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# UV Enhanced $NO_2$ Sensor at Room Temperature Based on ZnO Nanosphere and Urchin-like array

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**Abstract:**
As a widely employed semiconductor, zinc oxide (ZnO) was regarded as a promising candidate material for $NO_2$ detection. Furthermore, ultraviolet (UV) irradiation was found to be an efficient method to enhance sensing-properties of ZnOfor its intrinsic wide band gap. In this work, novel ZnO thin films withhollow nanosphere (HNS)and urchin-like (UL)array were designed and utilized for $NO_2$ sensing at room temperature.The morphological and spectroscopy properties of films were analyzed via scanning electronic microscopy (SEM), X-ray diffraction (XRD) and ultraviolet-visible spectroscopy (UV-vis).And $NO_2$-sensing properties of as-fabricated sensors were investigated with and without UV irradiation.After exposing to UV light, both HNS and UL film ZnO sensor achieved a tremendous enhancement in sensing performances. Moreover, ZnO sensor with ULarray showed superior performance with higher response and shorter response time compared with HNS ZnO. In addition, low detection limit (26 ppb) and good repeatability were also obtainedforUL film ZnO sensor. At last, the enhancement mechanism of different structuredZnO sensor was discussed.

**Key words:**$NO_2$sensor,ultraviolet enhancement, ZnO hollow nanosphere, Urchin-like ZnO

### Introduction

Nitrogen dioxide ($NO_2$) detection is one of the major projects in air quality monitoring. Many industrial circlesrequire high performance $NO_2$ sensor with great sensitivity, low detection limitation and rapid response [1].Up to now, various types of $NO_2$sensors have been investigated.Among them, resistance-type sensors were preferred for its simple structure and broad application potential. Base on this, a large amount of semiconductor namomaterials was utilized in gas sensors. Among them, ZnO was selected as a promising material because of its especial band gap and facile preparation process. Meanwhile, the sensing-characteristics of ZnO could be enhanced by UV light excitation. In this research, ZnO with novel hollow nanosphere (HNS) and urchin-like (UL)array structures were fabricated for $NO_2$detection at room temperature.The morphological, spectroscopy and $NO_2$-sensing properties were investigated. Moreover, the sensing mechanism was also discussed.

### Experimental details

The fabrication approach of ZnO HNS and UL array structure was schematized in Fig. 1. As reported in the previous work [2], a monolayer polystyrene (PS) sphere was prepared onto silicon substrate as templates. The diameter of PS sphere was reduced and controlled by $O_2$ plasma etching. Then, the ZnO layer was deposited on the surface of PS sphere by radio frequency magnetron sputteringfollowed by an annealing process at 500℃for 30 min in $N_2$to remove the inner PS template. After these, the HNS structure was formed. Moreover, the UL structure was fabricated based on processesabove followed by a hydrothermal procedure as follow. Zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$] and methenamine [$C_6H_{12}N_4$] with both the concentrations of 0.02M were mixed by magnetic stirring at 60℃ for 2h. After thorough mixing, ZnO HNS substrate was placed into as-prepared solution with constant temperature at 90℃for 3h by using water bath. Finally, the sample was rinsed and dried by water and nitrogen flow.

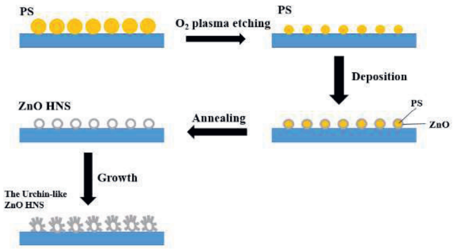


*Fig. 1. Schematic of processes to fabricateZnO HNS and UL array structures*

### Results and discussion

Thesurface morphology of ZnO film wascharacterized through SEM as shown in Fig. 2. It could be seen thata monolayer of ZnO HNS and ULarray structure is distributing on substrate. Thediameter of both ZnO HNS and UL is about 330 nm. A sphere structure with granular protuberance surface was formed for HNS due to the annealing procedure. Correspondingly, UL ZnO exhibited a sphere structure with nanorods on its surface (like urchin as shown in the inset). The specific surface area of UL structure was twice larger than that of HNS one based on BET results. The XRD and UV-Vis spectra were also measured, which indicate that ZnO nanorods were successfully synthesized and the wave length of excitation source could be chosen as 365 nm.

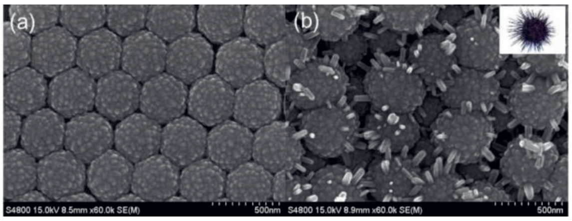


*Fig.2. SEM images of (a) HNS and(b)UL ZnO*

The sensing performances of sensors were testedtowardsvarious concentration of $NO_2$with different type of ZnO at room temperature under or without UV exposure. The result is depicted in Fig. 3. Sensors showedexcellent performance with negligible baseline drift towards different $NO_2$ under UV illumination, whereas they almost showed no response without UV. A larger response values (23% to 143%) and reduced response/recovery time (54~124 s) for UL structure ZnO sensor were obtained compared with HNS sensor (11% to 106%, 112~193 s), respectively, indicating that UL film ZnO sensor owned comprehensively superior sensing properties. Besides, the UL ZnO sensor possessed a good repeatability and low detection limit of $NO_2$ (20% @ 26 ppb).

The sensing mechanism of UL structure ZnO is diagramed in Fig. 4. Carrierswhich are excited by UV could enhance both the conductivity and the reactivity of ZnO. $NO_2$ would trap the photo-generated electrons on the surface of ZnO and then become $NO_2^-$. Besides, the resistance would increase owing to the reduction of carriers. Furthermore, more adsorption sites would be provided by UL structure attributed to its high specific surface area.

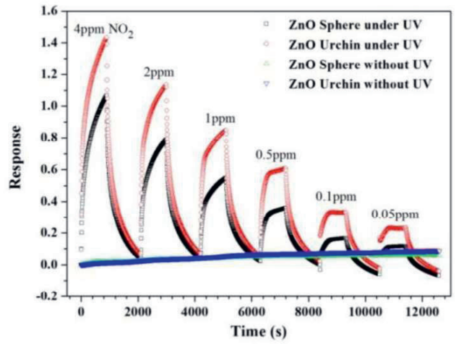


*Fig. 3. Dynamic response of HNS and UL ZnO sensor in different $NO_2$ concentration at room temperature*

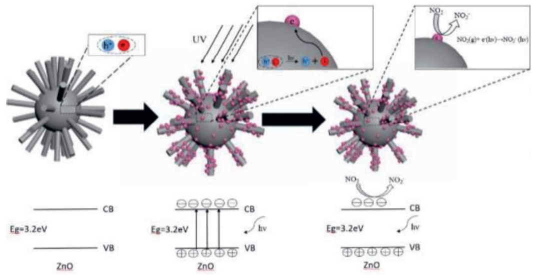


*Fig.4.Schematic diagram of the sensing mechanism*

## 4. Conclusion

ZnOfilms with novel HNSand ULstructureswere synthesized and utilized in $NO_2$ sensing at room temperature. Under UV illumination, both HNS and UL ZnO sensors obtained a significant enhancement than without UV. UL ZnO sensor exhibited comprehensively superior sensing performances with high sensitivity, short response time, good repeatability and low detection limit. This work provides a feasible strategy for $NO_2$ sensing.

### Reference

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