Rational design of Bi-doped rGO/Co_3O_4 nanohybrids for ethanol sensing

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Abstract

Gas sensors based on metal oxide semiconductors (MOSCs) and reduced graphene oxide (rGO) for sensing of organic volatile compounds often suffer from high operation temperature, low responses, poor selectivity, or narrow detection range. Herein, we design and fabricate Bi-doped rGO/Co_3O_4 (BGCO) nanohybrids with a flower morphology, which have been applied as a sensing layer for an ethanol sensor. This BGCO sensor exhibits a maximum *p*-type response of 178.1 towards 500 ppm ethanol at an optimum working temperature of 120 ºC. The sensor's detection range for the ethanol concentration is from 500 ppb to 500 ppm, and the sensor has an excellent selectivity to ethanol compared to other types of organic volatile gases and oxidizing gas such as NO_2. The enhanced ethanol sensing mechanism is attributed to the increased conductivity of Bi doped rGO/Co_3O_4 material. Additionally, incorporation of Bi dopant can promote the redox reaction, and the MOSCs act as the catalyst.

Keywords: semiconducting metal oxide, rGO, Bi doped Co_3O_4, ethanol sensor, resistive sensor

1. Introduction

With the rapid development of Internet of things, various sensor-based techniques are being extensively developed and applied for industry, agriculture, environment control, enhancement of life quality, and safety [1-4]. Among various types of sensors, chemiresistive gas sensors based on metal oxide semiconductors (MOSCs), such as Co_3O_4 [5], rGO/Co_3O_4 [6-8], Bi_2O_3 [9], SnO_2 [10], In_2O_3 [11], and WO_3 [12,13], as well as their nanocomposites [14-16], have many advantages including good sensitivity, selectivity, stability, cost effectiveness, and simple implementation for real-time control. All of these make them competitive for usages in environmental monitoring, food safety, industrial production, and disease diagnosis [17-19].

Volatile organic compounds (VOCs), including ethanol (C_2H_6O), formaldehyde (CH_2O), toluene (C_7H_8), methanol (CH_3OH), ethylene glycol ($(CH_2OH)_2$) and other aromatic carbohydrates, are hazardous to human health and can cause irritation of mucous membranes and upper respiratory tracts [20,21]. Nevertheless, our olfactory system is insensitive to accurately detect these types of harmful gases. Therefore, it is critical to develop high performance gas sensors not only for detection of toxic, explosive or flammable vapors (which could come from free emissions or destructive leakage), but also for quality or concentration control of living conditions, traffic routine inspections, rapid disease diagnosis and food inspection [22]. Ethanol (CH_3CH_2OH), for example, is one of the important VOCs used in food, biological and brewing industries. In recent years, studies for gas sensors for ethanol have been increased rapidly due to their extensive applications such as drunken-driving monitoring, safety tests for food package, and leakage detection in chemical factories [23,24]. Large quantity leakage or evaporation of ethanol may induce risk of explosion in brewery houses or storehouses [25]. Therefore, it is critically required for ethanol sensors with low operating temperature, fast detection, high sensitivity, and good selectivity.

The key working mechanism of these MOSCs based gas sensors is that the target gas molecules are chemisorbed and react with the oxygen species such as O^-, O_2^-, O^{2-} on the surface of the sensing material, which leads to changes of device's properties such

as electrical resistance [8,17]. To further enhance the gas sensing performance inlcuding low working temperature, sensitivity, selectivity, stablity, and reprodcibility, different strategies have been developed [26]. For example, doping of these MOSCs have been extensively studied to enhance the synergistic effects of the binary/ternary metal oxide materials (Bi_2O_3, SnO_2, MoO_3 and Co_3O_4) and increase the surface chemcial states of the electrons and high surface-to-volume ratios [27]. Heterostructures have also been widely used, including *n*-*n*, *p*-*p* and *p*-*n* junctions, where *p* is *p*-type semiconductor, *n* refers to *n*-type semiconductor. Many studies also applied composites of the MOSCs, for example, with the reduced graphene oxide (rGO), which can manipulate the Fermi energy level and large specific surface area [28-30].

Recently, there are studies reported using $Zn_{1-x}Fe_xO$/rGO [31], SnO_2-rGO [32], rGO-CuO [33] and MoO_3-rGO [34] nanocomposites for the ethanol sensors. However, rGO/Co_3O_4 [35], Co_3O_4/N-doped rGO nanocomposites [8], and rGO decorated hollow Co_3O_4 nano/microspheres [7], are still deserved to be further investigated due to their low responses and high operating temperatures. For instance, Liu's group synthesized rGO decorated hollow Co_3O_4 spheres using a solvothermal method and then applied them into an ethanol sensor. The sensor showed a *p*-type sensing behavior, and the response value is 13.5 towards 100 ppm ethanol, which is 3.7 times higher than that of the pure Co_3O_4 [35]. In 2019, Sun's group fabricated Co_3O_4 and rGO nanosheets, which have been used for ethanol sensing. They reported that the nanocomposite with 15 wt% of rGO has the best sensitivity when operated at 200 °C [7]. In 2020, Lin and co-workers reported that Co_3O_4/N-doped rGO nanocomposite with a mesoporous structure exhibited a *p*-type response for ethanol which can be operated at 200 ^oC [8].

In very recent years, various rGO/Co_3O_4 nanocomposites have been extensively studied as the ethanol sensing materials. However, the sensor's performance such as sensitivity, working temperature and selectivity of the rGO/Co_3O_4 based sensors is far from satisfactory, owing to their relatively high intrinsic resistance. One alternative strategy for enhancing sensing properties is to introduce other components (e.g., Bi, Zr, Ag) [36-38], especially for those elements with a high electronegativity. These elements can have a synergistic effect with Co to modulate the surface states, reactant adsorption,

and activation. According to the literature, the electronegativity of Bi is 1.9, which is beneficial in gas sensing because it is known to promote electron transfer [39]. In addition, the conductivity of Bi doped rGO/Co_3O_4 might be greatly improved because of the mismatch of lattice constants [40], which was induced by the doped Bi, because the radius of Bi atoms is larger than that of Co atoms. However, to the best of our knowledge, there are few reports on the ethanol sensing using Bi-doped rGO/Co_3O_4 nanohybrids. Therefore, in the present investigation, Bi-doped rGO/Co_3O_4 nanohybrids have been synthesized via one-pot solvent-thermal method. Based on this design methodology, we found that incorporation of 1% Bi (mass ratio) into rGO/Co_3O_4 nanohybrid can enhance the ethanol sensing performance (e.g., response and selectivity) significantly.

2. Experimental

2.1 Preparation of Bi-doped rGO/Co_3O_4 nanocomposite

All analytical grade reagents and chemicals were purchased from Aladdin (Shanghai, China), and used as received without any further purification. Mixtures of 747.2 mg $Co(Ac)_2 \cdot 4H_2O$, 7.472 mg $Bi(NO_3)_3 \cdot 5H_2O$, 500 mg 1,3,5 Trimesic acid ($C_9H_6O_6$), and 300 mg ammonium fluoride (NH_4F) were dissolved into the 40 ml absolute ethyl alcohol, and obtained a solution A. Graphene oxide (GO) nanosheets were synthesized from the natural graphite via the modified Hummers method, and then ultrasonically dispersed into 10 ml absolute ethyl alcohol at 250 W for 2 h, which obtained a solution B. Successively, the solutions of A and B were transfered into a 50 ml autoclave and heated at 180 °C for 24 h. The obtained products were centrifugated and washed with ethanol and water for 3 times, and dried at 80 °C for 12 h. The dark violet colored precursor was changed into black powder after calcination at 300 °C for 2 h. According to the mass ratio of $Co(Ac)_2 \cdot 4H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$, the prepared Bi-doped rGO/Co_3O_4 nanocomposite was denoted as 1%BGCO. Similarly, we prepared other three samples via changing the weight of $Bi(NO_3)_3 \cdot 5H_2O$ from 0 mg (0%), 22.416 mg (3%), to 44.832 mg (6%), and named them as 0%BGCO, 3%BGCO, and 6%BGCO, respectively.

2.2 Preparation of gas sensing set-up

In the typical sensor fabrication process, 100 mg 0%BGCO, 1%BGCO, 3%BGCO, 6%BGCO nanocomposites were mixed with *N*, *N*-dimethylformamide (DMF) to form paste, respectively. The paste was then drop-coated onto the surface of a ceramic tube with four platinum (Pt) electrodes to form a uniform coating. The coated ceramic tube with the BGCO were welded to a special six-polar pedestal. Finally, a Ni–Cr heating coil was inserted into the coated ceramic tube for heating purposes. The gas sensing performance was characterized using a gas sensing system (MA1.0, Narui Electronics Co. Ltd., China). The sensing response was calculated by the resistance ratio of the sensor resistance in sensing gases (R_g) to that in fresh air (R_a). The response time was defined as the time taken for the 90%-fold resistance alteration of gas sensors in the adsorption processes, whereas the recovery time was defined as the period taken by sensing device to reach 90% of its initial resistance after the exposed to air [41].

2.3 Materials Characterization

X-ray diffraction (XRD) patterns of the composites were obtained using a Bruker AXS (D8, advance, Cu Kα X-ray source) diffractometer at a scanning rate of 1° min^{-1}. The morphologies of the samples were investigated using a field emission scanning electron microscope (FE-SEM, Zeiss Gemini 500) and a high resolution transmission electron microscope (HR-TEM, JEOL-2100F 200 kV). The elemental mapping of the samples was performed using an energy dispersive X-ray spectroscope (EDX, Oxford Link-ISIS 300) at 15 kV. The spectra of X-ray photoelectron spectroscope (XPS) were recorded using a Termo Scientific Escalab 250xi instrument equipped with a monochromatic Al Kα source. The specific surface areas were determined by BET measurements (Autosorb iQ Station 1, USA). Experiments using ultraviolet photoelectron spectroscopy (UPS, Thermo Fisher Scientific Co.) was carried out in ultrahigh-vacuum environment with He I ($h\nu = 21.2$ eV).

3. Results and discussion

Fig. 1a presents the synthesis process of the BGCO sensing materials. Here, the BGCO nanohybrids were obtained via one-pot solvent-thermal method. Fig. 1b shows the surface morphologies and microstructures of the nanocomposite of Bi-doped

175 rGO/Co_3O_4 obtained using the FE-SEM. The surface of 1%BGCO composite shows a
176 flower-type morphology, and the lamellar structure of rGO could hardly be seen as the
177 substrate for the nucleation and growth of Co_3O_4. The surface also shows
178 interconnected pores, and the pore diameter is ranged from several nanometers to
179 several micrometers (Fig. 1c), which is consistent with the structure of the rGO [42].
180 Fig. 1d shows a TEM image, revealing the Co_3O_4 on the translucent layer of rGO [43].
181 Fig. 1e shows a HR-TEM image of the sample, where the two lattice fringes with
182 spacings of 0.47 nm and 0.24 nm are identified as the (111) and (311) lattice planes of
183 hexagonal Co_3O_4 [44,8]. To elucidate the elemental composition of the 1%BGCO
184 nanohybrids, EDX elemental mapping was performed (Fig. 1f to i), and the results
185 confirm that the sample of 1%BGCO contain C (Fig. 1f), O (Fig. 1g), Co (Fig. 1h) and
186 Bi (Fig. 1i), evenly distributed within the selected area. On the other hand, Bi elements
187 are sparsely scattered on the surface of 1%BGCO.
188
189
190 **Fig. 1.** (a) Illustration of the synthesis process of flower shaped Bi-doped rGO/Co_3O_4 nanohyrbids; (b) low-
191 magnification SEM and (c) high-magnification SEM of Bi-doped rGO/Co_3O_4 nanohyrbids; (d) low-magnification
192 TEM and (e) HR-TEM image of Bi-doped rGO/Co_3O_4 nanohybrids; the corresponding SEM-EDX elemental
193 mapping of the selected area (f - i).
194
195 Fig. 2 shows the crystalline phases of undoped rGO/Co_3O_4 (0%BGCO) composite
196 and Bi-doped rGO/Co_3O_4 nanohybrids obtained using the XRD. The diffraction peaks
197 of rGO/Co_3O_4 (0%BGCO) composite and Bi-doped rGO/Co_3O_4 including 1%BGCO,
198 3%BGCO, and 6%BGCO nanohybrids are the same with those of the cubic Co_3O_4
199 (JCPDS No. 43-1003). Due to the tiny doping amount of Bi sources in the preparation
200 of Bi-doped rGO/Co_3O_4 nanocomposite, no obviously crystalline phases corresponding
201 to the Bi or Bi compound such as Bi_2O_3 appeared in 1%BGCO, 3%BGCO, and
202 6%BGCO, which indicates that Bi doping did not obviously change the cubic structure
203 of Co_3O_4 (or that there are present below the minimum detection limit of XRD
204 diffraction). On the other hand, the Bi_2O_3 crystalline phase can be identified if the

doping amount of Bi is 10% in the 10%BGCO system (see Fig. S1, supporting information). Additionally, the diffraction peaks are sharp and strong, manifesting the good crystallinity and relatively small particle sizes, which are beneficial for the sensing performance [29].

Fig. 2. XRD patterns of 0%BGCO composite and BGCO nanohybrids of 1%BGCO, 3%BGCO and 6%BGCO.

Fig. 3a shows the high resolution XPS spectrum of C 1s, which indicates a high level oxidation of the graphene sheets, occurred during the exfoliation. There are three peaks with their binding energies at 284.2 eV, 286.1 eV and 289.7 eV, respectively, which can be assigned to the aromatic carbon (C-C), the epoxy or alkoxy (C-O) and the carbonyl carbon (C=O), respectively. Fig. 3b shows the deconvoluted O 1s spectrum of Bi-doped rGO/Co_3O_4 composites. The two peaks centered at 529.7 and 531.6 eV are attributed to the O^{2-} lattice oxygen, and chemisorbed oxygen species such as (O^-, O_2^- and O^{2-}), respectively, leading to the formation of electron depletion layer within the matrix of 1%BGCO [44,45]. Fig. 3c shows the binding energies of Co $2p_{1/2}$ and Co $2p_{3/2}$ in Co 2p XPS spectra, which are located at 794.5 eV and 779.86 eV, respectively. The difference between these two binding energy values is ~14.6 eV, suggesting that both Co^{3+} and Co^{2+} are co-existed in the nanohybrids of 1%BGCO [46,8]. Moreover, the other two satellite peaks located at 796.6 eV and 781.6 eV are linked to the Co^{2+} peak of two orbits [47]. Fig. 3d shows Bi 4f spectrum, and the binding energies for Bi $4f_{5/2}$ and Bi $4f_{7/2}$ are 164.90 and 159.56 eV, respectively. These show that all of the Bi species in the 1%BGCO sample are in the form of Bi^{3+}, which agrees well with the previous reports [1,48]. Additionally, the high resolution XPS spectra of other three samples of 0%BGCO, 3%BGCO, and 6%BGCO were analyzed, revealing that the samples surface is composed of the elements of Co, C, O and Bi, in which Bi acts as a decorating component (see Fig. S2 to 4, supporting information).

Fig. 3. XPS spectra of Bi-doped rGO/Co_3O_4 nanocomposites: (a) C 1s, (b) O 1s, (c) Co 2p and (d) Bi 4f, respectively.

Most of semiconductor-based sensors show temperature-dependent characteristics due to their unique electrical structures, which are strongly affected by temperature [49,50]. Thus, the different gas sensors have their individual optimum working temperatures. This is beneficial for improving the sensitivity and/or the selectivity according to the equation (1):

$$n_0 = 2(m_n^* k_0 T/2\pi\hbar)^{3/2}\exp(-(E_c - E_f)/k_0 T)) \quad (1)\ [1]$$

where T is Kelvin temperature scale, m_n^* is effective mass , k_0 is the Boltzmann constant, $\hbar$ is reduced Planck constant, E_c is the energy of conduction band bottom and E_f is the energy of Fermi level. We firstly tried to find the optimum operating temperature of the developed sensor. Fig. 4 shows the results of the sensing responses versus operating temperature (T) of the 0%BGCO and Bi-doped rGO/Co_3O_4 nanohybrids based sensor to 100 ppm ethanol. Through comparisons of the temperature dependent sensing characteristics in the temperature range of 80 - 200 ºC, we found that the sensors of the 0%BGCO, 1%BGCO, 3%BGCO and 6%BGCO exhibit their optimum sensing properties at temperatures of 150 ºC, 120 ºC, 130 ºC, and 140 ºC, respectively. Obviously, the sensor of 1%BGCO exhibits the outstanding sensing performance among all the sensors, and its optimum working temperature is 120 ºC.

Fig. 4. Sensing performances of the gas sensors toward 100 ppm ethanol gas at different operating temperatures.

To further reveal the changing trend of resistance (R_a) for the different BGCO sensors, the relationship curves between R_a values and the proportion of Bi dopant at different operating temperature from 80 to 200 ºC were obtained, and the results are shown in Fig. 5a. Obviously, the resistance values of 1%BGCO, 3%BGCO and 6%BGCO increase with the increase of Bi content in the BGCO nanohybrids at the same temperature, which indicates that the introduction of Bi element has significantly influenced the sensor's responses. The main reason can be ascribed to the fact that with a higher Bi content, the energy barrier and scattering cross-section could be increased, which would prevent the effective charge-transfer [51]. Additionally, the device's resistance decreases with the increase of the operating temperature, which is the

intrinsic characteristic of all the MOSCs. Furthermore, we also found that the resistance of 0%BGCO is the largest one among the samples of 1%BGCO, 3%BGCO and 6%BGCO. This phenomenon is in a good agreement with that reported in literature [39,52].

Fig. 5b exhibits the dynamic response and recovery characteristics of the sensors based on 1%BGCO and 0%BGCO to different ethanol concentrations from 500 ppb to 500 ppm tested at 120 °C. Obviously, the dynamic curves display a slow increase at a low ethanol concentration below 5 ppm. Afterwards the responses increase quickly after 5 ppm. In general, the 1%BGCO sensor exhibits much a higher response than that of 0%BGCO, which is mainly due to its increased content of Bi elements. Furthermore, the response of 1%BGCO sensor increases rapidly with the increasing concentration of ethanol, which can reach 178.1 at the ethanol concentration of 500 ppm. By taking the logarithm of R_a of samples of 0%BGCO and 1%BGCO, we found that the R_a of 1%BGCO exhibits a significant change with the increase of ethanol concentration, see Fig. 5c. On the other hand, it is worth mentioning that the R_a values of 1%BGCO, 3%BGCO, and 6%BGCO based sensors are much lower than that of 0%BGCO sensor due to the incorporation of Bi dopant, as shown in Fig 5d. Moreover, the resistance (R_a) of all the sensors can return to the baseline level (see Fig. 5d) which manifest that the BGCO materials have excellent recovery property when exposed to fresh air again from the target gas of ethanol. The detailed response and recovery performance will be discussed in the following section of this study. For comparisons, the dynamic response and recovery curves of the sensors based on 3%BGCO and 6%BGCO are given in Figs. S4 and S5 (Supporting Information). Clearly, the response of 1%BGCO is 6.35, which is ~8.17 times as large as those of 3%BGCO and 6%BGCO, respectively. Furthermore, the response of 1%BGCO is gradually reaching to the saturation stage when the ethanol concentration is above 200 ppm, as shown in Fig. 5e. Table 1 summarizes the sensing data of ethanol using the 1%BGCO and 0%BGCO. According to the data in the table, the 1%BGCO sensor shows a superior response than that of 0%BGCO sensor, mainly because of its larger specific surface area (67.795 m^2/g) and incorporation of Bi elements.

Table 1 The response data of 1%BGCO and 0%BGCO based sensors toward 100 ppm ethanol at 120 °C.

Materials	Concentrations (unit: ppm)							
	0.5	1	5	20	50	100	200	500
1%BGCO	2.5	8.2	15.0	59.8	104.6	136.7	157.6	178.1
0%BGCO	1.2	1.2	1.4	1.6	1.7	2.0	2.2	2.4

Fig. 5f shows a typical repeatable sensing results of the 1%BGCO and 0%BGCO sensors after five cycles to 100 ppm of ethanol at 120 °C. It is indicated that both the 1%BGCO and 0%BGCO sensors show a good reproducibility after the cycling test, manifesting their good stabilities. However, the 0%BGCO sensor has only a very low sensitivity of 2.0 (see Table 1). Similarly, the cycling test results of dynamic responses of 3%BGCO and 6%BGCO to 100 ppm ethanol at 120 °C were also studied, and the results are shown in Figs. S6 and S7 (Supporting Information). Based on all these results, we can conclude that the introduction of Bi can significantly enhance the sensitivity of the rGO/Co_3O_4 composite, meanwhile, the repeatability and stability of Bi-doped rGO/Co_3O_4 nanohybrids are well maintained.

Table 2 Gas sensing response values of various nanomaterials to ethanol gas.

Materials	Concn (ppm)	Temp (°C)	Response	Refs.
TiO_2/Co_3O_4	100	160	65	[53]
ZnO-Co_3O_4	1000	200	106	[54]
Co_3O_4/Al_2O_3	50	240	8.9	[55]
Pd@Co_3O_4-ZnO	200	240	59	[56]
α-$Bi_2Mo_3O_{12}$/ Co_3O_4	100	170	30.25	[57]
rGO/$CoTiO_3$	50	195	9	[58]
Co_3O_4 /N-doped carbon foam	100	100	10.4	[59]
3 wt% rGO-Co_3O_4	100	180	13.5	[35]
rGO/Co_3O_4	100	200	21	[7]
Co_3O_4/N-RGO-0.5	100	200	24.5	[8]
1%BGCO	100	120	150	This work

Fig. 5. (a) The initial resistance alteration trend of the Bi-doped rGO/Co_3O_4 (BGCO) nanohybrids induced by the proportion of Bi dopant at the different temperature from 80 to 200 °C; (b) Dynamic resistance changes of the 0%BGCO and 1%BGCO sensors when exposed to various ethanol gas toward 0.5-500 ppm ethanol at 120 ℃, respectively; (c) Continuous resistance curves of the 0%BGCO and 1%BGCO sensors to various concentrations of ethanol at 120 ℃; (d) The initial resistances (R_a) of the 0%BGCO, 1%BGCO, 3%BGCO and 6%BGCO sensors varied with the ethanol concentration at 120 ℃, respectively; (e) The response *vs* gas concentrations for 0%BGCO and 1%BGCO sensors, respectively; (f) Repeatability test of the 0%BGCO and 1%BGCO nanocomposite sensors to 100 ppm of ethanol at 120 ℃.

Figs. 6a and b compare the response and recovery times of the 1%BGCO sensor and 0%BGCO sensor exposed to 100 ppm ethanol at 120 °C. The τ_{res} of 0%BGCO sensor is 5 s, which is faster than that (89 s) of 1%BGCO sensor. On the other hand, both the sensors take a long time to recover 90% of its initial resistance, especially for the 1%BGCO (75 s). Most of the chemical sensors do not show good reversibility because the thermal energy is usually lower than the activation energy for desorption [60], which leads to a long τ_{rec}. In addition, the gas sensor based on the rGO and its hybrids exhibits a much longer recovery time, which has often been reported in literature [61,62]. The main reason is attributed to the lamellar structure of rGO and mesoporous structures in 1%BGCO, which cause the slow diffusion of the ethanol molecules.

The long-term stability is also a very important parameter for gas sensors, thus the sensing stability of 1%BGCO and 0%BGCO exposed to 100 ppm ethanol was studied once per 10 days at 120 °C for a period of two months to evaluate their long-term stable performance. After two months, the 1%BGCO sensor still maintains 92% of the initial value with a good stability, but no clear change of the 0%BGCO because of its low sensitivity (Fig. 6c).

It is practical to investigate the sensing performance of the sensors at differently humid conditions because the humidity could greatly deteriorate the sensing property of gas sensors. This has been investigated and the obtained results are shown in Fig. 6d.

The responses are maintained at around 150 in the relative humidity range of 30-50 %, but then decreases gradually with the further increase of the relative humidity. The response can still retain at 101.8 when exposed to 100 ppm of ethanol as the relative humidity reaches to 80 %, indicating that the 1%BGCO sensor can work at a relatively high humidity up to 80% for the detection of ethanol.

Fig. 6. (a) and (b) Dynamic resistance curves of the 0%BGCO and 1%BGCO sensors toward 100 ppm ethanol at 120 ℃; (c) Response stability of 0%BGCO and 1%BGCO sensors toward ethanol at 120 ℃ lasting for 10, 20, 30, 40, 50, and 60 days; (d) sensing performances of 0%BGCO and 1%BGCO sensors at different humidity with a concentration of 100 ppm ethanol gas 120 ℃.

The selectivity and cross-responses of 0%BGCO and 1%BGCO sensors to different gases (all with a volume of 100 ppm) including acetone (C_2H_6CO), isopropanol ($(CH_3)_2CHOH$), benzene ($C_6H_5CH_3$), ammonia (NH_3), trimethylamine (C_3H_9N) and NO_2 were tested at 120 °C. The obtained results are shown in Fig. 7a, which clearly indicates that the gas sensors are more sensitive to ethanol than the other gases as well as oxidizing gas of NO_2, especially for 1%BGCO sensor (Fig. 7a). According to the literature [63], the incorporation of Bi dopant can promote the redox reaction, whereas the MOSCs can act as the catalyst. Therefore, the incorporation of Bi in BGCO provides the obtained sensing material with a superior catalytic selectivity for the redox reaction between chemisorbed oxygen and ethanol molecules.

It is well-known that gas sensing performance is related to surface chemisorption and catalytic reaction. The sensing mechanism based on the changes of conductivity is mainly originated from the interaction between the adsorbed gaseous molecules and sensing materials as well as the reactions between the absorbed target molecules and oxygen molecules on the surface of sensing material. Therefore, the sensing performance of MOSCs is closely related to their composition, electronic structure, crystallinity and crystal size, as well as surface morphology, which significantly affect their capacities of adsorbing target gas and oxygen ions on the surface. When the 1%BGCO sensor are exposed to air, oxygen molecules (O_2) will be chemically

adsorbed onto the surface of the sensing materials to form oxygen ions (O^-) through binding free hot electrons from the conductance band (E_c) of 1%BGCO nanohybrids. The rGO nanosheets has a high electron mobility (μ), and could act as a medium to accept electrons. This facilitates the migration of carriers during the catalytic process, thus promoting the enhancement of sensing performances [31,32]. In this 1%BGCO nanohybrids system, when the sensing material was exposed to ethanol vapor gas, the ethanol molecules (CH_3CH_2OH) can react with the adsorbed oxygen species on the surface. Thereafter, the electrons are released back to the E_c and thereby the sensor resistance is increased greatly.

To further study the electron transfer behavior in the 1%BGCO nanohybrid system, UPS analysis was carried out. As shown in Fig. 7b, the cut off energy of 1%BGCO nanohybrids is 16.93 eV, indicating that the work function of the 1%BGCO nanohybrids is 4.27 eV, which facilitates the transportation of electrons [64]. On the other hand, when the Bi-doped rGO/Co_3O_4 nanohybrids are formed, conduction electrons of Bi-doped rGO grains are obtained from Co_3O_4 (if holes, to follow the opposite direction) to balance Fermi level (E_f), thus forming an electron depletion layer (EDL) at the interface Bi-doped rGO/Co_3O_4 and consequently increasing the R_a, according to the energy band diagram as schematically illustrated in Figs. 7c and d. The processes can be expressed using the following two reactions (2) and (3): [65].

$$O_2(ads) + 2e^- \rightarrow 2O^-(ads) \quad \text{..... (2)}$$

$$CH_3CH_2OH(ads) + 6O^-(ads) \rightarrow 2CO_2(ads) + 3H_2O(ads) + 6e^- \text{.....(3)}$$

Fig. 7. (a) The selectivity of the sensors based on 0%BGCO and 1%BGCO to different gases with a concentration of 100 ppm at 120 ℃; (b) UPS spectrum of 1%BGCO nanohybrids; (c) the energy band structure before contact of rGO and Co_3O_4 and (d) the energy band structure after contact of rGO and Co_3O_4.

4. Conclusions

In summary, the Bi-doped rGO/Co_3O_4 (BGCO) nanohybrids have been rationally designed and successfully synthesized via one-step solvothermal process, and their

ethanol-sensing performances were investigated. Specifically, the 1%BGCO sensor shows the superior sensing response of 150 at 120 ºC towards 100 ppm ethanol, a low detection limit (500 ppb). Moreover, the BGCO sensor shows excellent selectivity to ethanol compared to other organic volatile gases. The excellent gas sensing performance of 1%BGCO is mainly attributed to the appropriate content Bi and synergistic effect between Bi and rGO/Co_3O_4 system. Additionally, incorporation of Bi dopant can promote the redox reaction, whereas the MOSCs act as the catalyst. Thus, this study provides a new strategy for using the Bi-doped rGO/Co_3O_4 for ethanol sensing.

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Conflicts of interest

There are no conflicts to declare

Note

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643 **Fig. 1.** (a) Illustration of the synthesis process of flower shaped Bi-doped rGO/Co_3O_4 nanohyrbids; (b) low-
644 magnification SEM and (c) high-magnification SEM of Bi-doped rGO/Co_3O_4 nanohyrbids; (d) low-magnification
645 TEM and (e) HR-TEM image of Bi-doped rGO/Co_3O_4 nanohybrids; the corresponding SEM-EDX elemental
646 mapping of the selected area (f - i).
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650 **Fig. 2.** XRD patterns of 0%BGCO composite and BGCO nanohybrids of 1%BGCO, 3%BGCO and 6%BGCO.
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654 **Fig. 3.** XPS spectra of Bi-doped rGO/Co_3O_4 nanocomposites: (a) C 1s, (b) O 1s, (c) Co 2p and (d) Bi 4f, respectively.
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658 **Fig. 4.** Sensing performances of the gas sensors toward 100 ppm ethanol gas at different operating temperatures.
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662 **Fig. 5.** (a) The initial resistance alteration trend of the Bi-doped rGO/Co_3O_4 (BGCO) nanohybrids induced by the
663 proportion of Bi dopant at the different temperature from 80 to 200 °C; (b) Dynamic resistance changes of the
664 0%BGCO and 1%BGCO sensors when exposed to various ethanol gas toward 0.5-500 ppm ethanol at 120 ℃,
665 respectively; (c) Continuous resistance curves of the 0%BGCO and 1%BGCO sensors to various concentrations of
666 ethanol at 120 ℃; (d) The initial resistances (R_a) of the 0%BGCO, 1%BGCO, 3%BGCO and 6%BGCO sensors
667 varied with the ethanol concentration at 120 ℃, respectively; (e) The response *vs* gas concentrations for 0%BGCO
668 and 1%BGCO sensors, respectively; (f) Repeatability test of the 0%BGCO and 1%BGCO nanocomposite sensors
669 to 100 ppm of ethanol at 120 ℃.
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673 **Fig. 6.** (a) and (b) Dynamic resistance curves of the 0%BGCO and 1%BGCO sensors toward 100 ppm ethanol at
674 120 ℃; (c) Response stability of 0%BGCO and 1%BGCO sensors toward ethanol at 120 ℃ lasting for 10, 20, 30,
675 40, 50, and 60 days; (d) sensing performances of 0%BGCO and 1%BGCO sensors at different humidity with a

concentration of 100 ppm ethanol gas 120 ℃.

Fig. 7. (a) The selectivity of the sensors based on 0%BGCO and 1%BGCO to different gases with a concentration of 100 ppm at 120 ℃; (b) UPS spectrum of 1%BGCO nanohybrids; (c) the energy band structure before contact of rGO and Co_3O_4 and (d) the energy band structure after contact of rGO and Co_3O_4.