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Article

Co_{0.85}Se magnetic nanoparticles supported on carbon nanotubes as catalyst for hydrogen evolution reaction

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ABSTRACT

Co_{0.85}Se magnetic nanoparticles supported on carbon nanotubes were prepared by a one-step hydrothermal method. The saturation magnetization and coercivity of the MWCNTs/Co_{0.85}Se nanocomposites increased due to a decrease in the Co_{0.85}Se nanoparticle size in the MWCNTs/Co_{0.85}Se nanocomposites and an increase in the distance between the Co_{0.85}Se nanoparticles, which increased the specific surface area, thereby benefiting the electrocatalytic performance of the catalyst. Moreover, the MWCNTs/Co_{0.85}Se nanocomposites exhibited an excellent hydrogen evolution reaction performance owing to the presence of MWCNTs, which enhanced the mass transport during the electrocatalytic reactions. Furthermore, in an acid solution, the 30 wt% MWCNTs/Co_{0.85}Se composite catalyst exhibited a current density of 10 mA cm⁻² at a small overpotential of 266 mV vs. RHE, a small Tafel slope of 60.5 mV dec⁻¹, and good stability for HER.

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1. Introduction

As an eco-friendly and renewable clean energy, hydrogen (H₂) is considered a promising alternative to fossil fuels [1,2]. A large-scale, high-efficiency, and low-cost H₂ production technology is expected to be the cornerstone for developing H₂ energy [3]. Undoubtedly, electrochemical water splitting via the hydrogen evolution reaction (HER) is a favorable method for the generation of H₂. However, the commercialization of electrocatalytic H₂ evolution is limited by the slow dynamic processes, low catalytic performance, and poor stability of the catalysts [1]. Thus, to make the entire process more energy efficient, efficient HER electrocatalysts that deliver a high current at a low overpotential (η) have attracted extensive attention [4]. At present, materials based on noble metals such as Pt, Ir, Rh, and Ru are developed because of their superior catalytic

activity [5,6]. However, unfortunately, the high cost and rareness of noble metals restrict their application in the HER at a large scale. Therefore, it is important to find inexpensive, earth-abundant elements to prepare high-performance and durable electrocatalysts.

In recent years, low-cost earth-abundant transition metal compounds have been developed as possible alternatives, such as NiS₂/MoS₂ [7–9], CoP@ZnFeP [10], CoNi₂S₄ [11], and Co_xNi_{1-x}O [12]. Non-stoichiometric-phase cobalt selenide (Co_{0.85}Se), an important metal chalcogenide, has received extensive attention owing to its excellent performance in a variety of applications such as in the fields of dye-sensitized solar cells [13], potassium-ion batteries [14], water splitting [1,15,16], and CO₂ photo-reduction [17]. Interestingly, Co_{0.85}Se and its ternary compounds, having a weak ferromagnetic property, are usually used for wastewater treatment [18,19].

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Cobalt selenide is one of the promising HER electrocatalysts due to $t_{2g}^6 e_g^1$ separated from Co 3d electrons has a near-optimum electronic e_g filling [20]. Liu [21] et al. reported that an amorphous CoSe film electrodeposited on a Ti mesh needs an overpotential of 121 mV to drive the HER and exhibits a small Tafel slope (84 mV dec⁻¹). However, low-dimensional cobalt selenides have fewer active sites, poor dispersibility, and a low electron transmission capacity, which result in a poor electrocatalyst activity [11]. Therefore, to ensure more active sites to improve the charge and mass transfers for reaction, carbon materials (e.g., carbon nanotubes (CNTs), carbon cloth (CC), carbon nanofibers (CNFs), carbon fiber papers (CFPs), reduced graphene oxide (rGO), and graphdiyne) are used as high-conductivity materials to enhance the HER performance [22–24]. Multi-walled carbon nanotubes (MWCNTs) display various electronic properties such as metallic conductivity (possible electronic structure) and electron-storage capacity (one electron for every 32 carbon atoms) [25]. Hence, the specific structure of MWCNTs can effectively promote electron transfer from the electrocatalysts to the CNTs. Moreover, graphene is a zero-bandgap semiconductor in which the filled valence band and the empty conduction band are in contact with each other, thus giving rise to peculiar properties [26].

In this work, magnetic Co_{0.85}Se nanoparticles were synthesized by a one-step hydrothermal method without using any surfactant or structure-directing agent. MWCNTs were introduced into the Co_{0.85}Se electrocatalyst system to enhance the HER performance because of its high conductivity. The experimental results showed that the 30 wt% MWCNTs/Co_{0.85}Se nanocomposite displayed the lowest onset overpotential (266 mV vs. RHE at 10 mA cm⁻²) and the smallest Tafel slope (60.5 mV dec⁻¹) among all the electrocatalysts. Moreover, MWCNTs/Co_{0.85}Se exhibited excellent catalytic activity and retained its durability even after 1,500 cycles at a scan rate of 10 mV s⁻¹. This study provides a promising cost-effective hybrid electrocatalyst for HER.

2. Experimental

2.1. Materials and methods

Cobalt chloride (CoCl₂·6H₂O, AR), Se powder (Se, AR, Macklin), ammonium fluoride (NH₄F, AR), hydrazine hydrate (N₂H₄·H₂O, AR), and commercial 20 wt% Pt/C powder (AR) were purchased from Macklin (Shanghai, China). Graphene oxide (GO) and Nafion solution (5%) were purchased from Aladdin (Shanghai, China). MWCNTs with diameters ranging from 60 to 100 nm and lengths larger than 5 μm were purchased from Shenzhen Nanotech Port Co., Ltd.

2.2. Preparation of surface partially oxidized MWCNTs and GO dispersion solution

Before the partial surface oxidation, the nanotubes were immersed in 20% dilute nitric acid for 24 h to remove impurities. Then, they were washed to neutral, centrifuged, and dried at 60 °C for 12 h. Finally, surface partially oxidized MWCNTs

were prepared by adding 1 g of MWCNTs, 70 mL of 98% H₂SO₄, and 30 mL of 30% H₂O₂ into a 150 mL round-bottom flask and gently stirring the mixture at 50 °C for 12 h. After the mixture was cooled to room temperature, the product was taken out and washed with deionized water thoroughly until the pH reached 7. The as-prepared MWCNTs were then collected by filtration and washed thoroughly with water and ethanol. The MWCNTs were dried at 60 °C under vacuum overnight. Further, GO was prepared by a modified Hummers' method [27]. The GO powder was dispersed in water with a concentration of 1.0 mg mL⁻¹ and the GO solution was sonicated for several days. Finally, the dark brown solution was centrifuged at 7000 rpm for 4 min and the supernatant was obtained for further use [28].

2.2.1. Synthesis of Co_{0.85}Se and MWCNTs/Co_{0.85}Se nanocomposites

MWCNTs/Co_{0.85}Se nanocomposites were synthesized by a facile one-pot solvothermal method. First, 0.4 mmol of CoCl₂·6H₂O was dispersed in 84 mL of a mixed solvent composed of distilled water (72 mL) and N₂H₄·H₂O (12 mL). Then, 0.48 mmol of Se powder, 2 mmol of NH₄F, and 11.4 mg of oxidized MWCNTs were added sequentially. The solution was stirred for 20 min and then transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 24 h in an electric oven. After the autoclave was allowed to naturally cool to room temperature, the product was collected by centrifugation, washed with water and ethanol several times, and dried at 60 °C for 12 h in a vacuum oven to obtain the nominal 30 wt% MWCNTs/Co_{0.85}Se nanocomposite. Products with different MWCNTs-to-Co_{0.85}Se weight ratios were fabricated by the same method. Co_{0.85}Se nanoparticles were prepared by the same procedure in the absence of MWCNTs.

2.2.2. Synthesis of rGO/Co_{0.85}Se nanocomposites

Nominal 15 wt% rGO/Co_{0.85}Se nanocomposites were prepared by adding 5.8 mL of the GO dispersion solution into a solution of the prepared Co_{0.85}Se nanoparticles under the same synthesis conditions as mentioned above. The nominal rGO-to-Co_{0.85}Se weight ratios were adjusted to 10, 15, and 20 wt%, and the obtained samples fabricated by the same method are denoted as 10 wt% rGO/Co_{0.85}Se, 15 wt% rGO/Co_{0.85}Se, and 20 wt% rGO/Co_{0.85}Se, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer with a Cu radiation source ($\lambda = 0.1540$ nm). The Raman spectra were recorded under ambient conditions using a HORIBA JY LabRAM HR spectrometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained on a JEOL JSM-7610 Plus instrument and a FEI F20 instrument, respectively. The chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher EscaLab 250 Xi system. Magnetic hysteresis loops were recorded using a Quantum

Fig. 1. Schematic illustration of the preparation of MWCNTs/Co_{0.85}Se nanocomposite.

Design SQUID VSM at 300K.

2.4. Measurement of electrocatalytic properties

All electrocatalytic measurements were conducted on an electrochemical station (CHI660E) with a three-electrode system in a N₂-saturated 0.5 M H₂SO₄ solution. Platinum wire and Ag/AgCl were used as the counter electrode and reference electrode, respectively. Two milligrams of Co_{0.85}Se nanoparticles and MWCNTs/Co_{0.85}Se and rGO/Co_{0.85}Se nanocomposites were respectively dispersed into 1 mL of ethanol solution and sonicated for 40 min. Then, 10 μL of Nafion solution was added into the mixture solution. Thereafter, 10 μL of the above slurry was dropped on a polished glassy carbon electrode (GCE, *R* = 2 mm) as the working electrode and dried at room temperature before use. For comparison, commercial 20 wt% Pt/C was dispersed on a polished GCE in the same way. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s⁻¹ at room temperature and the electrodes were cycled for at least 20 cycles before taking any measurement to ensure the authenticity of data. Electrochemical impedance spectroscopy (EIS) was performed at -0.2 V vs. RHE in the frequency range of 0.05 to 10⁶ Hz with an AC voltage of 5 mV. To determine the stability of the electrocatalysts, were performed by LSV curves initially and after 1500 cycles at a scan rate of 10 mV s⁻¹ in 0.5 M H₂SO₄. Moreover, the effective active surface areas (ECSAs) of the samples were studied by cyclic voltammetry (CV) performed at various scan rates from 20 to 200 mV s⁻¹ in the potential range of 0.1 to 0.3 V (vs. RHE).

3. Results and discussion

CoCl₂·6H₂O as a cobalt ion source, Se powder as a Se source,

NH₄F as a mineralizer, and N₂H₄·H₂O as a reductant were used to synthesize Co_{0.85}Se nanoparticles. The process of synthesis can be expressed as the following equations [29].

N₂H₄·H₂O incomplete decomposition:

N₂H₄·H₂O complete decomposition:

First, cobalt ions reduce into elemental cobalt by the H₂ released from the decomposition of N₂H₄·H₂O. Then, elemental cobalt reacts with Se powder to form Co_{0.85}Se nanoparticles.

The XRD patterns of the samples are displayed in Fig. 2(a). The diffraction peaks at 33.3°, 44.7°, 50.5°, 60.3°, 61.8°, 69.9°, and 71.3° can be indexed to the (101), (102), (110), (103), (112), (202), and (004) crystal planes of hexagonal Co_{0.85}Se (PDF# 52-1008). However, the typical peaks around 26° corresponding to MWCNTs mostly disappear, which is attributed to the dilution of Co_{0.85}Se nanoparticles. Surprisingly, the XRD peaks of 30 wt% MWCNTs/Co_{0.85}Se are sharper than those of Co_{0.85}Se, which indicates the higher crystallinity of MWCNTs/Co_{0.85}Se. A possible explanation is that the MWCNTs are beneficial for the oriented growth of Co_{0.85}Se [30]. The interaction between Co_{0.85}Se and MWCNTs was further characterized by Raman spectroscopy; the Raman spectra are shown in Fig. 2(b). The peaks at 184 and 675 cm⁻¹ are attributed to the A_g and A_{1g} modes of CoSe₂, and the peaks at 466 and 520 cm⁻¹ are assigned to the E_g and F_{12g} modes of trivalent cobalt compounds, respectively [31]. In addition, the Raman spectra of MWCNTs and MWCNTs/Co_{0.85}Se show the characteristic peaks of Co_{0.85}Se as well as the disordered (D) and graphitic (G) peaks of MWCNTs at 1348 and 1583 cm⁻¹, respectively, which indicate the incorporation of Co_{0.85}Se in the MWCNTs. The D band originates from the vibration of sp³-hybridized carbon atoms in the disordered and defective region and is proportional to the number of defects and other carbon impurities in the MWCNTs samples. On the other hand, the G band is ascribed to the E_{2g} vibration mode of sp² carbon atoms [32]. The intensity ratios (*I*_D/*I*_G) are 1.23 and 1.02 for the MWCNTs and 30 wt% MWCNTs/Co_{0.85}Se, respectively (Fig. 2(b)). The *I*_D/*I*_G ratio exhibits the graphitization of carbon-based materials as well as

Fig. 2. XRD patterns (a) and Raman spectra (b) of Co_{0.85}Se, MWCNTs and 30 wt% MWCNTs/Co_{0.85}Se.

Fig. 3. High-resolution XPS spectra of Co 2p (a), Se 3d (b), and C 1s (c) for 30 wt% MWCNTs/Co_{0.85}Se.

the defect density. The defects on the surface of the MWCNTs, as suggested by a high I_D/I_G ratio, allowed the deposition of Co_{0.85}Se nanoparticles [25]. Furthermore, the peak at 2681 cm⁻¹ corresponds to the 2D band of the graphitic lattice vibration modes due to the created defects of MWCNTs.

XPS was performed to further analyze the surface chemical bonding states of 30 wt% MWCNTs/Co_{0.85}Se; the XPS profiles are shown in Fig. 3(a)–(c). As shown in Fig. 3(a), the 2p_{3/2} peak deconvoluted into Co³⁺ 2p_{3/2}, Co²⁺ 2p_{3/2}, and shakeup satellite peaks. The peaks at 785.9 and 802.8 eV are ascribed to the shakeup satellite peaks, respectively, which is consistent with the findings of a previous report [15]. The peaks with binding energies of 781.4 and 797.5 eV correspond to Co²⁺ and that at 778.2 eV corresponds to Co³⁺ [33]. The results indicate that cobalt is present on the surface as Co²⁺. Figure 3(b) and Figure 3(a) display the Se 3d and Co 3p spectra. The peaks at 54.2 and 55.4 eV are assigned to Se 3d_{5/2} and Se 3d_{3/2}, respectively, and the additional peak at around 60 eV deconvoluted into peaks corresponding to Se–O bonding structures and Co 3p [34,35]. The presence of SeO_x in the samples could be ascribed to surface oxidation, which is in good agreement with previous reports [36]. The high-resolution C 1s peak of MWCNTMWCNTs/Co_{0.85}Se (Fig. 3(c)) deconvoluted into three peaks located at 284.8, 286.2, and 288.9 eV, which are assigned to the C–C, C–O, and C=O groups, respectively [37,38]. The survey spectra of MWCNTs/Co_{0.85}Se, rGO/Co_{0.85}Se, and Co_{0.85}Se as well as Co 2p, Se 3d, and C 1s spectra are shown in Fig. S2(a)–(d).

SEM was performed to study the micromorphological features of the as-prepared samples (Fig. 4). Co_{0.85}Se nanoparticles display irregularly shaped particles with a size of approxi-

mately 50–100 nm with some degree of agglomeration, and a relatively rough surface (Fig. 4(a) and Fig. S4); thus, the structure of Co_{0.85}Se could provide abundant active sites. As shown in Fig. 4(b), the Co_{0.85}Se nanoparticles are well distributed on the surface of MWCNTMWCNTs, which are uniform with a diameter of approximately 50–60 nm and length in the micrometer scale. The Co_{0.85}Se magnetic nanoparticles were in intimate contact with the highly conductive MWCNTs support. A close contact between Co_{0.85}Se and MWCNTs is essential for an efficient electron transport toward the active sites of Co_{0.85}Se to MWCNTs. When GO was introduced in the reaction system, it converted into rGO nanoparticles during the hydrothermal reaction, which is confirmed by Raman analysis (Fig. S1). As shown in Fig. 4(b) and Fig. S3(a), the reduction in the size of Co_{0.85}Se is attributed to the space confinement effect of the nanotubes and rGO layers, which provide a space-confined environment, impeding the growth of Co_{0.85}Se nanoparticles [28,39].

The microstructures of the samples were analyzed by TEM and high-resolution TEM (HRTEM). The results shown in Fig. 5(a) corroborate that the Co_{0.85}Se nanoparticles have an irregular morphology, and the d-spacing value of 0.202 nm corresponds to the (102) plane (Fig. 5(b)). Moreover, Fig. 5(c) shows that Co_{0.85}Se nanoparticles with a size of ~50 nm are grown on the surface of MWCNTs. As can be seen in Fig. 5(c), the Co_{0.85}Se nanoparticles on the MWCNTs surface are smaller than the bare Co_{0.85}Se, which is ascribed to the presence of MWCNTs. The crystallite structure of Co_{0.85}Se in the nanocomposites showed no significant change. The interplanar distances of 0.27 and 0.18 nm correspond to the typical (101) and (110) planes of hexagonal Co_{0.85}Se, respectively (Fig. 5(d)). Furthermore, it is interesting that the entire observed area of the rGO/Co_{0.85}Se nanocomposite displays a typical monolayer rGO film and irregular nanoparticles (Fig. S3(b)). The formation of rich atomic interfaces between Co_{0.85}Se and rGO are ascribed to their strong coupling can be seen from red marks (Fig. S3(c)) [40]. Besides, the interlayer distance of 0.37 nm corresponds to the (002) lattice plane of rGO and the d-spacing value of 0.27 nm corresponds to the (101) plane of Co_{0.85}Se. Last but not the least, the scanning transmission electron microscopy (STEM) and EDX elemental mapping images confirmed the uniform dispersion of Co, Se, and C elements over the entire MWCNTs/Co_{0.85}Se nanocomposites (Fig. 5(e)). The Co and Se

Fig. 4. SEM images of Co_{0.85}Se (a) and 30 wt% MWCNTs/Co_{0.85}Se (b).

Fig. 5. TEM and HRTEM images of $\text{Co}_{0.85}\text{Se}$ (a,b) and MWCNTs/ $\text{Co}_{0.85}\text{Se}$ (c,d); (e) STEM and EDS mapping images of MWCNTs/ $\text{Co}_{0.85}\text{Se}$.

element mapping patterns overlapped adequately with the C element mapping pattern, which suggests the successful formation of the hybrid catalyst.

The magnetic hysteresis loops were measured to investigate the magnetic properties of $\text{Co}_{0.85}\text{Se}$ and MWCNTs/ $\text{Co}_{0.85}\text{Se}$ at room temperature (25 °C); the plots are shown in Fig. 6. The graphs show typical S-type curves, which indicate a ferromagnetic behavior. As shown in Fig. 6(a), the saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) values of $\text{Co}_{0.85}\text{Se}$ are 0.035, 0.0032 emu g^{-1} , and 55.09 Oe, respectively. The weak ferromagnetism can be attributed to the uncompensated spin on the surface of $\text{Co}_{0.85}\text{Se}$. Hence, as shown in Fig. 6(b), the M_s (0.118 emu g^{-1}), M_r (0.035 emu g^{-1}), and H_c (158 Oe) of MWCNTs/ $\text{Co}_{0.85}\text{Se}$ increased compared with those of $\text{Co}_{0.85}\text{Se}$ due to the decrease in $\text{Co}_{0.85}\text{Se}$ size in the MWCNTMWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites [41], which is consistent with the XRD and TEM results. The H_c increased from 55.09 Oe for the $\text{Co}_{0.85}\text{Se}$ nanoparticles to 158 Oe for the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites (Fig. 6(b)) due to the increase in the distance between the $\text{Co}_{0.85}\text{Se}$ nanoparticles, which resulted in weaker interparticle dipolar interactions [42,43]. The decrease in crystallite size and the increase in inter-nanoparticle distance enhanced the specific surface area of

the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ catalyst, which is beneficial for the electrocatalytic activity for HER [44].

The electrocatalytic activities of the as-prepared samples for HER were tested in 0.5 M H_2SO_4 on a GCE with a mass loading of approximately 0.16 mg cm^{-2} . In general, the commercial 20 wt% Pt/C catalyst shows the best HER property as a reference having a near zero onset potential and a large current density. The LSV curves of $\text{Co}_{0.85}\text{Se}$, 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$, and 20 wt% Pt/C are shown in Fig. 7(a). The results indicate the poor HER performance of the $\text{Co}_{0.85}\text{Se}$ nanoparticles with an overpotential of 319 mV (vs. RHE) at 10 mA cm^{-2} . In contrast, with the introduction of MWCNTs, the 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposite displayed better HER performance with a lower overpotential of 266 mV (vs. RHE) at 10 mA cm^{-2} . Fig. S5 shows the LSV curves of MWCNTs and MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites with different nominal weight percentages. When the mass ratio of MWCNTs increased from 15% to 30% in the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites, the onset potential decreased from 290 to 266 mV with an increase in current density from 60 to 83 mA cm^{-2} at -0.4 V (vs. RHE). This is possibly because the tubular structure of CNTs is conducive to the fast diffusion of electrolyte ions and the release of gaseous products of water electrolysis, which improved the electrocat-

Fig. 6. Magnetic hysteresis loops of $\text{Co}_{0.85}\text{Se}$ (a) and MWCNTs/ $\text{Co}_{0.85}\text{Se}$ (b) at 27 °C.

Fig. 7. Electrochemical measurements of the samples. LSV curves (a) and Tafel slopes (b) of $\text{Co}_{0.85}\text{Se}$, 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposite, and commercial 20 wt% Pt/C catalyst.

alytic activity [45]. However, the electrocatalytic property decreased when the MWCNTs content was increased to 45%. This is because with an increase in the mass ratio of MWCNTs in the composite, the active sites in the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites decreased [38]. All these results strongly indicate that the introduction of moderate MWCNTs can enhance the $\text{Co}_{0.85}\text{Se}$ nanoparticle HER performance because of improved conductivity and a reduction in the aggregation of $\text{Co}_{0.85}\text{Se}$ nanoparticles. Moreover, with an increase in the content of rGO, the overpotential of rGO/ $\text{Co}_{0.85}\text{Se}$ shows a similar trend as that of the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposites. The 15 wt% rGO/ $\text{Co}_{0.85}\text{Se}$ nanocomposite exhibited a significant HER at its lowest overpotential of 285 mV (vs. RHE) at 10 mA cm^{-2} (Fig. S5(b)). The Tafel slope is an inherent property of electrocatalysts, and a small Tafel slope indicates a strongly enhanced HER rate with a moderate increase in overpotential [46,47]. As shown in Fig. 7(b), the Tafel slope of 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ is the smallest, which indicates the favorable reaction kinetics of the nanocomposite. The HER catalyst inherent activity was further evaluated by the exchange current density (j_0). The smallest Tafel slope and the largest exchange current density of 0.07 mA cm^{-2} of 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ among all the as-synthesized catalysts further suggest that the HER occurred through a Volmer-Heyrovsky mechanism, in which the fast discharge of a proton is followed by the rate-limiting electro-

chemical recombination with an additional proton and a rate-determining step of the electrochemical desorption [48–50]. However, the MWCNTs/ $\text{Co}_{0.85}\text{Se}$ composites displayed a relatively small Tafel slope of 60.5 mV dec^{-1} among the Co-based HER catalysts, which is close to those of $\text{Co}_2\text{P}/\text{Co-Foil}$ and $\text{Co}_3(\text{PO}_4)_2/\text{N-C}$, but much better than that of CoP@ZnFeP nanocomposites (Table S1).

To investigate the interface reactions and electrode kinetics, EIS was performed; the EIS profiles of the $\text{Co}_{0.85}\text{Se}$ nanoparticles and 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ composite are shown in Fig. 8(a). As can be seen from EIS measurements, the 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ composite shows a lower impedance than the bare $\text{Co}_{0.85}\text{Se}$ samples under the same conditions, which is consistent with the results of Tafel slopes (Fig. 7(b)). This indicates the higher HER efficiency of MWCNTs/ $\text{Co}_{0.85}\text{Se}$, which can be attributed to the high electron-transfer ability and large surface area of MWCNTs [51,52]. Moreover, the effective ECSA, which is proportional to the amount of active sites for HER, was verified by capacitance measurements of the double layer at the solid-liquid interface [53]. To further demonstrate the superior catalytic performance of the 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ nanocomposite compared with that of $\text{Co}_{0.85}\text{Se}$, the double-layer capacitances (C_{DL}) were determined by performing CV at various scan rates (20–200 mV s^{-1}) in the potential range of 0.1–0.3 V (vs. RHE). As shown in Fig. 8(b) and Fig. S6(c), all the

Fig. 8. (a) Electrochemical impedance spectra of $\text{Co}_{0.85}\text{Se}$ and 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ composite at -0.2 V vs. RHE ; (b) CV curves of 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$; (c) estimated double-layer capacitances (C_{DL}) of $\text{Co}_{0.85}\text{Se}$ and 30 wt% MWCNTs/ $\text{Co}_{0.85}\text{Se}$ composite.

Fig. 9. (a) Durability test of 30 wt% MWCNTs/Co_{0.85}Se before and after 1500 cycles; (b) time dependence of current density of 30 wt% MWCNTs/Co_{0.85}Se at a static potential of 30 mV (vs. RHE).

CV curves exhibit a regular rectangular shape, which is the typical characteristic of double-layer capacitors. Fig. 8(c) exhibits the plot of the difference in the current densities of anode and cathode versus the scan rates, in which slopes are considered the electrochemical double-layer capacitances. It can be clearly seen that the C_{DL} of 30 wt% MWCNTs/Co_{0.85}Se (0.22 mF cm⁻²) is higher than those of Co_{0.85}Se and 15 wt% rGO/Co_{0.85}Se (0.04 and 0.17 mF cm⁻², respectively), which indicates the larger ECSA of 30 wt% MWCNTs/Co_{0.85}Se, and thus, the preferable HER [54].

The stability of electrocatalysts is another essential criterion for the evaluation of the electrocatalytic HER performance. To evaluate the stability of the catalysts, the polarization curves were measured at a scan rate of 10 mV s⁻¹ for 1500 cycles in an acid solution (Fig. 9(a), Fig. S7(a)). The 30 wt% MWCNTs/Co_{0.85}Se electrode exhibited better stability than Co_{0.85}Se in the acid solution because of its irregular tubular structure that can accommodate the volume expansion caused by H₂ gas [54]. In addition, the time-dependent graph of current density (Fig. 9(b)) displays a slight fluctuation in the HER performance of MWCNTs/Co_{0.85}Se. The possible reason is the

partial loss of the electrocatalytically active sites of the MWCNTs/Co_{0.85}Se nanocomposite during the violent bubble accumulation and release process (inset in Fig. 9(b)) [55].

The excellent activity of 30 wt% MWCNTs/Co_{0.85}Se for HER can be explained by the following factors: (1) the intrinsically good HER activity of nonstoichiometric Co_{0.85}Se because of its unique intrinsic half-metallic character due to the overlap of Co 3d and Se 4p spin-up electrons (high conductivity) [33]; (2) the Co_{0.85}Se nanoparticles synthesized using a polar organic solvent (N₂H₄·H₂O) may have a small crystal size, rough surface, and large specific surface area, which ensured a better reactive performance and afforded ample active sites [2]; and (3) the introduction of MWCNTs as a highly conductive material increased the conductivity of the entire electrode and facilitated charge transportation between the electrocatalyst and electrolyte [56].

4. Conclusions

In this study, we synthesized weak magnetic Co_{0.85}Se nanoparticles. MWCNTs were introduced into the Co_{0.85}Se catalyst

Graphical Abstract

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Co_{0.85}Se magnetic nanoparticles supported on carbon nanotubes as catalyst for hydrogen evolution reaction

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Co_{0.85}Se magnetic nanoparticles supported on carbon nanotube enhanced the performance of electrocatalytic hydrogen production, which possesses excellent activity than that of pure Co_{0.85}Se nanoparticle.

system as a highly conductive material to enhance the HER performance to reduce the aggregation of Co_{0.85}Se. The M_s values of Co_{0.85}Se and 30 wt% MWCNTs/Co_{0.85}Se were 0.035 and 0.118 emu g⁻¹, respectively. The MWCNTs/Co_{0.85}Se catalyst displayed a higher activity for H₂ evolution than Co_{0.85}Se in an acid solution, which gave rise to an overpotential of 266 mV at a current density of 10 mA cm⁻² and yielded a small Tafel slope of 60.5 mV dec⁻¹. The findings present a novel strategy for the development of highly active HER catalysts based on earth-abundant elements.

Conflict of Interest

The authors declare no conflict of interest.

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弱磁性Co_{0.85}Se纳米片负载碳纳米管作为电催化析氢催化剂

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摘要: 氢气是一种环境友好可再生的清洁能源, 电解水无疑是一种很好的制氢方法。然而, 电催化分解水产氢受到其缓慢的动力学过程、较低的催化性能和较差的稳定性的限制。为了使整个过程更节能, 具有高电流密度和低的过电势的高效电催化剂被广泛研究。非化学计量相硒化钴(Co_{0.85}Se)作为一种重要的金属硫属化合物具有优异的催化性能而广受关注。但是低维的Co_{0.85}Se活性位点少, 分散性差, 电子传递能力低, 导致其电催化剂活性差。多壁碳纳米管(MWCNTs)具有多种电性能, 包括金属导电性和电子存储能力等。因此, MWCNTs的特殊结构和高导电性可以有效地促进电子从电催化剂向碳纳米管的转移, 实现高效电分解水产氢性能。

本文在不使用表面活性剂和模板的情况下, 通过一步水热溶剂热法合成弱磁性Co_{0.85}Se纳米片负载碳纳米管电催化剂。采用磁滞回线研究Co_{0.85}Se和MWCNTs/Co_{0.85}Se的磁性能, 结果表明其有弱顺磁性, Co_{0.85}Se纳米片之间的空间距离增强导致粒子间偶极相互作用减弱, 从而使MWCNTs/Co_{0.85}Se纳米复合材料的矫顽力值增加到158 Oe。随着微晶尺寸的减小和纳米颗粒间距的增大, MWCNTs/Co_{0.85}Se催化剂的比表面积增大, 有利于提高其电催化活性。扫描电镜和透射电镜展示出Co_{0.85}Se纳米片分散性较差, 且团聚现象严重, 而MWCNTs/Co_{0.85}Se纳米复合催化剂显示Co_{0.85}Se纳米片均匀分散在MWCNTs表面, 且纳米片尺寸明显减小, 有利于Co_{0.85}Se纳米片暴露更多的活性位点。线性扫描伏安曲线测量表明, 在酸性溶液中Co_{0.85}Se纳米片在电流密度为10 mA cm⁻²时, 其过电势为319 mV (vs. RHE), 30 wt% MWCNTs/Co_{0.85}Se的过电势为266 mV (vs. RHE)。Co_{0.85}Se和MWCNTs/Co_{0.85}Se的Tafel斜率分别为92.6和60.5 mV dec⁻¹。此外, MWCNTs/Co_{0.85}Se的电流交换密度(*j*₀)为0.07 mA cm⁻²。较小的Tafel斜率和高电流交换密度表明, MWCNTs/Co_{0.85}Se具有良好的反应动力学和快速的质子分离速率。交流阻抗谱表明MWCNTs/Co_{0.85}Se比Co_{0.85}Se电阻更小, 电子传输速率更快。电化学活性表面积与双电层在固液界面处的电容测量值成正比。结果显示, 30 wt% MWCNTs/Co_{0.85}Se的双电层电容为0.22 mF cm⁻², 高于Co_{0.85}Se和15 wt%的rGO/Co_{0.85}Se(0.04 mF cm⁻², 0.17 mF cm⁻²), 这表明较大的电化学活性表面积有利于析氢反应进行。30 wt% MWCNTs/Co_{0.85}Se的循环稳定测试表明其具有较好的稳定性。

综上, 本文介绍了通过一步水热法合成具有弱磁性的Co_{0.85}Se和MWCNTs/Co_{0.85}Se电催化剂, 碳纳米管作为一种高导电性材料被引入Co_{0.85}Se纳米片中以减少Co_{0.85}Se的团聚, 使Co_{0.85}Se的活性位点增加, 进而提高电催化制氢性能。

关键词: 硒化钴; 纳米复合物; 磁性; 电催化剂; 析氢反应

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