

A Super-Nernstian pH Sensor using WO₃ Nanosheets Sensing Electrode

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Abstract

The effect of surface morphology of chemically synthesized WO₃ nanosheets (NSs) on pH sensing electrode is presented. Using a separated electrode (SE) of extended-gate field-effect transistor (SE-EGFET) configuration, WO₃ NSs pH sensor with a typical sensitivity of 63.60 mV/pH and good linearity (0.9970) is demonstrated for the first time. The super-Nernstian response is attributed to the high surface-to-volume (SV) ratio and dense sites at surfaces and intersections of WO₃ NSs in enhancing ion adsorption during pH sensing.

1. Introduction

Hydrogen ion concentration (pH) sensing devices play important roles in environmental, biological, and chemical detections.[1] For the past decades, configurations used for pH sensing has been evolved from Ion sensitive field-effect transistor (ISFET) type to extended-gate field-effect transistor (EGFET) type and then to a modified EGFET type with the sensing electrode serving as a separated extended gate.[1] The last one (short for SE-EGFET) has been widely used for bio and pH measurement,[2] which has the merits of low cost and easy use for having interchangeable sensing electrode.

In recent years, semiconducting metal oxides, such as ZnO, IGZO, AZO, ITO, etc. have been employed as pH sensing materials, because there can be easily miniaturized as solid-contact electrodes, less sensitive to interferences, higher mechanical strength, low cost, and high thermal stability.[3] Nevertheless, pH sensors based on these metal oxides usually show a low pH sensitivity and unstable in strong acid and alkali solutions.[4] Recently, pH sensing based on titanium dioxide (TiO₂) nanowire arrays and porous silicon (P-Si) with SE-EGFET configuration breaking through the super-Nernstian limitation with a pH sensitivity as high as 62 mV/pH and 66 mV/pH were reported.[4,5] The superior sensitivity is ascribed to a high surface area-to-volume (SV) ratio of the sensing element, which significantly enhances adsorption ion area to increase the potential voltage variation of the sensing electrode during pH sensing.[6]

Tungsten oxide (WO_x) based materials has been demonstrated for sensing applications owing to the advantages of controllable nanostructures, low cost, low processing temperature, and high chemical sensitivity.[7] In this work, chemical synthesis of WO₃ nanosheets (NSs) and their applications to SE-EGFET pH sensors is presented. WO₃-pH sensors with a pH sensitivity as high as 63.60 mV/pH and a good linearity (0.9970) are demonstrated. Effect of surface morphology on the pH sensitivity is studied. Influence of the surface-to-volume (SV) ratio in enhancing ions adsorption on the pH sensitivity are elucidated and discussed.

2. Experimental

The key fabrication processes for the preparation of nanosheet (NS)-like WO₃ are shown in Fig. 1. First, a tungsten foil (99.95%) was cleaned in a sonicating bath of acetone and isopropanol for 10 minutes and rinsed in deionized water for 10 minutes as shown in Fig 1(a). The tungsten foil was undergone a chemical bath with 1.0 M HNO₃ solution for 0.5 hour (h) at 90°C and followed by annealing at 300°C in air for 0.5 h [Fig. 1(b)]. Analogous to the dissolution-recrystallization growth mechanism,[8] a layer of tungstite (WO₃ · H₂O) was formed as tungsten was immersed in nitric acid.[9] It was then transformed into WO₃ NSs after thermal annealing. Figure 1(c) illustrates the package of the sensing electrode having a wire connection using silver (Ag) paste. Note that the size of the sensing area is 0.5 × 0.5 cm².

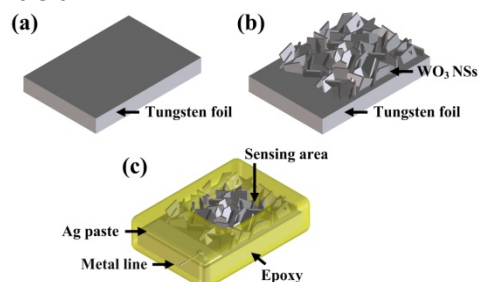


Fig. 1. The key fabrication processes of WO₃ NSs. (a) Tungsten foil, (b) synthesis of WO₃ NSs, and (c) wire connection and package.

Figure 2 shows the set-up for current-voltage (*I* – *V*) measurements of pH sensors with an SE-EGFET configuration. A Keithley 2636A and the n-MOSFET (CD4007UB) were used. The reference electrode (Ag/AgCl) and the sensing electrode were kept at a fixed distance of 2 cm. Both of them were immersed into a buffer solution (pH 2-12) at room temperature during pH sensing measurements. Results of the measured sensitivity and stability of the prepared pH sensors were presented and discussed.

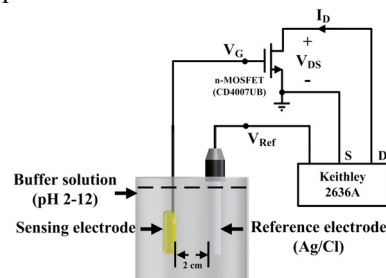


Fig. 2. Set-up of the *I*-*V* measurement of pH sensors.

3. Results and Discussion

The top-view SEM images of prepared samples are shown in Fig. 3. A tungsten foil shows a flat surface as shown in Fig. 3(a), while WO₃ NSs are with NS-like surface

on which NS are with a typical length and thickness ranging from 0.5-1 μm and 20-60 nm [Figs. 3(b) and (c)], respectively.

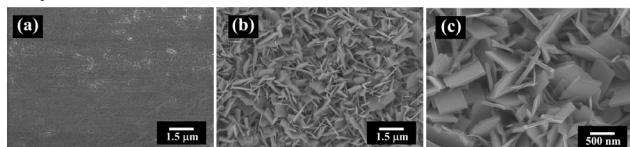


Fig. 3. The top-view SEM images of the prepared the samples. (a) Tungsten foil, (b) WO_3 NSs, and (c) high magnification of WO_3 NSs.

Figure 4 shows the XRD patterns (not drawn to scale) obtain from the prepared sample and the TEM images of a discrete NSs obtained. As revealed by XRD pattern, the strong diffraction peaks are indexed to be (002), (020) and (200) planes, the nanostructured layer could be classified as a monoclinic phase of WO_3 (PDF No. 43-1035). Figure 4(b) shows TEM and HRTEM images of a single NS and the corresponding SAED pattern. Clear strips of the lattice plane extending over the whole wire region were observed. Lattice-resolved fringes of 0.384 and 0.376 nm are evaluated from the HRTEM image, corresponding to the (002) and (020) planes of a monoclinic WO_3 structure. The corresponding SAED pattern also confirms that the NS is a single crystalline of WO_3 with [002] phase.

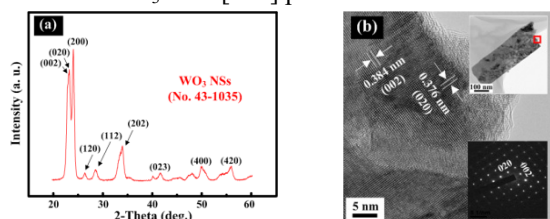


Fig. 4. (a) XRD analysis of the prepared sample. (b) TEM, HRTEM and SAED pattern of a discrete WO_3 NS.

Figure 5 shows the measured $I_D - V_{\text{Ref}}$ and $\Delta V_s - \text{pH}$ characteristics of WO_3 NSs in solutions with a pH level in the range of 2-12. As shown in Fig. 5(a), it is seen that the transfer curves shift toward the positive V_{Ref} - axis as pH level was increased because the decrease in H^+ (or the increase in OH^-) reduced the potential voltage of the sensing electrode. The voltage shift in the transfer curves of the EGFET at different pH levels is attributed to potential drop (ΔV_s) at dipole layer formed between the electrolyte interface and the WO_3 NSs sensing layer. Figure 5(b) shows the measured $\Delta V_s (= V_G - V_{\text{Ref}})$ as a function of pH level in the range of 2 to 12. It reveals that the adsorption of H^+ (or OH^-) results in a positive (or negative) ΔV_s which exhibits a linear relationship with the pH level. Note that the slope of the $\Delta V_s - \text{pH}$ curve reveals the sensitivity the WO_3 NSs pH sensor.

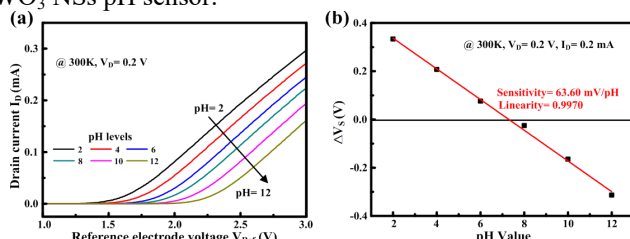


Fig. 5. The measured performance of the prepared pH sensing

electrode with (a) $I_D - V_{\text{Ref}}$ and (b) $\Delta V_s - \text{pH}$ characteristics.

The pH sensitivity of the prepared sample can be also evaluated from $V_{\text{Ref}} - \text{pH}$ ($@I_D = 0.2 \text{ mA}$) curves shown in Fig. 6(a). Note that a super-Nernstian response of the WO_3 NSs sensing electrode as high as 63.60 mV/pH and good linearity (0.9970) are obtained. Though the exact sensing mechanism governing the super-Nernst sensitivity is still under investigation, it could be due to WO_3 NSs offering a high SV ratio and dense sites at both the surfaces and intersections of WO_3 NSs to enhanced ion adsorption during pH sensing.

Figure 6(b) shows the results of stability test of the prepared WO_3 NSs pH sensor for a pH loop of 2 \rightarrow 12 \rightarrow 2 at $V_{\text{Ref}} = 3 \text{ V}$ and $V_D = 0.2 \text{ V}$. Note that each cyclic step has the same duration of 100 seconds (s). It reveals that the prepared WO_3 NSs pH sensor has repeatable sensing responses and stable operations in pH level in the range (2-12).

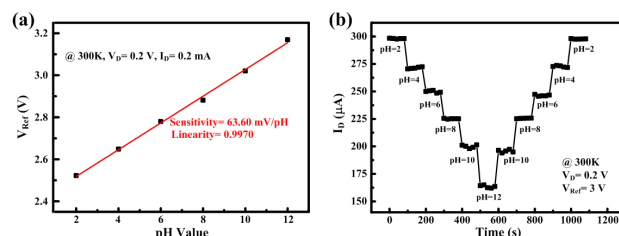


Fig. 6. (a) The measured $V_{\text{Ref}} - \text{pH}$ characteristics of the prepared pH sensor. (b) Stability test of the sensing responses of drain current (pH loop: 2 \rightarrow 12 \rightarrow 2).

4. Conclusions

The superior sensing performance of chemically synthesized of NSs-like WO_3 sensing electrode using SE-EGFET configuration has been demonstrated. WO_3 -pH sensors with a super-Nernstian response of 63.60 mV/pH, a good linearity of 0.9970 and superior reliability in 2-12 buffer solution levels are obtained, which is attributed to the WO_3 NSs sensing electrode offering a high SV ratio and dense sites at both the surface and intersections of WO_3 NSs to significantly enhance ion adsorption during pH sensing. It is expected that the pH sensor based on WO_3 NSs could be an effective for future pH sensing applications.

Acknowledgments

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References

- [1] Y. Qin et al., RSC Adv., **5**, (2015) 69086.
- [2] P. C. Yao et al., Solid State Sci., **28**, (2014) 47.
- [3] B. Eric, Advances in Potentiometry, Electroanalytical Chemistry, CRC Press, **1**, (2011)
- [4] S. J. Wang et al., Jpn. J. Appl. Phys., **53**, (2014) 06JG02.
- [5] N. H. Al-Hardan et al., Sensors, **16**(6), (2016) 839.
- [6] J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases, **70**, (1974) 1807.
- [7] L. Santos et al., ACS Appl. Mater. Interfaces, **6**, (2014) 12226.
- [8] R. B. Kale, Optik, **126**, (2015) 1109
- [9] E. Widenkvist et al., Cryst. Growth Des., **8**, (2008) 3750.