The CoTe$_2$ nanostructure: an efficient and robust catalyst for hydrogen evolution†

Tzu-Hsiang Lu,$^a$ Chih-Jung Chen,$^a$ Mrinmoyee Basu,$^a$ Chong-Geng Ma$^b$ and Ru-Shi Liu$^{a,c}$

Cobalt ditelluride nanoparticles in a diameter range of 20–50 nm were synthesized as a new electrocatalyst for the hydrogen evolution reaction in 0.50 M H$_2$SO$_4$($aq$). These nanoparticles can generate $-10$ mA cm$^{-2}$ at an overpotential of 246 mV without any decay up to 48 h of continuous reaction.

The energy crisis and environmental issues have continuously increased in recent years. Hydrogen, as a clean fuel, is a promising energy carrier in the hydrogen economy paradigm$^1$ because of its large mass storage density and long storage time.$^2$ 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 ($H_2$) in acidic solutions;$^3$ however, Pt is an expensive noble metal.$^4$ 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 MoS$_2$,$^5$ CoS$_2$,$^6$ WS$_2$,$^7$ CoSe$_2$,$^8$ W$_2$N,$^9$ NiMoN$_5$,$^{10}$ CoP,$^{11}$ FeP$_2$,$^{12}$ Ni$_3$P$_2$,$^{13}$ WP,$^{14}$ Mo$_6$C,$^{15}$ WC,$^{16}$ and MoB.$^{17}$ Cobalt is an interesting non-noble metal because of its catalytic power in hydrogen evolution. In this regard, scholars have focused on the development of Co-based complexes as HER catalysts. First-row transition-metal dichalcogenides (ME$_2$, M = Fe, Co, Ni; E = S, Se) have also been studied as active electrocatalysts for the oxygen reduction reaction in acidic electrolytes.$^{18}$ The high activity of dichalcogenides for HER has been recently confirmed.$^{19}$ Dai et al. indicated that anion is the active site of dichalcogenides for HER.$^{20}$ 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 $H_2$. As such, we predict that CoTe$_2$ presents a low adsorption strength for $H_2$ 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 the trigonal CdI$_2$-type and the orthorhombic marcasite-type,$^{21}$ with the latter being more stable. The present study is the first to introduce orthorhombic marcasite-type CoTe$_2$ as an electrocatalyst for HER. A hydrothermal method was used to synthesize CoTe$_2$, and CoTe$_2$ ink was subsequently prepared by dropping ethanol and Nafion on a rotating ring-disk electrode (RRDE). CoTe$_2$ nanoparticles (NPs) exhibit efficient electrocatalytic activity in acidic solutions, with an onset potential ($\eta$) of 198 mV and a Tafel slope of 45.9 mV dec$^{-1}$. CoTe$_2$ requires overpotentials of 217 and 246 mV to produce $-2$ and $-10$ mA cm$^{-2}$, respectively, and maintain electrocatalytic activity for 48 h. The CoTe$_2$ catalyst for HER shows high performance with high stability in acid solutions.

Centrifugation was then performed to separate CoTe$_2$ NPs and microsheets (MSs). The X-ray diffraction (XRD) pattern shows the diffraction peak of CoTe$_2$ NPs and MSs (Fig. 1). The strong peaks 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

---

$^a$ Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan. E-mail: rsliu@ntu.edu.tw

$^b$ College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

$^c$ Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 10609, Taiwan

† Electronic supplementary information (ESI) available: Full experimental details and additional data. See DOI: 10.1039/c5cc06806a

Fig. 1 Structural characterization of CoTe$_2$ NPs and MSs. XRD patterns of CoTe$_2$ NPs and MSs.
Miller indices (110), (011), (101), (111), (120), (200), (211), (002), (031), and (122), respectively. These peaks correspond to the characteristic diffraction peaks of the orthorhombic marnasite mattagamite (JCPDS-89-2091) (Fig. S1, ESI†). 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 the TeO2 impurity phase was also observed. The transmission electron microscopy (TEM) images of 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, low-magnification scanning electron microscopy (SEM) images further indicate the morphology of CoTe2 NPs and CoTe2 MSs (Fig. S2a and b, ESI†). The high-magnification SEM images show that numerous MSs and NPs are interconnected with each other (Fig. S2c and d, ESI†).

The compositions of CoTe2 NPs and MSs were determined by energy-dispersive X-ray (EDX; Fig. S3a and b, ESI†) and inductively coupled plasma-mass (ICP-mass; Fig. S4a and b, ESI†) spectroscopy. The measured atomic ratios of Co to Te are about 1:2.05 and 1:2.20 based on the EDX (Table S1a and b, ESI†) and ICP-mass (Table S2a and b, ESI†) results. We propose that TeO2 is partially generated on the surface during the hydrothermal reaction because the ratio of Co and Te is slightly higher than 2. Nevertheless, TeO2 dissolves in acidic solutions during HER measurements and is inert toward the electrochemical activity of CoTe2 materials.22 As such, the chemical state of the Co ions in CoTe2 was experimentally checked using Co K-edge X-ray absorption near edge structure (XANES) spectroscopy (Fig. 3). Co foil (Co with zero charge), CoO (Co with 2⁺ charge), Co3O4 (Co with mixed 2⁺ and 3⁺ charges), and Co3O4 (Co with 3⁺ charge) were used as standard materials. A chemical negative shift was observed in the Co K-edge jump for CoTe2, similar to the negative Co K-edge jump of CoS2 (pyrite) with respect to CoO.23 This phenomenon is attributed to the lower electronegativity of Te compared to that of O. Although the Co K-edge absorption of CoTe2 was determined between the Co foil and CoO, the chemical state of Co in CoTe2 is Co²⁺; hence, the form of Te in CoTe2 should be Te²⁻. CoTe2 is regarded as the sum of Co²⁺ and Te²⁻ from the ionic perspective, and this phenomenon is confirmed by the Mulliken charge analysis of our first-principles calculations (Table S3, ESI†). The band structure and partial and total densities of state (PDOS/DOS) diagrams for CoTe2 were theoretically calculated (Fig. S5 and S6, ESI†). The half-metallic nature can be easily concluded from the calculated position of the Fermi energy level E_F, and the mechanism underlying such a formation is provided in our previous work on CoSe2.24 The band structure for inorganic electrocatalysts near the Fermi level is dependent on the adsorption strength of the reactants.25 The optimal band structure to obtain high HER activity is the partially filled bands. The band gap for beta electrons (with down spin) in CoTe2 is indirect (SM → LD) and is equal to 1.063 eV. Comparison between CoTe2 and CoSe2 reveals that the 3d CF splitting between the t₂g and e₅g states for beta electrons in CoTe2 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 H₂SO₄(aq) electrolyte solution. The original polarization curve can be obtained using linear sweep voltammetry (LSV) (Fig. S7, ESI†). The Nyquist plots of CoTe2 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 were then fitted to the electrical model (Fig. 4a). The R_C of CoTe2 NPs indicates an overall series resistance of 0.84 ohm cm², whereas R_C represents the charge transfer resistance at the CoTe2/electrolyte interface (1.41 ohm cm²). Compared with those of CoTe2 NPs, the R_C and R_C values of CoTe2 MSs are 1.46 and 2.86 ohm cm², respectively. The R_C of CoTe2 NPs is lower than that of CoTe2 MSs; hence, CoTe2 NPs exhibits higher efficiency for HER because electrons can be rapidly transferred 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.\textsuperscript{6} 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 mechanisms through two steps.\textsuperscript{26} The first step is the discharge step (Volmer reaction: $\text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_\text{ads} + \text{H}_2\text{O}$), followed by the desorption step (Heyrovsky reaction: $\text{H}_\text{ads} + \text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$) or the recombination step (Tafel reaction: $\text{H}_\text{ads} + \text{H}_\text{ads} \rightarrow \text{H}_2$). $\text{H}_\text{ads}$ represents an H atom adsorbed at the active catalyst site. The rate-determining step in the HER mechanism could be the Volmer, Heyrovsky, or Tafel reaction with Tafel slopes of 29, 38, and 116 mV dec$^{-1}$. The Tafel plots ($\log|j|$ vs. $E$) of CoTe$_2$ NPs and MSs show that the Tafel slopes are located near the onset of current densities of 45.9 and 41.0 mV dec$^{-1}$ (Fig. 5), whereas the Tafel slope of Pt/C (20%) is 30.3 mV dec$^{-1}$. The Tafel slopes of CoTe$_2$ NPs and MSs do not match the expected Tafel slopes of 29, 38, and 116 mV dec$^{-1}$; as such, the Volmer–Heyrovsky reaction pathway with desorption reaction is the possible ratelimiting step for the 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 CoTe$_2$ NPs is about $5.9 \times 10^{-5}$ A cm$^{-2}$, which is about three orders of magnitude higher than the value of $9.9 \times 10^{-8}$ A cm$^{-2}$ for CoTe$_2$ MSs. The active surface area can also be estimated using $C_{dl}$ at the solid–liquid interface through cyclic voltammetry (CV) measurements (Fig. S9a and b, ESI†).\textsuperscript{27} The $C_{dl}$ values of CoTe$_2$ NPs and MSs are 26.7 and 4.15 mF cm$^{-2}$, respectively (Fig. S9c and d, ESI†). This finding indicates that more active sites exist in CoTe$_2$ NPs than in CoTe$_2$ MSs, which results in lower overpotential requirements for CoTe$_2$ NPs.

In addition to high current density, stability is another important factor for the development of electrocatalysts. The durability of the synthesized CoTe$_2$ was examined by continuous CV measurements at a scanning rate of 100 mV for 1000 cycles. The polarization curves (corrected) after 1000 cycles almost overlap with the initial curves (Fig. S10a and b, ESI†). The overpotential driven by a cathodic current of $-10$ mA cm$^{-2}$ exhibits cathodic shifts of 4 mV for CoTe$_2$ NPs and 5 mV for CoTe$_2$ MSs. A time-dependent potentiostatic electrolysis experiment at an overpotential-driven cathodic current of $-10$ mA cm$^{-2}$ was conducted within 48 h (Fig. 6a and b). The results show that current density does not evidently decay within the processing period. Orthorhombic CoSe$_2$ (marcasite) was prepared to compare the activity with that of CoTe$_2$. The XRD pattern corresponded to JCPDS-89-2003 (Fig. S11, ESI†). Although the overpotential of CoTe$_2$ is higher than marcasite CoSe$_2$ (218 mV at $-10$ mA cm$^{-2}$), the stability of marcasite CoSe$_2$ is not really high enough (Fig. S12a, ESI†). In a time-dependent potentiostatic electrolysis experiment, the current density of CoSe$_2$ decays by about 80% at $-246$ mV within 6 h (Fig. S12b, ESI†). This result depicts that CoTe$_2$ is much more eligible for practical application in H$_2$ evolution compared to CoSe$_2$.

In conclusion, we developed a simple hydrothermal method to fabricate CoTe$_2$ NPs and MSs. CoTe$_2$ NPs provided higher catalytic activity for HER than CoTe$_2$ MSs because NPs contain more active sites at the low morphological scale. The CoTe$_2$ 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.

This work was financially supported by the Ministry of Science, Technology of Taiwan (Contract No. MOST 104-2113-M-002-012-MY3) and Academia Sinica (Contract No. AS-103-TP-A06). C. G. Ma would also like to acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 11204393). We are grateful to Ms Chia-Ying Chien of the Instrumentation Center, National Taiwan University, for performing the TEM experiments.
Notes and references


