Atomic Scale Analysis of the Enhanced Electro- and Photo-Catalytic Activity in High-Index Faceted Porous NiO Nanowires

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Catalysts play a significant role in clean renewable hydrogen fuel generation through water splitting reaction as the surface of most semiconductors proper for water splitting has poor performance for hydrogen gas evolution. The catalytic performance strongly depends on the atomic arrangement at the surface, which necessitates the correlation of the surface structure to the catalytic activity in well-controlled catalyst surfaces. Herein, we report a novel catalytic performance of simple-synthesized porous NiO nanowires (NWs) as catalyst/co-catalyst for the hydrogen evolution reaction (HER). The correlation of catalytic activity and atomic/surface structure is investigated by detailed high resolution transmission electron microscopy (HRTEM) exhibiting a strong dependence of NiO NW photo- and electrocatalytic HER performance on the density of exposed high-index-facet (HIF) atoms, which corroborates with theoretical calculations. Significantly, the optimized porous NiO NWs offer long-term electrocatalytic stability of over one day and 45 times higher photocatalytic hydrogen production compared to commercial NiO nanoparticles. Our results open new perspectives in the search for the development of structurally stable and chemically active semiconductor-based catalysts for cost-effective and efficient hydrogen fuel production at large scale.

Hydrogen production through water splitting is regarded as a promising approach for clean renewable hydrogen fuel generation, a promising pathway towards solving worldwide energy and environmental issues1–4. Semiconductor-based catalysts play an important role in the clean and cost-effective energy fuels due to their unique properties, which can be tailored by composition and surfaces for improved performance, and their abundance5–7. However, the efficiency of energy conversion in semiconductor catalysts is still low, which is mainly due to inefficient catalytic redox reactions8. Co-catalyst is utilized to reduce activation energy and improve the semiconductor-based catalyst activity. Noble metals (mainly Ag, Au, Pd and Pt) have traditionally been the popular candidates as effective co-catalysts9–11. However, the high cost of noble metals especially the most effective HER co-catalyst, Pt9, has largely hindered the commercialization progress. Recently metal-oxide co-catalysts such as Co3O4 and NiO13–17 have been actively studied. To achieve sufficient catalytic activity, extensive efforts have been made to increase the specific surface area by reducing the size of metal oxide nanoparticles14,18,19. But such an increase in surface area cannot on its own lead to the desired catalytic performance and other new or fundamental approaches are necessary.

The catalytic properties of metal oxides can be manipulated by modifying the surface structure20,21. For instance, the [110] surface of Co3O4 was found to be much more catalytically active than the [100] surface20. Generally, compared to the low index facets (LIFs), the high index facets (HIFs) have higher surface energies which are therefore not energetically favored to appear at surfaces in equilibrium11. However, the presence of
Figure 1 | The morphology and microstructure of as-synthesized NiO NWs. SEM (a) and TEM (b) images of the as-synthesized NiO NWs. (c) HRTEM image of the as-synthesized NiO NWs composed of nanocrystals. Scale bar is 10 nm. (d) and (e) Atomic-scale surface structure analysis of the as-synthesized NiO NW. The observed curved surfaces consist of terraces, atomic steps. Scale bar is 2 nm.
Fundamentally, the difference in work function between HIF and adjacent low index terrace results in modulation of the spatial charge distribution of the neighboring surface facets23–26, and induces an electric field between the HIF and adjacent low index terrace. In the presence of the induced electric field, the decomposition of the adsorbed polarized molecules can be enhanced in the HER. In addition, the exposed HIF unique local structure environment also provides active sites for breaking chemical bonds23. Generally, the potential for a surface ion i contributing to surface potential of an ionic crystal can be written by27:

$$U_i = \frac{1}{2} \sum_j u_{ij}$$

where $u_{ij}$ is the potential induced by interaction between ion i and surrounding j ions. $u_{ij}$ can be expressed as:

$$u_{ij} = U_R(|\mathbf{r}_i - \mathbf{r}_j|) + e_i e_j \frac{\mathbf{p}_i \cdot \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^2} + e_i (\mathbf{p}_i \cdot \mathbf{r}_j) \frac{\mathbf{r}_i}{|\mathbf{r}_i|^3} + e_j (\mathbf{p}_j \cdot \mathbf{r}_i) \frac{\mathbf{r}_j}{|\mathbf{r}_j|^3} - \mathbf{p}_i \cdot \mathbf{r}_j \frac{3 (\mathbf{p}_i \cdot \mathbf{r}_j \mathbf{r}_i) \mathbf{r}_j - \mathbf{p}_j (\mathbf{r}_i \cdot \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^5}$$

where $\mathbf{r}_i$ is the displacement vector from ion j to i, $e_i$, $e_j$ represent the ionic charges, $\mathbf{p}_i$, $\mathbf{p}_j$ are the induced electric dipole moments. $U_R(|\mathbf{r}_i - \mathbf{r}_j|)$ stands for the short-range repulsive potential only for nearest neighbors. The second term is the long-range Coulomb potential. The last three terms represent the polarization energy due to the presence of surface induced dipoles. The surface polarization electric field $E_{\text{Di}}$ on ion i can be written as

$$\mathbf{E}_{\text{Di}} = \sum_j \left(3 \left(\frac{\mathbf{p}_i \cdot \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^5} \mathbf{r}_i - \frac{\mathbf{p}_j}{|\mathbf{r}_j|^3}\right) \right).$$

Falicov et al. have reported that only ions on the surface have non-zero dipoles while ions in bulk have zero dipoles29. Nickel oxide has a face-centered cubic (FCC) structure with octahedral Ni$^{2+}$ and O$^{2-}$...
sites, which is an ionic crystal. In a unit cell, each Ni$^{2+}$ has six nearest-neighbor ions. However, in terms of surface atoms, the Ni$^{2+}$ ion has a lower number of closest-neighbors due to the non-periodicity in the surface structure. In addition, HIF has lower symmetry compared to LIF$^{23}$. Generally, for ionic solids, HIFs have high concentration of low coordination number sites (steps and kinks) while LIFs have low concentration of low coordination number sites$^{24}$. With the presence of high index facets on the surface, the low symmetries and distortions of the surface structure induce non-zero dipoles on the terrace of the stepped surface. Higher density of exposed HIF atoms provides more non-zero dipoles at the step and kink sites, leading to larger electric dipole moments. As a result, a stronger polarization electric field is induced at the surface, which is simply the summation of each neighbour ions. However, in terms of surface atoms, the Ni$^{2+}$ ion has a lower number of closest-neighbors due to the non-periodicity in the surface structure. In addition, HIF has lower symmetry compared to LIF$^{23}$. Generally, for ionic solids, HIFs have high concentration of low coordination number sites (steps and kinks) while LIFs have low concentration of low coordination number sites$^{24}$. With the presence of high index facets on the surface, the low symmetries and distortions of the surface structure induce non-zero dipoles on the terrace of the stepped surface. Higher density of exposed HIF atoms provides more non-zero dipoles at the step and kink sites, leading to larger electric dipole moments. As a result, a stronger polarization electric field is induced at the surface, which is simply the summation of each surface dipole field over all ions on the surface as indicated in Eq. (3). A large local electric field on the surface assists in polarizing the incoming molecules with well-defined polarizability. Subsequently the covalent bonds in incoming molecules are broken apart, thereby facilitating chemical reactions. Additionally, a high density of surface defects (steps, kinks) favors the collisions between the reaction molecules and surfaces. The reaction probability can thus be increased by several orders of magnitude$^{25}$.

To evaluate the catalytic performance of as-synthesized NiO NWs, we first utilized the porous NiO NWs as catalyst for the electrocatalytic HER. Figure 4a shows the electrocatalytic activity of porous NiO NWs with different densities of exposed HIF atoms by the same mass loading of 0.28 mg/cm$^2$ onto the fluorine-doped tin oxide (FTO) substrates. The electrochemical catalytic performance follows an order of NiO$_{30\%}$ > NiO$_{10\%}$ > NiO$_{50\%}$ > commercial NiO. Tafel plot (Figure S7) indicates that NiO$_{30\%}$ sample has a small slope despite there is a large overpotential of ~800 mV. Since the morphology of the as-synthesized NiO is porous NWs, there is probably some pore blockage by evolved hydrogen gas and effective reduction in the electrode active surface area which might lead to the observed large overpotential$^{29}$. Significantly, the Faradaic efficiency curve of NiO$_{30\%}$ measured under a fixed potential of −0.88 V vs. RHE (Figure 4b) shows that the amount of hydrogen evolved is in accordance with the amount of hydrogen expected on the basis of 100% Faradaic efficiency, implying a high efficiency of charge transfer that facilitates the HER.

The stability of catalyst is another important requirement. The stability of the electrochemical activity of NiO$_{30\%}$ was measured by chronopotentiometry under a fixed current density of 10 mA/cm$^2$ (inset of Figure 4b). No significant change of the overpotential during the catalytic performance was observed. To further probe the correlation of surface structure and catalytic activity, we utilized as-synthesized NiO NWs with different densities of exposed HIF atoms as co-catalyst for the photocatalytic HER. Figure 4c shows different hydrogen production yield achieved in the photocatalytic HER, in which NiO$_{30\%}$ produced 45 times more hydrogen yield compared to the commercial NiO. In the absence of the as-synthesized NiO, the hydrogen production exhibits a substantial decrease (Figure S8, Supporting Information). The stable performance of NiO$_{30\%}$ as co-catalyst (Figure 4c inset) shows the amount of hydrogen gas is linearly dependent on time even after 12 hours of light irradiation, in which there was no significant rate decrease. Figure 4d shows a profile of hydrogen production as a function of NiO$_{30\%}$ weight percentage undergoing visible light irradiation ($\lambda > 420$ nm). The amount of hydrogen production rises with a weight increase in NiO$_{30\%}$ and it reaches the highest value of 90 $\mu$mol with amount of 2 wt% NiO$_{30\%}$. Further increase in the amount of NiO$_{30\%}$ resulted in a significant decrease in the hydrogen production yield. An excess weight percentage of NiO$_{30\%}$ could screen the active sites exposed on the surface and could also block the visible light absorbing material, leading to relatively poor photocatalytic performance. This non-linear behavior between the catalytic efficiency and the ratio of catalyst loading was also observed in other

Figure 3 | HRTEM images detailing surface structure of (a) NiO$_{10\%}$ with linear density of exposed HIF atoms of 1.25×10$^3$/cm, (b) NiO$_{30\%}$ with linear density of exposed HIF atoms of 2.92×10$^3$/cm, (c) NiO$_{50\%}$ with linear density of exposed HIF atoms of 8.32×10$^3$/cm, (d) commercial NiO with linear density of exposed HIF atoms of 1.24×10$^3$/cm. Scale bar is 5 nm. 3D models for the structure of the NiO nanoparticles for NiO$_{10\%}$ (e), NiO$_{30\%}$ (f) and NiO$_{50\%}$ (g). The step facets have been clearly indexed (detailed notation in Supporting Information). (h) The calculated energy difference between NiO high-index nanofacets and the electrochemical potential for H$_2$ in water for NiO$_{10\%}$, NiO$_{30\%}$ and NiO$_{50\%}$. The x-axis represents the number of atoms starting at the left most side of the cartoons. The lower energy difference facilitates electron transfer from the NiO to water for hydrogen reduction as is predominant for the NiO$_{30\%}$ sample.
The inset HRTEM image demonstrates the stability of NiO\(_{30}\%\) as co-catalyst after the photocatalytic HER where the highly exposed surface steps in the NiO\(_{30}\%\) sample prevail. This significant stability test validates for the first time, that those high-index facets responsible for the enhanced HER are conserved after long durations of reaction time. In addition, the crystal structure evolution of the dye-sensitized TiO\(_2\) materials loaded with NiO\(_{30}\%\) was also monitored by X-ray diffraction (XRD) (Figure S10, Supporting Information). The indexed XRD patterns confirm that the crystal phases of the NiO and TiO\(_2\) coexist all the time before and after hydrogen production experiments. It suggests excellent stability of porous NiO for the photocatalytic HER.

Figure 5 summarizes the photo- and electrocatalytic HER performance as a function of exposed HIF atom density. The measured BET value (Table S2, Supporting Information) is within the same order of magnitude in different NiO nanowires with slightly higher specific areas for the 10% and 50% NiOx nanoparticles compared to the 30%. This suggests that the specific surface area has lower or negligible influence on the catalytic activity in our NiO nanowires compared to surface defects. Under the effects of the induced electric fields at high-index facets, the decomposition of the adsorbed polar molecules is markedly enhanced, resulting in the increased chemical activity. In addition, the adsorbed molecules have a larger number of nearest neighbor ions at a step site compared to a flat surface. Therefore, there is an increased availability at the step site for adsorption and reaction. In terms of activation energy, the active sites reduce the potential energy in the chemical reaction by forming temporary chemical bonds with the adsorbed molecules. Providing more active sites, larger density of exposed HIF atoms induces a stronger polarization electric field arising from the summation of all adjacent surfaces and leads to a substantial enhancement of catalytic performance in both photocatalytic and electrocatalytic HERs.

Figure 4 | (a) The electrocatalytic activity of as-synthesized NiO NWs with different density of exposed HIF atoms. Inset is the zoom-in area. (b) The amount of hydrogen evolved by NiO\(_{30}\%\) over time based on the performed experiment and calculation. Inset shows the electrocatalytic stability performance of the NiO\(_{30}\%\) sample at a constant current density of 10 mA/cm\(^2\). (c) The amount of hydrogen evolution obtained by employing different density of exposed HIF atoms in the photocatalytic HER. Inset exhibits the stability performance of NiO\(_{30}\%\) as co-catalyst in the photocatalytic HER. (d) The amount of hydrogen evolution as a function of NiO\(_{30}\%\) loading mass ratio. The inset is the HRTEM image of NiO\(_{30}\%\) sample after the photocatalytic HER demonstrating stability of the high-index facets. Scale bar of inset is 5 nm.

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In summary, porous NiO NWs with highly exposed HIF were successfully synthesized via a cost-effective electrospinning method. Atomic-scale HRTEM analysis revealed that the high density of surface atomic steps conduces the exposure of the high-energy surfaces. The as-synthesized 1D porous NiO NWs exhibited high performance for both electrocatalytic and photocatalytic HER. The obtained correlation of exposed HIF density and catalytic performance provides guidance to engineer the surface structure to maximize the catalytic activity in the future for different material systems. Our study shows a potential route for the development of structurally stable and chemically active catalysts in new energy applications with high performance.

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