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CoTe₂ nanostructure: An efficient and robust catalyst for hydrogen evolution

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Cobalt ditelluride nanoparticles with a diameter range of 20–50 nm were synthesized as a new electrocatalyst for the hydrogen evolution reaction in 0.50 M H₂SO₄. These nanoparticles can generate ~10 mA/cm² at an overpotential of 246 mV without any decay up to 48 h of continuous reaction.

Energy crisis and environmental issues have continuously increased in recent years. Hydrogen as clean fuel is a promising energy carrier in hydrogen economy paradigm because of its large mass storage density and long storage time. Electrochemical reduction of water is a simple method for hydrogen production. Pt-based catalysts exhibit high performance for the hydrogen evolution reaction (HER), which reduces protons to molecular hydrogen (H₂) in acidic solutions; however, Pt is an expensive noble metal. Therefore, low cost and stable catalysts with a high current density must be developed for HER at low overpotentials. As an alternative to Pt, earth-abundant elements have been used to develop new less expensive acid-stable catalysts, such as MoS₂, CoS₂, WSe₂, CoSe₂, W₂N₃, NiMoN₅, CoP, FeP, Ni₃P₃, WH₄, MoC₁₅, WC₁₆, and MoB. Cobalt is an interesting non-noble metal because of its catalytic power toward hydrogen evolution. In this regard, scholars have focused on the development of Co-based complexes as HER catalysts. First-row transition-metal dichalcogenides (MₓEᵧ, M = Fe, Co, Ni, E = S, Se) have also been studied as active electrocatalysts for the oxygen reduction reaction in acidic electrolytes. The high activity of dichalcogenides for HER has been recently confirmed. Dai et al. indicated that anion is the active site of dichalcogenides for HER. This study also showed that electrocatalytic activity is strongly dependent on the adsorption strength of the hydrogen to the active site. If the adsorption strength is large, electrocatalytic activity is low because of the weak desorption of H₂. As such, we predict that CoTe₂ presents low adsorption strength for H₂ because of the low electronegativity of Te and thus exhibits electrocatalytic activity toward HER. In the composition range of Co:Te = 1:1–1:2, two different phases exist, which include trigonal CdI₂-type and orthorhombic marcasite-type, with the latter as more stable. The present study is the first to introduce orthorhombic marcasite-type CoTe₂ as an electrocatalyst for HER. Hydrothermal method was used to synthesize CoTe₂, and CoTe₂ ink was subsequently prepared by dropping ethanol and Nafion on the rotating ring-disk electrode (RRDE). CoTe₂ nanoparticles (NPs) exhibit efficient electrocatalytic activity in acid solutions, with an onset potential (η) of 198 mV and a Tafel slope of 45.9 mV/dec. CoTe₂ requires overpotentials of 217 and 246 mV to produce ~2 and ~10 mA/cm², respectively, and maintain electrocatalytic activity for 48 h. The CoTe₂ catalyst for HER shows high performance with high stability in acid solutions.

Centrifugation was then performed to separate CoTe₂ NPs and microsheets (MSs). The X-ray diffraction (XRD) pattern shows the diffraction peak of CoTe₂ NPs and MSs (Fig. 1). The strong peak observed at 21.8°, 26.8°, 28.3°, 31.7°, 32.9°, 33.6°, 43.5°, 46.5°, 49.1°, and 58.2° can be indexed with the Miller indices (110), (011), (111), (200), (211), (002), (031), and (122), respectively. These peaks correspond to the characteristic diffraction peaks of the orthorhombic marcasite mattagamite (JCPDS-89-2091) (Fig. S1). The peak of CoTe₂ MSs is not sharper than that of CoTe₂ NPs, which indicates that the primary particle size of CoTe₂ NPs is similar to that of CoTe₂ MSs. A small amount of TeO₂ impurity phase was also observed. The transmission electron microscopy (TEM) images of CoTe₂ NPs and MSs (Fig. 2a and 2b) show that their secondary diameter sizes are 20–50 and 200–400 nm, respectively. The TEM images also reveal the hexagonal MSs and NPs of CoTe₂. Moreover, the low-magnification scanning electron microscopy (SEM) images further indicate the morphology of CoTe₂ NPs and CoTe₂ MSs (Figs. S2a and S2b, ESI). The high-magnification SEM images show that...
Fig. 2 TEM images of (a) CoTe$_2$ NPs and (b) MSs.

The composition of CoTe$_2$ NPs and MSs was determined by energy-dispersive X-ray (EDX; Figs. S3a and S3b, ESI) and inductively coupled plasma-mass spectroscopy (ICP-mass; Figs. S4a and S4b, ESI). The measured atomic ratios of Co to Te are about 1:2.05 and 1:2.20 based on the EDX (Table S1a and S1b, ESI) and ICP-mass results (Tables S2a and S2b, ESI). We propose that TeO$_2$ is partially generated on the surface during the hydrothermal reaction because the ratio of Co and Te is slightly higher than 2. Nevertheless, TeO$_2$ dissolves in acid solutions during HER measurements and is inert toward the electrochemical activity of CoTe$_2$ materials. As such, the chemical state of the Co ions in CoTe$_2$ was experimentally checked by Co K-edge X-ray absorption near edge structure (XANES) (Fig. 3). Co foil (Co with zero charge), CoO (Co with 2$^+$ charge), Co$_2$O$_4$ (Co with mixed 2$^+$ and 3$^+$ charges), and Co$_3$O$_4$ (Co with 3$^+$ charge) were used as standard materials. A chemical negative shift was observed in the Co K-edge jump for CoTe$_2$, similar to the negative Co K-edge jump of CoS$_2$. This phenomenon is attributed to the lower electronegativity of Te than that of O. Although the Co K-edge absorption of CoTe$_2$ was determined between the Co foil and CoO, the chemical state of Co in CoTe$_2$ is Co$^{2+}$; hence, the form of Te in CoTe$_2$ should be Te$^{2-}$. CoTe$_2$ is regarded as the sum of Co$^{2+}$ and Te$^{2-}$ from the ionic perspective, and this phenomenon is confirmed by the Mulliken charge analysis of our first-principles calculation (Table S3, ESI). The band structure and partial and total densities of CoTe$_2$ is smaller because of longer Co–Te interionic distances. In addition, the Co–Te chemical bonding should be more covalent because of the strong hybridization between the Co-3d and Te-5p states, as shown in the DOS diagrams.

All measurements of HER activity were performed in 0.5 M H$_2$SO$_4$ electrolyte solution. The original polarization curve can be obtained using linear sweep voltammetry (LSV) (Fig. S7, ESI). The Nyquist plots of CoTe$_2$ NPs and MSs were measured at potentials of $-0.20$ and $-0.30$ V (near the onset potential) through electrochemical impedance spectroscopy (EIS). The experimental data was then fitted to the electrical model (Fig. 4a). The $R_p$ of CoTe$_2$ NPs indicates an overall series resistance of 0.84 ohm cm$^2$, whereas $R_p$ represents the charge transfer resistance at the CoTe$_2$/electrolyte interface (1.41 ohm cm$^2$). Compared with those of CoTe$_2$ NPs, the $R_p$ and $R_i$ values of CoTe$_2$ MSs are 1.46 and 2.86 ohm cm$^2$, respectively. The $R_p$ of CoTe$_2$ NPs is lower than that of CoTe$_2$ MSs; hence, CoTe$_2$ NPs exhibits higher efficiency for HER because electrons can rapidly transfer to the electrolyte. Nevertheless, the measured cathodic current could not present the original behavior of the catalysts because of the ohmic resistance effect. As such, IR loss was corrected to the initial data of the cathodic current and the background was removed (Fig. S8, ESI). After obtaining the EIS data, the polarization curves present the current density plotted against the applied potential, which were corrected for background removal and IR loss (Fig. 4b). The origin of the background current is complex and possibly caused by capacitive charging of the CoTe$_2$ surface. The current density of CoTe$_2$ NPs rapidly increases with further negative potential scans; thus, overpotentials of 217 and 246 mV are required to produce current densities of $-2$ and $-10$ mA/cm$^2$. By contrast, CoTe$_2$ MSs require overpotentials of 294 and 330 mV to produce current densities of $-2$ and $-10$ mA/cm$^2$. Pt/C (20%) could drive $-10$ mA/cm$^2$ at an overpotential of 10 mV. A two-electron reaction can be used to distinguish two kinds of mechanism through two steps.$^{26}$ The first step is the discharge step (Volmer reaction: H$_2$O$^+ + e^{-} \rightarrow$ H$_2$O$^*$, followed by the desorption step (Heyrovsky reaction: H$_2$O$^*$ + H$_2$O$^+ + e^{-} \rightarrow$ H$_2 +$ H$_2$O$^*$). The Tafel slopes of CoTe$_2$ NPs and MSs do not match the expected Tafel slopes of 29, 38, and 25 mV/decade. The Tafel slopes of Pt/C (20%) is 30.3 mV/decade. The Tafel slopes of CoTe$_2$ NPs and MSs were measured at potentials of $-0.20$ and $-0.30$ V through electrochemical desorption reaction is the possible rate-limiting step of HER. The onset potential was also determined from the start of the linear part of the Tafel plot CoTe$_2$ NPs, which were used as an efficient HER cathode, present an onset potential of $-198$ mV based on the linear part in the Tafel plot, whereas CoTe$_2$ MS demonstrate an onset
potential of ~−272 mV. The exchange current density can be typically extracted from the Tafel plot and applied to be proportional to the catalytically active surface area. The exchange current density of CoTe₂ NPs is about 5.9 × 10⁷ A/cm², which is about three orders of magnitude higher than the value of 9.9 × 10⁵ A/cm² for CoTe₂ MSs. The active surface area can also be estimated using Cdl at the solid-liquid interface through cyclic voltammetry (CV) measurements (Figs. S9a and S9b). The Cdl values of CoTe₂ NPs and MSs are 26.7 and 4.15 mF/cm², respectively (Figs. S9c and S9d, ESI). This finding indicates that more active sites exist in CoTe₂ NPs than that in CoTe₂ MPs, which results in lower overpotential requirements for CoTe₂ NPs.

In conclusion, we developed a simple hydrothermal method to fabricate CoTe₂ NPs and MSs. CoTe₂ NPs provided higher catalytic activity for HER than CoTe₂ MSs because NPs contain more active sites at a low morphology scale. The CoTe₂ NP catalyst coated on the RRDE exhibited high performance for HER with a small Tafel slope, large cathodic current at low overpotentials, and stability for more than 2 days. This novel material can be used in technological devices for solar water splitting.

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Fig. 5 Tafel plots show the HER mechanism of the CoTe₂ electrodes compared with Pt/C (20%).

In addition to high current density, stability is another important factor for the development of electrocatalysts. The durability of the synthesized CoTe₂ was examined by measuring continuous CV with a scanning rate of 100 mV for 1000 cycles. The polarization curves (corrected) after 1000 cycles almost overlap with the initial curves (Figs. S10a and S10b, ESI). The overpotential driven by a cathodic current of ~−10 mA/cm² exhibits cathodic shifts of 4 mV for CoTe₂ NPs and 5 mV for CoTe₂ MSs. Time-dependent potentiostatic electrolysis experiment at an overpotential-driven cathodic current of ~−10 mA/cm² was processed within 48 h (Figs. 5a and 5b). The results show that current density does not evidently decay within the processing period. The orthorhombic CoSe₂ (marcasite) was prepared to compare the activity with CoTe₂. The XRD pattern was corresponded to JCPDS-89-2003 (Fig. S11). Although the overpotential of CoTe₂ is higher than marcasite CoSe₂ (218 mV at -10 mA/cm²) but the stability of marcasite CoSe₂ is not really high enough (Fig. S12a). In time-dependent potentiostatic electrolysis experiment, current density of CoSe₂ decays about 80% at −246 mV within 6 h (Fig. S12b). This result depicts that CoTe₂ is much more eligible for practical application of H₂ evolution compared to CoSe₂.

Fig. 6 Time dependence of cathodic current density for (a) CoTe₂ NPs and (b) CoTe₂ MSs for 48 h at fixed overpotentials of ~−246 and ~−330 mV.

Notes and references
3 (b) H. B. Gray, Nat. Chem., 2009, 1, 7.