. The insets of (b, d) show the schematic illustration for interface structures. (a, c) TEM; (b, d) HRTEM (color online).

Upon achieving the facet control and interface control, we are now in a position to assess the performance of nanostructures in the proposed FA decomposition reaction. In the assessment, the usage dose of catalysts is maintained constant for all the catalysts (12.52 mg Pd). The obtained gas is collected by gas burette filled with sodium hydroxide solution, and determined by gas chromatograph (GC). Sodium hydroxide solution (1 M) is commonly used to absorb the yielded CO_2 gas, leaving H_2 or CO gas for further detection. To assess the efficacy of Pd{111}-TiO_2 interface in catalysis, we also use bare Pd octahedrons and tetrahedrons with {111} facets as reference catalysts in the evaluation of catalytic FA dehydrogenation activity.

As displayed in Table 1, TiO_2 is inactive for catalytic FA decomposition, while the reading of 8.1 mL in the control experiment should result from thermal expansion and is excluded from all the measurement data. According to the experiment results, the catalytic activity of Pd tetrahedrons is 1.5 times that of Pd octahedrons. It is worth mentioning that the proportion of surface atoms on tetrahedrons is significantly higher than octahedral and cuboctahedra shapes (see Figure S4). Considering the proportion of surface atoms on tetrahedrons (43.7% of surface atoms) and octahedrons (28.6% of surface atoms) [23], the $TONs_{surface}$ (TON=turn over number) of bare tetrahedrons and bare octahedrons are quite comparable (18.0 vs. 15.2).

Further with TiO_2 supports, the catalytic performance of both Pd tetrahedrons and Pd octahedrons is enhanced, indicating the contribution of interface effects to catalysis in Pd{111}-TiO_2 hybrid nanostructures. The volumes of produced H_2 gas are significantly increased with the addition of TiO_2 supports from 19.8 to 30.3 mL for Pd octahedrons and from 29.3 to 63.1 mL for Pd tetrahedrons, respectively. Specifically, the $TON_{surface}$ of Pd octahedrons-TiO_2 is twice higher than bare Pd octahedrons, and the $TON_{surface}$ of Pd tetrahedrons-TiO_2 is 3.4 times higher than bare Pd tetrahedrons. The enhancement in catalytic activity can be well understood based on the interfacial polarization between metal and semiconductor [10]. The different work functions between Pd and TiO_2 result in the accumulation of electrons at the Pd side [22]. The increase in the electron density of Pd surface, associated with the interfacial redistribution of charges, in turn promotes the catalytic FA decomposition [6].

Table 1 Experimental results of FA dehydrogenation reactions [a)]

	Dose$_{Pd}$ (mg)	Dose$_{TiO_2}$ (mg)	Light (mW/cm^2)	Volume (mL)	TON$_{total}$	TON$_{surface}$
Blank	–	–	–	8.1	0.0	0.0
TiO_2	–	50.0	–	8.1	0.0	0.0
TiO_2	–	50.0	1	8.1	0.0	0.0
Octahedrons	12.5	–	–	19.8	4.3	15.2
Tetrahedrons	12.5	–	–	29.3	7.9	18.0
Cuboctahedrons	12.5	–	–	18.7	3.9	11.9
Octahedrons-TiO_2	12.5	50.0	–	30.3	8.2	34.7
Octahedrons-TiO_2 [b)]	12.5	50.0	–	31.5	8.7	36.6
Octahedrons-TiO_2	12.5	50.0	1	32.5	9.1	38.2
Tetrahedrons-TiO_2	12.5	50.0	–	63.1	20.4	62.3
Tetrahedrons-TiO_2 [b)]	12.5	50.0	–	65.7	21.4	65.3
Tetrahedrons-C	12.5	50.0	–	25.1	6.3	19.3
Tetrahedrons-Al_2O_3	12.5	50.0	–	24.5	6.1	18.6
Tetrahedrons-TiO_2	12.5	50.0	1	71.8	23.7	72.2
Cuboctahedrons-TiO_2	12.5	50.0	–	25.7	6.5	15.0
Cuboctahedrons-TiO_2	12.5	50.0	1	28.9	7.7	17.7

a) Reaction conditions: 1 M aqueous FA solution (10 mL),120 min, 365 K, volume of H_2 is measured by gas burette. No CO has been detected in GC. b) Denotes the samples after extensive removal of capping agents.

Thus the Pd-TiO_2 hybrid nanostructures show a substantial enhancement on catalytic activity. In order to further confirm this interfacial polarization effect, the materials without a suitable band structure such as carbon (C) and aluminum oxide (Al_2O_3) are employed as substrates (Table 1). Pd tetrahedron-C and Pd tetrahedron-Al_2O_3 show comparable performance to that of bare Pd tetrahedron by considering that one face is blocked by substrates, as no interfacial polarization takes place.

Although the performance of both tetrahedrons and octahedrons is improved by TiO_2, the Pd{111}-TiO_2 interface shows an enhancement on Pd tetrahedrons-TiO_2 and Pd octahedrons-TiO_2 hybrid structures with different enhancement factors while the two samples share the same chemical environment, particle size and surface facet. Since the edge lengths of nanocrystals are identical, the lengths of interface edges should be consistent for these two nanostructures. The only difference between these samples is the angle of interface, which may alter the reaction process through a steric effect. The three surface facets of a tetrahedron or an octahedron are connected with TiO_2 substrate to form three angles of 109.5° or 70.5°, respectively. As the electronic polarization effect dramatically decays with the distance to the interface, the most active sites should be located at the surface of Pd tetrahedrons or octahedrons near the interface. In this case, the angle of Pd{111}-TiO_2 interface would be a key parameter to catalytic activity from the viewpoint of steric effect. It is known that the decomposition of FA is a combination of bond whirligig, wrench and cleavage processes, including formic acid adsorption, first dehydrogenation step ($HCOOH \rightarrow HCOO+H$), second dehydrogenation step ($HCOO \rightarrow CO_2+H$) and release of H_2 [17]. The large interface angle of Pd tetrahedrons-TiO_2 (109.5°) provides more space for the molecular bond whirligig/wrench during the reaction. To further demonstrate the importance of steric effect to FA decomposition, we employ Pd cuboctahedrons as a reference sample in the catalytic reaction under the same condition. Similarly to octahedral and tetrahedral nanocrystals, the TON$_{surface}$ of Pd cuboctahedrons-TiO_2 is higher than that of bare Pd cuboctahedrons. Although the Pd cuboctahedrons possess a smaller size (about 5 nm) and a larger number of surface atoms, the catalytic activity of Pd cuboctahedrons-TiO_2 is slightly lower than Pd octahedrons-TiO_2 nanostructures. This suggests that the small interface angle of Pd cuboctahedrons-TiO_2 (54.7°) may hinder the catalytic reaction (see Figure S5).

In the discussion of electronic structures and interface angles, one potential concern is the effect of capping agents on catalytic reactions. To further investigate the impact of capping agents on catalytic performance, Fourier-transform infrared spectroscopy (FTIR) has been employed to examine the existence of surface PVP on Pd tetrahedron-TiO_2 nanostructures. As displayed in Figure S6, most of PVP has been removed by a centrifugation and washing process. To more thoroughly clean the surface of Pd nanocrystals, a water steam treatment is employed to remove the residual surface PVP on samples [24]. Without the interference from PVP, both Pd tetrahdrons-TiO_2 and Pd octahedrons-TiO_2

show the slightly increased performance, which further proves the consistent chemical environment of samples. Based on the results, we can conclude that interfacial polarization plays an important role in the enhancement of catalytic activity.

It is worth pointing out that incident light can further improve the catalytic activity of Pd{111}-TiO_2 (Table 1), as the Schottky junction formed between Pd and TiO_2 can trap photoexcited electrons on Pd. This further verifies that FA decomposition can be promoted by the addition of electrons to Pd surface. Therefore, we can conclude that both electronic and steric effects play important roles in the process of catalytic FA decomposition. The electron density of Pd surface tuned by polarization effect or Schottky junction and the reaction space brought by controllable geometry structure are two factors for ensuring high catalytic activity. Moreover, the morphology of hybrid nanostructures is well maintained after the FA decomposition reaction (see Figure S7).

In summary, we have achieved the synthesis of Pd nanocrystals with identical surface facet and chemical environment through kinetic control, which can be integrated with TiO_2 supports at different interface angles. Even at the identical size, Pd tetrahedrons possess a larger portion of surface atoms (43.7% of surface atoms for 8-nm Pd tetrahedron), which leads to a great improvement on catalyst atomic economy. Furthermore, the polarization effect on the metal-oxide interface can largely improve the catalytic activity in FA decomposition. In the meantime, the steric effect associated with the interface angle between catalyst and substrate holds the key to further tuning FA decomposition efficiency. This investigation on the catalytic performance of controllable hybrid nanocatalysts provides fundamental information for interface design, and may serve as a new approach to further develop cost-effective and highly efficient catalysts in other reactions.

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

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