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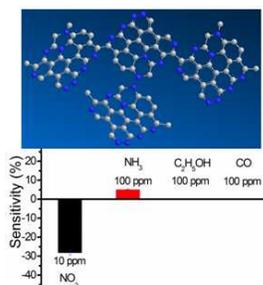
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Table of content



A p-type gas sensor based on C-rich carbon nitride exhibits good sensitivity and high selectivity toward NO₂ at room temperature.

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ARTICLE TYPE

Novel C-rich Carbon Nitride for Room Temperature NO₂ Gas Sensor

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Novel C-rich carbon nitride, prepared from thermal treatment of urea-derived porous g-C₃N₄ with addition of glucose-derived carbon, exhibits a nanoporous structure and is conductive at room temperature. As a p-type semiconductor, the porous carbon nitride displays a good sensitivity and selectivity toward NO₂ at room temperature.

Graphitic-C₃N₄ (g-C₃N₄) has attracted extensive research because of its semiconductivity, high thermal and chemical stability. It is a promising metal-free catalyst to generate hydrogen from water, oxidize benzyl alcohol and decompose pollutants,¹ and also a fluorescent sensor for metal ions detecting or anion contaminant monitoring based on the fluorescence quenching effect and complexation effect.² However, its poor electrical conductivity restricts its application in such fields as oxygen reduction reaction and gas sensing. It is reported that doping as in the cases of C-doped g-C₃N₄³ and P-doped g-C₃N₄⁴ can improve electrical conductivity of g-C₃N₄. For N-doped grapheme, managing the N content can control its electrical conductivity.⁵ Inspired by these, carbon nitride will be propitious for gas sensing via N-content controlling.

Previously, in our group, porously active g-C₃N₄ was prepared through the pyrolysis of urea under ambient pressure without additive assistance.^{6,7} On this basis, we obtained N-graphene with manageable N contents,⁸ the electrical properties of these materials get improved compared to g-C₃N₄. Therefore, carbon nitride with acceptable conductivity and appropriate N content for gas sensor can be realized in terms of the previous work.

Gas sensors based on graphene have been extensively researched due to the high surface area and electrical conductivity of graphene.⁹ However, pristine graphene has exhibited low sensitivity towards gases,^{10, 11, 12} which possesses a zero bandgap.¹³ Thus, semiconductors with similar structure to graphene were purchased for gas sensing, one of which, graphite carbon nitride was unexplored for its poor electrical conductivity.

Herein, conductive C-rich carbon nitride with nanopores of average 13.7 nm was synthesized in our study, according to the procedures in our previous reports⁸, which was synthesized through a two-step thermal treatment of glucose and urea. In which, glucose is a common natural product and it will effectively transform into carbons during high temperature treatment,¹⁴ while urea first generates porous g-C₃N₄ around 500 °C in air,^{6,7} and discomposes over 700 °C to release a nitrogen source in Ar. In our preparation method, the porous g-C₃N₄ not only supports nitride source, but also serves as a template during the second thermal step.

The resultant carbon nitride exhibits a porous structure and possesses a large amount of pyridine N. The pyridine N is occupied by negative charges, which shows strong affinity for adsorbed molecules. Especially, the carbon nitride with C/N atomic ratio of 2.6 has a propitious conductivity for gas sensor, and exhibits p-type semiconducting behavior in ambient conditions. The fabricated sensor performed a good sensitivity to NO₂ and high selectivity towards NO₂ among NO₂, NH₃, CH₃CH₂OH and CO.

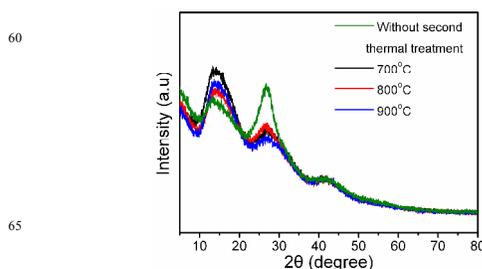


Fig. 1 The XRD patterns of the samples obtained with different second thermal treatment.

The obtained carbon nitride samples were characterized by XRD patterns, and the second treatment temperature was varied to clarify the structure of as prepared products. The appeared two peaks in the XRD patterns are typical of g-C₃N₄, with the two distinct peaks at 27.4° and 13.1° corresponding to (002) and (100) diffraction planes, as shown in Fig. 1, the widen peak at 27.4° demonstrates that the second thermal treatment causes the obvious decrease of the thickness of carbon nitride.

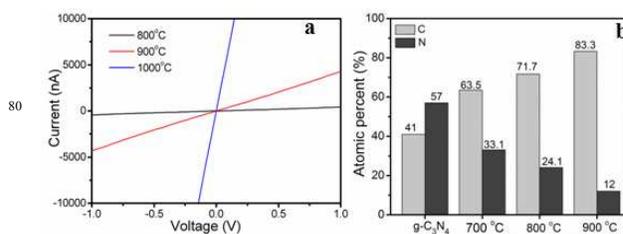


Fig. 2 (a) Current versus voltage, (b) atomic percent of C and N of the samples obtained with different second thermal treatment and g-C₃N₄,

The electric conductivities of these samples were measured, as shown in Fig. 2a, the slopes of the I-V curves obviously exhibit the conductivity get improved with the increasing thermal temperature. With the second treatment temperature increasing, not only the conductivity enhances, but also the nitrogen content decreases,^{8,15} as shown in Fig. 2b. Due to the modest conductivity

and N content, the sample obtained at 800 °C was tested in the gas sensing. The composition was studied using XPS, the results are exhibited in Fig. S1, C and N spectrum presents similar characters compared to g-C₃N₄^{6,7}, with the prominent difference is the peak-area ratio, demonstrating the obtained sample is one carbon nitride.¹⁶ The content of sp² C=C is found to be much higher than that in g-C₃N₄. Further, the main peak at 397.9 eV corresponds to sp² hybridized aromatic N bonded to carbon atoms (C=N-C) existed in graphitic carbon nitride⁶, also called pyridine N, which was proved to be reactive by theories and experiments.¹⁷ The C/N atomic ratio of 2.6 calculated from Fig. 2b is much higher than that of C₃N₄ (C:N=0.75), suggesting that this material is made up with one carbon nitride as a product of C-doped C₃N₄, here is denoted as C-rich carbon nitride. C₃N with the close atomic C/N ratio has been discovered as a low-energy structure for the carbon-rich phases of carbon nitride.¹⁸ Conjugated planar-ring structures with sp² hybridized carbon are most likely to be formed in C₃N,^{18,19} which is consistent with the result that a high content of sp² carbon is present in our sample.

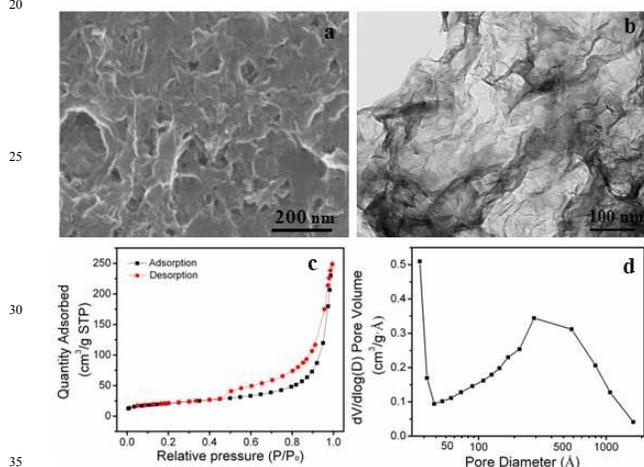


Fig.3 (a) SEM, and (b) TEM images of C-rich carbon nitride; N₂ adsorption/desorption isotherm (c) and corresponding BJH pore size distribution curve determined from the N₂ desorption isotherm (d) of C-rich carbon nitride.

The morphology of the obtained C-rich carbon nitride was studied by SEM and TEM. As shown in Fig. 3a and b, the carbon nitride sheets formed a film on the Si substrate, and the pores could be easily detected in the film, which demonstrate the porous sheet structure of the carbon nitride. The TEM image further reveals the typical layered platelet-like morphology. The porous structure was evidenced by N₂ adsorption-desorption isotherms and BJH measurements, as shown in Fig. 3c and d, the BET surface area was measured to be 74.4 m²/g, and the sample was measured to have a mesoporous structure with a wide pore size distribution, averagely 13.7 nm.

The nanoporous carbon nitride was found to be a p-type semiconductor according to the FET measurements based on the fabricated sensor, as shown in Fig. S2. Current versus voltage (I-V) curves of the carbon nitride exhibit linear ohmic behavior in both dry air and dilute NO₂, reflecting that the electrical contact plays a negligible role in the sensing process, as shown in Fig. 4a.²⁰ This phenomenon is similar with graphene, which lead us to believe the sensor mechanism is consistent with charge

transfer between the carbon nitride and the analytes. Fig. 4b exhibits that the resistance of the carbon nitride decreases notably upon NO₂ exposure, the corresponding sensitivity versus concentration was shown in Fig. 4b, which can apparently reveal the sensing character of carbon nitride. In the low concentration (0.5-2.0ppm), the sensitivity depends linearly on the concentration, and the linear response as a function of concentration can give the detection limit at sensitivity of 0.5%, which is about 140 ppb. The detection limit is much lower than the specified NO₂ concentration (2.4 ppm), suggesting that the carbon nitride is a novel and potential material for sensing NO₂ at ambient conditions.

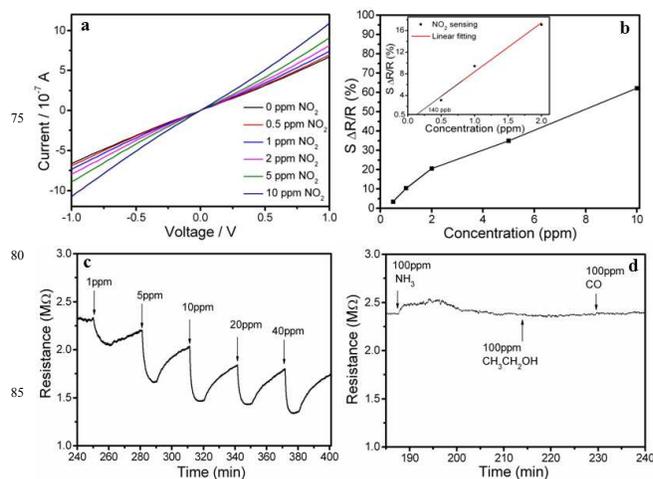


Fig. 4 (a) Current versus voltage in NO₂ with different concentration (response time = 10 min) at room temperature; (b) Sensitivity of C-rich carbon nitride based sensor vs. different NO₂ concentrations, with the inset is linear fitted response versus concentration (R-square = 0.965); (c) Real-time response to NO₂ from 1 ppm to 40 ppm at room temperature; (d) Real-time response to different gas at room temperature: NH₃, CH₃CH₂OH and CO.

To study the sensor dynamic range, sensors were tested against NO₂ with different concentrations at room temperature and ambient environment and the results are shown in Fig. 4c, with the ambient humidity measured to 65% RH. The same percentage of RH air was used as the carrier gas. Each step consists of 10 min exposure to NO₂ (adsorption) and followed by 20 min exposure to air (desorption). The sensor gives a large initial decrease in resistance of about 12%, followed by a partial recovery at room temperature. As the concentration increase, largely detectable changes occurred within 10 min and a region of saturation followed the initial rapid response. The slow change in desorption indicates that the gas molecule attached to the surface strongly at room temperature. As the concentration increases, we found that the sensor reached the saturation, which may due to the gas molecules covered the whole surface. The surface could get full recovery through prolonging the air exposure time, or via annealing or ultraviolet illumination as used for graphene based sensor.²¹ Fig. 4d shows that our devices exhibit little response to NH₃ and no response when exposed to a series of 100 ppm CO and CH₃CH₂OH. The device resistance is, in fact, increases upon exposure to reducing agents, while it decreases in an oxidizing environment, agreeing with the p-type semiconductor revealed in the I-Vg curve. Ethanol and CO are weak electron-donating dopants, therefore, they cannot change the resistance. The

response of the carbon nitride sensor to different humidity was also measured, as shown in Fig. S3. In the presence of humidity, the resistance increases, for the adsorbed water results in the formation of adsorbed terminal hydroxyl groups, which act as electron donors.²² The above phenomenon is similar to graphene, thus further shows the charge transfer mechanism.²¹

The C-rich carbon nitride contains a large amount of pyridine N as mentioned above in XPS, having a strong affinity to oxygen reported in ORR reaction.²³ Further, theory concerning the molecule adsorption of N-doped graphene reports that, N-doping will enhance the adsorption of NO₂ on the surface and the charge transfer.²⁴ Here, NO₂, an electron-withdrawing molecule, is mainly adsorbed by the pyridine nitrogen. The N atom, possesses negative electrons due to the higher electronegative compared with C. Usually fractions of the electronic charge, is transferred to the NO₂ molecule with consequent generation of a positively charged vacancy in the carbon nitride, giving reason for the p-type-like behavior. The above phenomenon indicates that NO₂ can be detected out of other gases. At the same time, the high number of pyridine N has a detrimental effect on the response time and detaching time, longish minutes are needed to establish equilibrium and desorb the molecules from the surface.

In conclusion, a novel p-type gas sensor based on C-rich carbon nitride was reported for the first time to our knowledge. The electrical conductivity of this carbon nitride with C/N atomic ratio of 2.6 gets enhanced significantly, which is appropriate for gas sensor. Furthermore, this carbon nitride exhibits porous structure and possesses a large amount of pyridine N occupied by negative charges. In light of these, NO₂ will adsorb on the pyridine N, and the electrons on the negative pyridine N can transfer to the NO₂ molecule, which accounts for the quite satisfactory sensitivity and high selectivity. Further work is underway to enhance its performance as an effective sensor under ambient conditions.

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Notes and references

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⁵⁰ † Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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