



# Boosting electrocatalytic activities of plasmonic metallic nanostructures by tuning the kinetic pre-exponential factor



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## ABSTRACT

The electrocatalytic activity of metallic nanostructures is commonly tuned by changing their structure, composition, size and morphology to decrease the activation energy of a rate-determining elementary step. Here, we report that the electrocatalytic activity of the excited plasmonic model Pd nanostructured electrocatalyst for oxygen reduction reaction (ORR) can be enhanced significantly by increasing the kinetic pre-exponential factor. The localized surface plasmon resonance (SPR) effect promotes a two-orders of magnitude increase in the apparent pre-exponential factor in the Arrhenius equation. Combined experimental and theoretical analyses of the kinetic H/D isotope effect indicate that the observed increase in the apparent pre-exponential factor is attributable to an increased quantum-mechanical proton tunneling arising from the local electric field enhancement upon SPR excitation. Intriguingly, the ORR activity enhancement can be observed under simulated solar light illumination, implying potential for fuel cell applications. The methodology developed in this study is applicable to other proton-coupled electron-transfer reactions, thus opening a promising route to manipulating electrocatalytic reactivity by tuning the kinetic pre-exponential factor and suggesting potential for fuel cell applications.

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## 1. Introduction

The efficient electrocatalysis of the oxygen reduction reaction (ORR) is important in many applications, including proton exchange membrane fuel cells and metal-air batteries [1–3]. In particular, ORR at the cathode is a key factor limiting the performance of fuel cells because of the exceptionally high O=O bond energy and the sluggish ORR kinetics, even on commonly used Pt- and Pd-based metallic nanostructured electrocatalysts [4,5]. According to transition-state theory, the rate constant ( $k$ ) of an electrochemical reaction could be tuned by either activation energy ( $E_a$ ) or pre-exponential factor ( $A$ ) of a rate-determining elementary step ( $k = Ae^{-E_a/RT}$ ) [6,7]. The conventional strategy for tailoring the activity and selectivity for ORR is to tune the intrinsic electronic and geometric effects of metallic nanostructures

[2,8,9]; these changes can lead to a decrease in the activation energy because the electron transfer of an inner-sphere electrocatalytic reaction occurs in an activated complex [10]. However, the effective control of electronic and geometric effects of metallic nanostructures, for example by alloying Pt and/or Pd with non-noble metals [11,12] and/or fabricating uncommon geometric metallic nanostructures [13–16], to decrease the ORR activation barrier has almost approached a technological bottleneck over the past thirty years. To alleviate this challenge, a crucial issue to be addressed is whether or not the electrocatalytic reactivity on metallic nanostructures can be further increased by tuning the kinetic pre-exponential factor.

Alternatively, by applying an external stimulus (e.g., temperature), the ORR kinetics could be altered. Electrocatalytically active nanostructures of noble metals, such as Pt and Pd, usually show a unique localized surface plasmon resonance (SPR) effect [17,18], which could be used as a promising external stimulus to directly drive heterogeneous photocatalytic reactions. Since the first report on the direct plasmonic photocatalysis for HCHO oxidation to CO<sub>2</sub>

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on optically insert SiO<sub>2</sub>-supported Au nanoparticles [19], direct plasmonic photocatalysis on Au and Ag nanostructures has been extensively investigated to improve the energy efficiency and selectivity of chemical reactions [20–23]. Recently, Linic and co-workers reported that plasmon excitation of the localized SPR on Cu nanoparticles resulted in a reduction of the surface Cu oxide, leading to a greatly improved selectivity for propylene epoxidation reaction [24]. The integration of bimetallic nanomaterials (such as Ag or Au) with another catalytically active metal (typically Pt and Pd) within one plasmonic nanostructure can efficiently accelerate some chemical reactions, induced by localized SPR excitation [25–27]. Similarly, if external radiative energy is applied to an inner-sphere electrocatalytic system, the local electric field near the surface of the metal nanostructures could be enhanced [28], which would boost the electrocatalytic reactivity [29]. Primary mechanistic studies on direct plasmonic photocatalytic systems have suggested that the reactivity enhancement is mainly caused by the transfer of energetic electrons to adsorbate orbitals. However, it is unclear if the enhancement in the reactivity was resulted from a reduction of the activation energy or an increase in the pre-exponential factor, or both.

Both the electrocatalytic reactivity and SPR feature of metallic nanostructures are highly dependent on the structure, composition, size and morphology of the nanostructures [30–32]; thus, the controlled synthesis of well-defined metallic nanostructures with tunable electrocatalytic and SPR properties is particularly important to the design of direct plasmonic electrocatalytic systems. We herein describe a simple but very efficient method for controlled synthesis of ultrathin Pd nanorods (NRs) with a diameter of ca. 1.5 nm and a tunable length of 4.9 to 22.6 nm from Na<sub>2</sub>-PdCl<sub>4</sub> by using CO as a reducing agent (see the [Supplementary Information](#) for details). The SPR can thus be tunable over a broad spectral range. Interestingly, we found that the ORR electrocatalysis on the plasmonic model Pd NRs electrocatalyst is greatly enhanced via the manipulation of the kinetic pre-exponential factor, although Pd is not the best electrocatalyst for the ORR. To the best of our knowledge, this work is the first report on the manipulating SPR to dramatically increase the pre-exponential factor of an electrocatalytic chemical reaction.

## 2. Methods

### 2.1. Catalyst preparation

In a typical synthetic procedure, 210 mg of PVP and 100 mL of 3.876 mM Na<sub>2</sub>PdCl<sub>4</sub>/methanol solution were added into a flask. 0.2, 0.6, and 1.0 mL of water were added into the above flask to control the length of the resultant Pd nanorods (NRs). High-purity N<sub>2</sub> at a flow rate of 200 mL min<sup>-1</sup> was used for de-aeration of the solution for 1 h under stirring. Then, high-purity CO by 200 mL min<sup>-1</sup> was introduced to the flask under gentle stirring. The reaction temperature was kept at 30.0 ± 0.1 °C unless stated otherwise. The products were washed with acetone and water for at least five times and recovered via a centrifugation. For a comparison, Pd sphere nanoparticles were prepared at 25 °C using a similar procedure but in aqueous solution.

### 2.2. Catalyst characterization

Transmission microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with an FEI Tecnai 30F microscope at an accelerating voltage of 200 kV. The sample was prepared by ultrasonically suspending the catalyst powder in ethanol. A drop of suspension was then placed onto a holey copper grid and dried in air for TEM measurement.

All the UV-Vis-near IR absorption spectra of Pd NRs and NPs samples were taken on the Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer at room temperature.

### 2.3. Electrochemical evaluation

Porous electrodes were prepared as follows [33]: 2 mg of the catalyst, 0.2 mL of Nafion (5 wt%, Aldrich) and 2.8 mL of ultrapure water were mixed ultrasonically. Then, 3 μL of this ink (about 2 μg of the nanocrystals) was transferred onto a glassy carbon disk (GC, 3 mm in diameter), and left to dry overnight. Electrochemical measurements were performed using a CHI 730 Potentiostat and a conventional three-electrode cell. The catalytic activity of the oxygen reduction reaction (ORR) was measured with a rotating disk electrode (Radiometer, France). The counter electrode was a GC plate, and a saturated calomel electrode (SCE) was used as the reference electrode. All the potentials, however, were referenced with respect to the standard hydrogen electrode (SHE). High-purity nitrogen or oxygen was used for de-aeration of the solutions. During the measurements, a gentle gas flow was kept above the electrolyte. The electrolyte used was either 0.1 M HClO<sub>4</sub> + H<sub>2</sub>O or 0.1 M DClO<sub>4</sub> + D<sub>2</sub>O. Before electrochemical measurements, the potential of Pd based electrodes was firstly held at -0.292 V (vs. SCE) in 0.1M HClO<sub>4</sub> for at least 5 min to remove the residual PVP [34]. Unless stated otherwise, the linear scanning voltammograms (LSVs) of the ORR were conducted in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup> and with a rotation speed of 1600 rpm. And the Koutecky-Levich plots of the ORR were obtained under the rotation speeds of 400, 900, 1600 and 2000 rpm, respectively.

To probe the surface of the catalysts, CO-stripping voltammetry was performed as follows: CO was pre-adsorbed onto the catalyst at a given potential of 0.20 V/SHE for 15 min by bubbling CO into 0.1 M HClO<sub>4</sub> solution with or without laser illumination. CO in the solution was subsequently removed by purging high-purity N<sub>2</sub> for 30 min. The electrochemical surface areas (ECSAs) of the catalysts were determined by H desorption peak and CO<sub>ad</sub> oxidation in CO stripping voltammograms over a potential range from 0.05 V to 1.28 V at a scan rate of 20 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub>. The H desorption charge, CO oxidation charge and PdO reduction charge on a Pd surface were assumed to be 210, 420 and 420 μC cm<sup>-2</sup>, respectively. All the electrochemical experiments were carried out at a temperature of 22.5 ± 0.1 °C.

### 2.4. Direct plasmonic electrocatalysis

We used the MBR-110 Ti sapphire laser as the monochromatic light source and the CEL-S500 Xenon light source to simulate solar light. Unless stated otherwise, the excitation wavelength is 850 nm with a power density of 0.2 W cm<sup>-2</sup>. The other photoelectrochemical measurement methods are the same as electrochemical measurement, as mentioned above.

### 2.5. Electromagnetic field simulation

The spatial distributions of local electric-field intensity around the Pd NRs were calculated by employing the Finite Difference Time Domain (FDTD) Method (Lumerical FDTD solutions). The simulations were conducted on individual Pd NRs with the same diameter (1.50 nm) and different lengths at respective resonance wavelengths (i.e. 4.9 nm@650 nm, 6.4 nm@765 nm, 11.8 nm@897 nm and 22.6 nm@945 nm) by referring the experimental observations. The Pd nanorods were illuminated from the top side by a plane wave polarized along the x-axis.

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