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Selective NO_2 Sensors Using MoS_2-MoO_2 Composite Yolk-shell Spheres

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Abstract

The gas sensing characteristic of MoS_2-MoO_2 composite yolk-shell spheres were investigated. MoO_3-carbon composite spheres were prepared by ultrasonic spray pyrolysis of aqueous droplets containing Mo-source and sucrose in nitrogen, which were converted into MoO_3 yolk-shell spheres by heat treatment at 400°C in air. Subsequently, MoS_2-MoO_2 composite yolk-shell spheres were prepared by the partial sulfidation of MoO_3. The MoS_2-MoO_2 composite yolk-shell spheres showed relatively low and irreversible gas sensing characteristics at < 200°C. In contrast, the sensor showed high and reversible response (S=resistance ratio) to 5 ppm NO_2 (S = 14.8) at 250°C with low cross-responses (S = 1.17-2.13) to other interference gases such as ethanol, CO, xylene, toluene, trimethylamine, NH_3, H_2, and HCHO. The MoS_2-MoO_2 composite yolk-shell spheres can be used as reliable sensors to detect NO_2 in a selective manner.

Keywords: Gas sensors, MoS_2 Yolk-shell Spheres, NO_2 Sensor, Selectivity

1. INTRODUCTION

Molybdenum disulfides (MoS_2) with 2-dimensional (2-D) layered nanostructures show distinctive electrical and electrochemical properties, which can be used for various applications such as Li-ion battery [1], field effect transistor [2], and gas sensors [3]. In particular, the MoS_2 nanostructures with high surface area to volume ratio and thinness are regarded as promising platform to design chemiresistors that can be operated at relatively low sensing temperature [3].

Various form of MoS_2 nanostructures were investigated as chemiresistive materials, which include chemically or mechanically exfoliated flakes [3,4], thick oriented film [5], and atomic layer prepared by chemical vapor deposition [6]. However, the researches of high performance gas sensors using MoS_2 nanostructures are still in the nascent stage.

Yolk-shell nanostructures, thin hollow spheres containing movable single or multiple yolks, are superior electrode materials for Li ion batteries on account of their high surface area, nanoarchitectures to buffer the structural strain, and short diffusion length of Li ion [7]. Moreover, the reforming of specific analyte gas within yolk-shell micro reactors can provide a new strategy to design selective and sensitive gas sensors [8-10].

In this contribution, MoS_2-MoO_2 composite yolk-shell spheres are prepared by the partial sulfidation of MoO_3 yolk-shell spheres and their gas sensing characteristics are investigated. Main focus of the study is directed at the selective and reversible detection of specific gas using MoS_2-MoO_2 composite yolk-shell spheres.

2. EXPERIMENTAL

2.1 Preparation of MoS_2-MoO_2 yolk-shell spheres

The MoO_3-carbon composite spheres were prepared by the ultrasonic spray pyrolysis of aqueous droplets containing 0.1 M of MoO_3 (Kanto Chemical Co., Inc., 99.5%), 0.1 M of sucrose (Sigma-Aldrich, 99.5%), and H_2O_2 (Sigma-Aldrich, 29.0-32.0%) at 900°C (carrier gas: nitrogen, flow rate: 10 L/min). The MoO_3-carbon composite spheres were converted into multiple-shelled MoO_3 yolk-shell spheres by heat treatment at 400°C. The oxidation of Mo-source and the partial combustion of carbon at

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the outer part, the contraction of inner MoO_3-carbon composite spheres, and repetition of these procedures leaded to the formation of MoO_3 yolk-shell spheres. The MoO_3 yolk-shell spheres were placed in crucible and converted into MoS_2-MoO_2 composite yolk-shell spheres by flowing H_2S (generated by flowing H_2/Ar to Thiourea) at 400°C for 6 h.

2.2 Gas sensing characteristics

The MoS_2-MoO_2 composite yolk-shell spheres were dispersed in ethanol and small amount of slurry was coated on the alumina substrate (1.5 mm × 15 mm × 0.25 mm) with two Au electrodes. The sensor was dried at room temperature for 2 h and heat treated at 250°C for 6 h to remove the residual water solvent in the sensing materials. A flow-through technique with a constant flow rate of 500 cm^3min^{-1} was used and a 4-way valve was used to switch the gas atmospheres. The responses of the sensors (R_g/R_a for NO_2 and R_a/R_g for other reducing gases: R_g: resistance in gas, R_a: resistance in air) were measured with varying sensor temperature using electrometer interfaced with a computer.

3. RESULTS AND DISCUSSIONS

3.1 Materials characterization

The X-ray diffraction pattern of powders by sulfidation of MoO_3 yolk-shell spheres through flowing H_2S at 400°C for 6 h

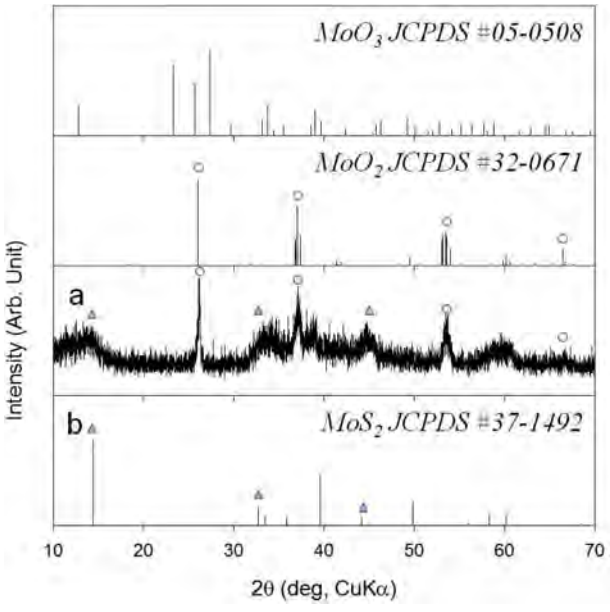

Fig. 1. X-ray diffraction pattern (XRD) of MoS_2-MoO_2 composite yolk-shell spheres.

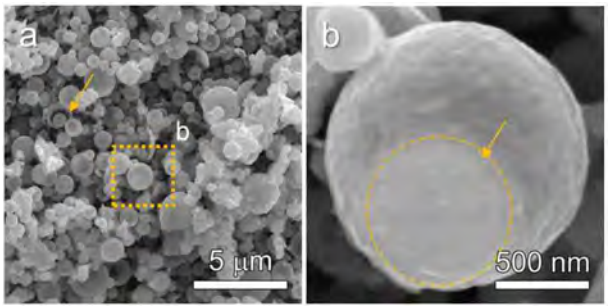

Fig. 2. Scanning electron microscopy (SEM) images of MoS_2-MoO_2 composite yolk-shell spheres.

was shown in Fig. 1. The powders were identified as the composite between MoS_2 (JCPDS #37-1492) and MoO_2 (JCPDS #32-0671). The reduction of Mo^{6+} into Mo^{4+} and the formation of MoS_2 phase were attributed to the partial sulfidation reaction. The MoS_2-MoO_2 composite powders showed the spherical morphology (Fig. 2a). The diameters of spheres ranged from 0.2 to 2.0 mm. The yolk-shell morphology was frequently observed in broken spheres (arrow in Fig. 2a), which was confirmed again by the different contour within a sphere in high magnification SEM image (Fig. 2b). It is known to convert MoO_3 phase into phase pure MoS_2 phase by heat treatment under H_2S atmosphere [11]. Thus, the co-existence of MoO_2 and MoS_2 in the present study can be attributed to the lower heat-treatment temperature and insufficient heat treatment time [12].

3.2 Gas sensing characteristics

The sensor using MoS_2-MoO_2 composite yolk-shell spheres showed the low response to analyte gases at <200°C. Moreover, the sensor resistance did not completely recover to original resistance in air after gas sensing reaction (not shown). Thus, it was difficult to measure the reliable gas sensing characteristics at <200°C. Accordingly, the gas sensing characteristics were measured at 200 and 250°C. Fig. 3 shows the sensing transients to 5 ppm NO_2, C_2H_5OH, CO, xylene, toluene, trimethylamine (TMA), NH_3, H_2, and HCHO at 250°C. The R_a value at 250°C was ~ 0.2 MΩ. It increased upon exposure to oxidizing gas such as NO_2, while it decreased upon exposure to all other reducing gases. This indicates that the MoS_2-MoO_2 composite yolk-shell spheres in the present study show n-type gas sensing behaviors. It is natural considering that MoS_2 and MoO_3 show the n-type gas sensing behaviors in the literature [3,13]. It should be noted that the sensor resistance was recovered completely upon exposure to air. The

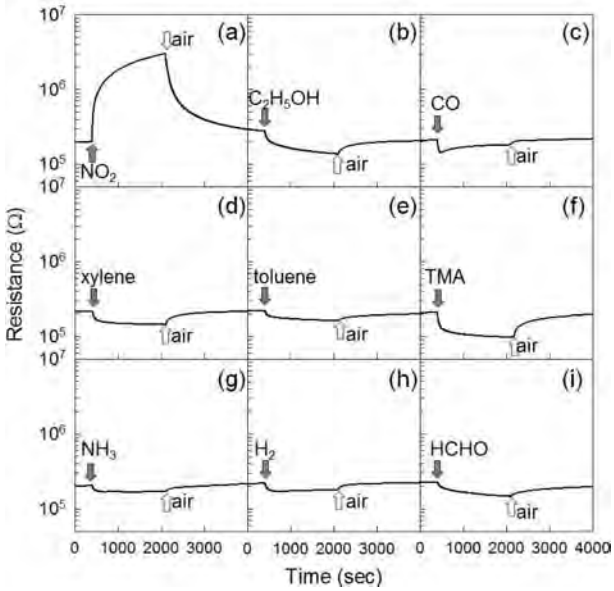

Fig. 3. Gas sensing transients to 5 ppm (a) NO_2, (b) C_2H_5OH, (c) CO, (d) *p*-xylene, (e) Toluene, (f) Trimethylamine, (g) NH_3, (h) H_2, and (i) HCHO of MoS_2-MoO_2 composite yolk-shell spheres at 250°C.

sensing transients at 200°C were also reversible. This says that the sensing temperature higher than 200°C is necessary to achieve reliable and reversible gas sensing characteristics in the sensor using MoS_2-MoO_2 composite yolk-shell spheres.

The gas responses at 200 and 250°C were summarized in Fig. 4. At both sensing temperatures, the variation of sensor resistance upon exposure to NO_2 is opposite to those upon exposure to reducing gases. Accordingly, in principle, NO_2 can be detected in a selective manner. However, when both NO_2 and reducing gases co-exist, the increase of sensor resistance by NO_2 can be nullified by the decrease of sensor resistance induced by other reducing gases. In particular, this problem becomes more significant when the cross-responses (R_a/R_g) to other interfering reducing gases are comparably high. In this perspective, the R_a/R_g values to reducing gases should be negligibly low to achieve selective NO_2 sensing. The response to 5 ppm NO_2 (R_g/R_a) at 200°C is 4.9, while those (R_a/R_g) to other 8 different analyte gases ranged from 1.04 to 2.66 (left in Fig. 4). In particular, high cross responses to CO (S=2.36), TMA (S=2.66), NH_3 (S=2.10), and H_2 (S=1.71) increase the possibility of sensor malfunction. In contrast, the response to 5 ppm NO_2 at 250°C (S=14.8) is significantly higher than those toward other 8 different reducing gases (S=1.17–2.13). Accordingly, the operation of sensor using MoS_2-MoO_2 composite yolk-shell spheres at 250°C is advantageous for selective, sensitive and reliable detection of NO_2.

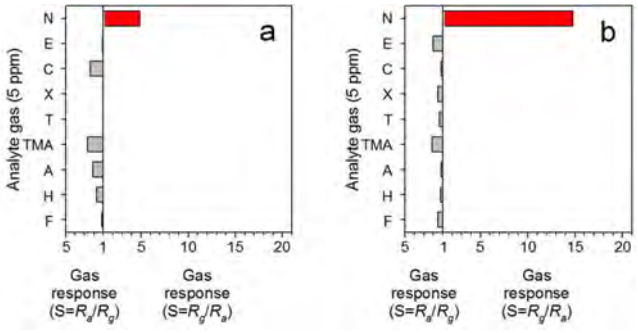

Fig. 4. Gas responses (S=R_a/R_g or S=R_g/R_a) to 5 ppm NO_2 (N), C_2H_5OH (E), CO (C), *p*-xylene (X), Toluene (T), Trimethylamine (TMA), NH_3 (A), H_2 (H), and HCHO (F) of MoS_2-MoO_2 composite yolk-shell spheres and at (a) 200°C and (b) 250°C.

3.3 Discussion

The sensor using MoS_2-MoO_2 composite yolk-shell spheres showed the reversible sensing behavior at 200 and 250°C, while it showed incomplete recovery at low sensing temperature. Donarelli et al. [3] measured NO_2 sensing characteristics of chemically exfoliated MoS_2 flakes annealed at 150 or 250°C. They observed n-type NO_2 sensing behavior (i.e. increase of sensor resistance) from the specimen annealed at 250°C and p-type sensing behavior from the specimen annealed at 150°C. They observed the incomplete recovery from sensing reaction at the sensor temperature of 25, 100 and 150°C. These results are consistent with those in the present study.

The increase of sensor resistance upon exposure to NO_2 can be explained by the adsorption of NO_2 with negative charge (NO_2^- (ads)) and consequent decrease of charge carrier concentration near the surface. Thus, the incomplete recovery from NO_2 sensing reaction means the sluggish kinetics of NO_2 desorption reaction. Thus, the rapid and complete recovery from NO_2 sensing at 200 and 250°C can be attributed to the thermal promotion of NO_2 desorption.

The selective detection of NO_2 is a key result in the present study. Yue et al. [14] reported the calculation that NO_2 and NH_3 weakly adsorbed on the monolayer MoS_2 played roles of acceptor and donor, respectively. This is consistent with Cho's report [6] and explains the decrease of sensor resistance upon exposure to NH_3 in the present study. However, the sensing mechanisms of other gases such as C_2H_5OH, CO, xylene, toluene, trimethylamine (TMA), H_2, and HCHO remain unclear and should be studied further. The sensor resistance was decreased upon exposure to reducing gases. Thus, the adsorption of oxygen with negative

charge and their reaction with reducing gases to produce electrons can be considered as a plausible explanation.

4. CONCLUSIONS

The MoS_2-MoO_2 composite yolk-shell spheres were prepared by the partial sulfidation of MoO_3 yolk-shell spheres and their gas sensing characteristics were investigated. The sensor showed low and incomplete gas responses at < 200°C, while it showed high and reversible gas sensing characteristics at 200 and 250°C. The response to 5 ppm NO_2 was 14.8 at 250°C, which is significantly higher than those towards other 8 different interference gases. The sensors MoS_2-MoO_2 composite yolk-shell spheres can be used to detect trace concentration of NO_2 in a highly selective, sensitive, and reversible manner.

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REFERENCES

[1] H. Hwang, H. Kim, and J. Cho, "MoS_2 nanoplates consisting of disordered graphene-like layers for high rate lithium battery anode materials", *Nano Lett.*, Vol. 11, pp. 4826-4830, 2011.

[2] H. Li, M. Si, S. Najmaei, A. T. Neal, Y. Du, P. M. Ajayan, J. Lou, and P. D. Ye, "Statistical study of deep submicron dual-gated field-effect transistors on monolayer chemical vapor deposition molybdenum disulfide films", *Nano Lett.*, Vol. 13, pp. 2640-2646, 2013.

[3] M. Donarelli, S. Prezioso, F. Perrozzi, F. Busti, M. Nardone, L. Giancaterini, C. Cantalini, and L Ottaviano, "Response to NO_2 and other gases of resistive chemically exfoliated MoS_2-based gas sensors", .*Sens. Actuators B*, Vol. 207, pp. 602-613, 2015.

[4] H. Li, J. Wu, Z. Yin, and H. Zhang, "Preparation and applications of mechanically exfoliated single-layer and multilayer MoS_2 and WSe_2 nanosheets", *Acc. Chem. Res.*, Vol. 47, pp. 1067-1075, 2014.

[5] J. K. Miremadi, R. C. Singh, S. R. Morrison, and J. Colbow, "A highly sensitive and selective hydrogen sensor from thick oriented films of MoS_2", *Appl. Phys. A,* Vol. 63, pp. 271-275, 1996.

[6] B. Cho, M. G. Han, M. Choi, J. Yoon, A. R. Kim, Y.-J. Lee, S.-G. Park, J.-D. Kwon, C. S. Kim, M. Song, Y. Jeong, K.-S. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, P. M. Ajayan, and D.-H. Kim, "Charge-transfer-based gas sensing using atomic-layer MoS_2", *Sci. Rep.*, Vol. 5, pp. 8052, 2015.

[7] Y. N, Ko, Y. C. Kang, and S. B. Park, "Superior electrochemical properties of MoS_2 powders with a MoS_2@void@MoS_2 configuration", *Nanoscale*, Vol. 6, pp. 4508-4512, 2014.

[8] Y. N. Ko, S. B. Park, J.-H. Lee, and Y. C. Kang, "Comparison of the electrochemical properties of yolk-shell and dense structured $CoFe_2O_4$ powders prepared by a spray pyrolysis process", *RSC Adv.*, Vol. 4, pp. 40188-40192, 2014.

[9] Y. J. Hong, J.-W. Yoon, J.-H. Lee, and Y. C. Kang, "One-pot synthesis of Pd-loaded SnO_2 yolk-shell nanostructures for ultraselective methyl benzene sensors," *Chem. -Eur. J.*, Vol. 20, pp. 2737-2741, 2014.

[10] J.-W. Yoon, Y. J. Hong, Y. C. Kang, and J.-H. Lee, "High performance chemiresistive H_2S sensors using Ag-loaded SnO_2 yolk-shell nanostructures," *RSC Adv.*, Vol. 4, pp. 16067-16074, 2014.

[11] Y.-C. Lin, W. Zhang, J.-K. Huang, K.-K. Liu, Y.-H. Lee, C.-T. Liang, C.-W. Chu, and L.-J. Li, "Wafer-scale MoS_2 thin layers prepared by MoO_3 sulfurization," *Nanoscale*, Vol. 4, pp. 6637-6641, 2012.

[12] I. H. Cho, Y. C. Kang, and S. B Park, "Thiophene hydrodesulfurization of unsupported Co-Mo catalysts prepared by spray pyrolysis method", *Korean J. Chem. Eng.*, Vol. 35, pp. 814-818, 1997.

[13] Y. H. Cho, Y. N. Ko, Y. C. Kang, I.-D Kim, and J. H. Lee, "Ultraselective and ultrasensitive detection of trimethylamine using MoO_3 nanoplates prepared by ultrasonic spray pyrolysis", *Sens. Actuators B*, Vol. 195, pp. 189-196, 2014.

[14] Q. Yue, Z. Shao, S. Chang, and J. Li, "Adsorption of gas molecules on monolayer MoS_2 and effect of applied electric field" *Nano Res. Lett.*, Vol. 8, pp. 425-431, 2013.