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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 overgrowth 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 characterizations, electrochemical studies and density function theory 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, $H_2O + e^- \rightarrow H_{ad} + OH^-$) and hydrogen recombination (the Heyrovsky step, $H_2O + H_{ad} + e^- \rightarrow H_2 + OH^-$, or the Tafel step, $2H_{ad} \rightarrow H_2$) [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 to composite metal-(hydroxyl) oxide systems. For example, $Ni(OH)_2$ 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 remain 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 enhancement.

Herein we report the exploration of metal nanocrystals decorated two-dimensional (2D) metal hydroxides as electrocatalysts for water reduction. Single-layer nickel hydroxide ($Ni(OH)_2$) nanosheets were

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first synthesized by liquid exfoliation of $Ni(OH)_2$ nanoplates [16,17]. Pt nanocrystals were then overgrown on these $Ni(OH)_2$ 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 functional 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 $Ni(OH)_2$ were documented in our previous reports (see the Supporting Information, Figs. S1 and S2) [16,17]. Pt nanocrystals were overgrown on the 2D $Ni(OH)_2$ 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-$Ni(OH)_2$ in the following discussion) show that the hexagonal nanosheets were evenly loaded with discrete nanocrystals of ~3 nm in diameter (Fig. 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 (Fig. 1b), indicating successful overgrowth of Pt on 2D $Ni(OH)_2$, as also evidenced by the line-profile elemental analysis based on energy-dispersive X-ray spectroscopy (EDS, see Fig. 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 (Fig. 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 (Fig. 1d).

Electron energy loss spectroscopy (EELS) was employed to probe the structural information of the metal-hydroxide interface (Fig. 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 Ni^{2+} 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 Ni^{3+}. 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 structure [18-20]. 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 (Fig. 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, Figs. 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 [21]. Fig. 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
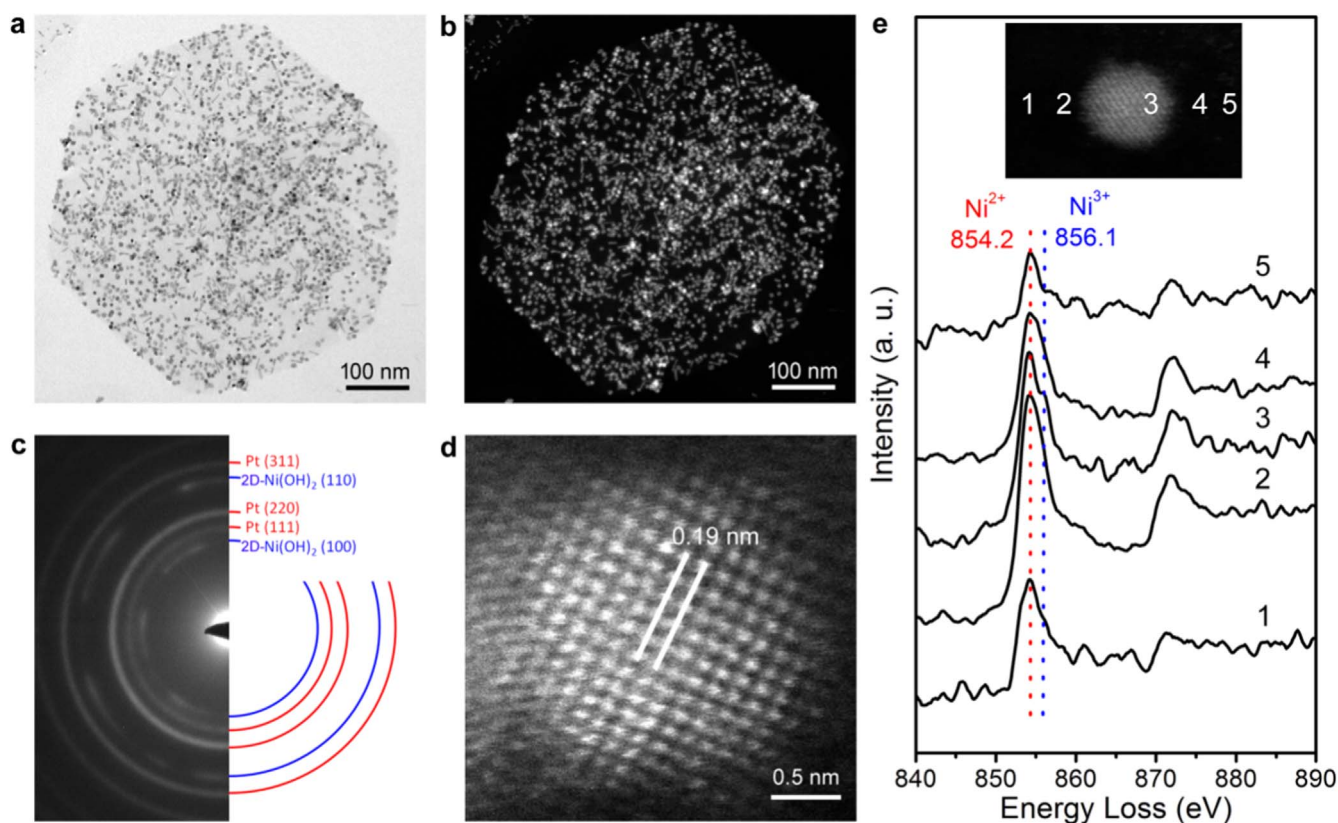

Fig. 1. Characterization of Pt@2D-$Ni(OH)_2$ nanocomposites. (a) Bright-field TEM, (b) HAADF-STEM images, and (c) SAED pattern collected for Pt@2D-$Ni(OH)_2$. HAADF-HRSTEM (d) image of a Pt nanocrystal. (e) EELS point scan of Pt@2D-$Ni(OH)_2$. Corresponding positions for EELS point scan are indicated by number in the inset HAADF-STEM image.