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Sensing Performance of EGFET pH Sensors with CZTSe Nanoparticles Fabricated on Glass Substrates

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In this work, the sensing membrane of an extended-gate field-effect-transistor (EGFET) pH sensor with CZTSe nanoparticles was fabricated on a glass substrate through a solution-based method. The CZTSe nanocrystals were synthesized successfully by using the metal sources in isophorondiamine (IPDA, $C_{10}H_{22}N_2$) solution under a N_2 flow at atmospheric pressure and at the reaction temperature of 235 °C. It was found that the average diameter of these nanoparticles was 20–30 nm. The resulting EGFET pH sensors with CZTSe nanocrystals exhibited good sensing performances owing to the large sensing surface-to-volume ratio. The pH sensitivity calculated from the linear relation between the drain-source current and the pH value was 7 μA/pH, and that calculated from the linear relation between the reference voltage and the pH value was 9 mV/pH.

Keywords: CZTSe, nanocrystal, isophorondiamine,,EGFET, pH

1. INTRODUCTION

Recently, modern diseases have become increasingly diverse, such as cardiovascular disease, diabetes, kidney disease, and so on. As a result, researchers are paying more and more attention to human health. The pH value of blood is an important index for the human body, and even a small change in body fluids can signify some problem or sickness. Therefore, pH sensors play important roles in many clinical applications such as environment monitors, blood monitors, biological analyses, chemical analyses, and clinical detection [1–3]. Semiconductor-based sensors have attracted intense attention and interest. Field-effect-transistor (FET)-based devices have been used widely in biosensors [4, 5]. Among such FET-based biosensors, extended-gate field-effect-transistors (EGFETs) possess several inherent advantages such as their facile fabrication process [6], low level of influence by optical illumination and operation temperature, and disposable gate. The EGFET consists of two parts: the sensing membrane structure and the metal-oxide-semiconductor field-effect-transistor (MOSFET) structure.

The material of the sensing membrane is the key point of the pH sensor. Recently, Cu_2-II–IV–VI_4 quaternary semiconductors such as $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS), and $Cu_2ZnGeSe_4$ have been investigated extensively as effective light-absorbing materials in solar cells. Of such systems, CZTSe has proved to be one of the most interesting materials for application in solar cells, since it is a direct p-type semiconductor with a reported optical band gap of 1.0–1.44 eV and an absorption coefficient larger than 10^4 cm^{-1} [7–11]. CZTSe is a promising membrane material owing to its stability, nontoxicity, and ideal biocompatible properties. In this study, the synthesis of Cu-based nanocrystals described is different from the general solution method using oleylamine (OLA) solvent [12–20]; we report a simple, continuous, scalable, and rapid synthesis of CZTSe nanocrystals, in which oleylamine is replaced by isophorondiamine (IPDA, $C_{10}H_{22}N_2$) and reactive metal salts are replaced by the cheaper elemental metal powders as reaction sources. The $Cu_2ZnSnSe_4$ nanocrystals presented here are highly crystalline and stable in solution, making them compatible with inexpensive and scalable solution-based processes. Therefore, the colloidal synthesis of $Cu_2ZnSnSe_4$ may extend the range of applications of this material to many other areas such as printable optics and electronics.

In this work, we present the synthesis of highly crystalline CZTSe nanoparticles through a simple, low-cost, convenient method, and discuss the pH sensor performance of the CZTSe nanoparticle structure and analyze its performance.

2. EXPERIMENTAL

2.1 Synthesis of CZTSe nanocrystals

$Cu_2ZnSnSe_4$ (CZTSe) powders were synthesized using three coordinating solvent method. In the synthesis procedure, Cu powder (1.0 mmol), Zn powder (0.5 mmol), Sn powder (0.5 mmol), and Se powder (2.0 mmol) were mixed and dissolved in 50 mL IPDA at room temperature; subsequently, the reaction temperature was kept at 235 °C for 20 h. After the reactions were cooled to room temperature, 50 mL acetone was added to precipitate the nanocrystal products, and the crystal structure of the nanocrystals obtained from the synthesis were characterized by powder X-ray diffraction (XRD) using CuKα radiation (λ=1.54 Å). The formation of CZTSe was further confirmed by Raman measurements; room-temperature Raman spectra were recorded with a Horiba's LabRam HR high-resolution spectrometer equipped with a multichannel CCD detection system in the backscattering configuration. An Oxford INCA energy-dispersive X-ray spectroscopy (EDS) detector was used to analyze the elemental composition. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) images were taken using a JEM 2100 microscope at an accelerating voltage of 200 kV.

2.2 Preparation of CZTSe sensing membrane

The as-prepared CZTSe microparticles were dispersed in isopropanol (IP) (95 wt% liquid and 5 wt% microparticles), and the mixture was stirred for 6 h. This part of the product was named solution A. Separately, ethyl cellulose (EC) was dissolved in IP by stirring for 6 h (90 wt% IP and 10 wt% EC). This part of the product was named solution B. A mixture was then prepared from solutions A and B in the volume ratio 5:1, and 0.1 wt% terpinol was added while the mixture was milled in an agate mortar. Finally, ink for screen printing was prepared and spun on a glass substrate, and the sensing membrane was finished.

2.3 Measurement system setup

For measurement of the sensing performances of the fabricated pH sensors, the sensing membrane and the Ag/AgCl reference electrode were dipped into the buffer solution (pH 4 to 10). The pH value of the buffer solution was varied from 4 to 10, depending on the concentration of H^+ ions in the detection solution. In order to achieve this, we used hydrochloric acid and sodium hydroxide to control the pH value. The CZTSe conducting layer of the EGFET was connected to the gate of a commercial MOSFET device. The sensing response of the pH sensors was measured using an Agilent 4156C analyzer. The measurement system is shown in Fig. 1.

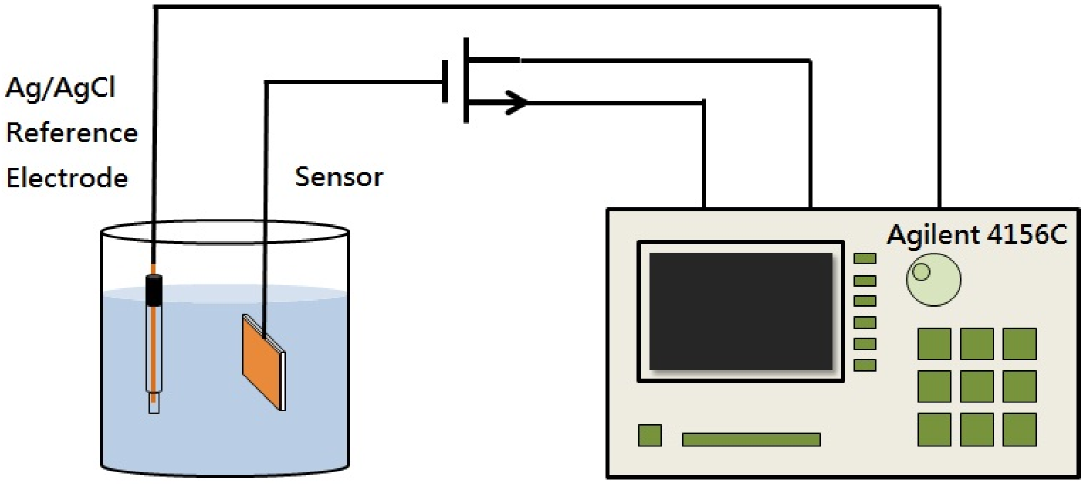

Figure 1. Measurement system of CZTSe-nanoparticle pH sensors.

3. RESULTS AND DISCUSSION

CZTSe nanocrystals were synthesized through the hot-injection method. The synthesis process is as follows: $2Cu + Zn + Sn + 4Se \rightarrow Cu_2ZnSnSe_4$ nanocrystals. The XRD pattern of the CZTSe nanocrystals synthesized using the thermal decomposition method is shown in Fig. 2; the CZTSe nanocrystals are composed of tetragonal CZTSe nanocrystals (JCPDS file No. 52-0868).

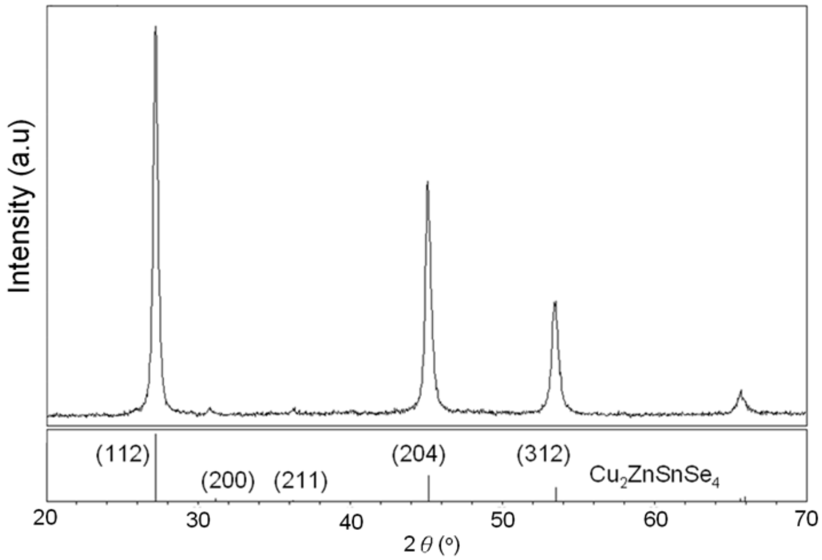

Figure 2. Powder XRD patterns of CZTSe nanocrystals

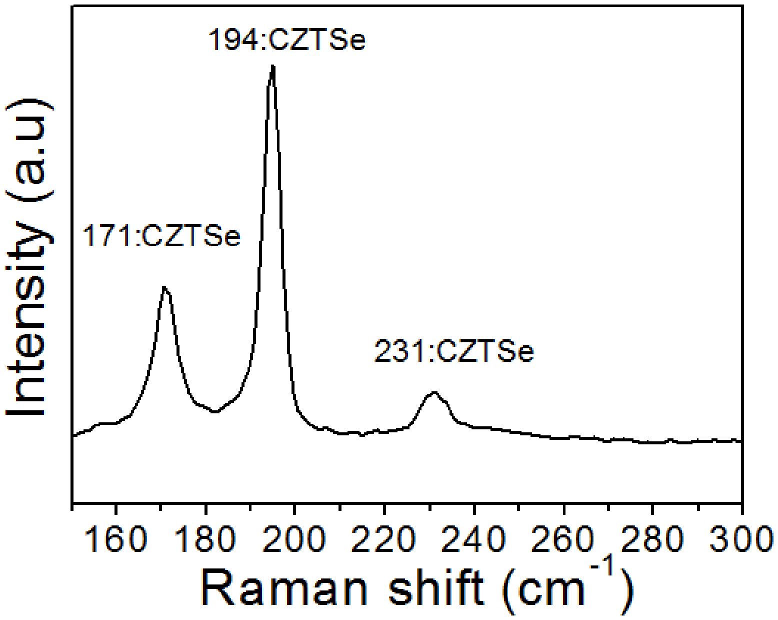

Figure 3. Raman characterization of as-synthesized CZTSe nanoparticles

We identified three major peaks corresponding to the (112), (204), and (312) planes. The crystal domain size was estimated from the full-width at half-maximum (FWHM) of the (112) peak by using the Scherrer equation:

$$D = \frac{0.9\lambda}{b\cos\theta} \qquad (1)$$

where D is the diameter of the crystallites forming the film, λ is the wavelength of the CuKα□ line, b is the FWHM in radians, and θ is the Bragg angle. The average size of the crystallite was 25.5 nm, and the XRD pattern of the nanocrystals shows d-spacings of 0.33 nm, characteristic of the (112) lattice plane for a stannite structure.

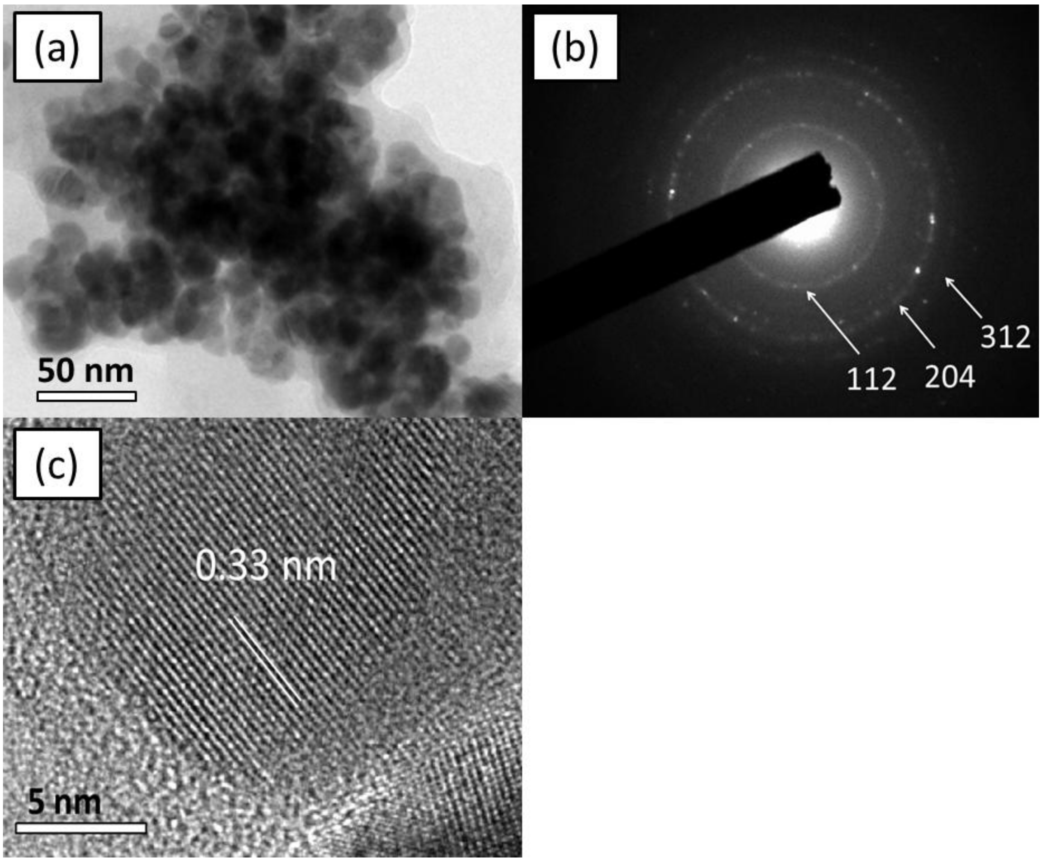

Figure 4. (a) TEM image of CZTSe nanocrystals dispersed in chloroform, with (b) SAED pattern and (c) HRTEM image

As confirmation of the presence of CZTSe, the samples were analyzed further through Raman scattering experiments. In the analysis, three main peaks were found at 171, 194, and 231 cm^{-1}, as shown in Fig. 3. These three peaks were identified as the main features of the CZTSe Raman spectrum [21–24], and the result corresponded with the XRD analysis, in which only a single quaternary phase was observed.

Fig. 4(a) shows the TEM and SAED images of the as-synthesized CZTSe nanocrystals dispersed in alcohol. We find that the average diameter of the CZTSe nanocrystals is 26±3 nm, which is very close to the particle size calculated from the Scherrer equation. The SAED patterns in Fig. 4(b) show a series of concentric rings corresponding to the (112), (204), and (312) orientations of the CZTSe nanocrystals. In Fig. 4(c), the lattice fringe calculated from the HRTEM image is 0.33 nm, corresponding to the (112) lattice plane for the chalcopyrite structure of CZTSe. Energy-dispersive X-ray spectroscopy (EDS) analysis of the nanoparticles (Table 1) revealed that the atom ratio of Cu, Zn, Sn, and Se approaches the stoichiometric ratio of 2:1:1:4, with the chemical composition Cu/(Zn+Sn) = 1.16 and Zn/Sn = 0.98. In our experiment, the crystals were slightly Cu-rich and Zn-poor in comparison with the stoichiometric composition. The average composition of the nanocrystals determined by EDS analysis takes the error of the EDS detector (approximately ±2 at%) into consideration.

Table 1. Chemical composition of the CZTSe nanoparticles obtained from the reaction at 235 °C for 20 h (in at%)

Element	Cu	Zn	Sn	Se
at%	28.58	12.09	12.28	47.05

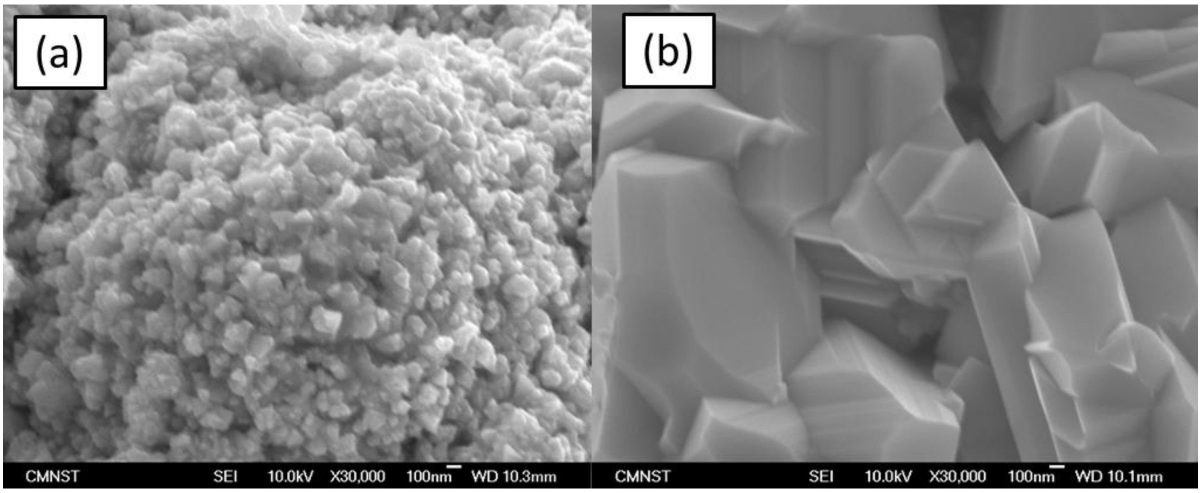

Figure 5. SEM images of CZTSe films: (a) as-cast CZTSe nanocrystal film on soda lime glass substrate, (b) CZTSe film after selenization at 550 °C for 30 min, showing complete recrystallization into large and densely packed grains

Fig. 5 shows SEM images of nanocrystal thin films prepared by drop-casting directly the desired amount of ink on soda lime glass and letting the solvent evaporate slowly. Multiple coatings could be applied to fabricate a thin film with the desired thickness. Selenization was usually carried out on the CZTSe thin film by annealing under selenium vapor to enhance the grain growth. Fig. 5(a) shows the top view of the nanocrystal film deposited on a soda lime glass substrate, which exhibits very dense packing of the CZTSe nanocrystals. The image of the CZTSe nanocrystal film selenized at 550 °C is shown in Fig. 5(b); the selenized film exhibits large and densely. Compared with the as-prepared CZTSe film, the film selenized under Se vapor pressure showed improved crystallization and a dramatically enlarged CZTSe grain size.

The dependence between the drain-source current (I_{DS}) and the drain-source voltage (V_{DS}) of the EGFET with CZTSe nanoparticles, operated at a reference electrode voltage (V_{REF}) of 3 V, was measured. The experimental results showed that when the pH value increased in the detection solution, I_{DS} decreased gradually. This was attributed to the accumulation of H^+ ions at the CZTSe surface under acidic conditions, which is equivalent to providing an extra positive voltage at the gate electrode. On the other hand, the accumulation of OH^- ions on the CZTSe surface in basic solution is equivalent to providing an extra negative voltage at the gate electrode.

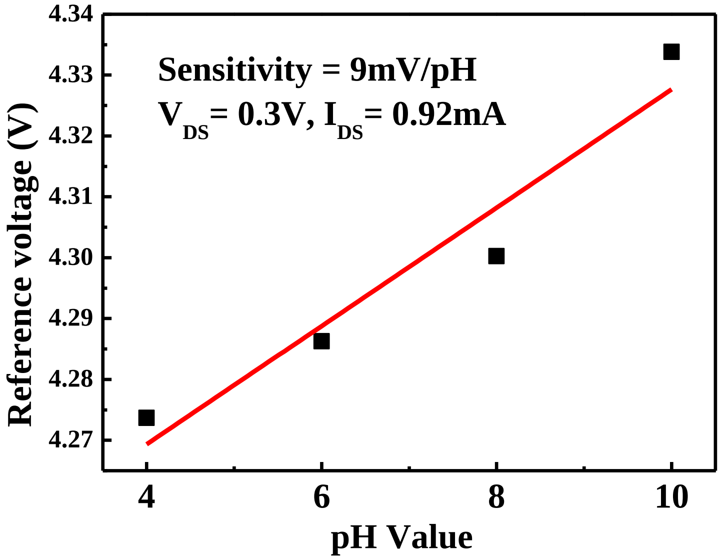

Figure 6. Reference voltage as a function of pH value

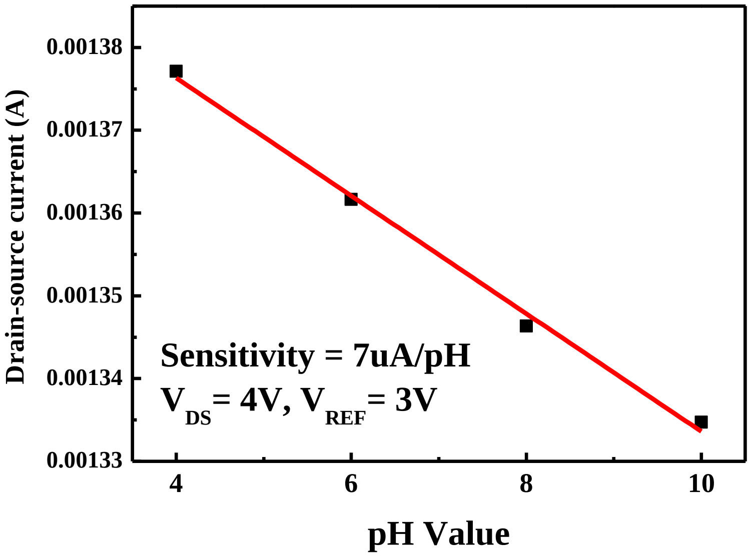

Figure 7. Drain-source current as a function of pH value

Figure 6 shows a linear relationship between V_{REF} and pH. The sensitivity is defined as the dependence of the obtained reference voltage on the pH value. so it could be calculated from the linear relationship between the reference voltage and the pH value. From the experimental results, the voltage sensitivity of the CZTSe nanoparticle EGFET was calculated to be 9 mV/pH. From the previous discussion, this indicates that when the pH was increased, the concentration of OH^{-} ions increased.

The measured drain-source current is shown as a linear function of the pH value in Figure 7, where the drain-source voltage (V_{DS}) of the MOSFET was 4 V and the reference electrode voltage (V_{REF}) was 3 V. The pH sensitivity was calculated from the linear relation between the drain-source current (I_{DS}) and the pH value. The sensing sensitivity of the pH sensors with CZTSe nanoparticles was 7 μA/pH.

According to the site binding theory [25, 26], the surface potential voltage of the extended gate is changed by the pH value of the electrolytic solution. The surface potential voltage (ψ_0) between the sensing layer and the solution can be expressed as [27]

$$2.303\left(pH_{pzc} - pH\right) = \frac{q\psi_0}{kT} + \sinh^{-1}\left(\frac{q\psi_0}{kT} \cdot \frac{1}{\beta}\right), \qquad (1)$$

where pH_{pzc} is the pH value at the point of zero charge, q is the electron charge, k is the Boltzmann constant, T is the absolute temperature, and β is the sensitivity parameter. The relation between β and the number of surface sites per unit area (N_S) can be given as [27]

$$\beta = \frac{2q^2 N_S (K_a K_b)^{1/2}}{kTC_{DL}}, \qquad (2)$$

where K_a and K_b are the acidic and basic equilibrium constants, respectively, and C_{DL} is the capacitance of the electrical double layer, as derived from the Gouy–Chapman–Stern model [28]. With a larger sensitivity parameter, a better linear response between the surface potential voltage and the pH could be derived from Eq. (1). In this work, CZTSe is an amphoteric material that can interact with either an acidic or a basic solution. In the solution, the surface of hydrous CZTSe would be protonated or deprotonated. The pH is dependent on the surface reaction between the H^{+} ions and CZTSe. The H^{+} ions of the surface charge are attributable to the production of OH^{-} or H^{+} ions through the protonation or deprotonation of CZTSe.

4. CONCLUSIONS

In this study, we have reported for the first time the synthesis of monodisperse CZTSe nanocrystals in solution through a thermal decomposition method. The CZTSe nanocrystals were prepared by using cheap and simple precursors of Cu, Zn, Sn, and Se powders in IPDA at a relatively low temperature of 235 °C. The CZTSe nanoparticle EGFET pH sensor is simple, low-cost, and convenient in terms of both its fabrication and application. According to our measured results, I_{DS} and V_{REF} have a certain relationship with the pH value, and the EGFET pH sensor with CZTSe nanoparticles exhibits a good sensing performance. The experimental results indicated that this nanoparticle sensor is a useful and successful device. Therefore, CZTSe nanoparticle sensors can indeed demonstrate a good performance for application in pH sensing.

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