Synthesis of Platinum-Nickel Hydroxide Nanocomposites for Electrocatalytic Reduction of Water

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Abstract. Water electrolysis represents a promising solution for storage of renewable but intermittent electrical energy in hydrogen molecules. This technology is however challenged by the lack of efficient electrocatalysts for the hydrogen and oxygen evolution reactions. Here we report on the synthesis of platinum-nickel hydroxide nanocomposites and their electrocatalytic applications for water reduction. An *in situ* reduction strategy taking advantage of the Ni(II)/Ni(III) redox has been developed to enable and regulate the epitaxial growth of Pt nanocrystals on single-layer Ni(OH)₂ nanosheets. The obtained nanocomposites (denoted as Pt@2D-Ni(OH)₂) exhibit an improvement factor of 5 in catalytic activity and a reduction of up to 130 mV in overpotential compared to Pt for the hydrogen evolution reaction (HER). A combination of electron microscopy/spectroscopy characterization, electrochemical studies and density functional calculations was employed to uncover the structures of the metal-hydroxide interface and understand the mechanisms of catalytic enhancement.

Water electrolysis represents a promising solution for storage of electrical energy generated from renewable but intermittent sources such as solar light and wind.^{1,2} This process generates hydrogen that could be used to feed fuel cells and power stationary and mobile devices. While electrolyzers operating with proton-exchange electrolytes generally suffer from the poor durability of oxygen evolution catalysts (oxides of Ir or Ru), the performance of alkaline electrolyzers is largely limited by the sluggish kinetics of water reduction at the cathode.^{3,4} It is generally believed that the water reduction in alkaline media involves water dissociation (the Volmer step, $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ad}} + \text{OH}^-$) and hydrogen recombination (the Heyrovsky step, $\text{H}_2\text{O} + \text{H}_{\text{ad}} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$, or the Tafel step, $2\text{H}_{\text{ad}} \rightarrow \text{H}_2$),^{7,8} albeit the different views present in the literature^{5,6}. Noble metals such as Pt and Pd are active for hydrogen recombination, but more oxophilic surfaces are demanded for the cleavage of the O-H bond in H_2O . The divergent requirements of catalytic properties have limited the performance of conventional alkaline electrolyzers employing single-component catalysts.

The design of hydrogen evolution reaction (HER) catalysts for alkaline electrolyzers has thus turned into composite metal-(hydroxyl)oxide systems. For example, $\text{Ni}(\text{OH})_2$ modified Pt single-crystal electrodes have been reported to exhibit enhanced HER activity, and the catalytic enhancement was ascribed to a synergy between the Pt surface for hydrogen recombination and the metal-hydroxide interface for water dissociation.⁹ Despite the extensive studies,¹⁰⁻¹⁵ structures of the metal-hydroxide interface still remains elusive, probably owing to the lack of synthetic control over the growth of metal hydroxides by electrochemical deposition methods. Such information is however important for fundamental understanding of the active sites on metal-hydroxide composite catalysts that account for the catalytic enhancements.

Herein we report the exploration of metal nanocrystals decorated two-dimensional (2D) metal hydroxides as electrocatalysts for water reduction. Single-layer nickel hydroxide ($\text{Ni}(\text{OH})_2$) nanosheets were first synthesized by liquid exfoliation of $\text{Ni}(\text{OH})_2$ nanoplates.^{16,17} Pt nanocrystals were then overgrown on these $\text{Ni}(\text{OH})_2$ nanosheets by coupling the Ni(II)/Ni(III) redox with the reduction of potassium tetrachloroplatinate (K_2PtCl_4). Our syntheses have generated surfactant-free composite nanostructures that were ready for electrocatalytic applications. A combination of electron microscopy/spectroscopy characterization, electrochemical studies and density function theory (DFT) calculations were employed to depict the structure-property relationships of the metal-hydroxide composite catalysts, based on which the active sites and mechanisms of catalytic enhancement for the HER are further discussed.

The growth and characterization of single-layer $\text{Ni}(\text{OH})_2$ were documented in our previous reports (see the Supporting Information, Figures S1 and S2).^{16,17} Pt nanocrystals were overgrown on the 2D $\text{Ni}(\text{OH})_2$ by *in situ* reduction of potassium tetrachloroplatinate (K_2PtCl_4) in formamide without adding any additional surfactant or reductant (see the experimental methods detailed in the Supporting Information). Transmission electron microscopy (TEM) images of the obtained product (denoted as Pt@2D- $\text{Ni}(\text{OH})_2$ in the following discussion) show that the hexagonal nanosheets were evenly loaded with discrete nanocrystals of ~3 nm in diameter (Figure 1a). High-angle annular dark-field scanning transition electron microscopy (HAADF-STEM) images of the composite nanostructures exhibit high contrast between the overgrown nanocrystals and the nanosheets (Figure 1b), indicating successful overgrowth of Pt on 2D $\text{Ni}(\text{OH})_2$, as also evidenced by the line-profile elemental analysis based on energy-dispersive X-ray spectroscopy (EDS, see Figure S4). The loading of Pt in the composite is determined to be 43% (wt.) by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Selected area electron

diffraction (SAED) patterns collected for Pt@2D-Ni(OH)₂ are composed of diffraction rings corresponding to the (100) and (110) planes (blue) of Ni(OH)₂, and the (111), (220) and (311) planes (red) of fcc Pt (Figure 1c). While the 2D Ni(OH)₂ possesses a polycrystalline nature, as described in our previous reports,¹⁷ the overgrown Pt nanocrystals were found to be single-crystal by STEM imaging, which displays coherent (200) lattice fringes of *fcc* Pt with an inter-plane spacing measured to be 0.19 nm (Figure 1d).

Electron energy loss spectroscopy (EELS) was employed to probe the structural information of the metal-hydroxide interface (Figure 1e). The EELS spectra collected for bare Ni(OH)₂ nanosheets, including those locations nearby (yet away from) the Pt nanocrystals, exhibit one peak at 854.2 eV which is a feature of Ni²⁺ within the Ni(OH)₂ nanosheets. An additional shoulder peak at 856.1 eV was observed in the spectra collected on top of the Pt nanocrystals and assigned to Ni³⁺. The later observation indicates that the overgrowth of Pt was associated with the redox conversion of Ni(II) to Ni(III) in the nanosheets, which is likely a result of charge transfer during epitaxial growth and formation of a Pt-O-NiOH type of interfacial structures.²⁵⁻²⁷ This is also in line with the finding that no Pt nanocrystals were obtained from the reaction in the absence of Ni(OH)₂ nanosheets (Figure S6), both demonstrating the important and indispensable role of the 2D Ni(OH)₂ in regulating the nucleation and growth of Pt nanocrystals to form metal-hydroxide heterostructures.

Further studies prove that the Ni-redox coupled reduction mechanism could be generalized to the overgrowth of other metal nanocrystals on the 2D Ni(OH)₂ (See the Supporting Information, Figures S7-S11). For example, Pd nanocrystals of about 15 nm in size were obtained by *in situ* reduction of potassium chloropalladate on Ni(OH)₂ nanosheets. Moreover, overgrowth

of Pt-Pd alloy nanocrystals were also achieved by co-reduction of potassium chloroplatinate and chloropalladate.

As no organic surfactant was used during the synthesis, the obtained Pt@2D-Ni(OH)₂ possesses a clean surface and could be directly applied as catalysts without subjecting to post-synthetic treatments.²⁸ Figure 2 summarizes the electrocatalytic performance of Pt@2D-Ni(OH)₂ (43 wt% of Pt) in comparison with Pt (10 wt% on XC-72 carbon black), the pristine 2D-Ni(OH)₂ nanosheets and physical mixtures of Pt and 2D-Ni(OH)₂ (43 wt% of Pt, denoted as Pt/2D-Ni(OH)₂). For convenience we will adopt in the following discussion potentials versus reversible hydrogen electrode (RHE), overpotentials given at the current density of 5 mA/cm²_{disk} and current densities read at the overpotential of 100 mV, unless otherwise specified. Pure 2D-Ni(OH)₂ nanosheets show very poor HER activity, less than 0.3 mA/cm² at -0.4 V. Pt@2D-Ni(OH)₂ shows substantially enhanced HER activity in 0.1 M KOH, achieving a current density of 4.2 mA/cm² and an overpotential of 123 mV, compare to 1.6 mA/cm² and 210 mV for Pt at the same loading (Figures 2a and d). Correspondingly, the current density of Pt@2D-Ni(OH)₂ manifests an improvement factor of 2.5 versus Pt at 0.1 V and a reduction of overpotential by 87 mV. It is noticed that the Pt@2D-Ni(OH)₂ composite is much more active than Pt/2D-Ni(OH)₂ in which Pt is only physically mixed with 2D-Ni(OH)₂; the latter is only slightly more active than plain Pt, with a mild reduction of overpotential by 22 mV (Figure 2a). This highlights the importance of epitaxial growth at the metal-hydroxide interface, as revealed by the characterizations in the case of Pt@2D-Ni(OH)₂, for enabling the synergetic effects for catalytic enhancement.

The HER activity of Pt@2D-Ni(OH)₂ in alkaline media was further boosted by replacing KOH with LiOH as the electrolyte. It was previously reported that Li⁺ cations interact more strongly with water molecules than K⁺ in an alkaline environment, and thereby could destabilize

the HO-H bond and lower the energy barrier for water dissociation.²⁹ As shown in Figure 2b, the overpotential for Pt@2D-Ni(OH)₂ in 0.1 M LiOH was further reduced to ~72 mV, which is ~130 mV lower than Pt in KOH and is merely 42 mV lower than that for Pt in HClO₄ (Figure 2b). The current density of Pt@2D-Ni(OH)₂ reached 8.2 mA/cm², representing an improvement factor of 3 compared to Pt (2.7 mA/cm²) in the same electrolyte and 5 compared to Pt in KOH. The Pt@2D-Ni(OH)₂ catalyst also shows substantially reduced slope in the Tafel plots, reaching 72 and 50 mV/dec in KOH and LiOH, respectively, in the potential range between -0.05 and -0.15 V, compared to 129 and 93 mV/dec for Pt (Figures 2 c and d). The reduced Tafel slopes indicate the superior performance of Pt@2D-Ni(OH)₂ at large current densities, which is usually the case in practical electrolyzers, and also suggest potential alterations to the rate-limiting factors due to the formation of the metal-hydroxide interface (see the discussion below on theoretical calculations).^{30,31} Stability studies show that the catalytic enhancement of Pt@2D-Ni(OH)₂ could sustain after intensive potential cycles for the HER (Figure S12).

After demonstrating the enhanced HER catalysis on the Pt@2D-Ni(OH)₂ catalysts, we also performed controlled synthesis to tune the Pt loading and studied its effect on the catalytic activity. For Pt@2D-Ni(OH)₂ nanocomposites with 19, 43, 64 and 83 wt% of Pt loading, the surface coverage of Pt nanocrystals on the Ni(OH)₂ nanosheets was estimated to be 3%, 30%, 59%, and 94%, respectively (Figures 3 a-c). All of these Pt@2D-Ni(OH)₂ catalysts exhibited superior HER activity compared to Pt/C. The improvement factors were consistently found to be nearly at ~2.5, except ~1.9 for the one with 94% coverage of Pt (Figures 3 d and e). While the drop of HER activity at the very high Pt loading could be due to the aggregation of Pt nanocrystals and blocking of active sites, it is more intriguing to observe that even the Pt@2D-Ni(OH)₂ catalyst

with a very low Pt loading (down to 3% of surface coverage and 19 wt% of Pt loading) could almost fully take advantage of the synergy between Pt and Ni(OH)₂ for catalytic enhancement.

The above results have revealed the important role of the metal-hydroxide interface in enhancing the HER electrocatalysis in alkaline media. We then employed periodic Density Functional Theory (DFT) calculations to develop fundamental understanding of the active sites and the HER pathway at the metal-hydroxide interface, based on a recently developed scheme for highly accurate prediction of Pourbaix diagrams.³² It was found that the interfacial structure changes with respect to the applied potential and differs from that of the rest of the Ni(OH)₂ nanosheet, with Pt-NiOH and Pt-O-NiOH types of interface being the stable phases at low (HER conditions) and high (e.g., open circuit) potentials, respectively. The later finding is consistent with the observation of Ni³⁺ present at the interface in the as-synthesized catalyst by EELS (Figure 1e). The Pt surface is likely covered by hydrogen (H) (>1 monolayer) under the HER conditions (Figure S17).^{33,34} To accomplish a full pathway of HER in alkaline, dissociation of two water molecules is considered. The first H₂O dissociates at the Pt-NiOH interface to form one *OH (* denotes adsorbates) on the Ni site at the edge and one *H on the Pt site neighboring to the interface, with a barrier of ~0.42 eV (Figure S18). For the hydrogen recombination step, we considered two possible pathways: direct H recombination (Figure 4a) and H diffusion/recombination (Figure 4b) (See the Supporting Information for more details of calculations). By assuming that the OH desorption/H₂O adsorption step is quasi-equilibrated, the net activation energy (corresponding to the overpotentials) in both cases is determined by the sum of the energy required to displace OH_{ad} with water (0.34 eV + eU_{RHE}) and the intrinsic water dissociation barrier (0.42 eV), namely the last and the first step shown in Figures 3 a and b, respectively, which has a similar value of 0.76 eV + eU_{RHE}. Thus, the two pathways described above likely run in parallel at

the Pt-NiOH interface with relatively low barriers compared to pure Pt (>1 eV, similar to the case shown in Figure S14), giving rise to the enhanced water reduction activity on the Pt@2D-Ni(OH)₂ catalyst.

In summary, we have synthesized Pt nanocrystals decorated 2D nickel hydroxides and explored their electrocatalytic applications for water reduction. An *in situ* reduction strategy taking advantage of the Ni(II)/Ni(III) redox has been developed for epitaxial growth of Pt nanocrystals on the single-layer Ni(OH)₂ nanosheets. These Pt@2D-Ni(OH)₂ nanocomposites were found to be highly active for the HER in alkaline media, exhibiting an improvement factor of 5 in catalytic activity and a reduction of up to 130 mV in overpotential compared to commercial Pt/C. A combination of electrochemical studies, electron microscopy/spectroscopy characterizations and DFT calculations reveals that the Pt@2D-Ni(OH)₂ nanocomposites possess a Pt-O-Ni-OH type of interface under ambient conditions, which is believed to transform into Pt-Ni-OH under the HER conditions. This type of interfacial structure facilitates both water dissociation and hydrogen recombination and accounts for the enhanced catalytic activity of the platinum-nickel hydroxide nanocomposites for water reduction. Our work emphasizes the controlled synthesis of nanocomposites for tailoring and fundamental studies of heterostructured interfaces for catalyzing complex chemical processes.

ASSOCIATED CONTENT

Supporting Information. Detail of experimental and computational methods, and more characterization results.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Key Project of National Natural Science Foundation of China (21433012), the National Basic Research Program of China (grant no. 2013CB933000), the National Natural Science Foundation of China (21273270), the Natural Science Foundation of Jiangsu Province (BK20130007). The work at Johns Hopkins University was supported by the National Science Foundation (CBET 1437219) and the JHU Catalyst Award. The work at Purdue University was supported by a DOE Early Career Award from the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract E-AC02-06CH11357. We gratefully acknowledge the computing resources provided on Blues and Fusion, a high-performance computing cluster operated by the Laboratory Computing Resource Center at Argonne National Laboratory. Use of computational resources through the National Energy Research Scientific Computing Center (NERSC) is also gratefully acknowledged.

Figure 1. Characterization of Pt@2D-Ni(OH)₂ nanocomposites. (a) Bright-field TEM, (b) HAADF-STEM images, and (c) SAED pattern collected for Pt@2D-Ni(OH)₂. HAADF-HRSTEM (d) image of a Pt nanocrystal. (e) EELS point scan of Pt@2D-Ni(OH)₂. Corresponding positions for EELS point scan are indicated by number in the inset HAADF-STEM image.

Figure 2. HER activities of (a) 2D-Ni(OH)₂, Pt/2D-Ni(OH)₂, Pt@2D-Ni(OH)₂ composite (43 wt% of Pt), and commercial Pt catalyst (10 wt% Pt on XC-72 carbon) in 0.1 M KOH and (b) Pt@2D-Ni(OH)₂ composite and commercial Pt catalyst in 0.1 M LiOH. Dot lines in (a) and (b) represent the commercial Pt catalyst in 0.1 M HClO₄. (c) Comparison of the HER activities of Pt, Pt/2D-Ni(OH)₂, and Pt@2D-Ni(OH)₂ in different electrolytes and the corresponding the Tafel slope. (d) Summary of the HER activities of Pt, Pt/2D-Ni(OH)₂, and Pt@2D-Ni(OH)₂ in different electrolytes.

Figure 3. TEM images of Pt@2D-Ni(OH)₂ nanocomposites with a) 19, b) 64 and c) 83 wt% of Pt; d) HER activities (in 0.1 M KOH), and e) current density versus the area coverage of Pt nanocrystals (NCs) on the Ni(OH)₂ nanosheets. Inset in e) is the enlarged image of Pt@2D-Ni(OH)₂ composite with 83 wt% of Pt. The area coverage was estimated from the TEM images by counting the number of Pt nanoparticles and measuring the particle sizes. Loading of Pt was controlled to be consistent at $\sim 1.13 \mu\text{g}/\text{cm}^2$ throughout the electrochemical measurements.

Figure 4. Calculated reaction pathways for water reduction at the Pt-NiOH interface: a) Direct H recombination which involves a first H₂O dissociation and then direct reaction between the generated ^{*}H and the nearest neighbor ^{*}H on Pt to form H₂; b) The H diffusion/recombination pathway in which the ^{*}H generated from the first water dissociation diffuses to react with a weakly adsorbed ^{*}H on Pt. The electrode potential is 0 V vs. RHE. Gray, green, red and white balls represent Pt, Ni, O and H, respectively.

O and H, respectively. The species involved in the reactions are highlighted in rose (O) and yellow (H).

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