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Solvothermal synthesis 2D ultrathin CdSe nanosheets and its photoelectrochemical properties

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This work synthesized ultrathin 2D CdSe nanosheets by a facile solvothermal method. The morphology, structure, composition, and thermal stability of the samples were studied and analyzed using transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD), infrared spectra (IR), and thermogravimetric (TG) methods. Results demonstrated that stable wurtzite-structured CdSe nanosheets with 2-3 nm thickness were successfully fabricated. UV-Vis absorption spectroscopy (UV-Vis) and fluorescence spectroscopy analysis exhibited the characteristic absorption peaks and fluorescence emission peaks of CdSe nanosheets with narrow full-width half-maximums (fwhm) and slight Stokes shift, implying ultrathin structure. Photoelectrochemical (PEC) measurement declared a fast and stable photo-response for the as-prepared CdSe ultrathin nanosheets. With the reaction temperature increasing, the PEC activity enhanced due to the decreased nanosheets thickness. This paper provides a new route for the synthesis of CdSe ultrathin nanosheets and their application in the field of photoelectrochemical catalysis.

Keywords: CdSe; ultrathin nanosheets; solvothermal method; PEC properties

1. INTRODUCTION

With the development of science and technology, nanomaterials have attracted extensive attention due to their unique chemical and physical properties. The preparation of nanomaterials with unique structure and excellent performance is the current research hot spot [1]. Two-dimensional semiconductors have attracted extensive research due to their atomic layer thickness, large specific surface area, and special electric and optical features, broadly applied in solar cells, photocatalysis, photoelectrochemistry, and photoluminescence [1-3]. Among II-VI nano-semiconductors, CdSe nanomaterials have the advantages of unique surface effect, high anisotropic growth, and dielectric effect, which are widely used in light-emitting diodes, biomarkers, spectral analysis, photosensitive elements, and solar cells. 2D ultrathin CdSe nanosheets, a new type of colloidal nanocrystals, have large lateral

dimensions, usually up to 10-100 nm, and very thin thickness, with only a few single atomic layers thickness. Hence, they only induce significant quantum confinement effects in the thickness direction [4]. This special structural feature makes CdSe nanocrystals promising for applications in electrochemical sensors, environmental chemistry, and photoelectrochemistry [5].

The preparation methods for 2D nanosheets mainly include liquid phase exfoliated, chemical vapor deposition (CVD), and chemical etching-assisted methods [6-11]. Among them, liquid phase exfoliation has been recognized as an effective method to overcome weak van der Waals forces [12]. Recently, inorganic-organic hybrid intermediates solvothermal methods have been proposed to synthesize single-atomic layer 2D materials. This method has been developed and applied rapidly because of the low cost, low technical requirements, and simple operation [13]. However, the cadmium selenide ultra-thin structure was fabricated mainly through the chemical etching-assisted method and thermal injection method, which have many disadvantages such as multiple steps [14], inconvenient to operate and/or requiring special precursor (Cadmium Stearate (Cd(St)2) [15], selenocarbamate, trioctylphosphine or tri-n-octylphosphine-selenium) [16, 17]. Therefore, exploiting new effective strategies is necessary to obtain CdSe ultrathin nanosheets.

CdSe is a narrow bandgap semiconductor with well visible light absorption and can be applied in fluorescent materials, photocatalysis, and optoelectronic devices fields [18]. Two-dimensional cadmium selenide with a thickness of one or more atoms can quickly diffuse electrons and holes to its surface, which is beneficial to the separation of carriers. Furthermore, it has an ultra-high specific surface area, producing more active sites [19]. Therefore, 2D ultrathin nanomaterials would have higher PEC activity than bulk materials [19].

In this paper, a facile solvothermal method with Se powder as selenium source was used to synthesize ultrathin CdSe nanosheets, whose morphology and structure were characterized by TEM, AFM, and XRD. Stable wurtzite-structured CdSe nanosheets with 2-3 nm thickness were fabricated. In addition, the photoelectrochemical performance of CdSe ultrathin nanosheets was studied, and the effect of reaction temperature on optical response and PEC activity was discussed. As far as we know, the synthesis of free-standing 2D cadmium selenide nanosheets using the solvothermal method has not been reported.

2. EXPERIMENTAL PART

2.1 Experimental reagents

Selenium Powder (99.0%, Sinopharm Chemical Reagent Co., Ltd.), Cadmium Chloride (CdCl₂·2.5H₂O) (99.0%, Sinopharm Chemical Reagent Co., Ltd.), Cadmium Nitrate Tetrahydrate (Xilong Chemical Co., Ltd.), octylamine (C₈H₁₉N, 90.0%, Aladdin reagent), oleylamine (C₁₈H₃₇N, 80.0-90.0%, Aladdin reagent), all of the above reagents are of analytical grade.

2.2 Preparation of ultrathin 2D CdSe nanosheets

0.275 g of cadmium chloride, 5 ml of octylamine, and 5 ml of oleylamine were poured into a 25 ml Teflon autoclave, reacted at 120 °C for 2 h to obtain the precursor of cadmium chloride. And 0.355 g of selenium powder, 2.5 mL of octylamine, and 2.5 ml of oleylamine were poured into the other 25 ml Teflon autoclave, which was maintained at 200 °C for 10 h to prepare a selenium dispersion. Finally, the Se dispersion and the cadmium chloride precursor solution were mixed uniformly, and poured into a 25 ml autoclave, reacting at different temperatures for 17 h. After cooling to room temperature, ethanol was added to precipitate the product, which was washed 3 times with 50% ethanol and absolute ethanol, respectively. The residue was freeze-dried to obtain a yellow powder. The preparation process is shown in Fig.1.



Figure 1. CdSe nanosheets preparation process.

2.3 Material Characterization

The crystal structures of the as-synthesized samples were analyzed by PANalytical X'Pert PRO X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418$ Å) in the range of 10 to 90°. The microstructures and thickness of the as-prepared samples were measured by transmission electron microscopy (TEM, JEOL, JEM-2100F) and atomic force microscopy (AFM, NanoFirst-2000). Thermal stability was tested by thermometer (SDT Q600). The UV–vis absorption spectra of the as-obtained samples were recorded by a UV/VIS/NIR Spectrometer (PerKinElmer, Lambda 750) in the 200 to 800 nm range. BaSO₄ was used as the standard reflectance material. The Fluorescence specwere was measured by Fluorescence Spectrometer (Hitachi, F7000).

2.4 Photoelectrachemical performance measurement

Firstly, we prepared photo-anode by the following method. In a typical experiment, the CdSe nanosheets were dispersed in ethanol solution, which was spin-coated onto the clean ITO surface, naturally dried to obtain an ITO/CdSe film electrode. Then, the electrode was annealed at 300° C for 1h under Ar protection. All the as-prepared film electrodes were fabricated to a 1 cm × 1 cm a by using silicone rubber.

The photoelectrochemical performance has been investigated on an electrochemical workstation (CHI 660E, CH Instruments). The fabricated samples were used as photo-anode, with a Pt wire as a

counter electrode and a saturated calomel electrode (SCE) as a reference electrode in a 0.5 M Na₂SO₄ solution (pH=6.8) to set up a three-electrode system. The illumination source (Beijing Perfectlight Technology Co., CHF-XM 500W Xe lamp) was calibrated to one sun (100 mW/cm²) using a spectroradiometer (Beijing Au-light Co., CEL-NP2000). The photocurrent-potential measurement was recorded from 0 to 1 V vs. SCE at a scan rate of 0.01 V/s, and the light was chopped manually at regular intervals. The amperometric i-t curves were measured at the bias potential of 0.5 V vs. SCE. The measured potential vs. SCE was converted to the reversible hydrogen electrode (RHE) scale by using the Nernst equation:

$$E(RHE) = E(SCE) + 0.059 \times pH + 0.2412V$$

3. RESULTS AND DISCUSSION

Fig. 2 is the XRD pattern of the CdSe nanosheets prepared by the solvothermal method. It can be observed from Fig.2 that the three diffraction peaks are located at $2\theta=24.74^{\circ}$, 25.95° , and 28.09° , corresponding to (100), (002) and (101) crystal planes of CdSe with hexagonal wurtzite structure, respectively, which is consistent with the literature results [20]. The significantly widened base and sharpened peaks suggest typical characteristics of such highly crystallized ultrathin nanosheets. The sharp peaks are multiplied signals from the highly oriented two dimensional textures laying curled up on the substrate [5], hinting the as-prepared CdSe nanocrystals could own the structure of ultrathin nanosheets.



Figure 2. XRD diagram of CdSe nanosheets.

To study the thermal stability, thermogravimetric tests were performed on the CdSe nanosheets. Fig. 3 displays that from 150 °C to 300 °C, the weight loss is 22.2%s mainly due to the decomposition of organic molecules such as octylamine and oleylamine. From 300 °C, the weight loss slows down, and CdSe begins to lose crystal water. It shows that the cadmium selenide nanosheets have good stability before 300 °C.

Fig. 4 is an infrared spectrum of CdSe nanosheets. As shown in Fig.4, the C=C stretching

vibration absorption peak appears at 1640 cm⁻¹, δ C-H stretching vibration of -CH₃ located at 1400 cm⁻¹, stretching vibrations of –NH₂ at 2980 cm⁻¹ and 2900 cm⁻¹, and stretching vibration peak of O-H bond at 3420 cm⁻¹. These characteristic peaks may come from the reaction mixtures introduced by octylamine, oleylamine, and solvent ethanol. A small amount of octylamine and oleylamine can help the cadmium selenide nanosheets be uniformly dispersed in ethanol and prevent agglomeration.



Figure 3. Thermal gravimetric curves of CdSe Nanosheets.



Figure 4. The infrared spectrum of CdSe nanosheets.

The high resolution TEM image in Fig. 5 presents that the cadmium selenide is flakes-structure, mostly oval and uniformly dispersed. Lattice stripes can be seen in Figure 5b-c, with an interplanar spacing of 0.34 nm, assigned to the (002) plane of wurtzite CdSe [21], which is consistent with the XRD

data. We can also find that the length and width of the nanosheets are about 50-100 nm, and the morphology is uniform and regular.



Figure 5. The TEM Figure of CdSe Nanosheets.



Figure 6. (a) AFM images of CdSe nanosheets. (b) AFM height profiles across the edges of CdSe nanosheets.

To further prove the morphology of CdSe nanosheets are 2D structures, the atomic force microscopy (AFM) was used. Fig. 6a is the AFM image of the CdSe sample, which displays that the

shape of CdSe is nanosheets-like. The AFM height map (Fig. 6b) shows that the thickness of the CdSe nanosheets is between 2-3 nm.



Figure 7. UV-visible absorption spectra of CdSe nanosheets were obtained at different temperatures.



Figure 8. UV-visible absorption Fluorescence spectra of CdSe nanosheets were obtained at 120 °C.

Temperature plays an important role in the optical properties of nanomaterials. It can be seen from Fig. 7 that CdSe nanosheets synthesized at 100 °C have two absorption peaks locate at 431 nm and 456 nm, which correspond to electron/light hole transfer and electron/heavy hole transfer, respectively. It is a common and important feature of two-dimensional nanosheets in the absorption spectrum, which

is the hole energy level splitting caused by the special structure of two-dimensional nanosheets [22]. When the reaction temperature increased to 120 °C, two peaks blue-shifted to 428 nm and 454 nm, respectively, and the peaks became narrower and stronger. It manifests the CdSe nanosheets' thickness at 120 °C is thinner and more uniform.

The Fluorescence spectra of CdSe nanosheets obtained at 120 °C (as seen from Fig.8b) manifests the emission spectra with full width half-maximums (fwhm) <10 nm and the slights Stokes shift between the first exciton. And the platelet emission is below 10 meV compared with quantum dots and quantum rods with the significant Stokes shifts. The very narrow fwhm implies the thinner thickness is consistent with those reported in the literature [23]. Results revealed that the ultrathin cadmium selenide nanosheets with uniform thickness and appropriate fluorescence properties were successfully prepared by the solvothermal method.

Among Group II-VI semiconductors materials, Cadmium selenide (CdSe) has potential application in the optoelectronic device, luminescence materials, lasers, and photocatalysis fields due to excellent visible-light absorption and narrow band gap (~1.7 eV) [24, 25]. Hence, CdSe as a narrow bandgap semiconductor could display significant photocatalytic activities under visible light irradiation. Especially, CdSe quantum dots (QDs) have shown good photocatalytic activities for H₂ evolution by water splitting under visible light, owing to the quantum confinement effect and strong visible light absorption in a wide range of wavelengths [26, 27]. Hence, CdSe nanosheets with ultrathin structure could also exhibit excellent photocatalytic performance. To prove this speculation, we carried out the photoelectrochemical measurement.

Fig. 9a shows the transient photocurrent-time curves of the CdSe nanosheets electrode under 0.6 V bias. At the moment of illumination, the photocurrent of the sample increases rapidly until a stable value. Once the light turns off, the current drops sharply to zero, indicating that the CdSe ultrathin nanosheets are highly responsive to visible light. Moreover, with the increase in synthesis temperature, the photocurrent of CdSe nanosheets promotes significantly. Since UV-fluorescence spectroscopic analysis proved that the higher the reaction temperature is, the thinner the thickness of the as-prepared CdSe nanosheets are, it revealed that the thinner CdSe nanosheets have the higher PEC activity. The light-switching current-potential curves (Fig.9b) of CdSe nanosheets illustrate that the photocurrent of CdSe nanosheets prepared at 120 °C is largest at the same potential consistent with Fig.9a. At 1.0 V, it reaches 0.43 mA/cm², 1.7 times that of the sample obtained at 100 °C. Linear sweep voltammetry tests on CdSe nanosheets synthesized at different temperatures (in Fig.9c) show that the current generated by the sample under illumination is significantly higher than the dark current, displaying that the sample has an intensive response to light. It is worth mentioning that the photocurrent is significantly enhanced when the synthesis temperature is above 110 °C, meaning 110 °C is the required temperature for achieving the ultrathin structure of CdSe. Among them, the CdSe nanosheets fabricated at 120 °C generated the highest PEC signal, consistent with the results in Figure 9a-b. This may be ascribe that thinner CdSe nanosheets have larger specific surface area, more active sites, and shorter carrier transport paths. Furthermore, the ultrathin structure induces a quantum confinement effect, which is beneficial to separation and migration of photogenerated charges. The photocurrent density of pure ultra-thin CdSe nanosheets (this work) is comparable with other photoanode materials of the same type used for photocatalytic decomposition of water (in table 1). As shown in Fig.8, CdSe nanosheets emit strong

fluorescence, suggesting dramatic recombination of photo-induced electron and hole. Maybe, this is the reason that the PEC activities of pure CdSe nanosheets is not optimal. In future research, we could further improve PEC properties of 2D CdSe nanosheets by constructing heterojunctions or using co-catalyst to suppress the carrier recombination. 2D CdSe nanosheets. This implies that CdSe ultrathin nanosheets have important application prospects in the field of PEC water splitting.



Figure 9. (a) Photocurrent-time curves at the bias potential of 0.5 V vs. SCE. (b)Linear sweep voltammogramss from 0 to 1 V vs. SCE at a scan rate of 0.01 V/s. (c)Linear sweep voltammograms of CdSe nanosheets prepared at different temperatures, the curves were recorded from 0 to 1 V vs. SCE at a scan rate of 0.01 V/s.

Table 1. Comparison of the photoelectrochemical performance of similar materials.

Photoanode Materials	Photocurrent density	Ref.
CdSe/Ag/TiO ₂	0.11 mA/cm ²	[28]
Au/CdSe	7.1 mA/cm^2	[29]
CdSe/S,N-GQDs	$42.86 \ \mu A/cm^2$	[30]
CdSe/TiO ₂	1.6 mA/cm^2	[31]
Pure CdSe ultrathin nanosheets	0.43 mA/cm ²	This work

4. CONCLUSION

In this work, we adopted a facile solvothermal method to synthesize CdSe ultrathin nanosheets with uniform thickness at 120 °C for 17 h. XRD, TG and IR analysis showed that the cadmium selenide

nanosheets were wurtzite phase and relatively stable below 300 °C. Characterization of TEM and AFM testified that the lateral dimentions of the nanosheets were in the range of 50-100 nm, and the thickness was 2-3 nm, manifesting that the CdSe ultrathin nanostructures were successfully prepared. The asprepared CdSe nanosheets displayed two strong absorption peaks with narrow peak spacing and fluorescence emission peak with small Stokes shift. The PEC measurements demonstrated that the CdSe nanosheets have good light responsiveness, and the photocurrent of the CdSe nanosheets synthesized at 120 °C can reach 5.4 μ A/cm², which is 1.8 times that of samples at 100 °C. The results show that the thinner the nanosheets, the more specific surface area and reactive sites. At the same time, the photogenerated charge transport path is shortened, which is conducive to carrier separation, thereby improving the photoelectrochemical performance. This paper provides a new route for the synthesis of CdSe ultrathin nanosheets and their application in the field of photoelectrochemical catalysis.

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