



# Electrocatalytic reduction of nitric oxide on Pt nanocrystals of different shape in sulfuric acid solutions

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## ABSTRACT

Pt tetrahedral (Pt-TTH) nanocrystals enclosed with 24  $\{hk0\}$  facets, Pt nanothorns (Pt-Thorn) with a high surface density of atomic steps, and congeries of Pt nanoparticles (Pt-NP) were prepared and served as catalysts to study the electrocatalytic reduction of both adsorbed and solution nitric oxide. The structure sensitivity for the reduction of a saturated NO adlayer on the Pt nanocrystals (NCs) of different shape was studied by cyclic voltammetry (CV) and *in situ* FTIR spectroscopy in sulphuric acid solutions. The results revealed that two types of NO adsorbates can be reduced independently at separated potentials, i.e. the reduction of linear bonded NO ( $\text{NO}_L$ ) on the Pt-NP electrode gives rise to a current peak at  $-0.01$  V (vs. SCE), while the bridge adsorbed NO ( $\text{NO}_B$ ) yields a current peak at  $-0.08$  V. The *in situ* SNIPTIRS results confirmed the assignment of NO adsorbates, i.e. the  $\text{NO}_B$  species yielding a IR absorption bipolar band with its negative-going peak at  $1636\text{ cm}^{-1}$  and positive-going peak around  $1610\text{ cm}^{-1}$ , and the  $\text{NO}_L$  species giving rise to a bipolar band with its negative-going peak at  $1809\text{ cm}^{-1}$  and positive-going peak around  $1720\text{ cm}^{-1}$ . It has determined that the  $\text{NO}_L$  species can be preferentially formed on the Pt NCs with open surface structure, i.e. the more open the surface structure of the Pt NCs, the larger the relative quantity of  $\text{NO}_L$  versus  $\text{NO}_B$ . It has also revealed that the Pt NCs with a high surface density of atomic steps exhibit superior electrocatalytic activity for the reduction of solution NO species. The steady-state current density of NO reduction on Pt-TTH NCs is 7.5–12 times as large as that on Pt-NP, and that on Pt-Thorn is 2.5–4 times of that on Pt-NP in the reduction potential region of electrochemical dynamic control.

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## 1. Introduction

Nitric oxide (NO) is a key intermediate in environmentally important reactions such as reduction of nitrate (nitrite) and oxidation of ammonia [1–17]. It also plays a key role in signal transduction and cytotoxicity [18,19]. From an electrocatalytic point of view, nitric oxide can serve as an ideal model molecule to study surface structure effect of metal electrocatalysts. The bonding of NO to metal surface is considered to be contributed by two components. The first involves the donation of electron density from  $\sigma$ -orbital of N atom to the metal, and the second concerns the back-donation from d-orbital of metal to the  $\pi^*$ -orbital of N atom. This bonding description is very similar to that between CO and metal surface. However, within the M–N–O group, the metal–nitrogen bond is usually strong, whereas the N–O bond is relatively weak. This is in contrast with the metal carbonyl linkage, where the M–C bond is relatively weak and the C–O bond is strong [20].

The electrode materials employed in the studies of electrochemical reduction of NO were usually noble transition metals [21,22]. Pt was confirmed as one of the best catalysts. Early studies of the adsorption and reactions of NO were mainly conducted on Pt single crystal planes in solid–gas interfacial environment by using IRRS, TPD, UPS, XPS, AES and *ab initio* density functional calculations [23–31]. Dunn et al. [23] found that the absorption bands of NO in infrared spectra spread over the wavenumber range of  $1450\text{--}1780\text{ cm}^{-1}$ , depending on the temperature and the coverage of adsorbed NO ( $\text{NO}_{\text{ad}}$ ) on the polycrystalline Pt foil. The coverage dependent shifts of IR bands in the spectra are due to the strong short-range interactions between adjacent NO molecules rather than the conversion from bridge to linear adsorption sites. DFT calculations [29,30] proposed the N–O stretching frequency bands and the corresponding sites:  $1450\text{--}1645\text{ cm}^{-1}$  for threefold coordinated NO,  $1640\text{--}1710\text{ cm}^{-1}$  for bridge adsorbed NO and  $1700\text{--}1850\text{ cm}^{-1}$  for linear adsorbed NO. It was also pointed out that the characteristic frequency ranges for the different sites depend on the surface structure on which adsorption occurs. The activity of different Pt single crystal planes for nitric oxide adsorption and decomposition was studied by Masel et al. [24–26] and Sugai et al. [27,28]. These studies have

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arrived at a consensus that the activity varies significantly with the geometry of the exposed Pt surfaces. They concluded that the order of activity for the NO decomposition on Pt surfaces is as follows: (410) > (310) > (100) > (210) > (110)  $\cong$  (111). The decomposition of NO is sensitive not only to the steps but also to the geometrical structure of the atoms in the step [31]. What is interesting consists in the observation that there is a close correlation between the properties of adsorbed NO molecules in the liquid phase and under ultrahigh vacuum (UHV) [3–5,32–34]. It has been established that the NO adsorbate on platinumized Pt electrode is transformed to N<sub>2</sub>O at the potentials above 0.35 V (versus RHE), and reduced to NH<sub>4</sub><sup>+</sup> and NH<sub>2</sub>OH at lower potential in the electrochemical system [32]. In recent years, a series of studies [3–5,34–39] have been done concerning the reduction of NO<sub>ad</sub> in acid media both on single crystal and polycrystalline Pt electrodes by using FTIR, CV and DEMS. It was indicated that the vibrational behaviour of the NO adlayer is greatly influenced by the coverage. The process of NO reduction is structure sensitive in terms of coverage-dependence site occupation.

However, it has been rarely reported about studies of Pt nanocrystals (NCs) for the reduction of NO in liquid phase. The activity of Pt NCs is sensitive to the packing of atoms on the surface and the exposed facets of a nanocrystal [40,41]. Tian and co-workers [42] have synthesized Pt tetrahedral nanocrystals (Pt-THH NCs) enclosed by {730} and vicinal high-index facets, which exhibit a much improved electrocatalytic activity and stability for the oxidation of small organic fuel molecules, such as formic acid and ethanol. The success in synthesis of Pt-THH NCs presents an exciting approach to improve the catalytic property of Pt nanocatalysts through shape-controlled synthesis of nanocrystals enclosed with high-index facets.

In this paper, Pt nanocrystals of different shape, i.e. the tetrahedra (Pt-THH) and thorns (Pt-Thorn), were prepared and used as electrocatalysts in investigation of NO reduction. It has revealed that the Pt nanocrystals with a high surface density of atomic steps (e.g. Pt-THH and Pt-Thorn) exhibit much higher catalytic activity for the reduction of NO than that of congeries of Pt nanoparticles. The results also demonstrated that the linear bonded NO species can be preferentially formed on the open surface structure of Pt NCs.

## 2. Experimental

### 2.1. Preparation of Pt-NP, Pt-Thorn and Pt-THH

Pt NCs of different shape were prepared by electrodeposition method. The glassy carbon (GC) substrate ( $\Phi = 3$  mm, Takai Carbon Co., Ltd., Tokyo, Japan) was polished mechanically by successively using alumina powder of sizes 5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.3  $\mu\text{m}$ , and cleaned in an ultrasonic bath prior to the electrodeposition. The Pt nanoparticles (Pt-NP) were deposited electrochemically onto GC substrate in cyclic voltammetric (CV) conditions in  $2 \times 10^{-3}$  M K<sub>2</sub>PtCl<sub>6</sub> + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. 50 cycles of potential cycling between –0.25 V and 0.40 V at a scan rate of 50 mV s<sup>–1</sup> were applied in the deposition. The Pt tetrahedral (Pt-THH) nanocrystals were synthesized according to Ref. [42], and the Pt nanothorns (Pt-Thorn) were made by using the procedure described in Ref. [43].

The electrochemical studies were carried out in a three-electrode electrochemical cell connected to a PAR 263A potentiostat (EG&G) with a platinum foil counter electrode and a saturated calomel electrode (SCE). All electrode potentials were quoted versus the SCE scale. The solutions were prepared with Millipore water (18 M $\Omega$  cm) provided by a Milli-Q Labo apparatus (Nihon Millipore Ltd.). The chemical reagents of K<sub>2</sub>PtCl<sub>6</sub> (AR), H<sub>2</sub>SO<sub>4</sub> (GR) and NaNO<sub>2</sub> (GR) were purchased from China Medicine Shanghai Chemical Reagent Corporation. Sulphuric acid-d<sub>2</sub> (D<sub>2</sub>SO<sub>4</sub>, 99.5%) and deuterium oxide (D<sub>2</sub>O, 99.9%) were purchased from Dabeii Corporation

of Peking University. The solutions were deoxygenated by purging with high-purity N<sub>2</sub> prior to each experiment, and protected by a flow of N<sub>2</sub> gas over it during the experiment. All experiments were carried out at room temperature.

### 2.2. Pt NCs characterization

The electrochemical characterization of the Pt NCs electrodes was performed in a three-electrode cell on a CHI 660B working station (Chenhua Shanghai). In the present study the hydrogen evaluation potential on electrodes of Pt NCs of different structure supported on GC substrate is not the same (see Fig. 2), so the oxygen adsorption charge that is integrated from CV curves with the same potential range for all Pt electrodes was used to calculate the electroactive surface area, and a smooth polycrystalline Pt electrode was employed in the calibration of electroactive surface area of Pt NC electrodes (see Supplementary information). The morphologies and structure of the Pt NCs were characterized by using scanning electron microscopy (SEM, Hitachi S-4800 SEM) and transmission electron microscopy (TEM, TECNAI F30).

### 2.3. Formation of a saturated NO adlayer on Pt NCs electrodes

A saturated NO adlayer was prepared by immersing the clean Pt NCs electrode in a  $2 \times 10^{-2}$  M NaNO<sub>2</sub> + 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at open circuit potential for 5 min, after which the electrode was rinsed with Millipore water and transferred quickly to the electrochemical cell containing NO-free 0.1 M H<sub>2</sub>SO<sub>4</sub> solution [1–5,44–47]. In the Infrared experiment, the NO adlayer was generated in the similar way, while using solutions made of D<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>O. In the experiment of reduction of solution NO, the 0.1 M H<sub>2</sub>SO<sub>4</sub> solution was saturated with NO (99.9%) for 30 min after deaeration. The solubility of NO is  $2.05 \times 10^{-3}$  M in water at room temperature [48]. The NO saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution was newly prepared for each experiment. The transient current and steady state current measurements were recorded in the electrochemical cell containing 0.1 M H<sub>2</sub>SO<sub>4</sub> with saturated NO.

### 2.4. In situ Fourier transform infrared reflection spectroscopy (in situ FTIRS)

Electrochemical *in situ* FTIR spectroscopic measurements were carried out on a Nexus 870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector and an infrared microscope (IR-plan Advantage, Spectra-Tech, Inc.). A CaF<sub>2</sub> disk was used as IR window, and an IR cell of thin layer configuration between electrode and IR window was approached by pushing the electrode against the window during FTIR measurements. The incident infrared beam was aligned at about 60° to the normal of electrode surface. Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) was employed, which is ideally suitable for studying adsorbed species that are stable at both E<sub>R</sub> and E<sub>S</sub> potentials [49]. The resulting spectrum was reported as the relative change in reflectivity that is calculated as,

$$\frac{\Delta R}{R} = \frac{\sum R(E_S) - \sum R(E_R)}{\sum R(E_R)} \quad (1)$$

where  $\sum R(E_S)$  and  $\sum R(E_R)$  are the sum of single-beam-spectrum collected at sample potential E<sub>S</sub> and reference potential E<sub>R</sub>, respectively. In all *in situ* SNIFTIRS experiments, E<sub>R</sub> was set at 0.60 V which is the open circuit potential (OCP) of Pt NCs with a saturated NO adlayer in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. It has been confirmed that NO can be adsorbed stably on the Pt NCs electrodes at this potential. 1000 interferograms were collected and co-added into each single-beam spectrum, and the spectral resolution was 8 cm<sup>–1</sup>.

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