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- Authors: Bao Yu Xia, Jun-Ye Zhang, Hongming Wang, Yifan Tian, Ya Yan, Qi Xue, Ting He, Hongfang Liu, Chundong Wang, and Yu Chen

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Substituted Anodic Hydrazine Oxidation Assisting Energyefficient Hydrogen Production Based on Bifunctional Cobalt Perselenide Nanosheet Electrode

Jun-Ye Zhang,^a Hongming Wang,^b Yifan Tian,^c Ya Yan,^d Qi Xue,^e Ting He,^a Hongfang Liu,^a Chundong Wang,^{c,*} Yu Chen,^{e,*} and Bao Yu Xia ^{a, f*}

Abstract: Water electrolysis is promising source for hydrogen production yet challenging. Intensive efforts have been riveted on developing highly efficient and earth-abundant electrocatalysts for water splitting. In this work, we propose an effective strategy through replacing sluggish oxygen evolution by the substituted anodic hydrazine oxidation to assist the energy-efficient hydrogen production based on a bifunctional tubular cobalt perselenide nanosheet electrode. Specifically, this electrode can afford a current density of 10 mA cm⁻² at -84 mV for hydrogen evolution and -17 mV for hydrazine oxidation in 1.0 M KOH and 0.5 M hydrazine electrolyte. An ultralow cell voltage of only 164 mV is required to afford the current density of 10 mA cm⁻² during the 14 hours stable water electrolysis.

The paradox of increasing energy demand and decreasing fossil fuel urges the human society to develop the sustainable and clean

- [a] J Zhang, T He, Dr. Prof. H Liu, Dr. Prof. B. Y. Xia Key Laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Wuhan National Laboratory for Optoelectronics Huazhong University of Science and Technology (HUST) 1037 Luoyu Road, Wuhan 430074, PR China E-mail: <u>byxia@hust.edu.cn</u>
- [b] Dr. Prof. H. Wang Institute for Advanced Study, Nanchang University, 999 Xuefu Road, Nanchang, PR China
- [c] Y Tian, Dr. C. Wang School of Optical and Electronic Information, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan 430074, PR China, E-mail: <u>apcdwang@hust.edu.cn</u>
- [d] Dr. Prof. Y. Yan School of Materials Science & Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, PR China
- [e] Q Xue, Dr. Prof. Y. Chen

Key Laboratory of Macromolecular Science of Shaanxi Province, Key Laboratory of Applied Surface and Colloid Chemistry (MOE), Shaanxi Key Laboratory for Advanced Energy Devices, School of Materials Science and Engineering, Shaanxi Normal University 199 Chang'an Rd, Xi'an 710062, PR China E-mail: <u>ndchenyu@gmail.com</u>

[f] Dr. Prof. B. Y. Xia

Shenzhen Insitute of Huazhong University of Science and Technology, 9 Yuexing Road, Shenzhen 518000, PR China

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energy sources.^[1] Hydrogen energy is well-though-out as one of the auspicious candidates due to its high caloric value and clean product.^[2] The large-scale hydrogen production with high purity is therefore of great significance to prompt hydrogen energy technologies.^[3] Compared with steam reforming and coal gasification, hydrogen production from water splitting by renewable energy is energy-efficient and eco-friendly for the reformation of energy system.^[4] Generally, water electrolysis can be divided into cathodic hydrogen evolution reaction (HER: 4H₂O + 4e⁻ \rightarrow 2H₂ + 4OH⁻) and anodic oxygen evolution reaction (OER), and efficient electrocatalysts for HER and OER is necessary to reduce the overall voltage of full cell.^[5] So far, noble metal basedcatalysts (such as Pt and IrOx) have exhibited excellent activities for electrolysis reactions, but their practical application is still restricted by the high cost and unsated stability.^[6] Continuous efforts have been devoted to developing highly efficient and stable earth-abundant electrocatalytic composites (such as sulfides, hydroxides etc.) to prompt the HER and OER.[7]

Nanotechnology has successfully engineered and advanced the nanocatalysts design for water splitting.^[8] However, even using the best HER catalyst Pt and OER catalyst IrOx to drive water splitting, the overall voltage at 10 mA cm⁻² is much higher than 1.50 V,^[9] as the theoretical voltage of water electrolysis is mainly determined by the sluggish anodic OER (1.23 V vs. RHE).^[10] In particular, hydrazine, a kind of rocket fuel and aqueous contaminant, could be electrochemically oxidized by transitional-metal catalyst composites (sulfides,[11] phosphides,[12] etc.) at -0.33 V vs. RHE.[13] Inspired by hydrazine fuel cells and chloro-alkaline industry, the substituted anodic reaction such as hydrazine oxidation (HzOR: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$) may be another effective and valuable approach to lower the overall electrolysis voltages.^[14] Therefore, with the assistance of earthabundant electrocatalysts, the substituted anodic hydrazine oxidation could reduce the cost and overpotential of whole electrolysis cell,^[15] thus realizing the production of pure hydrogen with lower power implementations. Meanwhile the reaction is accompanied with other benefit like the degradation of aqueous hydrazine contaminants to nitrogen and water.[16]

Herein, we report an effective approach for the electrochemical production of hydrogen, assisted by the substituted anodic hydrazine oxidation in water electrolysis, which is based on a bifunctional tubular cobalt perselenide (CoSe₂) nanosheet electrode. Specifically, the as-fabricated CoSe₂ electrode

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performs a superior catalytic activity and strong durability for HER and HzOR, which can output a current density of 10 mA cm⁻² at -84 mV for HER and -17 mV for HzOR respectively. An ultralow cell voltage of only 164 mV is required to afford the current density of 10 mA cm⁻² during the 14 hours stable water electrolysis, which is gratifyingly superior than the minimum theoretical voltage of water splitting (1.23 V). This work provides not only an effective and earth-abundant electrode for hydrogen evolution, but more importantly, a low-energy and eco-friendly philosophy to render electrochemical hydrogen production by substituted anodic oxidation reaction.



Figure 1. SEM (a, b) and (HR)TEM images (c-f) of tubular $CoSe_2$ nanosheets. Inset of (f) layered structure and model structure of nanosheets.

The tubular CoSe₂ nanosheets electrode is prepared by a facile two-step hydrothermal method, the first step is the preparation of dihydroxycarbonate precursors followed by the subsequent transformation of tubular CoSe2 nanosheet through the hydrothermal selenization method (Experimental Section for the details). Scanning electron microscopy (SEM) image shows the luxuriant bunch structure grows on the nickel foam substrate (Figure 1a), similar to the morphology of previous dihydroxycarbonate precursor (Figure S1, SI). The as-obtained tubes have a uniform diameter of ~ 250 nm, which is larger than the smooth precursor nanofibers (~ 100 nm). There are enormous number of lace-structured and gauzy nanosheets surrounding on the outer wall surface of tubular CoSe₂ (Figure 1b). Transmission electron microscopy (TEM) observation in Figure 1c confirms the tubular structure (Figure S2, SI), and the outer surface composes of dense interconnected nanosheets (Figure 1d). High-resolution (HR) TEM image further displays that the lattice spacing of the (211), (210) and (200) planes are 0.237, 0.265, and 0.295 nm and the lateral dimension of such a thin nanosheets (number of layers = 2~5) is only around 5.0 nm with an interlayer space of 0.67 nm, respectively (Figure 1e, 1f). The folded edges of gossamer nanosheets are clearly observed (Figure 1f), which corresponds to the different layers of CoSe2. In particular, some crystalline distortions are observed as the crystal fringes along the curled edge are discontinuous, which would result in the rich defects and open edges (Figure 1f). Moreover, the Se-Co-Se atom structure is also clearly visible together with the expanded Se-Co-Se band (Figure 1f inset).^[17] The formation of tubular structured CoSe₂ nanosheets might involve the ion exchange and diffusion process

during the hydrothermal selenization. Such hierarchical nanosheet structure with interconnected configuration endows an excellent accessibility of abundant active sites, interfacial contact, mass transport and gas diffusion for electrochemical reactions (Figure S3, SI).^[18]



Figure 2. XRD pattern (a) ("*" is ascribed to the signal peaks of nickel substrate), Raman spectrum (b), Co 2p (c) and Se 3d (d) XPS spectra of CoSe₂.

X-ray diffraction (XRD) pattern shows evident peaks at 30.49°, 34.19°, 37.57°, 43.66°, and 51.70° which are in accord with the faces of (200), (210), (211), (220), and (311), respectively, indicating the diffraction peaks of CoSe₂ electrode are in well agreement with the cubic phase (JCPDS: 89-7184) (Figure 2a).^[19] Raman spectroscopy in Figure 2b signifies a characteristic signal peak at 182 cm⁻¹, which is related to the Se-Se stretching mode of cubic CoSe₂.^[20] Moreover, the corresponding energydispersive X-ray (EDX) results illustrate the symmetrical and homogenous elements distribution (Figure S4, SI). The elemental content of Co and Se from EDX are 32.82% and 67.18%, which is consistent with the ICP-OES (Co:Se = 33.65%:66.35%) and Xray fluorescence (XRF) analysis (Figure S5, SI), demonstrating the element ratio of Co and Se to be approximately 1:2. X-ray photoelectron spectroscopy (XPS) is performed to investigate the surface chemistry of as-obtained CoSe2. The Co 2p spectrum shows that both peaks of 781.48 eV and 797.24 eV are assigned to Co(II) 2p_{3/2} and Co(II) 2p_{1/2}, respectively (Figure 2c). Notably, there is a pair of peaks at 779.54 eV and 794.49 eV are assigned to Co(III) 2p_{3/2} as well as Co(III) 2p_{1/2}, accompanying with two satellite peaks at 784.83 eV and 803.0 eV.[21] There is significant difference between cobalt precursor and as-obtained CoSe₂ samples, indicating that cobalt species in CoSe₂ mainly exists in high valence (Figure S6a, SI).^[22] Furthermore, XPS spectrum of Se 3d reveals that both peaks at 54.9 eV and 55.6 eV are attributed to Se $3d_{3/2}$ and $3d_{5/2}$, respectively, which is consistent with cobalt perselenides reported.^[23] A peak at 59.75 eV would be ascribed to the Se-O bond due to the surface oxygen adsorption/oxidation (Figure 2d).^[24] Moreover, surface oxygen is further examined by O 1s XPS spectrum as demonstrated by Se-O bond at 531.47 eV (Figure S7, SI).[25]

The electrochemical performance of $CoSe_2$ electrode for hydrogen evolution is investigated in 1.0 M KOH solution using standard three-electrode system (graphite rod as counter electrode). The overpotentials at a current density of 10 mA cm⁻²

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 (η_{10}) of cobalt precursor and nickel foam substrate are 193 mV and 241 mV, respectively (Figure 3a). While the η_{10} of CoSe₂ electrode is only 79 mV to achieve a current density of 10 mA cm⁻ ². This is comparable with commercial Pt/C (38 mV) and lower than those of selenium-based or cobalt-based HER electrocatalysts reported in alkaline electrolyte (Table S1, SI). Moreover, Pt/C catalyst shows the smallest Tafel slope value (48 mV dec⁻¹), owing to its mediocre reaction ΔG (Figure 3b). As expected, CoSe₂ electrode exhibits a smaller Tafel slope (84 mV dec⁻¹) compared with cobalt precursor (106 mV dec⁻¹) and nickel foam substrate (121 mV dec-1), revealing a facile kinetics for hydrogen generation. Meanwhile, the electrochemical impendence spectroscopy (EIS) results shows four samples have a similar ohmic resistance (R_s) due to the same Ni foam substrate (Figure S8, SI). However, compared to cobalt precursor and pristine nickel foam, CoSe₂ electrode has a much smaller charge transfer resistance (R_{ct}) at the interface of electrocatalyst and electrolyte, suggesting an excellent interfacial contact and faster charge transfer between the hierarchical nanosheets structure and electrolyte. Furthermore, the double-layer capacitance (C_{dl}) of CoSe₂ electrode is 4.45 mF cm⁻² (Figure S9, SI), which is 50 times higher than that of cobalt precursor electrode (0.08 mF cm⁻ ²). This momentous difference suggests that the excellent HER performance of CoSe₂ electrode is triggered by the increased electrochemically active surface area enabled by the hierarchical nanosheet structure and excellent exposure of massive active sites to the reactants. Moreover, density functional theory (DFT) calculation results reveal that Co site is favorable for adsorption of water molecular, while the transformation of Hads to H2 occurs on the active Se sites (Figure S10, SI). Based on above electrochemical results and DFT calculations, the intrinsic electrocatalytic HER activity of CoSe2 nanostructures is ascribed to the nature of Co sites and the formation of Co-Se bonds together with the enhanced electric behavior.^[26] The outstanding electrochemical stability of as-prepared electrode is also demonstrated by the steady whole 50 h durability test (Figure 3c). The catalytic current remains stable and no dramatic η_{10} loss after 50 h test (Figure 3d). Raman and SEM results also suggest the robust electrode also remains the intact morphology and structure after this long-term test (Figure S11, S12, SI).



Figure 3. *I*R-corrected LSV polarization curves (a) and corresponding Tafel slopes (b) of CoSe₂, Pt/C on Ni substrate, nickel foam substrate and cobalt precursor. (c) 50 h stability test of CoSe₂ at a current density of 10 mA cm⁻². (d) LSV curves of before and after 50 h stability test. All the experiments are implemented in 1.0 M KOH solution.

To guarantee the general function of hydrogen production cell as proposed, it is also significant to ascertain that the as-composed CoSe₂ electrode could successfully work in the alkaline electrolyte hydrazine. With increasing containing the hydrazine concentration, no obvious changes happen in the potential difference at the current density of over 10 mA cm⁻², only a negative shift for onset-potential is mainly due to the standard redox potential of hydrazine (Figure 4a). Even in the 1.0 M KOH with 0.5 M hydrazine solution, the as-obtained CoSe₂ electrode still shows an outstanding catalytic activity on hydrogen evolution which is evidenced by a small η_{10} of 84 mV, similar to the results in KOH electrolyte without hydrazine involved (Movie S1, SI). Additionally, the catalytic capability of CoSe₂ electrode is further acknowledged in KOH electrolyte containing various hydrazine concentrations (Figure 4b). Obviously, CoSe₂ anode generates negligible current corresponding to its oxidation process in the absence of hydrazine in the electrolyte. However, the introduction of hydrazine (0.1 M N₂H₄ solution) into the electrolyte gives a significant current response. Also there is a decrease onset potential (till -44 mV vs. RHE) and increase in current densities for HzOR with the increased hydrazine concentration (Figure S13. SI), approving the effective approach to lower anodic overpotential by the substituted anodic hydrazine oxidation reactions. Compared with cobalt precursor, nickel foam and IrO₂, CoSe₂ electrode demonstrates the excellent activity for the hydrazine oxidation (Figure S14 and S15, SI), approving that the presence of CoSe₂ phase is active for HzOR (Movie S2, SI). The hydrazine oxidation process (N₂H₄ + 4OH⁻ \rightarrow N₂ + 4H₂O + 4e) is proposed in Figure S16.^[27] Moreover, CoSe₂ electrode exhibits the comparable, even surpassed activity than Pt/C electrode at higher potentials for HER in 1.0 M KOH electrolyte containing 0.5 M hydrazine (Figure 4c). CoSe₂ electrode achieves anodic current densities of 10 and 100 mA cm⁻² at -17 mV and 170 mV, respectively, much more negative than that of Pt/C electrode, which are 51 mV and 280 mV respectively. These results certainly certify the noteworthy role of earth-abundant CoSe₂ nanostructure as the bifunctional electrode for efficient hydrazine oxidation assisting-water electrolysis.



Figure 4. (a) Hydrogen evolution and (b) hydrazine oxidation LSV polarization curves of $CoSe_2$ in 1.0 M KOH containing different hydrazine concentration; (c) LSV polarization curves of $CoSe_2$ and Pt/C for HER/HzOR couple in 1.0 M KOH with 0.5 M N₂H₄ solution; (d) LSV polarization curves comparison of $CoSe_2$ for water electrolysis assisting with or without hydrazine anodic oxidation; (e) Faradic efficiency of hydrogen production and (f) Cell stability test based on a $CoSe_2/CoSe_2$ couple at 10 mA cm⁻² in 1.0 M KOH with 0.5 M hydrazine solution.

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Afterwards, the combined electrochemical results of CoSe₂ electrodes for overall water electrolysis in KOH with and without hydrazine electrolyte are compared (Figure 4d). The comparable HER performance is observed for CoSe₂ electrodes, similar potentials of -84 mV (with hydrazine) and -90 mV (without hydrazine) vs. RHE are required to achieve a cathodic current density 10 mA cm⁻². For the anodic oxidation, CoSe₂ electrode exhibits an excellent oxygen evolution performance, 1.513 V vs. RHE to achieve an anodic current density of 10 mA cm⁻². But even though, the full cell voltage of an assembled cell for water splitting by CoSe₂ electrodes or Pt∥IrO₂ couple may be higher than 1.5 V to afford the considerable current density of 10 mA cm⁻² (Figure S17, SI). However, CoSe₂ electrodes demonstrates an impressive electrochemical HzOR activity at -17 mV and 170 mV vs. RHE to afford the anodic current density of 10 and 100 mA cm⁻², respectively. It endows an ultralow voltage for a complete water electrolysis assembled by anodic HzOR and cathodic HER. Such a full cell design reveals that the sluggish anodic oxidation is responsible for the energy consumption mainly for electrochemical hydrogen production. Fortunately, the hydrazine oxidation can replace the cathode water oxidation reaction, and thus remarkably reduce the full cell voltage and achieve the energy-saving purpose in water electrolysis technologies. Moreover, the cathodic CoSe₂ electrode displays a high hydrogen production faradic efficiency of 98.3% (Figure 4e), suggesting the complete electron utilization during the hydrogen production. Figure 4f shows the potential response of two-electrode HER/HzOR electrolyzer utilizing the bifunctional CoSe₂ electrode. The paired CoSe₂ electrode only requires 0.164 V to generate a current density of 10 mA cm⁻² for 14 hours stable hydrogen production, which is very little value compared to the theoretically thermodynamical potential of water splitting (1.23 V). Moreover, vigorous gas bubbles are produced from the both electrodes when the assembled cell is driven by a commercial 1.5 V AA battery (Movie S3, SI), demonstrating the promising potential for future practical application.

In summary, we demonstrate an effective approach for energyefficient hydrogen production by a substituted anodic hydrazine oxidation to replace the sluggish oxygen evolution based on a bifunctional tubular CoSe2 nanosheet electrode. In the presence of hydrazine, CoSe₂ electrode exhibits an excellent activity even better than Pt/C electrode, as evidenced by low potentials of -84 mV for HER and -17 mV for HzOR. The assembled HER/HzOR electrolyzer system merely requires an ultralow voltage of 0.164 V to drive a current density of 10 mA cm⁻² for hydrogen generation during a stable 14h electrolysis operation. This work not only provides an efficient and robust electrocatalyst for water splitting, but also delivers a philosophy for the energy-saving full electrolysis cell design by integrating both corresponding anodic oxidation and cathodic reduction reactions, thus grasps great potentials in the future energy conversion and storage technologies, sustainable environmental issues and beyond.

Experimental Section

Experimental Details, DFT calculations, SEM, TEM, XPS, Raman and other electrochemical measurements.

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Keywords: Cobalt perselenide • Bifunctional electrocatalyst • Hydrogen evolution • Hydrazine oxidation • Water electrolysis

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Entry for the Table of Contents

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Sweet Synergy of Reaction and Catalyst: An effective philosophy of replacing sluggish oxygen evolution by anodic hydrazine oxidation is developed for energy-saving water electrolysis based on a low-cost and bifunctional cobalt perselenide electrode.

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Cell	-	+ 4e ⁻
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L.		

Jun-Ye Zhang,^a Hongming Wang,^b Yifan Tian,^c Ya Yan,^d Qi Xue,^e Ting He,^a Hongfang Liu,^a Chundong Wang,^c Yu Chen,^{e, *} and Bao Yu Xia^{a, f*}

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