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# Trapezohedral platinum nanocrystals with high-index facets for high-performance hydrazine electrooxidation

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## Abstract

Direct hydrazine fuel cell is a promising portable energy conversion device due to its high energy density and free of carbon emissions. To realize the practical applications, the design of highly efficient electrocatalysts for hydrazine oxidation reaction (HzOR) is crucial. Metal nanocrystals with high-index facets have abundant step sites with reactivity. In this study, we prepared trapezohedral Pt nanocrystals (TPH Pt NCs) enclosed by {311} high-index facets and investigated the catalytic performance for hydrazine oxidation. TPH Pt NCs possess a specific activity of 39.1 mA·cm<sup>-2</sup> at 0.20 V, much higher than {111}-faceted octahedral (13.9 mA·cm<sup>-2</sup>) and {100}-faceted cubic Pt NCs (9.11 mA·cm<sup>-2</sup>). Meanwhile, TPH Pt NCs also show superior stability. Density functional theory (DFT) calculation indicates that Pt(311) facilitates the deprotonation of N<sub>2</sub>H<sub>4</sub>\* to N<sub>2</sub>H<sub>3</sub>\* (the rate-determining step) and improves the HzOR activity. This study is helpful for the design of advanced electrocatalysts for HzOR, especially high-index faceted Pt nanocatalysts.



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**Keywords:** Hydrazine oxidation reaction, trapezohedral Pt nanocrystals, high-index facets, electrocatalysis

## INTRODUCTION

Hydrazine ( $\text{N}_2\text{H}_4$ ) is one of the most promising substitutes for hydrogen in fuel cells<sup>[1-3]</sup>. In comparison with other candidates (e.g., methanol, ethanol, and formic acid) applied in direct fuel cells, hydrazine is a carbon-free fuel with high energy density ( $5.5 \text{ kW}\cdot\text{h}\cdot\text{L}^{-1}$ ). Therefore, direct hydrazine fuel cells (DHFCs) have been recognized as one of the promising energy conversion devices due to their high theoretical potential of 1.56 V, remarkable power density, a wide range of operating temperature and no harmful products<sup>[4,5]</sup>. Furthermore, the substitution of sluggish oxygen evolution reaction in the water electrolysis system with hydrazine oxidation reaction (HzOR), which is thermodynamically more favorable ( $\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^-$ ,  $-0.33 \text{ V vs. RHE}$ ), can significantly reduce energy consumption for green hydrogen production<sup>[6,7]</sup>.

Despite the great progress in the recent developments on DHFCs, the actual open circuit voltage is still significantly lower than the theoretical one, and a large amount of energy is consumed by the overpotential of the HzOR<sup>[8]</sup>. Therefore, the design of highly active electrocatalysts is crucial for the practical applications of DHFCs. Current studies of HzOR mainly focus on the design and fabrication of efficient electrocatalysts such as noble metal and intermetallic compounds<sup>[9-13]</sup>, non-noble metals and their single atoms<sup>[14-17]</sup>, and non-metallic materials<sup>[18]</sup>. The catalytic activity is closely related to the surface and electronic structure of the catalysts<sup>[19-25]</sup>. However, the effect of surface structure of metal nanocrystals on HzOR is rarely studied, especially that of high-index facets. Rosca and Koper<sup>[26,27]</sup> reported that the HzOR on bulk Pt single-crystal electrode is structure-sensitive, and the electrocatalytic activity increases in the order of  $\text{Pt}(110) > \text{Pt}(100) > \text{Pt}(111)$ , indicating step sites are more active for HzOR. Because the high-index facets have a high density of atomic steps and ledges, which usually are active sites to control molecular adsorption and desorption, including oxygen reduction reaction<sup>[28]</sup>,  $\text{CO}_2$  reduction reaction<sup>[29]</sup>, nitrogen reduction reaction<sup>[30]</sup>, and small organic molecules oxidation reaction<sup>[31-33]</sup>, it is anticipated that metal electrocatalysts with high-index facets will improve the HzOR performance. Previously, Liu *et al.* investigated the HzOR concave trisoctahedral Au nanocrystals (TOH Au NCs) enclosed by  $\{551\}$  high-index facets, which exhibit higher activity than Au sphere<sup>[8]</sup>. Pt group metals (e.g., Pt and Rh) are much more active than Au for HzOR<sup>[34]</sup>. However, to the best of our knowledge, there are no reports about HzOR on Pt NCs with high-index facets.

Herein, we carried out the HzOR on high-index faceted Pt NCs for the first time. We prepared trapezohedral Pt nanocrystals (TPH Pt NCs) enclosed with  $\{311\}$  high-index facets, octahedral Pt NCs with  $\{111\}$  facets and cubic Pt NCs with  $\{100\}$  facets by electrochemical method. It was found that TPH Pt NCs show much higher catalytic activity and stability of HzOR than octahedral and cubic Pt NCs. The activity of TPH Pt NCs just decreased by only 28% after 5000 s test, while 57% and 48% decline are observed on octahedral and cubic Pt NCs, respectively. Density functional theory (DFT) calculation demonstrates that the rate-determining step of HzOR on the three Pt surfaces of  $\text{Pt}(311)$ ,  $\text{Pt}(111)$  and  $\text{Pt}(100)$  is the first-step dehydrogenation of  $\text{N}_2\text{H}_4^*$  to  $\text{N}_2\text{H}_3^*$ , and  $\text{Pt}(311)$  shows the lowest energy barrier, which is beneficial for the HzOR activity.

## EXPERIMENTAL

Electrochemical preparation of Pt NCs was performed in a standard three-electrode cell with a saturated calomel electrode (SCE) as reference electrode and a platinum plate as counter electrode. The working electrode was a glassy carbon rod ( $D = 6 \text{ mm}$ , Takai Carbon Co., Ltd., Tokyo, Japan), which was controlled

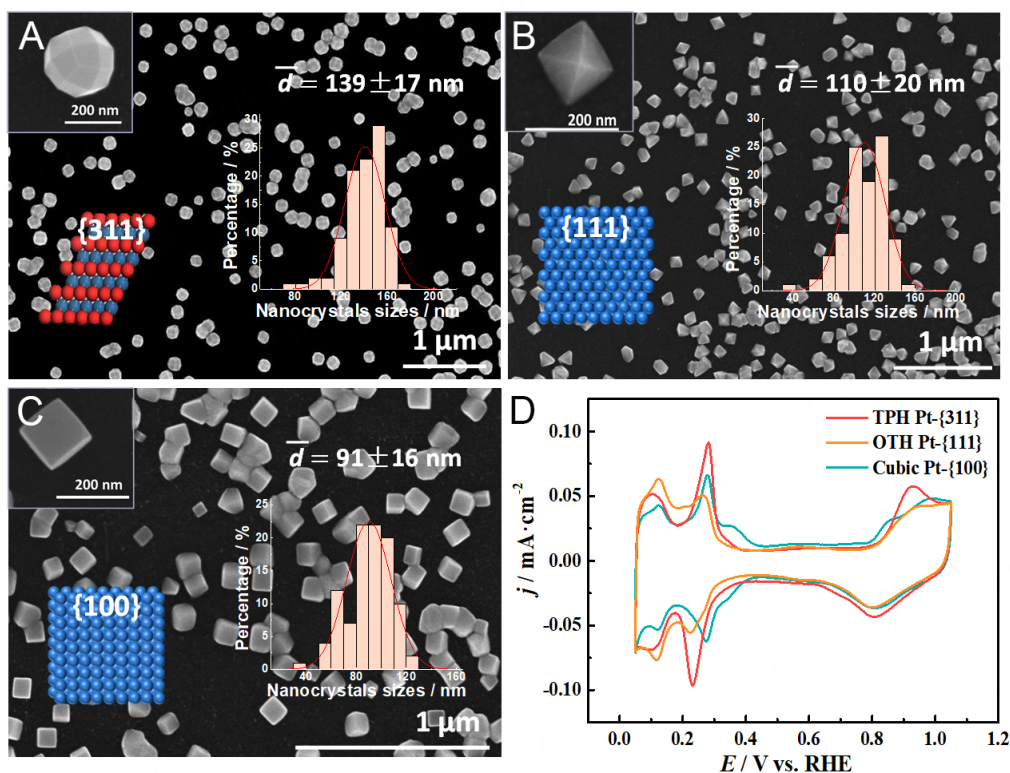
by a 263A potentiostat (EG & G) with an electrochemical square-wave potential (SWP) program [Supplementary Table 1]. All potentials are versus the reversible hydrogen electrode (RHE) scale. Before electrodeposition, the glassy carbon was mechanically polished successively with alumina powder of the size of 1.0 and 0.3  $\mu\text{m}$ . For preparation of Pt NCs, electrochemical cleaning was performed at 1.5 V for 2 s and nucleation process was conducted at 0.28 V for 0.14 s. TPH Pt NCs were prepared in the solution of 2 mM  $\text{H}_2\text{PtCl}_6$  + 0.1 M  $\text{H}_2\text{SO}_4$ , with SWP of lower potential ( $E_L$ ) at 0.42 V and upper potential ( $E_U$ ) at 1.39 V for 30 min ( $f = 100$  Hz)<sup>[35]</sup>. Cubic Pt NCs were obtained by electrochemically etching THH Pt NCs in 0.1 M  $\text{H}_2\text{SO}_4$  with SWP of  $E_U$  at 1.5 V and  $E_L$  at 0.45 V for 15 min ( $f = 100$  Hz)<sup>[36]</sup>. The OTH Pt NCs were electrochemically prepared in 2 mM  $\text{H}_2\text{PtCl}_6$  + 0.1 M  $\text{Na}_2\text{SO}_4$  with SWP of  $E_L$  at 0.38 V and  $E_U$  at 1.30 V for 8 min ( $f = 100$  Hz). The morphology and structure of Pt NCs were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100 at 200 kV).

Prior to each electrochemical measurement, the electrolyte solution was deoxygenated by bubbling high-purity  $\text{N}_2$  for 20 min. The electrochemical measurements of HzOR were conducted in 0.5 M  $\text{N}_2\text{H}_4$  + 1 M KOH solution and the scan rate is 10  $\text{mV s}^{-1}$ . The electrochemical impedance spectroscopy (EIS) was recorded in a frequency range from 0.1 Hz to 1 MHz at 0.20 V.

## RESULTS AND DISCUSSION

The Pt NCs are electrodeposited on a glassy carbon electrode using a programmed square-wave potential method [Supplementary Table 1]. The SEM images of TPH Pt NCs, OTH Pt NCs, and cubic Pt NCs are shown in Figure 1. The corresponding average sizes were about 139, 110 and 91 nm, respectively. The inset provided the atomic model of the corresponding facets: TPH Pt NCs are enclosed by 24  $\{hkk\}$  ( $h > k > 0$ ) high-index facets, OTH and cubic Pt NCs are enclosed by  $\{111\}$  and  $\{100\}$  low-index facets, respectively. The Miller indices of TPH Pt NCs were determined by measuring the plane angle in the TEM image along the  $[001]$  orientation [Supplementary Figure 1]. The average values of angles  $\alpha$  and  $\beta$  were  $142.0^\circ$  and  $128.1^\circ$ , respectively, which are near to the theoretical values of  $143.1^\circ$  and  $126.9^\circ$  for  $\{311\}$  facets, and thus the TPH Pt NCs are denoted as TPH Pt- $\{311\}$  NCs. The  $\{311\}$  facet is composed of a two-atomic-width (100) terrace separated by a monatomic (111) step. The 4-fold-symmetrical SAED pattern confirms that the nanoparticle is of single crystalline. From HRTEM image of TPH Pt NC [Supplementary Figure 2], the  $\{311\}$  step sites could be observed directly. The formation of high-index faceted Pt NCs can be ascribed to the repetitive adsorption/desorption of oxygen species on the Pt NCs induced by the SWP<sup>[35]</sup>. However, over intensive etching at high  $E_U$  of SWP can remove Pt step atoms and result in the formation of cubic or octahedral Pt NCs<sup>[36]</sup>.

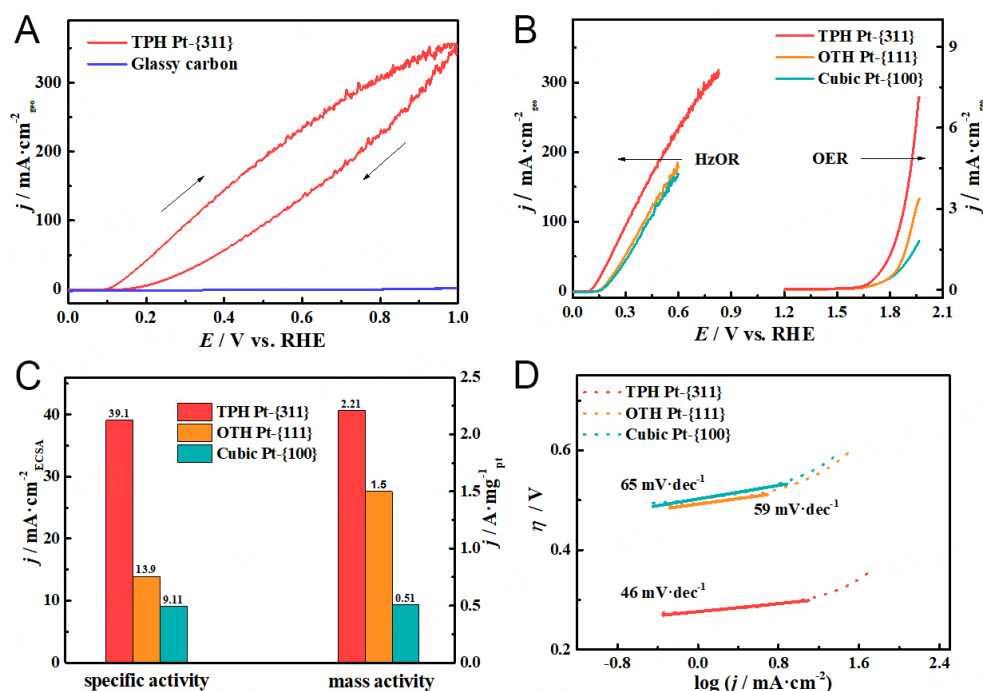
The surface structure of the as-prepared Pt NCs was further characterized by cyclic voltammetry (CV) in deaerated 0.1 M  $\text{H}_2\text{SO}_4$  solution. As shown in Figure 1D, the obtained CV curves could be divided into three regions, including the  $\text{H}_{\text{UPD}}$  (underpotentially deposited hydrogen) region at the potential of 0.05 ~ 0.40 V (vs. RHE), the double layer region at 0.40 ~ 0.70 V, and the region of oxygen species adsorption at 0.70 ~ 1.05 V. The electrochemically active surface area (ECSA) could be determined by the charge of hydrogen adsorption/desorption ( $Q_{\text{H}}$ ) normalized by 210  $\mu\text{C}\cdot\text{cm}^{-2}$ . The CV curves could also provide characteristic fingerprints of the Pt NCs. For example, the small shoulder at around 0.36 V on cubic Pt- $\{100\}$  NCs is a characteristic peak of two-dimensional (100) surface domains or (100) terrace<sup>[31,37]</sup>. TPH Pt- $\{311\}$  NCs hold the highest peak of (100) step at around 0.28 V, and the OTH Pt- $\{111\}$  NCs show the highest peak of (111) step at around 0.12 V. In the region of oxygen species adsorption, the current related to the adsorption/desorption of oxygen species on the TPH Pt- $\{311\}$  NCs is 0.049  $\text{mA}\cdot\text{cm}^{-2}$ , which is considerably larger than that on OTH Pt- $\{111\}$  NCs (0.031  $\text{mA}\cdot\text{cm}^{-2}$ ) and cubic Pt- $\{100\}$  NCs (0.027  $\text{mA}\cdot\text{cm}^{-2}$ ). This initial oxygen adsorption at low potentials is mainly attributed to oxygen atoms



**Figure 1.** SEM images of (A) trapezohedral (TPH) Pt NCs; (B) octahedral (OTH) Pt NCs; and (C) cubic Pt NCs. The inset presents high magnification SEM image, size histogram and atomic model of the facet. (D) Cyclic voltammograms of the TPH, OTH, and cubic Pt NCs recorded in 0.1 M  $\text{H}_2\text{SO}_4$  at  $50 \text{ mV s}^{-1}$ .

adsorbed on Pt step atoms with low coordination numbers<sup>[32]</sup>. This result supports that TPH Pt- $\{311\}$  NCs have a high density of step atoms.

The performance of the as-prepared catalysts for HzOR was evaluated. Figure 2A shows the CV curve of HzOR on TPH Pt- $\{311\}$  NCs in an Ar-saturated 0.5 M  $\text{N}_2\text{H}_4$  + 1.0 M KOH solution at room temperature. High oxidation current can be seen on TPH Pt- $\{311\}$  NCs and the current increases with the increase of potential, while the bare glassy carbon electrode is almost inert to the HzOR. The onset potential of HzOR on TPH Pt- $\{311\}$  NCs is about 0.1 V, close to the value on bulk Pt(110) with step atoms, much lower than that of Pt(100) and Pt(111) reported previously<sup>[27]</sup>. The hysteresis loop in the CV curve of HzOR on TPH Pt NCs might be caused by the decrease of  $\text{N}_2\text{H}_4$  concentration near electrode surface in the positive scan due to the intensive HzOR, and the formation of some poisoning species. Figure 2B compares the linear sweep voltammetric (LSV) curves of the as-prepared catalysts, where the current density is normalized by the geometric area. The current density on TPH Pt- $\{311\}$  NCs is  $41.7 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$  at 0.20 V, which is much higher than  $13.4 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$  on OTH Pt- $\{111\}$  NCs and  $9.7 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$  on cubic Pt- $\{100\}$  NCs, demonstrating that the TPH Pt- $\{311\}$  NCs have a high activity for HzOR. The catalysts were further tested for oxygen evolution reaction (OER) in 1.0 M KOH solution [Figure 2B]. Obviously, the TPH Pt- $\{311\}$  NCs only need 0.12 V to acquire a current density of  $6.0 \text{ mA}\cdot\text{cm}^{-2}_{\text{geo}}$  in HzOR, which is much lower than the potential of 1.94 V in OER. This result indicates that the substitution of OER with HzOR in the water electrolysis system can significantly improve energy conversion efficiency.

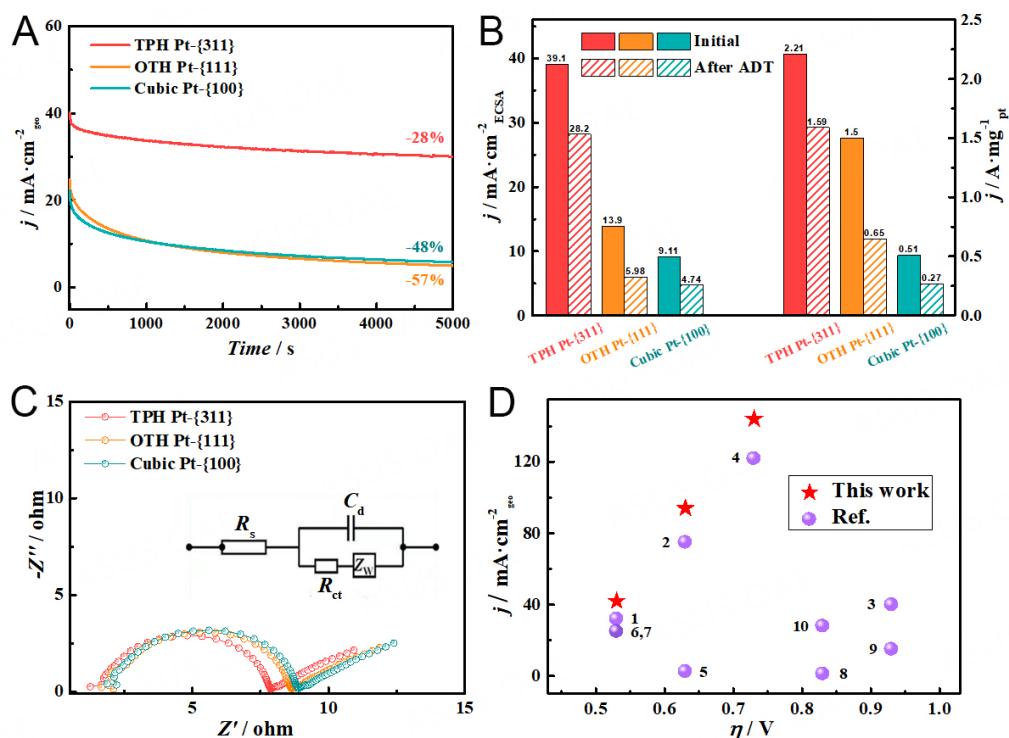


**Figure 2.** (A) CV curves of HzOR on TPH Pt-{311} NCs and bare glassy carbon electrode in an Ar-saturated 0.5 M N<sub>2</sub>H<sub>4</sub> + 1.0 M KOH solution; (B) LSV curves of the catalysts for HzOR and OER; (C) Specific activity and mass activity of the catalysts at 0.20 V; (D) Tafel plots of the catalysts.

The currents of HzOR on different catalysts were also normalized to the ECSA and the estimated Pt loading of the catalysts [Supplementary Tables 2 and 3], as shown in Figure 2C. The specific activity and estimated mass activity of TPH Pt-{311} NCs are 39.1 mA·cm<sup>-2</sup><sub>ECSA</sub> and 2.21 A·mg<sub>Pt</sub><sup>-1</sup> at 0.20 V, respectively. The specific activity of TPH Pt-{311} NCs is 2.8-fold that of OTH Pt-{111} NCs (13.90 mA·cm<sup>-2</sup><sub>ECSA</sub>) and 4.3-fold that of cubic Pt-{100} NCs (9.11 mA·cm<sup>-2</sup><sub>ECSA</sub>). The high activity of TPH Pt-{311} NCs could be attributed to the high density of step sites on the surface. The Tafel slope was calculated to compare the catalytic kinetics during the HzOR [Figure 2D]. From the linear fitting of the plot of  $\eta$  versus  $\log(j)$ , the Tafel slope of TPH Pt-{311} NCs is measured to be 46 mV·dec<sup>-1</sup>, which is lower than that of OTH Pt-{111} NCs (59 mV·dec<sup>-1</sup>) and cubic Pt-{100} NCs (65 mV·dec<sup>-1</sup>), revealing that the TPH Pt-{311} NCs have a fast charge transfer kinetic.

The stability of the catalysts for HzOR was evaluated, as shown in Figure 3A. A sudden decrease in the current density at the initial stage can be observed for all the three catalysts. The current density of the TPH Pt-{311} NCs only decreased by 28% of the initial activity after 5000 s at 0.20 V; however, the OTH Pt-{111} NCs and cubic Pt-{100} NCs decreased by 57% and 48%, respectively. After the stability test, the remained specific activity of the TPH Pt-{311} NCs is 28.2 mA·cm<sup>-2</sup><sub>ECSA</sub>, which was 4.7-fold (5.98 mA·cm<sup>-2</sup><sub>ECSA</sub>) that of OTH Pt-{111} NCs and 5.9-fold (4.74 mA·cm<sup>-2</sup><sub>ECSA</sub>) that of cubic Pt-{100} NCs [Figure 3B]. The estimated mass activity of the TPH Pt-{311} NCs is 1.59 A·mg<sub>Pt</sub><sup>-1</sup>, which is 2.4-fold (0.65 A·mg<sub>Pt</sub><sup>-1</sup>) that of OTH Pt-{111} NCs and 5.9-fold (0.27 A·mg<sub>Pt</sub><sup>-1</sup>) that of cubic Pt-{100} NCs. These results indicate a high catalytic stability of TPH Pt-{311} NCs. After 5000 s of the HzOR electrolysis, the shape of TPH Pt NCs is still well preserved [Supplementary Figure 3], indicating that the catalyst structure has not been damaged significantly. The 28% activity decline of TPH Pt NCs observed here may be mainly caused by the poisoning of the catalyst by the formation of the \*NO<sub>x</sub> and \*N, which may strongly adsorb on the catalyst surface and poison the catalyst<sup>[38,39]</sup>.



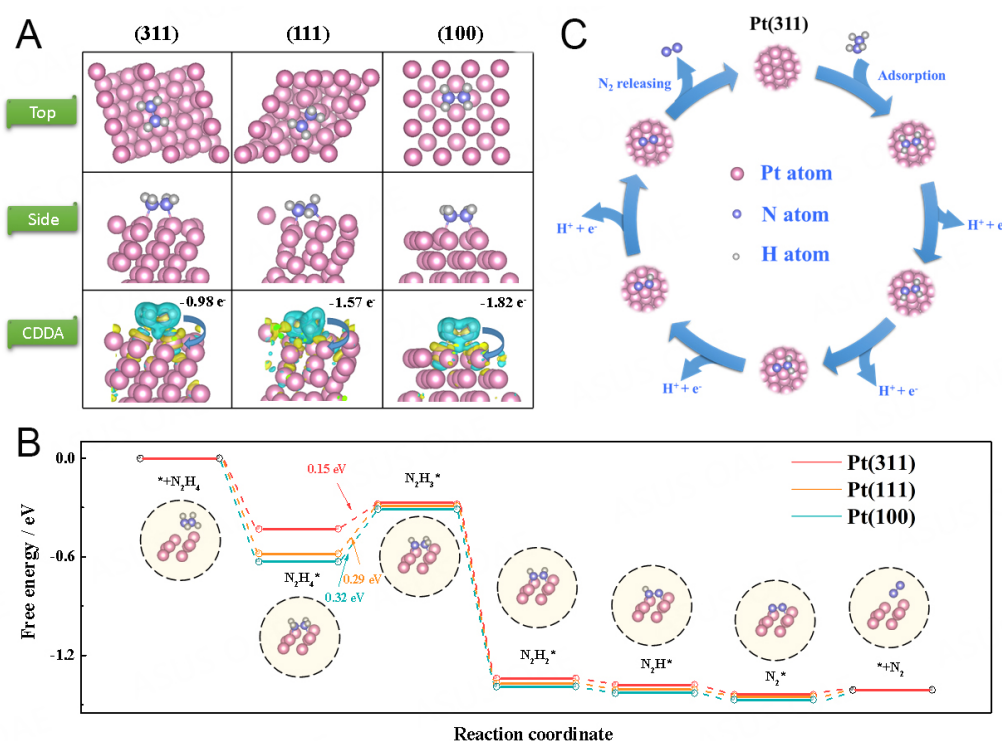


**Figure 3.** (A) Chronoamperometric test of the as-prepared catalysts at 0.20 V vs. RHE in 0.5 M  $\text{N}_2\text{H}_4$  + 1 M KOH solution; (B) Specific activity and mass activity at 0.20 V of the as-prepared catalysts before and after accelerated durability tests (ADT) of 5000 s at 0.20 V; (C) EIS of TPH Pt-{311} NCs, OTH Pt-{111} NCs and cubic Pt-{100} NCs at 0.20 V (inset: equivalent circuit used for data analyses,  $R_s$  and  $R_{ct}$  are the ohmic and charge-transfer resistance, respectively); (D) HzOR activities of TPH Pt-{311} NCs compared with the reference results shown in Supplementary Table 4.

Figure 3C shows the electrochemical impedance spectroscopy (EIS) of the as-prepared catalysts at 0.20 V. The charge-transfer resistance ( $R_{ct}$ ) reflects the kinetics of electrocatalysis on the catalysts, and a lower  $R_{ct}$  value corresponds to a faster reaction rate. TPH Pt-{311} NCs exhibit a smaller  $R_{ct}$  of 6.4  $\Omega$  than that of OTH Pt-{111} NCs (7.0  $\Omega$ ) and cubic Pt-{100} NCs (7.2  $\Omega$ ), indicating that a fast charge transport rate at the catalyst/electrolyte interface of TPH Pt-{311} NCs, which is consistent with the activity tendency observed in the LSV test for HzOR. Compared with the catalysts reported in recent studies<sup>[40-42]</sup>, TPH Pt-{311} NCs exhibit an outstanding activity for HzOR, as shown in Figure 3D and Supplementary Table 4.

To understand the reaction mechanism and different catalytic activity of TPH Pt-{311} NCs, OTH Pt-{111} NCs and cubic Pt-{100} NCs, density functional theory (DFT) calculation of HzOR on Pt(311), Pt(111) and Pt(100) planes are conducted. The slab models of  $\text{N}_2\text{H}_4$  adsorption on Pt(311), Pt(111) and Pt(100) are first given to reveal the charge density difference of  $\text{N}_2\text{H}_4^*$  [Figure 4A]. Charge density difference analysis (CDDA) indicates prominent charge transfer from the N atoms in  $\text{N}_2\text{H}_4$  to the nearby Pt atoms. The Bader charge analysis indicates that the electron transferred is -0.98, -1.57, and -1.82  $e$  on Pt(311), Pt(111), and Pt(100), respectively. Less electron transfer suggests weaker interaction between  $\text{N}_2\text{H}_4^*$  and Pt(311). The N-H bond length in  $\text{N}_2\text{H}_4^*$  on Pt(311) (1.027-1.029  $\text{\AA}$ ) becomes longer relative to the free molecule (1.024-1.026  $\text{\AA}$ ), indicating a weaker N-H bond of  $\text{N}_2\text{H}_4^*$  and thus accelerating the HzOR process.

The elementary reactions for stepwise  $\text{N}_2\text{H}_4$  dehydrogenation ( $\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_4^* \rightarrow \text{N}_2\text{H}_3^* \rightarrow \text{N}_2\text{H}_2^* \rightarrow \text{N}_2\text{H}^* \rightarrow \text{N}_2^*$ ) are investigated on the three Pt planes. The adsorption of  $\text{N}_2\text{H}_4$  on all the three Pt planes is thermodynamically spontaneous, which makes the catalysts easily covered by the  $\text{N}_2\text{H}_4^*$  at the initial stage.



**Figure 4.** (A) The structural model of  $N_2H_4$  adsorption on Pt(311), Pt(111), and Pt(100) planes, and the corresponding CDDA, where the yellow and cyan regions indicate the accumulation and depletion of the charge, respectively; (B) Free energy profiles of stepwise dehydrogenation of  $N_2H_4$  on different Pt planes; (C) Proposed pathway of the HzOR on Pt(311). The pink, blue and grey balls represent Pt, N and H atoms, respectively.

The initial dehydrogenation of  $N_2H_4^*$  to  $N_2H_3^*$  is endothermic on all the studied surfaces, and is the rate-determining step (RDS) of HzOR since this step holds the highest energy barrier. For Pt(311), the energy barrier of the initial dehydrogenation of  $N_2H_4^*$  to  $N_2H_3^*$  is 0.15 eV, which is much lower than that on Pt(111) and Pt(100) (0.29 and 0.32 eV, respectively). The lower energy barrier of RDS on Pt(311) compared with that of Pt(111) and Pt(100) verify that Pt(311) is a highly active surface for HzOR. Note that unlike  $N_2H_4$  oxidation on Au high-index planes where each step dehydrogenation from  $N_2H_4^*$  to  $N_2H$  is endothermic<sup>[8]</sup>, only the  $N_2H_4^*$  to  $N_2H_3^*$  on Pt is endothermic and the  $N_2H_4^*$  can adsorb on Pt strongly due to high reactivity of Pt.

From the free energy profiles of  $N_2H_4$  stepwise dehydrogenation [Figure 4B], the low RDS energy barrier of  $N_2H_4^*$  to  $N_2H_3^*$  mainly comes from the low adsorption energy of  $N_2H_4^*$  on Pt(311). This is an unexpected phenomenon, because the low-coordinated Pt step atoms [coordination number (CN) = 7] on Pt(311) high-index plane can interact with adsorbates more strongly than flat Pt(111) and Pt(100) (CN = 9 and 8, respectively), yielding a higher adsorption energy. We then analyzed the Pt-N bond length and adsorption configuration. The Pt-N bond length of  $N_2H_4^*$  on Pt(311) is 2.153-2.155 Å, which is longer than that of Pt(111) (2.146-2.148 Å) and Pt(100) (2.132-2.134 Å). Longer Pt-N bond length indicates weaker adsorption of  $N_2H_4^*$  on Pt(311), which is favorable for the reduction of the energy barrier from  $N_2H_4^*$  to  $N_2H_3^*$ , because the binding of  $N_2H_4^*$  is too strong according to the free energy profile curve [Figure 4B]. We analyzed the adsorption structure of  $N_2H_4^*$  on Pt(311). It is *via* two N atoms preferentially coordinating with two low-coordinated Pt atoms on the surface. Because the *s* and *p* orbitals of N atoms are relatively discrete and the rich step sites on high-index plane will result in large space steric effect, the adsorption of  $N_2H_4^*$  on Pt(311) will elongate the adjacent Pt-Pt distance (increasing from 2.774-2.776 to 2.793-2.795 Å after the

**Table 1. Calculated Gibbs free energies of elementary steps for electrocatalytic hydrazine oxidation reaction on Pt(311), Pt(111) and Pt(100), respectively**

Elementary steps	Gibbs free energies ( $\Delta G$ )/eV		
	Pt(311)	Pt(111)	Pt(100)
$N_2H_4 + * \rightarrow N_2H_4^*$	-0.43	-0.58	-0.63
$N_2H_4^* \rightarrow N_2H_3^* + H^+ + e^-$	0.15	0.29	0.32
$N_2H_3^* \rightarrow N_2H_2^* + H^+ + e^-$	-1.06	-1.08	-1.08
$N_2H_2^* \rightarrow N_2H^* + H^+ + e^-$	-0.04	-0.04	-0.04
$N_2H^* \rightarrow N_2^* + H^+ + e^-$	-0.04	-0.04	-0.04
$N_2^* \rightarrow N_2 + *$	0.03	0.04	0.05
$N_2H_4^* \rightarrow 2NH_2^*$	0.26	0.47	0.74
$N_2H_3^* \rightarrow NH^* + NH_2^*$	0.67	0.73	0.85
$N_2H_2^* \rightarrow 2NH^*$	0.34	0.52	0.59

adsorption), which will increase the system energy. In contrast, the Pt-Pt distance just changes slightly on Pt(111) (increasing from 2.774-2.776 to 2.780-2.782 Å) and Pt(100) (increasing from 2.774-2.776 to 2.776-2.778 Å). This viewpoint provides a reasonable interpretation of the unexpected low adsorption energy of  $N_2H_4^*$  on high-index Pt(311) plane. Most reports about DFT calculations of HzOR mechanism only consider the change of free energy and the  $\Delta G$  of transient state<sup>[43-46]</sup>. Accompanied by the four-electron transfer in the oxidation reaction of hydrazine ( $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$ ), the free energy of adsorbed intermediates is also calculated. As shown in Table 1, the calculated Gibbs free energies of elementary steps for electrocatalytic HzOR on Pt(311), Pt(111) and Pt(100) surfaces are listed and the optimized intermediates are concomitantly displayed in Figure 4B. In our work, the analysis of Pt-N bond length and adsorption configuration provides new insight into the HzOR mechanism on Pt high-index planes.

The dehydrogenation process of HzOR on Pt is given [Figure 4C and Supplementary Figures 4 and 5]. The mechanism of HzOR on Pt(311) can be described as follows. First, as  $N_2H_4$  is close to the surface of Pt(311), it is easily adsorbed on the step sites forming  $N_2H_4^*$ . Then,  $N_2H_4^*$  stepwise-dehydrogenated and finally converted to  $N_2$ , and the N-H bond cleavage and the retention of N-N bonds are facilitated by the chemisorption of  $N_2H_4$  through both nitrogen atoms<sup>[47]</sup>.

## CONCLUSIONS

In summary, we synthesized TPH Pt NCs with {311} high-index facets, OTH Pt-{111} NCs, and cubic Pt-{100} NCs by electrochemical square-wave potential method. The structure-reactivity relationship of electro-oxidation of hydrazine was investigated. At 0.20 V vs. RHE, the specific activity is 2.8 and 4.3 times that of OTH Pt-{111} NCs and cubic Pt-{100} NCs, respectively. The catalytic activity of TPH Pt-{311} catalyst decreased by only 28% after 5000 s, while 57% and 48% are dropped on OTH Pt-{111} NCs and cubic Pt-{100} NCs, respectively. These results show that TPH Pt-{311} NCs with abundant step sites are more beneficial to HzOR than OTH Pt-{111} NCs and cubic Pt-{100} NCs. DFT calculation demonstrates that on the three Pt planes, the rate-determining step of HzOR is the first-step deprotonation from  $N_2H_4^*$  to  $N_2H_3^*$ , and Pt(311) has the lowest energy barrier for this step, which is beneficial to the HzOR activity. The low energy barrier mainly comes from the unexpected weak adsorption of  $N_2H_4^*$  on stepped Pt(311), since the adsorption can induce the elongation of the adjacent Pt-Pt distance. This study is of importance for the design of hydrazine oxidation electrocatalysts.



## DECLARATIONS

### Authors' contributions

Conceived the idea of the project: Tian N, Hu SN, Lou YY

Made substantial contributions to conception and design of the study, performed data analysis and interpretation and wrote the draft of manuscript: Tian N, Zhou ZY, Hu SN, Lou YY, Li MY, Xiao C

Performed data acquisition and provided administrative, technical, and material support: Sun SG, Tian N, Zhou ZY

Discussed and revised the manuscript: Tian N, Zhou ZY, Hu SN, Lou YY

Finalized the manuscript: Sun SG, Tian N, Zhou ZY

### Availability of data and materials

Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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