GQDs-TiO₂ Heterojunction Based Thin Films for **Volatile Organic Compounds** sensor with Excellent Performance at Room Temperature

Shaofeng Shao,^{*a} Wei Wang,^a Kai Zhou,^a Fan Jiang,^a Hongyan Wu,^a and Ralf Koehn^b

^a School of Physics and Optoelectronic Engineering, Nanjing University of Information Science & Technology, Nanjing, China.

^b LMU, Chemistry and Biochemistry, Butenandtstr. 5-13, Munich, Germany.

*Corresponding: ssfshao@nuist.edu.cn.

Crystalline nanoporous GQDs-TiO₂ thin films are synthesized under a 120 °C water vapour hydrothermal treatment, and water soluble GQDs are successfully loaded in the thin film in optimum density to form novel GQDs-TiO₂ heterojunctions. The optimum sensing performance is achieved at GQDs content of 1.6 wt%, with the isopropanol response value up to 13.8 at 50 ppm and a short response time of ~ 18 s at room temperature. In general the synthesis procedure described in this work has the advantage of being easy, cost efficient, and highly suitable for the fabrication of gas sensor with the application for monitoring specific harmful and toxic volatile organic compounds (VOCs) in early diagnosis of cancer.

Key words: graphene quantum dots; TiO₂; Sensors; VOCs; Thin films

Introduction

Early diagnosis of cancer is significant for applying effective treatment to improve the survival rates of patients. [1] To achieve these goals, the chemiresistors have obtained considerable attention because it is a cost-effective, power-efficient, and highly sensitive VOCs detection tool.[2] However, in breath analysis research, developing a low cost and facial VOCs gas sensor that possesses high sensitivity to low concentration of VOCs at room temperature still remains a challenge.

Recently, TiO₂ decorated with nanoscale carbon materials have attracted much attention.[3, 4] Combining the advantages of the graphene nature and quantum dots, GQDs have been recognized as an emerging nanomaterial and applied in numerous areas, such as bio-imaging, sensors and optoelectronic devices.[5-7] Long *et al.* performed theory calculations to characterize the interfacial electronic structure and carrier transfer between GQDs and TiO₂ interface.[8, 9] The conjugated π structure of GQDs in the sensing materials would play an important role for their improved sensing performance, such as facilitating the adsorption of VOCs.[10] The strong chemical interaction between the GQDs and TiO₂ nanoparticles should make sensing materials

more stable and the charge transfer between them more efficient, leading to high sensitivity, and quick response time. Nevertheless, developing ordered nanoporous GQDs-TiO₂ sensing films for efficient sensing performance at room temperature is still rare.

In this work, we developed a flexible, sensitive, and rapid VOCs gas sensor based on ordered nanoporous GQDs-TiO₂ thin film. The GQDs-TiO₂ sensing film was synthesized in situ on the sensing device with the water vapor hydrothermal treatment. Compared with the pristine TiO₂ thin film, the GQDs-TiO₂ thin film obtained higher ordered nanostructure, smaller grain size, and larger surface area, making them promising candidates for preparing highly sensitive gas sensors. The effective synthetic procedure opens an efficient pathway to develop highly sensitive and low cost gas sensor for early diagnosis of cancer.

Experimental Section

The Ti precursor solutions were prepared by dissolving 1.0 g TiCl₄ in 0.3 mol ethanol in the presence of 4×10^{-5} mol F127 polymer ([HO(CH₂CH₂O)₁₀₆-(CH₂CH(CH₃)O)₇₀-(CH₂CH₂O)₁₀₆H, EO₁₀₆PO₇₀EO₁₀₆], Sigma). 0.8 ml 12 M HCl dropped in 8ml GQDs solution (2 mg/ml), then mixed with the above solution under constant stirring for overnight. Sensing films were prepared by spin-coating 40 μ l of the GQDs-Ti precursor solution onto one sensor device at 4000 rpm for 60 s under 20% relative humidity, and then dried at 60°C for 2 h. The films exposed to a water vapor hydrothermal treatment, 90% relative humidity, at 120°C for 96 h. The films were then heat treated by annealing at temperature of 250 °C for 2 h with an up ramp rate of 1.0°C/min, and further treated at 300 °C under nitrogen atmosphere for 1 h.

Results and Discussion

The WAXRD pattern (Fig. 1a) of GQDs-TiO₂ thin film exhibits five discrete *hkl* reflection at 25.2°, 37.8°, 48.1°, 53.9° and 55.1°, respectively, corresponding to the crystallographic planes of anatase TiO₂. However, no diffraction peak can be attributed to GQDs in the WAXRD patterns. The grain size is 3.5 nm for the GQDs-TiO₂ thin film, and 6.2 nm for the pristine TiO₂ thin film. The Raman spectrum of scratched pristine TiO₂ thin films (Fig. 1b), four strong peaks correspond to the E_{g(1)}, B_{1g(1)}, A_{1g}+B_{1g(2)}, and E_{g(3)} modes of anatase TiO₂, respectively. In the case of the scratched GQDs-TiO₂ thin films, besides four TiO₂ peaks, two additional peaks of the GQDs are observed at 1581 and 1375 cm⁻¹, corresponding to the G and D bands of GQDs. As shown in Fig.

1c, all TiO₂ samples give typical IV isotherms, typical for the nanopore shape.[11] The average pore size of scratched GQDs-TiO₂ films with one large hysteresis loop (P/P₀=0.4-1.0) is 5.4 nm. For pristine TiO₂, the average pore size is 13.5 nm with poor nanopore distribution. The specific surface areas of pristine and GQDs-TiO₂ scratched films are 62.4, and 167.3 m² g⁻¹, respectively. The TEM image in Fig. 2a shows that the nanopore arrays are packed in an ordered arrangement with a repeating distance. The inset image shows the magnification of selected regions, where the regular arrangements of ordered channels are attributable to the hexagonal ordered arrangement of nanopores. The presence of the GQDs in the thin film is further confirmed by the HRTEM image, as displayed in the Fig. 2b, this real-space image shows that the GQDs consist of almost defect-free graphene. Moreover, an obvious crystal structure is observed, with an interplanar spacing of 0.21 nm corresponding to that of graphene (100) planes. Cross-sectional HRSEM image shown in Fig. 2c reveals that the GQDs-TiO₂ thin film has a network of uniform nanopores. From the inset cross-sectional TEM image, one can see the presence of many interconnected nanoparticles with long-range nanoporous periodicity. The STEM image shown in Fig. 2d, gives more details about the dispersion of GQDs inside the nanoporous titania thin film. It shows that there are many bright spots with diameter size about 5 nm in thin film, which are detected as GQDs. An EDX line measurement obtained from on area in Fig. 2d depicts the presence of carbon and titanium in the crystalline nanopore wall. From the above TEM/STEM images of the GQDs-TiO₂ thin film, the GQDs are well dispersed throughout ordered nanoporous TiO₂ thin films with a firm and close contact to form GQD-TiO₂ heterojunctions.

The response curves of GQDs-TiO₂ based gas sensor measured under various vapor concentrations ranging from 2 to 500 ppm are shown in Fig. 3a. The tests switch from low to high concentration, and then converse. GQDs-TiO₂ sensing film exhibits the best isopropanol-sensing performance, with high response to isopropanol concentrations ranging from 2 to 500 ppm. Moreover, the GQDs-TiO₂ sensor also exhibits a response to acetone, methanol, ethanol, butanol, and toluene vapours, as shown in Fig. 3b. The 50 ppm isopropanol response (13.8) becomes more than 2 times as high as that of acetone. Thus, the GQDs-TiO₂ sensor exhibits not only high response but also high isopropanol selectivity against ethanol and other gases at low concentration. The response curve exhibits excellent reproducibility with a slight fluctuation, *i. e.* the sensors also show excellent stability, as shown in Fig. 3c. The response time defined as the time necessary to

reach 90 % of the maximum response is about 18 s, and the recovery time is about 11 s. For comparative study, the response of the pristine TiO₂ films was not obvious (not shown for brevity). The GQDs-TiO₂ sensor shows high sensitivity and excellent selectivity to the isopropanol gas, suggesting that the GQDs play an important role in the room temperature gas sensing properties. As shown in Fig 3d, we determine that GQDs can be well dispersed within the TiO₂ thin films, and thus the optimum GQD-TiO₂ heterojunctions at the nanoscale can be established at the low decorating level. The presence of GQDs in the films can effectively inhibit the electron-hole pair recombination due to the planar π -conjugation structure, and form more stable thick space-charge layer and high potential barrier.[12] GQDs may create a Schottky contact at the interface between GQDs (~0.8 eV) and TiO₂ (3.2 eV) nanoparticles, the synergistic effect of TiO₂ nanoparticles and GQDs occurs, the interface of GQDs/TiO₂ nanopartilces belongs to a forward-biased Schottky barrier, which can contribute to more easy capture or migration of the electrons.[13] Esfandiari *et al.* reported that the addition of graphene based materials led to high rate and amount of electronic sensitizations with faster responses and more sensitivity in a wide range of target gases concentrations at low working temperatures.[14] Therefore, for the design of GQD-based gas sensors with excellent gas sensing performance, it is of crucial importance to construct nanoparticle heterojunctions that can effectively inhibit the high sensitivity to low concentration of isopropanol gas with quick response and recovery at room temperature.

Conclusions

An efficient and facile sensing system made of GQDs-TiO₂ heterojunction based ordered nanoporous thin films was used to detect VOCs vapours at room temperature. Especially for isopropanol vapour, the sensing materials exhibited highly sensitive, rapid, and reversible response. The GQDs-TiO₂ sensing films showed excellent sensitivity with the response value of 13.8 at 50 ppm. Moreover, the gas sensor had a fast response (ca. 18 s) and recovery (ca. 11 s) behaviour, excellent room temperature selectivity and stability. The GQDs-TiO₂ gas sensors have potential applications for monitoring specific harmful and toxic VOCs in early diagnosis of cancer.

Acknowledgments

The work supported by the Startup Foundation for Introducing Talent of NUIST, and NSF

(BK20160091).

References

- [1] M. Hakim, Y.Y. Broza, O. Barash, N. Peled, M. Phillips, A. Amann, H. Haick, *Chem. Rev.* 112 (2012) 5949-66.
- [2] J. Zhang, X. Liu, G. Neri, N. Pinna, *Adv. Mater.* 28 (2015) 795-831.
- [3] H. Sun, L. Wu, W. Wei, X. Qu, *Mater. Today* 16 (2013) 433-442.
- [4] Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou, L. Qu, *Adv. Mater.* 23 (2011) 776-80.
- [5] S. Zhu, L. Wang, B. Li, Y. Song, X. Zhao, G. Zhang, S. Zhang, S. Lu, J. Zhang, H. Wang, H. Sun, B. Yang, *Carbon* 77 (2014) 462-472.
- [6] S. Umrao, M.H. Jang, J.H. Oh, G. Kim, S. Sahoo, Y.H. Cho, A. Srivastva, I.K. Oh, *Carbon* 81 (2015) 514-524.
- [7] S. Zhu, J. Zhang, S. Tang, C. Qiao, L. Wang, H. Wang, X. Liu, B. Li, Y. Li, W. Yu, X. Wang, H. Sun, B. Yang, *Adv. Funct. Mater.* 22 (2012) 4732-4740.
- [8] J.N. Gavgani, A. Hasani, M. Nouri, M. Mahyari, A. Salehi, *Sens. Actuators, B* 229 (2016) 239-248.
- [9] J. Shen, Y. Zhu, X. Yang, C. Li, *Chem. Commun.* 48 (2012) 3686-99.
- [10] H. Yu, Y. Zhao, C. Zhou, L. Shang, Y. Peng, Y. Cao, L.-Z. Wu, C.-H. Tung, T. Zhang, *J. Mater. Chem. A* 2 (2014) 3344.
- [11] K. Sing, D. Everett, R. Haul, L. Moscou, R. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 57 (1985) 603.
- [12] D. Pan, J. Jiao, Z. Li, Y. Guo, C. Feng, Y. Liu, L. Wang, M. Wu, *ACS Sustainable Chem. Eng.* 3 (2015) 2405-2413.
- [13] Y. Dong, H. Pang, S. Ren, C. Chen, Y. Chi, T. Yu, *Carbon* 64 (2013) 245-251.
- [14] A. Esfandiari, S. Ghasemi, A. Irajizad, O. Akhavan, M.R. Gholami, *Int. J. Hydrogen Energy* 37 (2012) 15423-15432.

Fig. 1 (a) WAXRD patterns of GQDs-TiO₂ and TiO₂ thin film calcined at 300°C; (b) Raman spectrum of GQDs-TiO₂ and TiO₂ thin films; (c) N₂ adsorption/desorption isotherms for scratched GQDs-TiO₂ and TiO₂ thin films.

Fig. 2 (a) TEM image of GQDs-TiO₂ film. The inset shows the magnification of selected regions; (b) HRTEM image of the GQDs-TiO₂ film. The inset shows the magnification of selected region; (c) Cross-sectional SEM image of the GQDs-TiO₂ film. The inset shows the Cross-section TEM image of the selected region; (d) STEM image of the GQDs-TiO₂ film.

Fig. 3 (a) Response curves of GQDs-TiO₂ sensors measured under various gas concentrations; (b) Response curves of GQDs-TiO₂ sensor to 50 ppm VOCs. (c) Response and recovery curves of the sensor to isopropanol gas at 50 ppm. (d) Schematic illustration of the mechanism governing the isopropanol gas sensing in thin film.

Fig. 1

Fig. 2

Fig. 3