Self-assembled NiTe₂ nanocrystals as highly efficient and stable electrocatalyst for hydrogen evolution reaction

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Abstract. To develop high-efficient electrocatalysts with excellent stability for hydrogen evolution reaction (HER) is a crucial way to alleviate the serious energy crisis. Recently, transition metal tellurides have been reported as promising catalysts for HER. Herein, self-assembled NiTe₂ nanostructures including nanocrystals (NCs) and nanoplates (NPs) were synthesized in different solvents by a facile solvothermal method. As novel electrocatalysts, NiTe₂ nanostructures show highly efficient HER performance in acidic medium. Particularly, NiTe₂ NCs exhibit much faster kinetics for HER. Compared with NiTe₂ NPs, NiTe₂ NCs demonstrate superior HER performance with a low onset overpotential of 317 mV vs. RHE and a very small Tafel slope of 36 mV dec⁻¹, which is close to that of noble platinum (Pt) catalyst (30 mV dec⁻¹). Moreover, it exhibits excellent stability with more than 95% high current retention after being tested for 1500 voltammetry cycles. The outstanding HER activity of NiTe₂ NCs is attributed to its unique interconnection nanostructure and high conductivity. It is promising for NiTe₂ NCs as a highly efficient non-noble-metal electrocatalyst to replace Pt-based materials for hydrogen evolution.

1. Introduction

The development of sustainable, cheap and green energy is extremely urgent because of the severe depletion of fossil fuels.[1] Up to now, hydrogen has been considered as one of the most environmental-friendly energies to replace fossil fuel due to its clean and high calorific value.[2] Recently, water electrolysis has been identified as the most promising way to produce hydrogen and has been triggered great attention. As we all known, platinum (Pt) is regarded as the best electrocatalyst for the hydrogen evolution reaction (HER) due to its fast HER reaction rate.[3] However, the exorbitant price and severe scarcity on the earth prevent their broad applications for the hydrogen generation. Hence, searching for inexpensive, highly active and non-Pt electrocatalysts becomes an urgent task.

Recently, transition metals sulfides,[4] selenides,[5] and tellurides,[6] have been reported as highly active and stable electrocatalysts for HER and other electrochemical reactions.[7] In general, the HER performances of these catalysts are strongly limited by their conductivity and the number of exposed active sites. Hence, the electrocatalysts with high conductivity can provide effective electron transmissibility, and thus boosting the HER reaction. Compared to sulfides and selenides with relatively low conductivity, tellurides with metallic characteristics have good electronic conductivity.
Owing to the lower electronegativity of Te than Se and S, transition metals tellurides exhibit more metallic character than transition metals chalcogenides and have smaller bandgaps for efficient charge transfers.[6] Therefore, it is believed that transition metals tellurides with metallic characteristics are promising electrocatalysts for HER.

Herein, self-assembled NiTe$_2$ NCs were synthesized by a facile solvothermal method. As a novel electrocatalyst, the NiTe$_2$ NCs show highly efficient HER performance in acidic solution. Compared with NiTe$_2$ NPs, it demonstrates superior HER performance with a low onset overpotential of 317 mV vs. RHE and a very small Tafel slope of 36 mV dec$^{-1}$, which is close to that of noble platinum (Pt) catalyst (30 mV dec$^{-1}$). In addition, it also exhibits excellent long-term stability after being tested for 1500 voltammetry cycles. The outstanding HER activity of NiTe$_2$ NCs is attributed to its unique interconnection nanostructure and high conductivity. This study presents a facile method to fabricate metal tellurides as non-Pt electrocatalysts to replace Pt-based catalysts for hydrogen evolution.

2. Experimental

2.1. Synthesis of NiTe$_2$ nanocrystals and NiTe$_2$ nanoplates

In a typical procedure, the NiTe$_2$ nanocrystals were synthesized as follows. First, 2 mmol of Na$_2$TeO$_3$ and 1 mmol of Ni(AC)$_2$·3H$_2$O were dissolved in 34 mL of DMF (dimethylformamide) under magnetic stirring. Then, 6 ml of hydrazine hydrate was added into the solution. After stirring for 1 h, the above solution was transferred into a 50 mL of Teflon-lined autoclave, and then heated at 180 °C for 24 h. For comparison, NiTe$_2$ nanoplates were synthesized as the same procedure, while using DETA (diethylenetriamine) as the solvent.

2.2. Characterizations

The morphologies of NiTe$_2$ NCs and NiTe$_2$ NPs were carried out by Scanning electron microscope (SEM, JEOL) and transmission electron microscope (TEM, Tecnai F20). The crystal phase and structure of NiTe$_2$ NCs and NiTe$_2$ NP were characterized via X-ray diffraction analyzer (XRD, Rigaku D/MAX-rA diffract-ometer). The chemical composition of NiTe$_2$ NCs was analyzed through X-ray photoelectron spectroscopy (XPS, Kratos XSAM800).

2.3. Electrochemical Measurements

Electrochemical measurements of NiTe$_2$ NCs and control samples were performed in 0.5 M H$_2$SO$_4$ electrolyte using a three-electrode system at an electrochemical station (CHI660D). A saturated calomel electrode (SCE) and graphite rod were employed as reference and counter electrodes, respectively. The working electrodes were prepared as follows. 4 mg of NiTe$_2$ NCs was added into a mixed solution containing 700 µL pure water and 250 µL ethanol. And the mixed solution was sonicated to obtain a homogeneous suspension. Then, 50 µL of Nafion solution was added into the suspension and sonicated at least 30 min to form a homogeneous ink. Finally, 10 µL of the above ink was dropped onto a glassy carbon electrode with a diameter of 3 mm and then dried at 60 °C for 10 min. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV/s. AC impedance was carried out at - 0.4 V vs. RHE in the frequency range $10^{-1}$ to $10^5$ Hz. The stability was evaluated by 1500 cyclic voltammetry cycles at a scan rate of 100 mV s$^{-1}$. For comparison, the HER performances of Pt/C and NiTe$_2$ NPs were performed at the same procedure. In 0.5 M H$_2$SO$_4$, the potentials are calibrated to the RHE based on the equation. \( E_{\text{RHE}} = E_{\text{SCE}} + 0.254V \).

3. Results and discussion

The crystal structure and phase of as-prepared NiTe$_2$ samples were characterized by X-ray diffraction (XRD). Figure 1 presents the XRD patterns of the NiTe$_2$ NCs and NiTe$_2$ NPs. It can be seen that both NiTe$_2$ NCs and NiTe$_2$ NPs have similar XRD patterns. The crystal phase of NiTe$_2$ shows high crystallinity and all the diffraction peaks match well with the hexagonal NiTe$_2$ structure (JCPDS card No. 88-2278). Besides, there are no characteristic XRD peaks for impurities are detected,
demonstrating the pure phase of NiTe₂ obtained by different solvents. The diffraction peaks at 16.88°, 26.78°, 31.76°, 33.8°, 43.82°, 47.24°, 57.98°, 59.24°, 66.26°, and 77.72° correspond to the (001), (100), (011), (002), (012), (110), (201), (112), (202) and (121) crystal planes of NiTe₂, respectively.

**Figure 1.** XRD patterns of NiTe₂ NCs and NiTe₂ NPs.

The chemical states of NiTe₂ NCs were investigated by X-Ray photoelectron spectroscopy (XPS) experiments. In Figure 2a, the Ni 2p spectrum shows two shakeup satellites and two spin-orbit doublets. The peaks appeared at 853.1 and 870.1 eV correspond to Ni²⁺ in NiTe₂ NCs.[8] While the peaks at 55.6 and 873.3 eV can be attributed to the inevitable surface oxidation of NiTe₂ NCs.[8] Moreover, the peaks at about 861.1 and 879.2 eV are designated to the corresponding shakeup satellites.[8] As shown in Figure 2b, the peaks at 572.9 and 583.3 eV correspond to Te 3d₅/₂ and Te 3d₃/₂ in NiTe₂ NCs, respectively, and the strong two peaks at 576.4 and 586.8 eV are assigned to the surface oxidation species of Te.[8]

**Figure 2.** XPS spectra of NiTe₂ NCs: (a) Ni 2p and (b) Te 3d.

The morphologies of NiTe₂ NPs and NiTe₂ NCs were first investigated by SEM measurement. Figure 3a shows that the NiTe₂ NPs possess a hexagonal shape with smooth surfaces. However, NiTe₂ NCs have no definite shape with a rough surface (Figure 3b). Furthermore, TEM was used to further
identify the structure of NiTe$_2$ nanocrystals. As shown in Figure 3c, it can be seen that NiTe$_2$ NCs are composed of ultra-thin nanocrystals, which connect with each other. It is no doubt that the interconnection nanostructure will immensely enhance the charge transfer between the highly conductive NiTe$_2$ nanocrystals.[9] Furthermore, we can easily find that the nanocrystals with rich edges are multiscale and uneven, which can afford much more exposed edges as well as more active edge sites for HER. In addition, the HRTEM image shows the lattice spacings are 0.282 nm (Figure 3d), which can be assigned to the (101) crystal planes of NiTe$_2$, implying the formation of hexagonal phase NiTe$_2$ nanocrystals.[8] To further investigate the morphology of NiTe$_2$ NCs, the EDS mapping analysis was performed on the typical area in Figure 3e. Figure 3f and 3g illustrate that the Ni and Te elements are homogeneously distributed on the crystalline NiTe$_2$ nanocrystals.

The electrochemical activity of NiTe$_2$ NCs was investigated by a three-electrode electrochemical cell setup (CHI1660D) in 0.5M H$_2$SO$_4$. Figure 4a shows the polarization curves of NiTe$_2$ NCs, NiTe$_2$ NPs, and Pt/C. It is observed that NiTe$_2$ NCs show a low onset overpotential of 317 mV vs. RHE and a low overpotential of 398 mV vs. RHE at -10 mA cm$^{-2}$, which surpasses the activity of NiTe$_2$ NPs. Generally, the Tafel slope can be used to assess the HER efficiency of the catalysts and a smaller Tafel slope corresponds to a high-efficiency catalytic reaction. To further probe the mechanism of NiTe$_2$ NCs in the HER process, the Tafel slopes of NiTe$_2$ NCs, NiTe$_2$ NPs, and Pt/C were calculated from
Tafel plots based on the Tafel equation \( y = m \log(J) + n \), where \( m \) is the Tafel slope and \( J \) corresponds to the current density.\[10\] In Figure 4b, the Tafel slope of NiTe_2 NCS is only 36 mV dec\(^{-1}\), which is much lower than that of 64 mV dec\(^{-1}\) for NiTe_2 NPs. The result suggests that the NiTe_2 NCS show remarkably enhanced HER catalytic reaction compared to NiTe_2 NPs. Particularly, the Tafel slope of NiTe_2 NCS (36 mV dec\(^{-1}\)) is very close to that of Pt/C (30 mV dec\(^{-1}\)), indicating its superior intrinsic HER activity. According to the previous report, the NiTe_2 NCS follow the Volmer–Tafel reaction mechanism, which is the same as Pt/C, further revealing its high-efficient HER activity.\[10\]

As a powerful technique, the electrochemical impedance spectroscopy (EIS) was used to investigate the HER kinetics on the electrode’s surface. As shown in Figure 4c, the Nyquist plots of NiTe_2 NPs and NiTe_2 NCS can be fitted to the equivalent circuit (the inset), where \( R_c \) represents the interfacial charge transfer resistance and \( R_s \) corresponds to the solution resistance.\[11\] After fitting, the \( R_c \) value of NiTe_2 NCS is 69 \( \Omega \), which is much lower than that NiTe_2 NPs (1380 \( \Omega \)), indicating the fast interfacial charge transfers in the HER process. Compared to NiTe_2 NPs, the fast charge transfers could be attributed to the unique interconnection nanostructure and high conductivity of NiTe_2 NCS.

Besides high-efficient HER activity, durability is also another key parameter to evaluate a valuable catalyst. To study the stability of NiTe_2 NCS in acidic solution, a continuous cycling test (1500 cycles) was performed at a scan rate of 100 mVs\(^{-1}\). As shown in Figure 4d, the LSV curve after 1500 cycles nearly overlaps with the initial one, and the high current retention of 95% at 400 mV vs RHE is presented after 1500 cycles, indicating the long-term HER stability of NiTe_2 NCS in acidic medium.

**Figure 4.** (a) Polarization curves and (b) corresponding Tafel plots of Pt/C, NiTe_2 NPs and NiTe_2 NCS. (c) Nyquist plots of NiTe_2 NPs and NiTe_2 NCS. (d) Durability test of NiTe_2 NCS after 1500 CV cycles.

**4. Conclusions**

In conclusion, self-assembled NiTe_2 NCS were synthesized by a facile solvothermal method. As a novel electrocatalyst, NiTe_2 NCS exhibit a low onset overpotential of 317 mV vs. RHE and a low overpotential of 398 mV vs. RHE at -10 mA cm\(^{-2}\). Particularly, the Tafel slope of NiTe_2 NCS is very close to that of Pt/C, indicating its superior intrinsic HER activity. In addition, it also shows long-term stability with high current retention of 95% after 1500 voltammetry cycles. Compared with NiTe_2 NPs,
the outstanding HER activity of NiTe₂ NCs is attributed to its unique interconnection nanostructure and high conductivity. The interconnection nanostructure can enhance the charge transfer between the highly conductive NiTe₂ nanocrystals. Moreover, the NiTe₂ nanocrystals with rich edges can afford much more active edge sites for HER. This work presents a facile method to synthesize metal tellurides as non-Pt electrocatalysts to replace Pt-based catalysts for hydrogen evolution.

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