Research Article

Ammonia Gas Detection by Tannic Acid Functionalized and Reduced Graphene Oxide at Room Temperature

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Reduced graphene oxide (rGO) based chemiresistor gas sensor has received much attention in gas sensing for high sensitivity, room temperature operation, and reversible. Here, for the first time, we present a promising chemiresistor for ammonia gas detection based on tannic acid (TA) functionalized and reduced graphene oxide (rGO$_{TA\ functionalized}$). Green reductant of TA plays a major role in both reducing process and enhancing the gas sensing properties of rGO$_{TA\ functionalized}$. Our results show rGO$_{TA\ functionalized}$ only selective to ammonia with excellent respond, recovery, respond time, and recovery times. rGO$_{TA\ functionalized}$ electrical resistance decreases upon exposure to NH$_3$ where we postulated that it is due to n-doping by TA and charge transfer between rGO$_{TA\ functionalized}$ and NH$_3$ through hydrogen bonding. Furthermore, rGO$_{TA\ functionalized}$ hinders the needs for stimulus for both recovery and respond. The combination of greener sensing material and simplicity in overall sensor design provides a new sight for green reductant approach of rGO based chemiresistor gas sensor.

1. Introduction

There has been a growing interest in detection of ammonia gas to serve the purpose of detection and monitoring for the field of environmental, automotive, chemical industry, and medical diagnostic [1]. Ammonia gas detection also contributes to explosive detection as ammonium nitrate based explosive releases a trace of ammonia gas when gradually decomposes [2]. On top of that, leakage detection and environment pollution monitoring are the primary concerns as the toxic and corrosive behaviours of ammonia possess severe threat to human skin, eyes, and respiratory tract. The conventional solid state sensor and conducting polymer sensor are suffering from low detection under room temperature. Besides, solid state sensor has the drawbacks of selectivity and complex fabrication process while conducting polymer sensor is often irreversible [3–7]. The emerging of carbon nanocomposites based chemiresistor especially reduced graphene oxide (rGO) has demonstrated high potential in gas sensing due to high sensitivity, room temperature operation, low power consumption, miniaturization potential, and reversibility, in which posing a trend of surpassing

the conventional solid state and conducting polymer sensor. However, rGO chemiresistor is suffering from drawback of poor selectivity where functionalization and use of arrays are often the solution to improve selectivity [8, 9]. Generally, environmental harmful reductant such as hydrazine or sodium borohydride are usually employed in synthesize of rGO. Thus, there is a demand in finding environment benign approach such as green, electrochemical, and solvothermal reductants [10–14].

Tannic acid (TA) is a water soluble phenolic hydroxyl-rich compound and is widely present in woods such as oak, walnut, and mahogany [15, 16]. TA has demonstrated itself as an effective green reducing and stabilizing agent on synthesis of graphene, noble metal nanoparticles, and noble metal nanoparticles/graphene nanocomposites [17–20]. Recently, Zhang et al. have reported TA functionalized rGO with silver nanoparticles decorated for H$_2$O$_2$ and glucose sensing application [19]. However, TA functionalized rGO solely as gas sensor is rarely reported, in particular on ammonia gas detection. In this paper, for the first time, we demonstrate a simple yet green chemiresistor sensor for ammonia gas detection which comprises just overlapping comb electrode
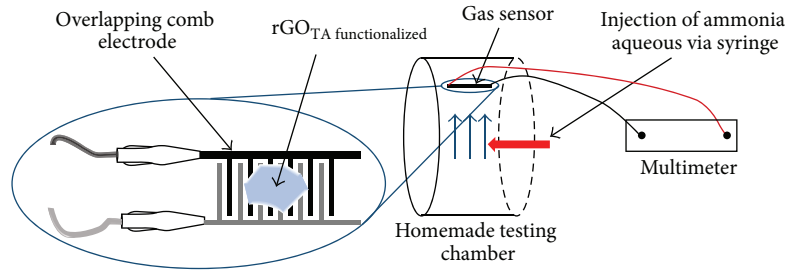
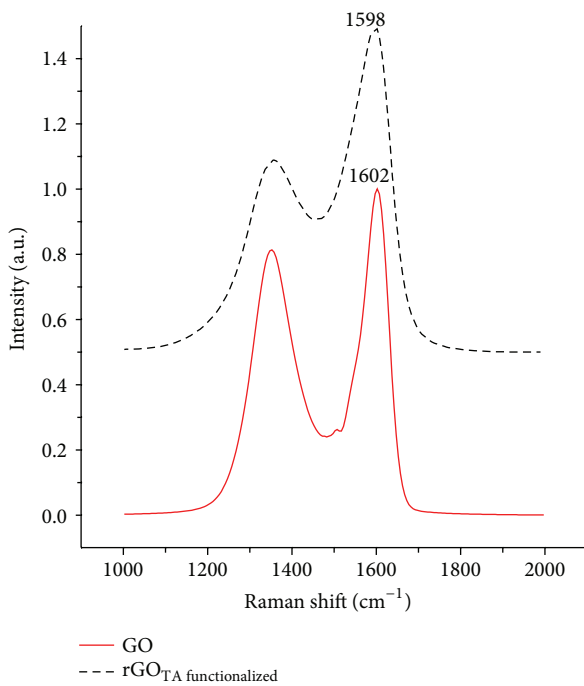FIGURE 1: Schematic diagram of experiment set up for gas testing.

FIGURE 2: Raman spectra of GO and rGO$_{TA\ functionalized}$. I_G peak blue shifted from 1602 nm (GO) to 1598 nm (rGO$_{TA\ functionalized}$). I_D/I_G ratio is diminished from 0.81 (GO) to 0.59 (rGO$_{TA\ functionalized}$).
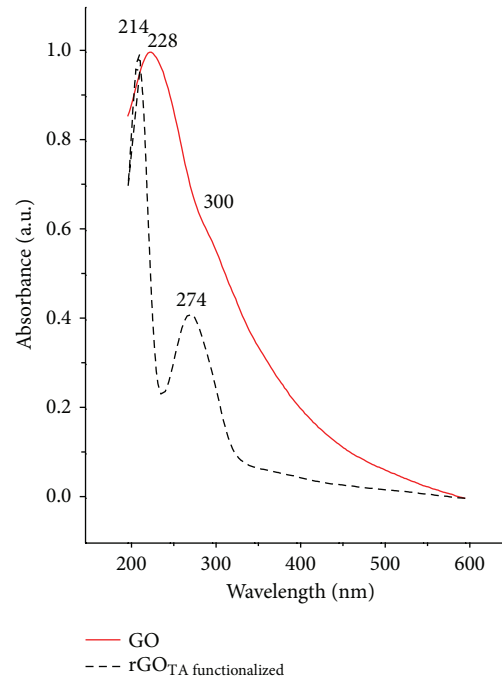

FIGURE 3: Absorption peak of GO and rGO$_{TA\ functionalized}$. GO has absorption peaks at 228 nm and around 304 nm (small shoulder peak). TA has absorption peaks around 213 and 276 nm which are assigned for Π-Π^* aromatic units and C=O groups, respectively.

with drop-casted rGO$_{TA\ functionalized}$. We employed the green reductant of TA to serve as both reducing and functionalizing agent for rGO$_{TA\ functionalized}$, where TA plays a major role in reduction process and enhancing the gas sensing properties. Experimental findings indicate that rGO$_{TA\ functionalized}$ has fulfilled all the aspects to be considered as an excellent sensor for ammonia gas detection. In addition, rGO$_{TA\ functionalized}$ has the advantages of room temperature operation, has wide range detection, and hinders the need of stimulus such as current, purging of gas, and UV illumination for recovery/response.

2. Experimental Section

2.1. Preparation of rGO$_{TA\ functionalized}$. Reduction of GO by TA was referring to a method reported by Lei et al. in 2011 with modification where reduction time was elongated to 24

hours and pH was adjusted to 9, with the aim to promote the degree of reduction and absorption of TA on rGO [21]. Graphene oxide (XF002) was obtained from XF Nano Inc., China. Tannic acid was obtained from Tianli Chemical Reagent Co. Ltd, China, without further purification. GO was dissolved in DI water and subjected to sonication. TA was dissolved in 90 mL of DI water and temperature was raised to 80°C. Sodium hydroxide was added to adjust the pH to 9. GO was then dropwise added into TA solution. The reaction mixture was kept continuous stirring and maintained at 80°C for 24 hours. The resultant suspension showed a black solution which indicated the reduction of GO to rGO. The resultant suspension was collected and washed three times. The sample was recorded as rGO$_{TA\ functionalized}$. rGO$_{TA\ functionalized}$ was drop casted onto an array of electrode (overlapping comb electrode) and dried in oven.

(a)

(b)

(c)

(d)
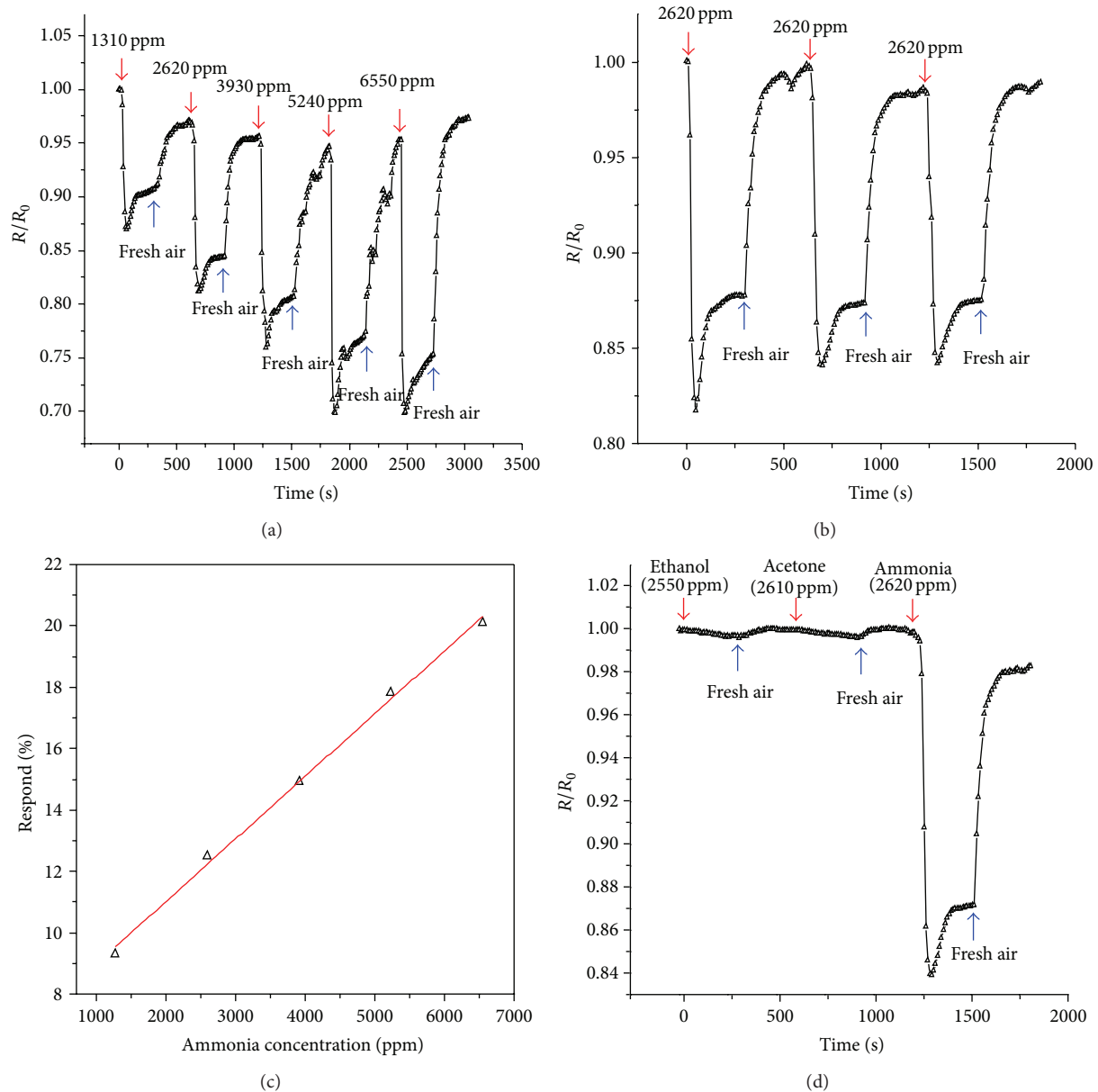
FIGURE 4: (a) Respond towards variation of NH_3 concentration. (b) Respond when exposed to cycles of NH_3. (c) The linear respond with increase of NH_3 concentration. (d) Selectivity respond when exposed to ethanol, acetone, and ammonia.

2.2. Material Characterization and Gas Testing. All the UV-vis absorption spectra were conducted on a Hitachi U-3010 spectrophotometer. Raman spectra were conducted by Horiba Jobin Yvon HR 800 with 514 nm excitation. Raman spectra were fitted by Voigt function using peak fitting function of Origin 9.0.

Keithley Multimeter 2000 was used as electrical resistance measurement. Ammonia gas sensing experiments were carried out in a simple homemade testing chamber as shown in Figure 1 with a net volume of 5655 cm^3. The ammonia aqueous was injected into chamber with a distance of 10 cm from sensor. Various concentrations of ammonia aqueous and organic solutions were introduced to the chamber manually via injection at the humidity of 26% and temperature of

25°C. The door of chamber was opened to introduce fresh air for recovery process.

3. Result and Discussion

3.1. Synthesis and Characterization of $rGO_{TA\ functionalized}$. From Raman spectra (Figure 2), I_G peak is found blue shifted from 1602 nm (GO) to 1598 nm ($rGO_{TA\ functionalized}$) upon reduction. The blue shifting of I_G peak indicated the recovery of hexagonal network upon reduction. The I_D/I_G ratio which was often used to indicate the degree of disorder or defects in rGO is diminished from 0.81 (GO) to 0.59 ($rGO_{TA\ functionalized}$) which is suggesting the possible decrement in disorder due to reduction process. GO is reduced by TA via two-step S_N2
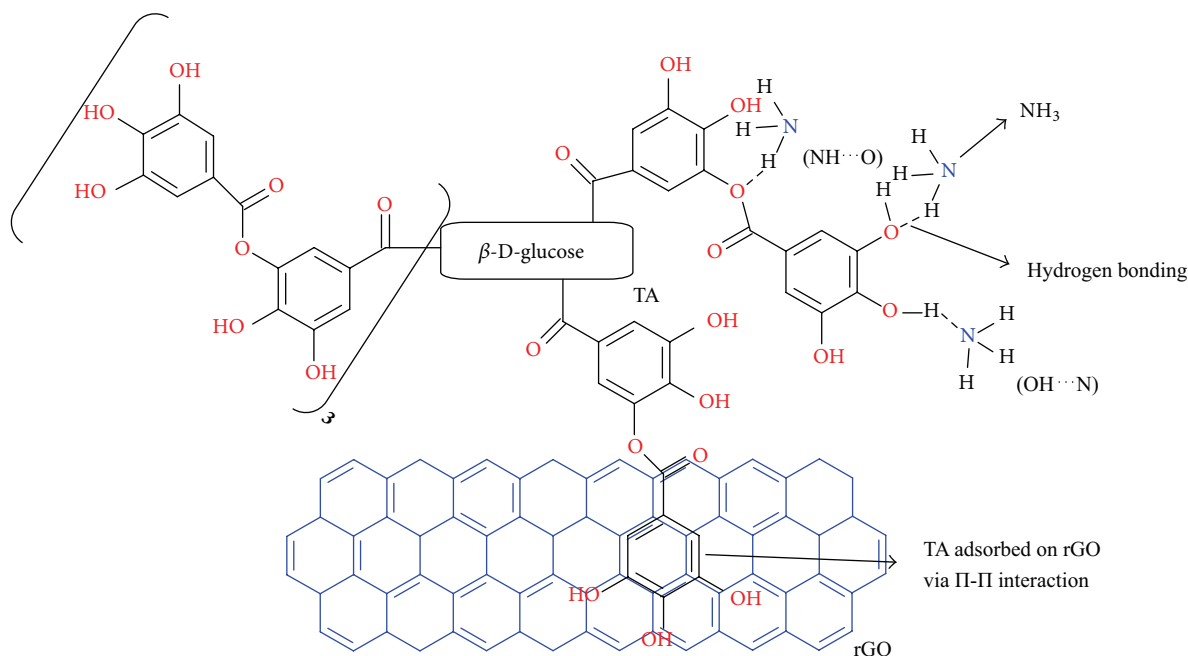
FIGURE 5: Illustration diagram of hydrogen bonding between hydroxyl and NH_3 (OH$\cdots$N), hydroxyl and NH_3 (NH$\cdots$O), and epoxide and NH_3 (NH$\cdots$O).

nucleophilic reactions and followed by elimination [21, 22]. From Figure 3, UV-Vis spectra of GO have absorption peaks at 228 nm and around 304 nm (small shoulder peak) due to Π-Π^* transition of aromatic C–C and n-Π^* transition of C=O [2]. Upon reduction, the absorption peaks disappeared and new peak is found around 270 nm which again suggested the restoration of electronic conjugation [23, 24]. TA has absorption peaks around 213 and 276 nm which are assigned for Π-Π^* aromatic units and C=O groups, respectively. Thus the absorption peak of $rGO_{TA\ functionalized}$ around 213 nm clearly indicated the sorption of TA [25]. The recovery of hexagonal networks is allowing the TA to adsorb on rGO with aromatic rings binding to the surface carbon rings via Π-Π interactions [21, 26].

3.2. Gas Sensing Characteristic of $rGO_{TA\ functionalized}$. The exposure of $rGO_{TA\ functionalized}$ to ammonia gas (NH_3) responded by decrement in electrical resistance ratio R/R_0 (Figure 4(a)). R and R_0 are electrical resistance values with and without ammonia gas, respectively. Electrical resistance respond ratio r_{RES}, which is defined as ratio in percentage: $(R_0 - R/R_0) \times 100\%$, is inversely proportional to NH_3 concentration in linear (Figure 4(c)). A plausible sensing mechanism is established. TA is known to be electron donating molecules. TA molecules sorption via Π-Π stacking n-doped the rGO, which is intrinsically p-type. The interaction between NH_3 with $rGO_{TA\ functionalized}$ would be expecting the donation of negative charge carrier to $rGO_{TA\ functionalized}$ from NH_3, in which NH_3 is acting as donor characteristic [27]. Thus, the charge carrier transfer greatly enhances the negative charge carrier density of $rGO_{TA\ functionalized}$, leading to decrement

in overall electrical resistance which agreed well with the experimental observation [28, 29].

The exposure of $rGO_{TA\ functionalized}$ to continuous cycles of NH_3 has demonstrated good consistency and reversibility of $rGO_{TA\ functionalized}$ in NH_3 gas detection (Figure 4(b)). As from Figure 4(d), $rGO_{TA\ functionalized}$ gave negligible electrical resistance ratio reading of conductance increment when exposed to organic vapours such as ethanol ($\approx$ 0.31% R/R_0) and acetone ($\approx$ 0.32% R/R_0) in compare to NH_3 ($\approx$ 12.5% R/R_0). It clearly suggests the strong selectivity of $rGO_{TA\ functionalized}$ towards NH_3. The strong selectivity towards NH_3 may due to NH_3 strong reducing and donor behaviour among the introduced vapours, where we evaluated that NH_3 injected a much higher amount of negative charge carrier into $rGO_{TA\ functionalized}$ compared to other introduced vapours. Therefore greatly enhancing the negative charge carrier density of $rGO_{TA\ functionalized}$.

Analysis of curves in Figure 4 revealed that it is an immediate sharp response of decrement in resistance followed by gradual recovery and saturation upon exposure to NH_3. The gradual recovery region arises from desorption of the weak molecular adsorption onto low energy binding sites such as sp^2 bonded carbon. Whereas saturation region arises from molecular interaction with higher energy binding sites, in particular oxygen functional group that is introduced by TA and residual oxygen functional group from incomplete reduction, which is substantially stronger [4, 30, 31]. The molecular interaction of NH_3 with $rGO_{TA\ functionalized}$ occurred through hydrogen bonding with hydroxyl and epoxide groups (Figure 5). The hydrogen bonding between NH_3 and hydroxyl group is either occurred by coordination of the N in NH_3 to the H in hydroxyl group (OH$\cdots$N) or

TABLE 1: Respond ratio/r_{RES}, respond time/t_{RES}, recovery ratio/r_{REC}, and recovery time/t_{REC} of rGO$_{TA\ functionalized}$ towards different concentration of NH$_3$/C$_{NH_3}$.

C_{NH_3} (ppm)	r_{RES}	t_{RES} (s)	r_{REC}	t_{REC} (s)
1310	9.3%	40	66.45%	170
2620	12.5%	40	88.87%	90
3930	14.9%	40	93.80%	250
5240	17.8%	20	100.00%	260
6550	20.1%	20	100.00%	100

coordination of one of the H atoms in NH$_3$ to the O in hydroxyl group (NH$\cdots$O). Whereas hydrogen bonding of NH$_3$ with epoxide group is coordination of one of the H atoms in NH$_3$ to the O of epoxide group (NH$\cdots$O) [32, 33].

Strikingly, saturation region is recoverable quickly without the needs of stimulus in which recovery of molecular interaction is usually slow or unrecoverable [4]. This attributes to the good recovery ratio r_{REC} and fast recovery time t_{REC} (Table 1). r_{REC} is defined as ratio in percentage: $((R - R_a)/(R - R_0)) \times 100\%$. R_a is electrical resistance values after ammonia gas desorption. t_{REC} is defined here as time required reaches 90% of initial resistance amplitude. It is to highlight that recovery ratio r_{REC} and recovery time t_{REC} of rGO$_{TA\ functionalized}$ do not deteriorate with increases of NH$_3$ concentration C_{NH_3} even in regime of dense concentration (>3000 ppm).

The sorption of TA provides abundant amount of hydroxyl (–OH) and epoxide (=O) which serve as active site for gas absorption, thus enhancing the respond time and sensitivity [34]. The excellent respond times t_{RES} and recovery times t_{REC} (40 s and 260 s, resp., for 1310–6550 ppm of NH$_3$) are assuring the good detection efficiency. Respond ratio r_{RES} and recovery times are paramount in practical application. In addition, rGO$_{TA\ functionalized}$ has shown great improvement in dense concentration regime compared to previous studies, in particular on recovery ratio r_{REC}, respond ratio r_{RES}, and recovery times t_{REC} where rGO$_{TA\ functionalized}$ demonstrated respond time t_{RES} of 40 s, recovery ratio of 93.8%, and recovery time of 260 s [31, 35].

4. Conclusion

In summary, we demonstrated a green yet simple NH$_3$ gas sensor based on rGO$_{TA\ functionalized}$. Electrical resistance decreases upon exposure to NH$_3$ where we postulated that it is due to n-doping by TA and charge transfer between rGO$_{TA\ functionalized}$ and NH$_3$ through hydrogen bonding. Experimental findings revealed that rGO$_{TA\ functionalized}$ has high potential value to be explored for detection of NH$_3$ based on excellent selectivity, respond times, and recovery times, especially under dense concentration regime (>3000 ppm). The stimulus-free, wide range detection capability and room temperature operation do favour the practical use of rGO$_{TA\ functionalized}$ in NH$_3$ gas sensing.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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