SYNTHESIS AND APPLICATION OF GRAPHENE/SILVER NANOWIRES/GOLD NANOPARTICLES HYBRID FOR AMMONIA GAS SENSING

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ABSTRACT

Graphene material synthesized from chemical method (reduced Graphene Oxide – rGO) is a promising candidate for gas sensors due to their unique properties. With structure of single layer of bonded sp^2 carbons in a two-dimensional (2D) lattice, rGO have large surface to volume ratio, high conductivity and electron mobility at room temperature. Meanwhile, the different oxygen-containing functional groups (contain dangling bonds) decorated on carbon networks make rGO easily respond with compatible gas molecules. However, the investigating of structure of rGO in micrometer scale shows that the chemical method often results in non-uniform film thickness on substrate due to overlap of rGO sheets. These may disrupt the conductive paths in rGO films and decrease their conductivity. Therefore, gas sensing signal of pristine rGO based sensors is tarnished and the sensors do not recover to their baseline at room temperature. In this study, silver nanowires (AgNWs) and gold nanoparticles (AuNPs) are combined with rGO material to form rGO/AgNWs/AuNPs hybrid. With one-dimensional nanostructure, the AgNWs connects effectively together many rGO islands and reduce significantly their contact resistance so that NH_3 sensing signal is improved and complete recovery of the sensor is nearly achieved at room temperature. Especially, all these signals are further enhanced when the AuNPs (diameter ~ 30 nm) are added into the hybrid.

Keywords: reduced graphene oxide (rGO), NH_3 gas sensor, silver nanowires, gold nanoparticles, hybrid.

1. INTRODUCTION

Many researchers have reported the fabrication and testing of rGO based gas sensors. The interactions of gas molecules with rGO were studied by density functional theory calculations. Results indicate that the adsorption of gas molecules on rGO is generally stronger than that on pristine graphene because of the presence of diverse active defect sites, such as the hydroxyl and epoxy functional groups and their neighboring carbon atoms [1]. However, non-uniform film

thickness and overlap of rGO sheets on substrate are causes for the low sensitivity and poor selectivity of rGO. Fortunately, it is well-known that noble metals, such as Au, Ag, Pd, and Pt, have been widely used to combine with rGO, forming a new type of sensing material for highly selective and sensitive gas sensors [2]. For example, compared to graphene without Pt, significantly improved H_2 detection sensitivity was observed with 1.0 nm Pt film coating [3]; Ag or Au nanoparticle -decorated rGO hybrids improved NH_3 sensing properties over bare rGO [2, 4]; selectivity of NO_2 gas was drastically enhanced by the decoration of Al nanoparticle [5].

Noble metal nanostructures are functional materials with unique physical and chemical properties, which are closely related to their size, shape, composition and structure [6]. For example, in the functionalization of graphene with metal nanomaterial a sizable energy gap can be opened up in graphene through the quantum confinement effect [7]. This is favorable for using the rGO/metal nanomaterial hybrids to make devices (super capacitors, solar cells, and sensors…). In gas sensor, the combination of metal nanoparticles and graphene can modulate the electronic properties of graphene, leading to enhancement of selectivity and sensitivity in gas-sensing characteristics [5].

In this work, we prepared and combined AuNPs or/and AgNWs materials with rGO films to produce hybrids of two or three nanomaterials and studied effect of these metals to NH_3 sensing signal of bare rGO film.

2. EXPERIMENTAL

2.1. Synthesis of nanomaterials

2.1.1 Synthesis of gold nanoparticles (AuNPs)

Seed solution was prepared when 0.5 mL of 2.0 mg/mL trisodiumcitrate (Na_3-citrate) was added to 0.34 mL of 1.0 mg/mL $HAuCl_4$ and vigorously stirred for 15 min. After that, 1.0 mL of 0.04 mg/mL sodium borohydride ($NaBH_4$) dissolved in 0.2 mL of 2.0 mg/mL Na_3-citrate was slowly added dropwise to the Au precursor solution, which was followed by stirring for 120 min.

Growth solution was created by using 0.875 mL of 10.0 mg/mL $HAuCl_4$ precursor solution, 3.6445 g Hexadecyltrimethylammonium bromide (CTAB), 0.08 mL of ascorbic acid (1M) and 0.08 mL of NaOH (1M) dissolved in 97.5 mL deionized water and stabled for 24 h.

To synthesize ~ 30 nm AuNPs-1, the seed solution and the growth solution were mixed together in 20 ^{o}C temperature condition meanwhile 30 ^{o}C temperature was condition for synthesis of ~ 40 nm AuNPs-2. In the case of synthesizing ~ 50 nm AuNPs-3, 1.750 mL of 10.0 mg/mL $HAuCl_4$ precursor solution was used in growth solution (increase two times), synthesis temperature is 30 ^{o}C and other data were unchanged.

2.1.2 Synthesis of rGO film and AgNWs material

rGO films: GO solution was prepared from purified natural graphite by a modified Hummers method. GO films were exposed to hydrazine agent and thermal treatment at 350 ^{o}C to reduce to rGO films. Experimental details are given in the literature [8, 9].

AgNWs material: The AgNWs were synthesized through polyol method using $AgNO_3$ precursor and ethylene glycol reducing agent. Experimental details are given in the literature [10].

2.2. Fabrication of gas sensor devices and gas-sensing measurement

The gas sensor reported herein was fabricated on a quartz wafer, followed by a standard cleaning process. The rGO film was coated directly onto substrate. Two silver planar electrode arrays were deposited on the rGO film using thermal evaporation method. We used spray-coating method to disperse AgNWs or/and AuNPs arranged between two electrodes to complete our gas-sensing devices.

In order to demonstrate NH_3 gas sensing property of the rGO-based gas sensors, we measured its resistance change exposed to analyte gas. Sensitivity was defined as $\Delta R/R_a = (R_g - R_a)/R_a$, where R_a and R_g represent resistance of the sensor to be exposed to Ar and NH_3 gas, respectively.

3. RESULTS AND DISCUSSION

3.1. Degree of AuNPs with different size and shape

The SEM images in Fig. 1 show surface morphology of AuNPs materials with different size and shape, sphere AuNPs-1 with diameter ~ 30 nm, sphere AuNPs-2 with diameter ~ 40 nm and triangle AuNPs-3 with edge ~ 50 nm. This result is attributed to the difference in conditions of synthesis and the UV-Vis absorption spectra in Fig.1 confirm this with the plasmon resonance bands of difference colloidal AuNPs solutions. A surface plasmon resonance peak appears at 529 nm, 545 nm, and 560 nm for AuNPs-1, AuNPs-2 and AuNPs-3, respectively. According to Mie theory, the band peak of surface plasmon resonance depends on the size, type, shape, composition, and dielectric constant at metal surface, which affect the electron charge density on particle surface [6].
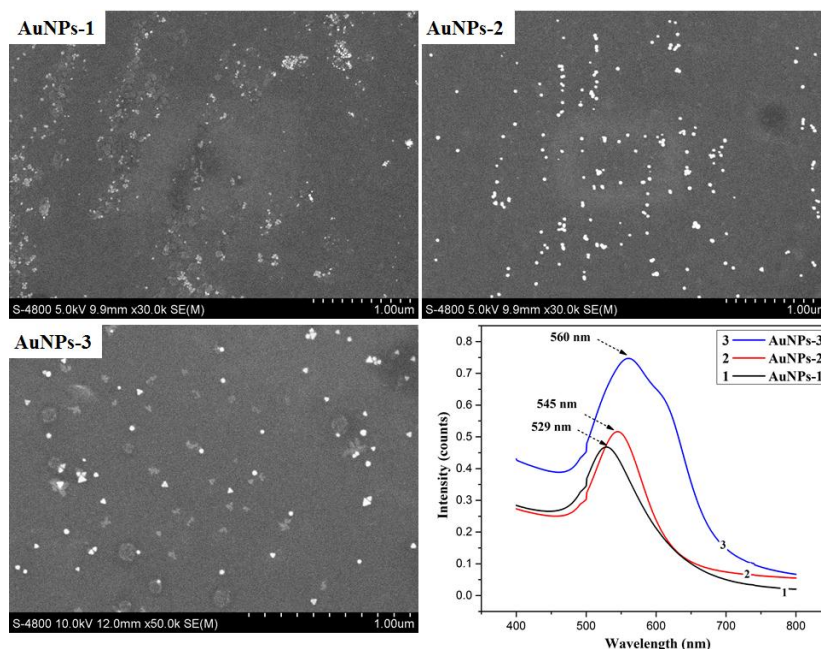

Figure 1. SEM images and UV-Vis absorption spectra of AuNPs-1, AuNPs-2, AuNPs-3 materials.

3.2. Ammonia gas response of rGO/AgNWs and rGO/AuNPs hybrids

The sensors made from hybrids of two nanomaterials are used in this study, rGO films are combined with different structure metal nanomaterials (one-dimensional nanostructure – AgNWs or zero-dimensional nanostructure – AuNPs). Besides, a gas-sensing device using bare rGO is also fabricated as a reference.

The bare rGO material which contains the different oxygen-containing functional groups on its carbon network is attributed p-type semiconductor. In the sensors based on rGO film, rGO is the main material plays the role of response with NH_3 gas, the NH_3 gas molecules are adsorbed on the rGO surface, act as donors and increase resistance of rGO material. This is sensitivity of the sensors. More details are given in the literature [10, 11].

The data in Fig. 2 shows that the NH_3 sensitivity of bare rGO material is improved significantly by adding nanomaterials. In comparison with the sensitivity of bare rGO material (6 %) (Fig. 2a), the increase of sensing signal of the rGO/AuNPs sensor (16 %) is higher than the increase of sensing signal of the rGO/AgNWs sensor (13 %), however the recovery of rGO/AgNWs sensor is better than rGO and rGO/AuNPs sensors. Besides, Fig. 2b presents that the smaller of AuNPs diameter the higher of the NH_3 sensing signal of rGO/AuNPs sensor. Diameter of AuNPs-1 is smallest (~30 nm) and the sensing signal of rGO/AuNPs-1 is highest (16 %).

This phenomenon can be explained based on the quantum confinement effect in small size and the large fractions of surface atoms of AuNPs [5 - 7, 12], meanwhile the AgNWs (length ~ 10 μm) play the role of bridges connecting together many rGO islands to improve electrical conductance of rGO/AgNWs hybrid. On the other hand, the connecting many rGO islands significantly decreases the initial resistance (R_a) of rGO/AgNWs hybrid so the recovery of sensor is improved.
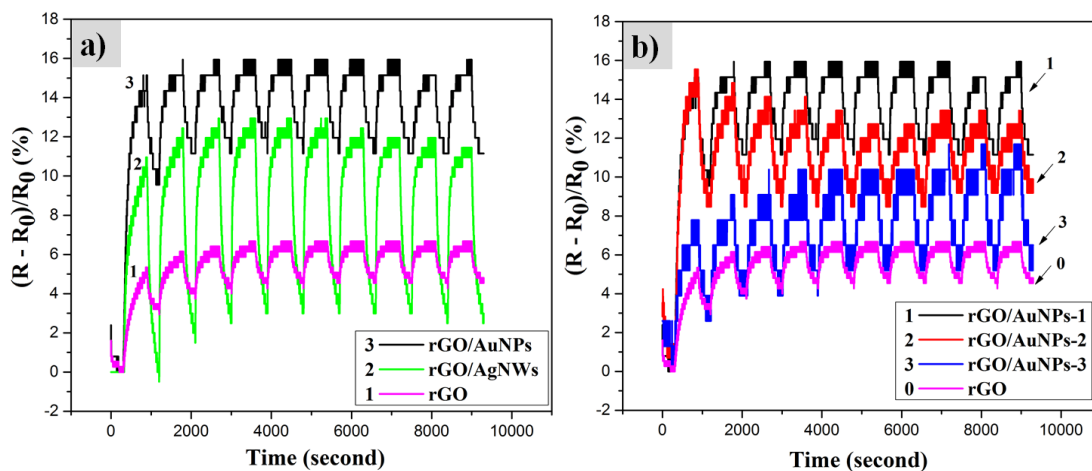

Figure 2. (a) Response of the bare rGO, rGO/AgNWs and rGO/AuNPs sensors to NH_3 gas; (b) Response of rGO/AuNPs sensors with different diameter AuNPs (30 nm, 40 nm and 50 nm) and bare rGO sensor to NH_3 gas.

To further confirm the immobilization of rGO, AgNWs and AuNPs in the hybrids and investigate the unique role of each component, XPS was conducted. The results from Fig. 3a, b, d, e demonstrated that there are a number of functional groups on the surface of rGO therefore rGO easily respond with NH_3 gas molecules [13]. Figure 3c and Fig. 3f present the Ag 3d and Au

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4f peaks in XPS spectra of rGO/AgNWs and rGO/AuNPs hybrids, respectively [13, 14], evidences the combination of target metal materials into rGO-based hybrids. Moreover, comparison XPS spectra peak C1s of bare rGO and rGO/AgNWs shows that there is not appearance of any new peaks which are formed by combination of rGO and AgNWs materials (Fig.3a, b). This indicates that the AgNWs only play the role of bridges connecting together many rGO islands and improve electrical conductance of this hybrid. In the cases of the rGO/AuNPs hybrid, the C peaks shift to higher binding energies when AuNPs are combined with rGO (Fig.3d, e). It can attribute that this phenomenon derived from modulation the intrinsic property of rGO by AuNPs material [6], therefore the enhancement of NH_3 gas sensing signal of rGO/AuNPs hybrids is higher than rGO/AgNWs hybrid in comparison with sensitivity of bare rGO film.
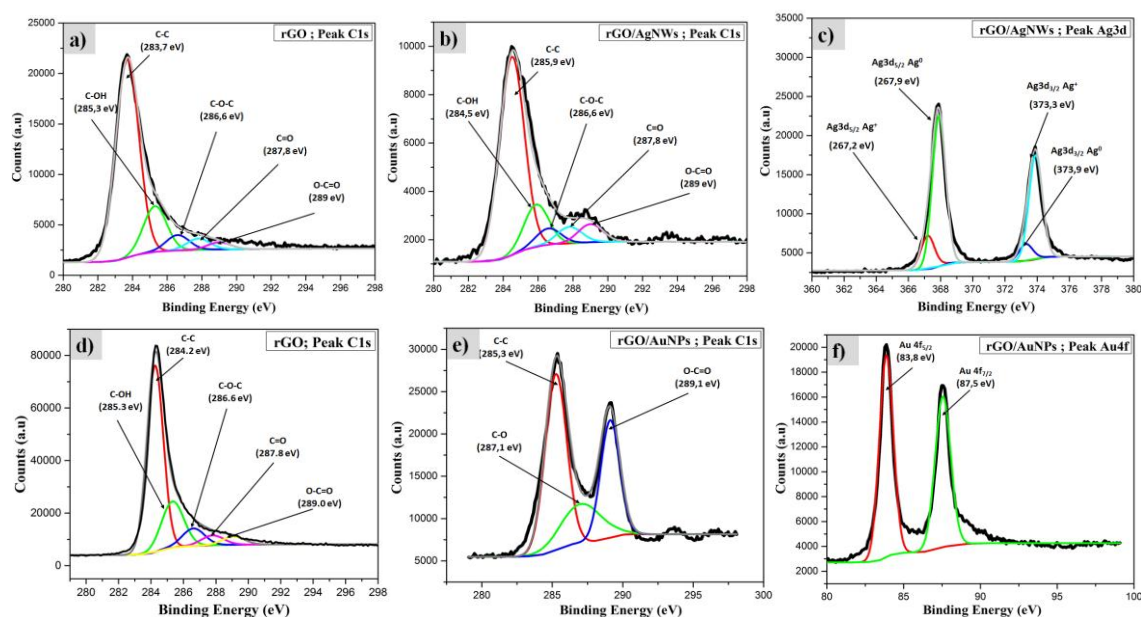

Figure 3. High-resolution C1s XPS spectra of as deposited rGO (a, d); C1s XPS spectra of rGO/AgNWs and rGO/AuNPs hybrids (b, e); Ag3d and Au4f XPS spectra of rGO/AgNWs and rGO/AuNPs hybrids (c, f).

3.3. Ammonia gas response of rGO/AgNWs/AuNPs hybrids

Rely on the inherent properties of bare materials: (i) rGO film is the main material plays the role of response with NH_3 gas; (ii) the AgNWs play the role of bridges connecting together many rGO islands and improve electrical conductance of this hybrid; (iii) the AuNPs can modulate the intrinsic property of rGO. In this study, we made a better sensor based on a hybrid created from three nanomaterial layers, rGO/AgNWs/AuNPs sensor.

The result from Fig. 4 shows that, NH_3 sensing signal of rGO/AgNWs/AuNPs sensor was enhanced significantly comparison with bare rGO sensor (~ 3.0 times), rGO/AuNPs hybrid sensor (~ 1.2 times) and rGO/AgNWs hybrid sensor (~ 1.6 times). In addition, the nearly complete recovery of this sensor at room temperature make it becomes more perfect than the sensors based on original rGO material and rGO/AuNPs hybrid. However, further study is required for a more understanding of the gas-sensing mechanism in rGO/metal hybrid systems.
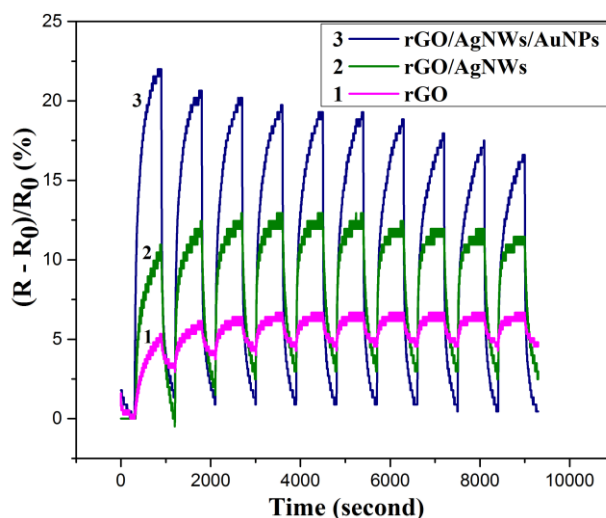
Figure 4. Response of the bare rGO, rGO/AgNWs and rGO/AgNWs/AuNPs sensors to NH_3 gas.

4. CONCLUSION

We investigated the effect of metal nanomaterials combination on the sensing characteristics of rGO-based sensors for NH_3. Each metal nanomaterial plays unique role in the hybrids dependent on its sharp and size. With one-dimensional nanostructure, the AgNWs connects effectively together many rGO islands which improved sensing signal from 6 % of rGO sensor to 16 % of rGO/AgNWs sensor and complete recovery is nearly achieved at room temperature. The AuNPs with zero-dimensional nanostructure and diameter ~ 30 nm can modulate the electronic properties of hybrid which are further enhanced sensing signal (to 20 %) when they are added into the rGO/AgNWs/AuNPs hybrid.

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TÓM TẮT

TỔNG HỢP VÀ ỨNG DỤNG TỔ HỢP LAI GRAPHENE/DÂY NANO AG/HẠT NANO AU VÀO VIỆC NHẠY KHÍ AMMONIAC (NH_3)

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Graphene tổng hợp theo phương pháp hóa học (Graphene oxide được khử - rGO) là một ứng viên sáng giá cho ứng dụng chế tạo cảm biến khí do các tính chất tuyệt vời của chúng. Với cấu trúc của lớp đơn nguyên tử cacbon liên kết trong mạng tinh thể 2 chiều, rGO có tỉ lệ diện

tích bề mặt so với khối lượng lớn, tính dẫn điện và độ linh động điện tử cao ở nhiệt độ phòng. Trong khi đó, các nhóm chức chứa oxy (chứa dựng các liên kết dư thừa) được đính kết trên mạng lưới carbon làm cho rGO dễ dàng hồi đáp với các phân tử khí tương thích. Tuy nhiên, nghiên cứu cấu trúc rGO ở kích thước micromet cho thấy, phương pháp hóa học thường tạo nên các màng có độ dày không đồng đều do sự chồng lấp của các mảng rGO. Điều này đã phá vỡ các đường dẫn của màng rGO và làm giảm độ dẫn điện của chúng. Do đó, tín hiệu nhạy khí của cảm biến tạo thành từ rGO thuần sẽ bị mờ nhạt và chúng không hồi phục về trạng thái ban đầu ở điều kiện nhiệt độ phòng. Trong nghiên cứu này, các dây nano bạc (Agnws) và các hạt nano vàng (Aunps) được kết hợp với rGO để tạo thành tổ hợp lai rGO/Agnws /Aunps. Với cấu trúc nano một chiều, các Agnws kết nối hiệu quả các mảng rGO và làm giảm đáng kể điện trở tiếp xúc của chúng nên tín hiệu NH_3 được cải thiện và sự phục hồi hoàn toàn của cảm biến gần như đạt được ở nhiệt độ phòng. Đặc biệt, tất cả các tín hiệu này được tăng cường hơn nữa khi Aunps (dimetter ~ 30 nm) được thêm vào tổ hợp.

Từ khóa: graphene oxide được khử (rGO), cảm biến khí NH_3, dây nano Ag, hạt nano Au, tổ hợp lai.