

EFFECT OF SILVER NANOWIRE DIMENSION TO AMMONIA ADSORPTION OF GRAPHENE-SILVER NANOWIRES HYBRID

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Abstract. *In this report, we study the effect of silver nanowires (AgNws) dimension to electrical properties of rGO/AgNws hybrid. The alteration of these electrical properties leads the difference of ammonia sensibility of the rGO/AgNws hybrid based sensing devices. When the rGO is accompanied by AgNws of different sizes from ~ 500 nm to > 10 μ m, the ammonia sensitivity of these hybrids change from 60% to 340% alteration compared with the bare rGO material.*

Keywords: reduced graphene oxide, Hummers method, silver nanowires, polyol method, NH₃ gas sensing.

I. INTRODUCTION

Graphene is an allotrope of carbon and constructed by a single two-dimensional (2D) layer of sp^2 hybridized carbon atoms and has many excellent electrical properties. As a result, Graphene and related materials, such as Graphene Oxide (GO) and reduced Graphene Oxide (rGO), have demonstrated significant potential as materials for chemical sensing because of their 2-dimensional structure results in a high sensing area per unit volume and the low noise compared to other solid state sensors. Many research groups have reported the use of graphene or graphitic materials for detecting gases and vapors [1, 2]. Especially, some of the articles attempted to connect the advantages of nanoscale metals with that of graphene for improving of gas sensor applications [3–7], due to growth, the morphology, shape, size, and composition of these metals can be tailored to impart enhanced functionalities.

The ability to detect ammonia (NH₃), an explosive and hazardous gas, in a sensitive and selective manner is critically important for a variety of applications. Chemically reduced graphene oxide (rGO) using hydrazine or/and thermal reduction procedure show excellent performance for the detection of this gas [5–7]. However, it is challenging to maintain the structural and electrical

advantages because rGO synthesized by chemical methods has many defects and composes of small sheets. Therefore, rGO-based gas sensors have some disadvantages; one of them is the uncompleted recovery of gas sensors.

In this study, we investigate using silver nanomaterials (including Ag nanowires and Ag nanoparticles) with different sharp and size which play the role of small bridges connecting many rGO islands together to improve electrical properties of rGO/Ag nanomaterial hybrids and results in higher NH_3 gas sensitivity and more complete recovery. Besides, this is desirable to develop a general method to achieve rGO/Ag nanomaterial hybrids while maintaining the inherent advantages of each component for enhanced electrochemical applications.

II. EXPERIMENT

II.1. Synthesis of silver nanowires (AgNws) with different sharp and size

The Ag nanomaterials are synthesized through polyol method [8–11]. This process need two steps: seeding process and nanomaterial-growing process. First step, 17 mg of NaCl, 20 mg of AgNO_3 and 15 mg of KBr are added into 30 ml of ethylene glycol (EG) and then this solution is slowly heated from room temperature to 170°C . In this period, AgNO_3 is reduced to form the nucleus seeds. Second step, 250 mg of AgNO_3 and 300 mg of poly vinyl pyrrolidone (PVP) are added dropwise into the solution. This solution is regularly stirred and stabilized at 170°C for 1 hour. In this condition, the newly generated Ag atoms would selectively deposit onto the seeds to induce the 1D growth at a relatively high concentration.

During the nanomaterials synthesis, ethylene glycol (EG) serves as both solvent and reducing agent. Under the reduction of EG at high temperature, Na nanoparticles are formed from NaCl material which play the role of homogeneous seeds and then Ag nanoparticles are also formed immediately via these seeds with the introduction of Ag^+ ions (source from 20 mg of AgNO_3) into the solution. Particularly, there are a few reports on the effect of NaCl during the polyol process [8, 10]. They claim that, the main product of this method is Ag nanoparticles without the addition of NaCl. This phenomenon is interpreted as follows: For creating of initial Ag nanoparticle seeds, 20 mg AgNO_3 is used in the first step of the polyol process with reduction of Ag^+ ions to Ag^0 atoms. If the Cl^- ions, arise from 17 mg of NaCl, are not added into the solution, the reaction between Cl^- ions and Ag^+ ions for formation of AgCl would be unsuccessful. So, this causes the high Ag^+ ions concentration which enhances the reduction of Ag^+ ions to Ag^0 atoms. Hence, only some Ag nanoparticles grow as multitwin particles and others as micrometer-sized particles. Sahin Coskun et al. show that [8], addition of NaCl leads to the presence of Ag in a compound form (AgCl) and slows down the reduction of Ag^+ ions. These slow reaction conditions enable Ag nanoparticles to grow as multitwin particles, which would then grow in the form of nanowires (Fig. 1).

Besides, chemical adsorption of PVP molecules onto the surfaces of as-formed Ag nanoparticles is the reason for them to remain at nanoscale. With the passivation of some facets of these particles by PVP, some nanoparticles can grow into multi-twin particles. A common attitude is that PVP interacts more strongly with Ag atoms on the (100) faces than those on the (111) faces, which act as a structure-directing agent as well as the capping agent preventing aggregation. As a result, the multi-twin particles grow into Ag nanowires when AgNO_3 and PVP are successively

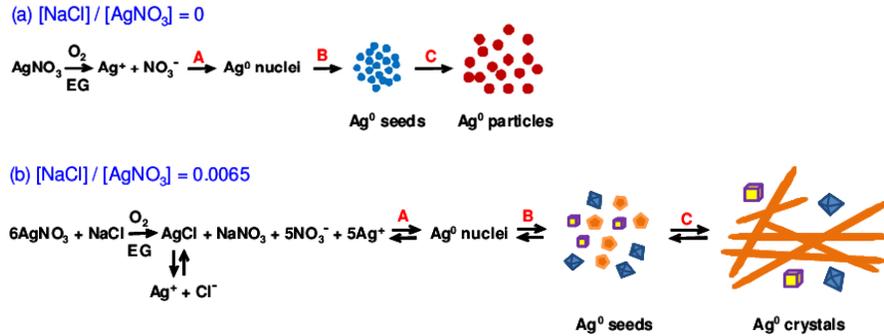


Fig. 1. Possible nucleation and growth mechanisms of Ag nanostructures at different molar ratios of $[\text{NaCl}]/[\text{AgNO}_3]$ [10].

added into the solution (Fig. 2). Thereby, the final morphologies of Ag nanostructures at the end of the polyol process are strongly dependent on the PVP: AgNO_3 molar ratio [8, 11–14].

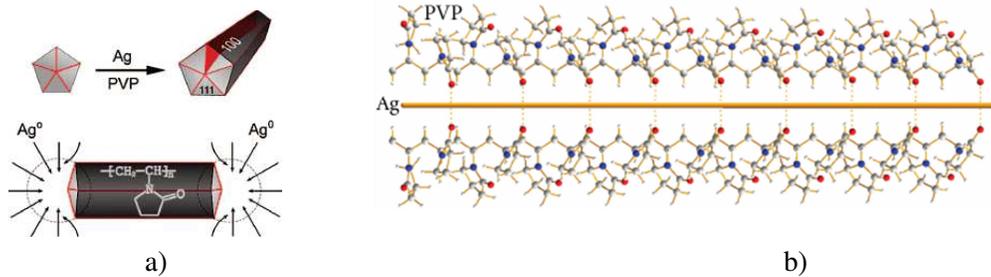


Fig. 2. a) Once twinned seeds lengthened into wires. PVP selectively adsorbed on the (100) side facets so that Ag atoms could only add to the (111) facets at the ends of each wire [14]. b) Schematic diagram of 1D structure for PVP-Ag coordination compound [12].

In this work, we examine effect of sodium chloride (NaCl) and polymer to AgNO_3 ratio (PVP: AgNO_3) on sharp and size of Ag nanomaterials produced in the polyol process. When NaCl is not added in first step of the polyol process, the main product is Ag nanoparticles. On the other hand, when a sufficient amount of NaCl is added in this step the main product is Ag nanowires and the changing of PVP: AgNO_3 ratio at the same time forms Ag nanowires with different length. Then, we investigate the interconnection level of these products on many rGO islands so that improve electrical properties of rGO/Ag material hybrids. As a result, this changes ammonia (NH_3) gas sensitivity of gas sensors based on rGO/Ag material hybrids in comparison with the bare rGO based gas sensor.

II.2. Preparation of gas sensing devices and measurement system

The gas sensor reported herein was fabricated on a quartz wafer with thermal evaporation and two silver electrodes (Fig. 3). The GO solution was spin-coated directly onto a clean quartz wafer. Subsequently, these dry GO films were exposed to hydrazine agent and thermal treatment at 250°C in the high vacuum of $\sim 10^{-6}$ Torr to reduce to rGO films. After that, two silver planar electrode arrays were deposited on the rGO films using thermal evaporation method with 6 mm distance between them. Finally, we used spray-coating method to disperse AgNWs on rGO surface area between two electrodes to complete our gas-sensing devices (Fig. 3) [9].

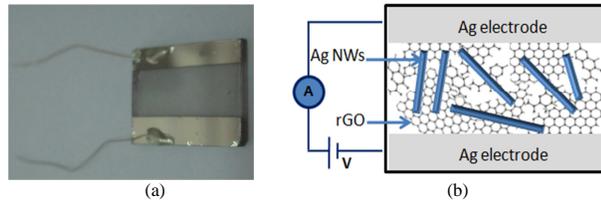


Fig. 3. Image of gas sensing device with two planar electrodes (a) and scheme of a gases detection measuring (b).

The devices are mounted in the test chamber. The measurement included two processes: absorption and desorption. In absorption process, the flowing NH_3 target gas (consisting of Ar carrier gas) from the bubbler into the test chamber for the period time and the change in resistance of sensor were recorded in that time. Moreover, we let the Ar purge gas flow through the test chamber to re-establish the rGO initial resistance. That step will give information about desorption ability of sensor in desorption process. All of the above procedures were controlled by computer [9].

III. RESULTS AND DISCUSSION

III.1. Degree of silver nanostructures with different shape and size

In the polyol process, we study the effect of PVP: AgNO_3 molar ratio (in a range of 0.4:1; 1.4:1; 1.6:1) and NaCl on the final products. In the following experiments, we keep all the parameters constant except the one being investigated.

a) Effect of NaCl. NaCl is an important factor creating about shape of nanometer produces (Ag nanoparticles or Ag nanowires) in polyol method. In our experiment, we also have the same result with the Refs. [8, 10]: i) Without the addition of NaCl, the main product is Ag nanoparticles; ii) When a sufficient amount of NaCl is added, the main product is Ag nanowires.

b). Effect of PVP: AgNO_3 molar ratio. Chemical adsorption of PVP molecules onto the surfaces of as-formed Ag nanoparticles in seeding process is a reason for the final morphologies of Ag nanostructures. With the amount of PVP increasing in comparison of the amount of AgNO_3 (in a range of 0.4:1; 1.4:1; 1.6:1 ratios), the yields of the Ag nanowires have different sizes and almost no particles could be observed in the product with 1.4:1; 1.6:1 ratios.

Fig. 4a shows that the peaks at 38° and 44° correspond to (111) and (200) planes of Ag, respectively and no impurities are detected from this pattern within the resolution limit of XRD. The ratio of diffraction intensity between the (111) and (200) planes for Ag nanoparticle sample and Ag nanowire samples with the PVP: AgNO_3 ratio in a range of 0.4:1; 1.4:1; 1.6:1 are as follow 1.4; and 2.66; 3.27; 2.3, respectively. In comparison of the samples, this ratio is the lowest for the Ag nanoparticle sample while this ratio is higher for Ag nanowire samples. Following the Refs. [8, 11, 12], from these ratios we have a beginning forecast for size and shape of the products, the peak at 38° features for the length of Ag nanowires while the peak at 44° features for the diameter of Ag nanowires and Ag nanoparticles. Besides, Fig.4b shows the UV-visible absorption spectra of

Ag colloid solutions synthesized with different conditions as above mention. The appearance of a peak at ~ 380 nm and the shoulder around ~ 350 nm indicate that the main product is Ag nanowires when making conditions are addition of NaCl and using of different PVP:AgNO₃ molar ratios [8, 11, 12]. Unanimously, a weak peak at ~ 405 nm indicates the formation of Ag nanoparticles at a relatively low concentration. In the absence of NaCl, the peaks at 350 nm, 380 nm and 405 nm of final product disappear and there is only another large peak around 445 nm. This peak suggests that the final product is Ag nanoparticles with a large range of different diameters [5, 11, 12].

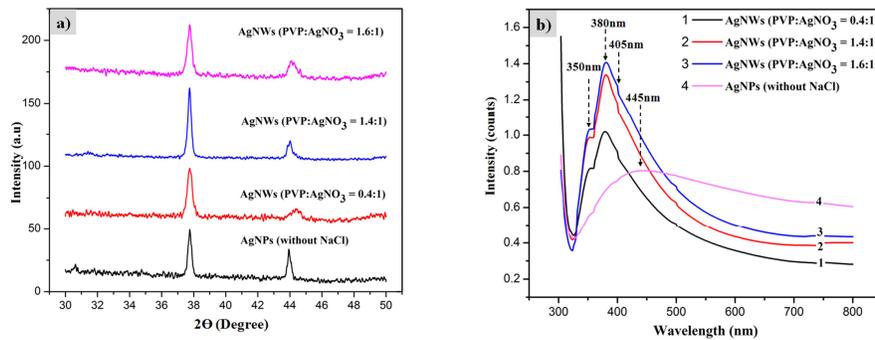


Fig. 4. XRD spectra of Ag nanomaterials (a), and UV-vis spectra of Ag nanomaterials (b).

In order to obtain the general view and the detailed structural information of the Ag nanomaterials, the SEM observation of the nanoparticles synthesized with the sample without NaCl and the Ag nanowires synthesized (in the present of NaCl) with different PVP:AgNO₃ molar ratios of 0.4:1, 1.4:1 and 1.6:1 are shown, respectively. According to Fig. 5, this observation indicates that all the synthesized products with addition NaCl and different PVP:AgNO₃ molar ratios contain a majority of Ag nanowires. When the PVP:AgNO₃ molar ratio is 0.4:1, the passivation of (100) faces of multi-twin particles is insufficient and Ag nanostructure growth occurs on both (111) and (100) faces. So, Ag nanowires synthesized at this low PVP:AgNO₃ molar ratio have the larger diameter. At the same time, the multi-twin particles that could not grow into nanowires agglomerate and form large amounts of micrometer-sized Ag particles (Fig. 5b). As the PVP:AgNO₃ molar ratio increases (1.4:1 and 1.6:1), the diameter of the nanowires decreases gradually while their length increases evidently (Fig. 5c, d). However, increasing of the length of the nanowires has disadvantages. The pressure of the carrier gas flow in sensor preparation process can break these nanowires into the

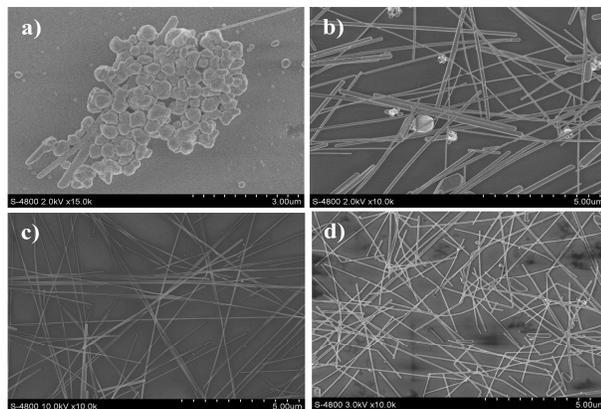


Fig. 5. SEM images of Ag nanomaterials: a) AgNPs (without NaCl), b) AgNWs (PVP : AgNO₃ = 0.4 : 1), c) AgNWs (PVP : AgNO₃ = 1.4 : 1) and d) AgNWs (PVP : AgNO₃ = 1.6 : 1).

shorter nanowires (Fig. 5d). Besides, as the presentation in II.1 the sample without NaCl contains a majority of Ag nanoparticles and rarely has nanowires (Fig. 5a).

III.2. Ammonia adsorption of rGO-silver nanostructure hybrid

Firstly, we examine the structure of rGO-Ag nanomaterial hybrids which is the most importance component in our gas sensing devices by using AFM image, resistance change of these hybrids and XPS spectrum. From Fig. 6, the AFM image of rGO-AgNWs hybrid reveals that rGO which is synthesized by chemical method includes small dimension sheets (called an island). The AgNWs are used to play the role of bridges connecting together many rGO islands to improve electrical properties of rGO-AgNWs hybrid. As a result, the resistance of the rGO-Ag nanomaterial hybrids decrease remarkably in dependence on the dimension of Ag nanowires. In comparison with the resistance of bare rGO material ($4.78\text{k}\Omega$), the resistance of the rGO-AgNWs hybrids decrease $2.8\text{ k}\Omega$, $2.39\text{ k}\Omega$ and $1.2\text{ k}\Omega$ with the increase of dimension of AgNWs materials is $\sim 5\text{ }\mu\text{m}$, $\sim 10\text{ }\mu\text{m}$ and $> 10\text{ }\mu\text{m}$, respectively. The resistance of the rGO-AgNPs decreases slightly ($4.68\text{ k}\Omega$) when rGO is combined with the AgNPs material which has the short dimension ($\sim 500\text{nm}$). This means that the AgNWs with the long dimension connect much more efficient than the AgNPs.

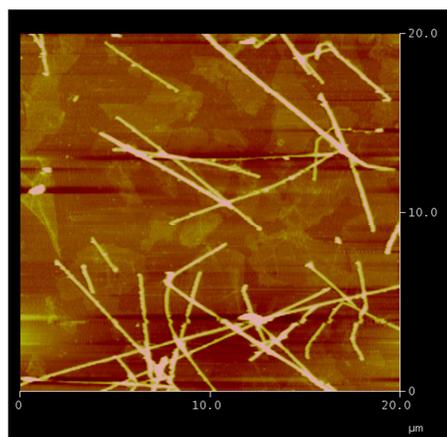


Fig. 6. AFM images of rGO-AgNWs hybrid expressed the connecting role of AgNWs between rGO islands.

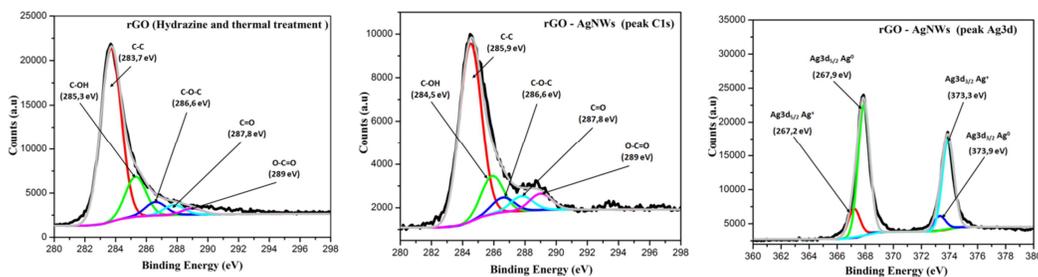


Fig. 7. High-resolution C1s XPS spectra of as deposited rGO, C1s XPS spectra of rGO-AgNWs hybrid and Ag3d XPS spectra of rGO-AgNWs hybrid.

Moreover, XPS spectra show that apart from the peaks of bare rGO and AgNWS materials there is not appearance of any new peaks which are formed by combination of rGO and AgNWs materials (Fig. 7). This indicates that the AgNWs only play the role of bridges connecting together many rGO islands and improve electrical properties of these hybrids while maintaining the inherent properties of each original component.

Secondly, we investigate the sensitivity ability NH_3 of bare rGO material and its hybrids with AgNPs or AgNWs. These experiment processes are performed in the same condition (room

temperature and atmospheric pressure). The data in Fig. 8 shows that the sensitivity ability of original rGO material is improved significantly by silver nanomaterials. In comparison with the sensitivity of bare rGO material (10%), the increase of sensitivity of the rGO-AgNWs hybrids is 21%, 35% and 44% with the increase of dimension of AgNWs materials is $\sim 5\mu\text{m}$, $\sim 10\mu\text{m}$ and $>10\mu\text{m}$, respectively, while the sensitivity of the rGO-AgNPs also increases to 16% (the dimension of AgNPs is $\sim 500\text{nm}$). Particularly, recovery of gas sensors based on rGO-AgNWs is better than recovery of gas sensors based on original rGO material and rGO-NPs hybrid.

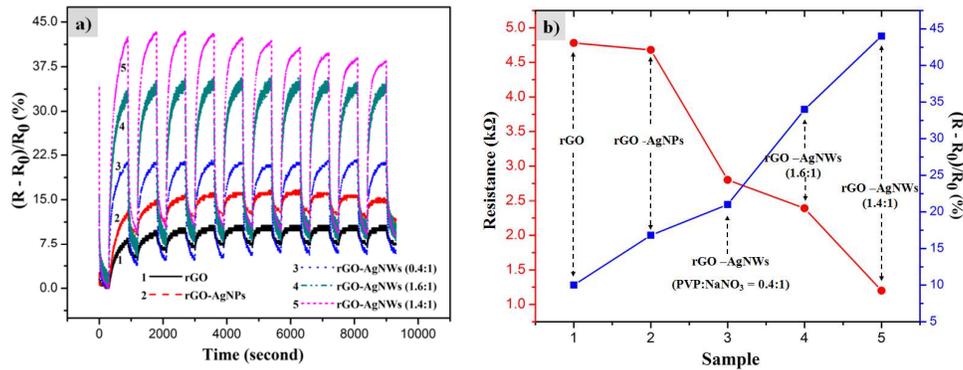


Fig. 8. (a) Response of the bare rGO sensor and rGO-Ag nanomaterial sensors to NH_3 gas; (b) Changes resistance and sensitivity of different hybrids in comparison with these of bare rGO material.

In our experiment, the rGO-AgNWs based gas sensor using PVP:AgNO₃ molar ratio 1.4:1 has the highest NH₃ sensibility (44%) which is improved 4.4 times compared with the ammonia sensibility of bare rGO based gas sensor (10%). This result is more effective than results of Refs. [6, 7]. Madhav Gautam *et al.* show that, decorating Pt nanoparticles on the surface of the graphene film by a vacuum evaporation method enhances the NH₃ response from 5% to 12% (increase 2.4 times) and improves recovery of device [6]. While the NH₃ sensibility of the graphene surface modified with Au nanoparticles and the as-prepared graphene surface are the same (8%), only improves the reliability, recovery and repeatability of this hybrid [7].

Finally, the negligible resistance change of the AgNWs based sensor when is exposed in NH₃ gas medium (Fig. 9) indicates that AgNWs material is not response with NH₃ molecule. This result confirms that AgNWs material plays the role of bridges connecting together many rGO

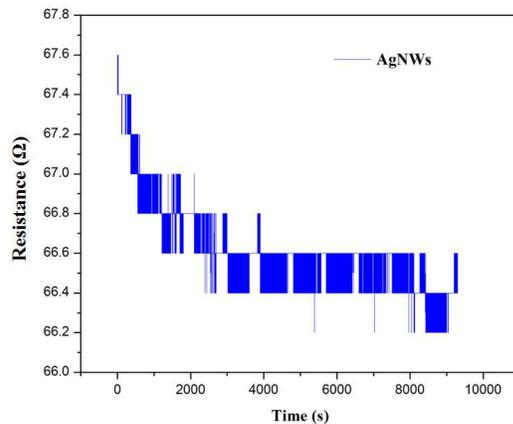


Fig. 9. Response of the AgNWs sensor to NH_3 gas.

islands for improving electrical properties of the hybrid; rGO is the main material which plays the role of response with NH₃ gas.

IV. CONCLUSION

In this study, we have investigated the effect of silver nanostructure dimension to NH₃ adsorption of rGO-silver nanostructure hybrids. These silver nanostructure materials play the role of bridges connecting together many rGO islands and improve electrical properties of the hybrids. The resistance of rGO-silver nanostructure hybrid material decreases when the dimension of silver nanowires materials increases. So, the sensitivity ability NH₃ of these hybrids increases as a result. This effect caused 68%–340% enhancement of the sensitivity ability for the rGO-silver nanostructure hybrids compared with the bare rGO material throughout the dimension of AgNPs (~500nm) and the longest dimension of AgNWs (>10μm). Particularly, this is desirable to develop a general method to achieve rGO/Ag nanostructure hybrids while maintaining the inherent advantages of each component for enhanced electrochemical applications which is confirm by XPS spectrum.

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