Fabrication of Self-powered Heterostructure MoS_2/Cu_2O Photoelectrochemical Biosensor

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Abstract--**Abstract- In this study, chemical vapor deposition (CVD) was used to grow the MoS2 thin films, and electrochemical deposition was used to grow the Cu2O thin films. We applied mechanical grinding to polishing the surface of the grown Cu2O and made the first treatment of the grown MoS2. Then we transferred MoS2 to Cu2O which had been polished to complete our heterostructure. The analysis of the transmission electron microscopy (TEM) is used to observe the crystal structure of the MoS2 flakes. By observing periodicity diffraction points from the corresponding selected area diffraction pattern (SAD) on Cu2O thin film indicates the monocrystalline with our grown sample. In addition, the measurements of Raman spectroscopy, Multiphoton excitation microscope, Atomic force microscope (AFM) and Photoluminescence (PL), we will able to confirm the monolayer structure of the MoS2 flakes. After preliminary processing of the grown MoS2 flakes, the sample transfer to a Cu2O thin film to complete the p-n heterojunction structure. We analyzed the luminous energygap of the p-n heterojunction structure by using the measurements of Scanning electron microscope (SEM), Second-harmonic generation (SHG), and Raman mapping. It showed that Cu2O thin film prepared by the deposition environment pH value 12 had a highly regular crystallinity and its crystal lattice is complete, while MoS2 is a single-layer structure. Subsequently, we measured the biosensor through the UV-Visible spectrometer and the micro-current meter. Through the steps of the above process, we successfully manufactured a photoelectrochemical biosensor. We used it for photo-response measurement of two cancer cells with different stages of cancerization. Then we obtained the photo-response characteristics and the working wavelength range of our biosensor. In this cancer cell measurement experiments, the characteristic response of biochips to cancer cells and the different cancerous staging characteristics were verified.**

keywords—**Photoelectrochemical; Chemical Vapor Deposition (CVD); MoS_2; Cu_2O**

Introduction

In recent years, two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs), including MX_2 (M = Mo, W; X = S, Se), have attracted a great deal of attention because of their unique structure as well as remarkable physical and chemical properties. Molybdenum disulfide (MoS_2), a typical TMDC with a direct band gap of 1.8 eV for the monolayer and a layer number dependent band structure, has been used to tackle the zero-bandgap problem of graphene. Mechanical exfoliation is widely used in fundamental research because of the possibility to fabricate high quality 2D materials. Bulk MoS_2 is an indirect band gap semiconductor with a band gap of 1.3 eV. The chemical vapor deposition (CVD) method is one of the most practical methods to prepare 2D materials, including graphene, boron nitride (BN), and MoS_2-like TMDCs.

The Cu_2O layers are prepared by several techniques such as the sputtering technique, the thermal oxidation of a metallic Cu sheet, anodic oxidation, photochemical deposition and electrodeposition in an aqueous solution containing copper sulfate hydrate and lactic acid. Cu_2O has a small band gap of ~2.0 eV and suitable conduction band, which gives it efficient visible light absorption. Furthermore, copper is naturally abundant, which makes for possible large-scale fabrication of p-tpye Cu_2O photoelectrodes, offering potential competitiveness over other semiconductors. The p-n heterogeneous structure was prone to photoelectrochemical reactions and self-powered.

Method

The results presented in this paper were reproduced more than five times, and the phenomenon of the domain shape change in the same place on the chip along the flow direction always existed. We used CVD to grow MoS_2 with one furnace to control the temperature of MoO_3 and S separately, and a ceramic boat to create a wider change in MoO_3 concentration on the substrates. Growth substrates were Si with a 300 nm layer of SiO_2. Substrates were cleaned in acetone for 10 min and then isopropyl alcohol for 10 min, followed by DI-water for 10 min. After being cleaned, four substrates were tightly aligned and placed face down above a ceramic boat containing 10 mg of molybdenum(VI) oxide (MoO_3) powder (10um 99.95%, Gredmann). Quartz tube together with another boat containing 1 g of sulfur powder (≥99.98%, Gredmann). They were then put into furnace (furnace having MoO_3 and S is in far away). The CVD growth occurred at atmospheric pressure while ultra-high-purity argon was flowing. The CVD system was 100 sccm of Ar gas for 1.25 h when the temperatures was on 700℃, held at the setting temperature for 45 min.

The Cu_2O film was formed by electrochemical deposition. The electrolyte was made of 0.4M $CuSO_4$ and 85% lactic acid. pH was regulated by adjusting the concentration of NaOH. Three electrolytes with different pH were used to determine the photo-chemical response of the biosensor chip.

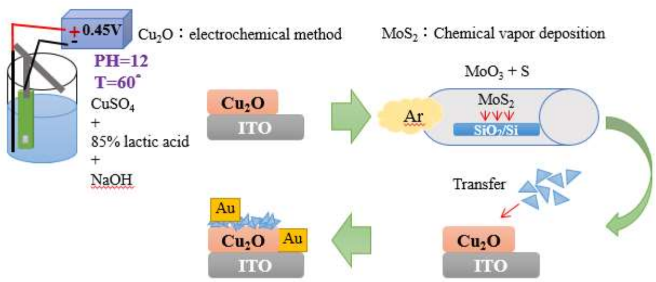

Fig. 1. Fabrication of Monolayer n-type MoS_2 grown by Chemical vapor deposition on p-type Cu_2O Photoelectrochemical.

Results and discussions

The SEM images of the p-Cu_2O with mechanical smooth is show in Fig.2. The SEM images of the p-Cu_2O with mechanical smooth is show in Fig.2. Measurements indicate that the Cu_2O thin films are mchanical panarization about 2 μm and that the Cu_2O film thickness for AFM image Z range is 94.623nm and rms is 3.849nm show in Fig.3. The microstructure and properties of the MoS_2 crystals were measured by SEM, Raman spectra, AFM, and PL spectra, confirming that the MoS_2 film was a uniform, single layer with high crystallinity. In addition, the effects of MoO_3 precursor temperature and Ar gas flow rate on MoS_2 crystal shape were also investigated. Two characteristic Raman vibration modes can be seen in the spectra in Fig.4 the $E^1{}_2g$ mode representing the in-plane vibration of molybdenum and sulfur atoms and the A_1g mode related to the out-of-plane vibration of sulfur atoms. The fitting results show that these two modes are located at 384.7 and 405.0 cm^{-1} , respectively, giving a frequency difference Δk of 20.4 cm^{-1} . Most of the domain has a Δk of <20 cm^{-1}, confirming a homogeneous monolayer. Fig.5a shows the typical PL spectra from a synthesized MoS_2 domain. A strong PL signal is located at 675 nm. Panels b of Fig.4 show corresponding PL intensity maps for a large triangular MoS_2 domain.

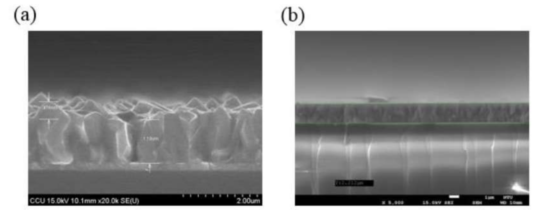

Fig. 2. SEM images of the p-Cu_2O/ITO, Mechanical smooth SEM of Cu_2O.

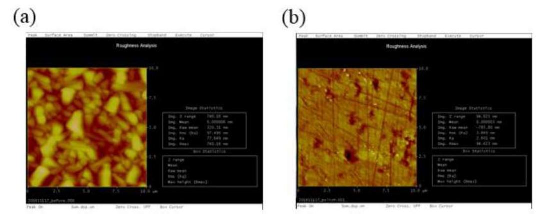

Fig. 3. AFM image for Cu_2O mechanical smooth, the Z range is about 94.623nm and the rms is 3.849nm.

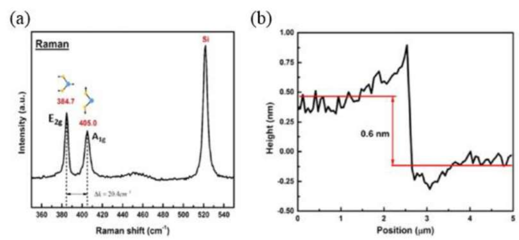

Fig. 4. (a) Raman spectrum of the MoS_2 domain, plotting the spatial variation of the magnitude of the frequency difference between A_1g and $E^1{}_2g$. (b) The height profile of AFM image for MoS_2 domains.[1]

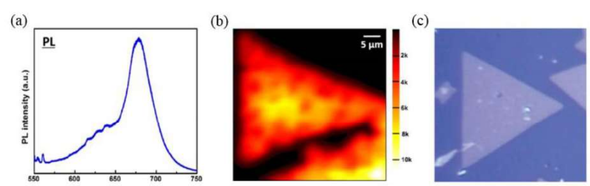

Fig. 5. (a) Photoluminescence (PL) spectrum of a synthesized MoS_2 domains. (b) 2D image of the PL intensity of triangular MoS_2 domains. The excitation wavelength is 532 nm. (c) The image of the optical microscope of monolayer MoS_2. [1]

Conclusion

The Cu_2O could be combined with certain ntype semiconductors of the more positive conduction bands such as MoS_2, ZnO, rGO, etc., forming the n–p junction to allow the efficient transport of photogenerated electrons from Cu_2O to the n-type semiconductor conduction band that results in the improved photostability of Cu_2O. After MoS_2 grown on 300 nm SiO_2/Si substrate by CVD process, the MoS_2 flakes were transferred to Cu_2O thin film to finish the p-n heterogeneous structure. The p-n heterogeneous structure was prone to photoelectrochemical reactions and self-powered. We researched electrical properties variety and characteristic of photovoltaic without requiring an extra bias voltage. We hope the different biosensor of cancer level cells can be applied in the future.

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