

Communication

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Size-Dependent Electrocatalytic Reduction of CO₂ over Pd Nanoparticles

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Supporting Information Placeholder

ABSTRACT: Size effect has been regularly utilized to tune the catalytic activity and selectivity of metal nanoparticles (NPs). Yet, there has been a lack of understanding on size effect in the electrocatalytic reduction of CO₂, an important reaction coupling with intermittent renewable energy storage and carbon cycle utilization. We report here a prominent size-dependent activity/selectivity in the electrocatalytic reduction of CO₂ over differently-sized Pd NPs, ranging from 2.4 nm to 10.3 nm. The Faradaic efficiency for CO production varies from 5.8% at -0.89 V (vs. reversible hydrogen electrode) over 10.3 nm NPs to 91.2% over 3.7 nm NPs, along with an 18.4 fold increase in current density. Based on the Gibbs free energy diagrams from density functional theory calculations, the adsorption of CO₂ and the formation of key reaction intermediate COOH* are much easier on edge and corner sites than on terrace one of Pd NPs. In contrast, the formation of H* for competitive hydrogen evolution reaction is similar on all three sites. A volcano-like curve of the turnover frequency for CO production within the size range suggests that CO₂ adsorption, COOH* formation and CO* removal during CO₂ reduction can be tuned by varying the size of Pd NPs due to the changing ratio of corner, edge and terrace sites.

The accelerated depletion of fossil fuel resources leads to increasing accumulation of greenhouse gas, CO₂, in the atmosphere, which raises serious environmental concerns.¹ To reduce our dependence on the fossil fuel, renewable energy sources, such as solar and wind energies, are growing up rapidly, whereas, these renewable electricities are difficult to be merged into the electricity grid due to their intermittent and local nature, and further expansion is highly limited by the lack of efficient energy storage and conversion techniques.² Electrocatalytic reduction of CO₂ to fuel and chemical feedstock, powered by intermittent renewable electricity, is an attractive route for simultaneous conversion of CO₂ and renewable energy sources.³ However, there are several fundamental challenges in the electrocatalytic reduction of CO₂, such as high overpotential, low Faradic efficiency due

to the competitive hydrogen evolution reaction (HER), etc.^{4,5} Key points in addressing these issues, are the successive CO₂ adsorption,⁶⁻⁹ intermediates formation^{10,11} and product removal^{12,13} on active sites during the electrocatalytic reaction.

Various metallic electrodes have been screened thoroughly, and it is found that the trends on product composition and distribution are strongly dependent on the binding energy of intermediates on metals.¹⁴ For instance, CO₂ is converted into CO on Au, Ag and into hydrocarbons on Cu due to the adsorption strength of CO* intermediates on metals.¹⁴ Varying the particle size has also shown a size effect on the electrocatalytic reduction of CO₂, where the dependence of Faradaic efficiency and current density on particle size has been observed on Ag¹⁵, SnO₂¹⁶, Cu¹⁷ and Au^{18,19} nanoparticles (NPs). However, there have been limited studies looking into the size effect among NPs smaller than 10 nm, which are most commonly used in catalysis. Recently, studies on the CO₂ reduction reactivity trends over Au NPs within a very narrow size range of ~1-8 nm¹⁸ or 4-10 nm¹⁹ were reported. Current density for both CO and H₂ production increases obviously with decreasing the size of Au NPs along with the decrease in Faradaic efficiency toward CO production. Density functional theory (DFT) calculations reveal that the edge site on Au NPs is much more active than terrace and corner sites for CO₂ reduction to CO, while corner sites are highly active for competitive HER. In contrast to the behavior of Au NPs, we report here Faradaic efficiency for CO production increases with decreasing Pd NP size in a size range of 2.4-10.3 nm, which varies from 5.8% at -0.89 V (vs. reversible hydrogen electrode, RHE) over 10.3 nm NPs to 91.2% over 3.7 nm NPs, along with an 18.4 fold increase in current density for CO production. DFT calculations indicate that corner and edge sites (small Pd NPs) facilitate the adsorption of CO₂ and formation of key reaction intermediates COOH* during CO₂ reduction compared with terrace one (large Pd NPs), while the formation of H* for competitive HER is similar on all three sites. Furthermore, a volcano-like curve of the turnover frequency (TOF) for CO production within the size range suggests that CO₂ adsorption, COOH* formation and CO* removal during CO₂ reduction can be tuned on differ-

ently-sized Pd NPs due to the changing ratio of corner, edge and terrace sites.

A series of carbon-supported Pd NPs were prepared using sodium citrate as a stabilizing agent and NaBH₄ as a reductive agent. The particle size of Pd NPs was controlled by adjusting the ratio of sodium citrate to PdCl₂ and the reduction temperature. For distinction, the average size of Pd NPs in each sample was used in the sample name, for instance, 3.7 nm-Pd indicates that Pd NPs in the Pd/C catalyst has an average particle size of 3.7 nm. Figure 1 and Figure S1 show transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of six Pd/C catalysts with different sizes. The NPs are uniformly deposited on carbon support, and typical Pd(111) plane with the characteristic lattice spacing of 0.23 nm is observed. Figure S2 shows the corresponding histograms of particle-size distribution of six Pd/C catalysts by counting more than 200 particles for each from the TEM images. The particle size distribution gradually broadens with increasing NP size. X-ray diffraction (XRD) patterns of the Pd NPs are shown in Figure S3, and the average crystalline size of Pd NPs was calculated from the (220) diffraction peak (Table S1). Obviously, both TEM and XRD results confirm that a series of Pd NPs in a narrow size range are successfully prepared. The actual loadings of Pd in all the Pd/C catalysts are 18.3 ± 0.5 wt%, as measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) as listed in Table S1. The consistent loading of Pd in Pd/C catalysts allows us to directly compare CO₂ reduction activities of different Pd/C catalysts and investigate the size effect of Pd NPs.

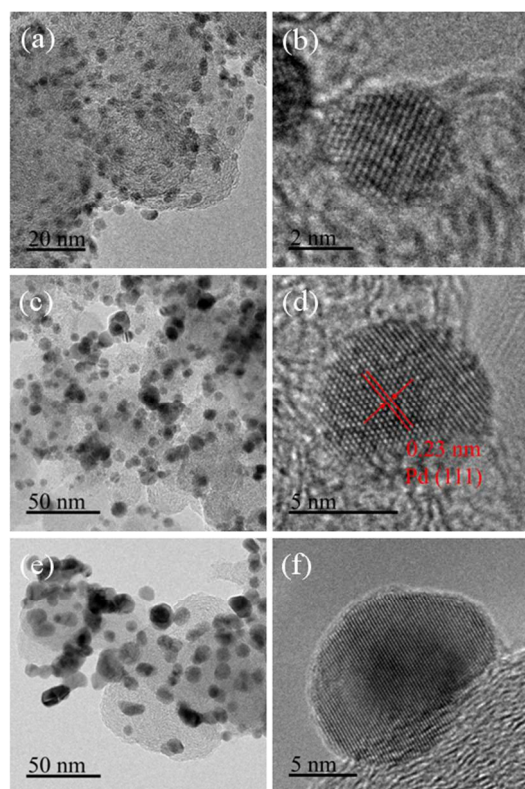


Figure 1. TEM image and HRTEM images of (a, b) 3.7 nm-Pd, (c, d) 6.2 nm-Pd and (e, f) 10.3 nm-Pd.

Controlled potential electrolysis of CO₂ was performed in an H-cell (separated by Nafion 115) filled with 0.1 M KHCO₃ solution (pH=6.8) as shown in Scheme S1. Under the reported reaction conditions, CO and H₂ were major products as detected by an on-line micro gas chromatography (GC), and only trace amount of formate with a Faradaic efficiency of 0.37-1.3% (Table S2 and Figure S4) was detected by nuclear magnetic resonance (NMR). Figure 2a-b shows the applied potential dependence of Faradaic efficiency and current density for CO production over Pd NPs. All the Faradaic efficiencies for CO production firstly increase with applied potential, despite the size of Pd NPs. The competitive HER is facile at low overpotentials and CO₂ reduction is prone to occur with increased applied potential. However, the Faradaic efficiency decreases at high applied potentials, which is probably caused by the limited mass transport of CO₂ in 0.1 M KHCO₃ solution. On 2.4 nm Pd and 3.7 nm-Pd, all the Faradaic efficiencies at different potentials exceed 80%, and the maximum value of 91.2% is reached at -0.89 V (vs. RHE), which is much higher than that over Pd wire electrode (<6%).²⁰ The Faradaic efficiencies for CO production over 2.4 nm Pd and 3.7 nm-Pd are also comparable to those over Au and Ag NPs.^{15,18,19,21}

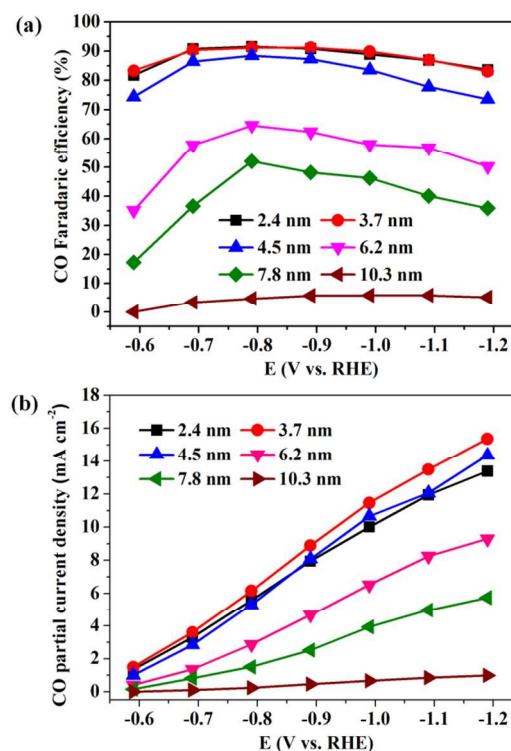


Figure 2. The applied potential dependence of (a) Faradaic efficiencies and (b) current densities for CO production over Pd NPs with different sizes.

The current density for CO production increases with applied potential (Figure 2b), indicative of accelerated reaction rate for CO₂ reduction at high applied potentials. Figure S5 summarizes the mass activities of Pd NPs for CO production at various potentials. The mass activity reaches $23.9 \text{ A g}^{-1}_{\text{Pd}}$ at -0.89 V (vs. RHE) on 3.7 nm-Pd, which is higher than that on 4 nm-Au NPs¹⁹ in the case of a similar metal loading on car-

bon and is comparable to that on ultrathin Au nanowire.²¹ It should be noted that the mass activity of Pd NPs was measured based on gas diffusion electrode, which can be directly used in practical compact electrolysis cells. Therefore, these Pd/C catalysts demonstrate promising applications for practical industrial CO₂ electrocatalytic reduction processes.

Interestingly, the Faradaic efficiencies and current densities for CO formation over Pd NPs with different sizes are quite different at various potentials. The current densities for CO production on 2.4 nm-Pd are smaller than that on 3.7 nm-Pd with nearly the same Faradaic efficiency. Further increasing the size of Pd NPs, both Faradaic efficiencies and current densities for CO production decrease saliently. The Faradaic efficiency decreases sharply from 91.2% to 5.8% over a particle size ranging from 3.7 nm to 10.3 nm at -0.89 V (vs. RHE). The current densities for CO production also change in the same trend, and the current density on 3.7 nm-Pd has an 18.4 fold increase compared to that over 10.3 nm-Pd, which is in contrast to the case of Au NPs.^{18,19} To the best of our knowledge, the unique particle size dependence of the Faradaic efficiencies and current densities toward CO₂ reduction has not been reported previously.

In order to understand the relationship between the CO₂ reduction reactivity and the size of Pd NPs, DFT calculations were conducted. It is still a computational challenge to directly simulate the CO₂ reduction over Pd NPs with different sizes by means of DFT calculations. However, it is possible to simulate the process over three different reaction sites (terrace, edge and corner) of Pd NPs, represented by flat Pd(111) surfaces, stepped Pd(211) surfaces and Pd₅₅ (or Pd₃₈) clusters, respectively. Furthermore, according to the ratio of three kinds of reaction sites (terrace, edge, and corner) on ideal Pd NPs with different sizes, it is reasonable to build the intrinsic relationship between catalytic properties and NPs size.²² CO₂ weakly adsorbs on Pd(111), Pd(211), Pd₅₅ with 0.23, -0.11 and -0.21 eV respectively and CO₂ prefers to be away from Pd(111) (Figure S6). The calculated Gibbs free energy diagrams for CO₂ reduction into CO on Pd(111), Pd(211), Pd₅₅ and Pd₃₈ at 0 V (vs. RHE) are shown in Figure 3 according to the methodology proposed by Nørskov et al.²³ It is seen that on Pd(111), the formation of COOH*, a key reaction intermediate of CO₂ reduction, is associated with an increase in free energy (0.22 eV). While on Pd(211) and Pd₅₅, COOH* is very stable with a release of -0.15 and -0.53 eV, respectively. Therefore, the formation of reaction intermediate COOH* becomes easier from terrace (Pd(111)), stepped (Pd(211)) to corner (Pd₅₅). Pd₃₈ has a free energy similar to Pd₅₅. On these models, the formation of CO*, another reaction intermediate, are all exergonic with very similar Gibbs free energy changes with those of COOH*, due to that the conversion of COOH* to CO* is typically facile.^{21,24} Therefore, it is concluded that the formation of COOH* is a key electrochemical step for CO₂ reduction to CO. The main reason for different changes of Gibbs free energies on different reaction sites is that the adsorption of COOH and CO become stronger from terrace, step to corner site (Figure 3 and Figure S7). These calculations well explain that Pd NPs have positive shifts in the position of the reduction peak of Pd(OH)₂ in the cathodic scan²⁵ between 0.9 V and 0.5 V with increasing particle size (Figure S8). The reduction peak potential of Pd(OH)₂ shows a linear decrease with increasing the size of Pd NPs (Figure

S8c), since a stronger hydroxyl adsorption on defects (corner and edge sites), corresponding to small Pd NPs, than on terrace sites for large Pd NPs.²⁶ The strong adsorption of CO on Pd NPs could be probed by the electrochemical CO stripping voltammetry method.²⁵ As shown in Figure S9, a broad CO stripping profile with a dominant peak around 1.03 V (vs. RHE) occurs on 2.4 nm-Pd, 3.7 nm-Pd and 4.5 nm-Pd, whereas there is a sharp peak around 0.9 V (vs. RHE) with a shoulder peak around 1.03 V (vs. RHE) on 6.2 nm-Pd, 7.8 nm-Pd and 10.3 nm-Pd. The negative shift on peak potential and the reduced current density at 1.03 V (vs. RHE) with increasing particle size suggest the weakened adsorption of CO* on Pd NPs, in consistent with the DFT calculations (Figure S7). From the calculated Gibbs free energy diagrams, the formation of H₂ has tiny differences on these models (Figure S10), and the overall Gibbs free energy changes is much smaller than that for the formation of CO*, indicating that CO₂ reduction is predominant under the present experimental conditions.

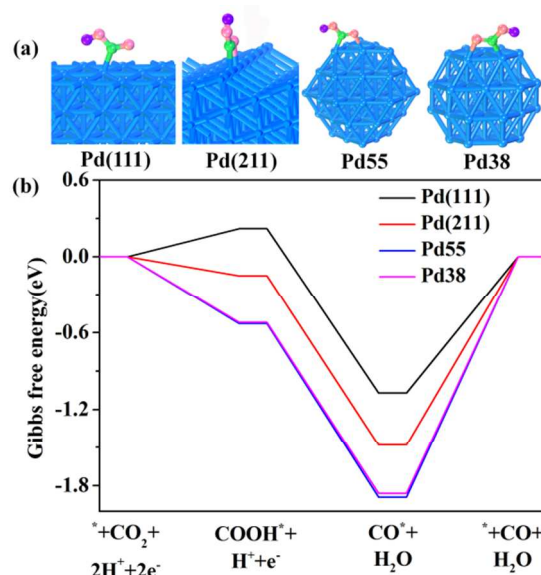


Figure 3. (a) The adsorption of COOH and (b) Free energy diagrams for CO₂ reduction to CO on Pd(111), Pd(211), Pd₅₅ and Pd₃₈.

According to the DFT calculation results, the corner and edge sites on Pd NPs are considered active for CO₂ reduction, and the corner, edge and terrace sites are all active for HER. TOF for CO or H₂ production on Pd NPs at various potentials was calculated according to the ratio of corner and edge or the ratio of corner, edge and terrace in Pd NPs (Figure S11). Figure 4 shows the size dependence of TOF for CO production at various potentials. The maximum TOF varies from 3.7 nm-Pd to 4.5 nm-Pd when the applied potential is shifted from -0.59 V to -0.89 V (vs. RHE) gradually. The sluggish removal of CO* at a high coverage on 3.7 nm-Pd, having a higher ratio of corner and edge sites, probably retards the increase of TOF with the potential, compared with that on 4.5 nm-Pd. The difference of TOF for CO production over differently-sized Pd NPs is enlarged at high applied potentials, revealing that the electrochemical step for formation of HCOO* and CO* becomes dominant on

the reaction rate. The increase of TOF on 2.4 nm-Pd and 10.3 nm-Pd is much less sensitive with the applied potential than that on Pd NPs with the middle sizes (Figure S12a), which suggests that the non-electrochemical step plays very important roles on 2.4 nm-Pd and 10.3 nm-Pd, probably associated with the strong adsorption of CO on step and corner sites and weak adsorption of CO₂ on terrace site, respectively. TOF for H₂ production increases with the increasing size of Pd NPs at various potentials (Figures S12b and S13). The formation of H⁺ is similar on corner, edge and terrace sites, which participates both CO₂ reduction and HER. The increase of TOF values for H₂ production in the size range from 2.4 nm to 4.5 nm is sluggish because H⁺ on corner and edge sites (small Pd NPs) might mainly participate in the formation of COOH* and CO* in CO₂ reduction. On the contrary, H₂ production increases drastically in the size range from 4.5 nm to 10.3 nm because H⁺ on terrace site (large Pd NPs) is less influenced by the formation of CO and is converted to H₂ predominantly.

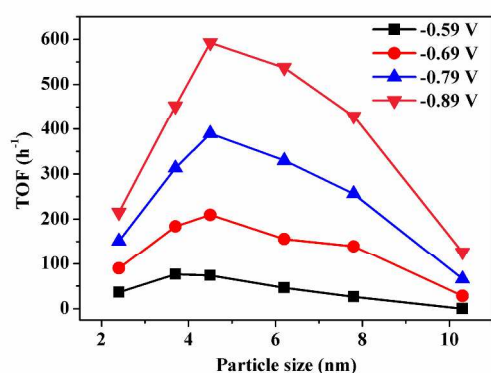


Figure 4. Size dependence of TOF for CO production on Pd NPs at various potentials.

In summary, a unique particle size dependence of Faradaic efficiencies and current densities for CO₂ reduction has been demonstrated over Pd NPs with the narrow size range of 2.4 nm to 10.3 nm. DFT calculations found that corner and edge sites on Pd NPs were more active than terrace one toward CO₂ reduction and that competitive HER was similar on all three sites. The volcano-like curve of TOF for CO production within the size range suggests that CO₂ adsorption, COOH* formation and CO* removal during CO₂ reduction can be tuned by varying the size of Pd NPs due to the changing ratio of corner, edge and terrace sites.

ASSOCIATED CONTENT

Supporting Information

Experimental details, TEM and HRTEM images, XRD patterns, mass activities for CO production, cyclic voltammograms and DFT calculation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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Table of Contents

