Polypyrrole-Bonded Quaternary Semiconductor LiCuMo$_2$O$_{11}$−Graphene Nanocomposite for a Narrow Band Gap Energy Effect and Its Gas-Sensing Performance

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ABSTRACT: In this study, we demonstrate the fabrication and characterization of a new quaternary semiconductor nanocomposite of LiCuMo$_2$O$_{11}$/graphene oxide/polypyrrole (LCMGP) via a hydrothermal method and testing of an NH$_3$ and H$_2$SO$_4$ sensor operating in gaseous states at room temperature. We used X-ray diffraction, transmission electron microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy to characterize the properties of LCMGP nanostructures. Our sensor is capable of detecting NH$_3$ and H$_2$SO$_4$ and quantifying their concentration in the gas flow. These results have been confirmed by exposing the sensor to different concentrations of NH$_3$ and H$_2$SO$_4$ (100–1000 ppm). The obtained results confirm the exceptional sensing properties of the graphene−polymer-combined quaternary semiconductor nanocomposite related to the oxidation−reduction process that can be used for detection, identification, and quantification purposes.

1. INTRODUCTION

Solid-state gas sensors, which can identify toxic gases and natural fumes with high sensitivity, have extraordinary potential in numerous fields, for example, ecological checking, medicinal diagnosis, and industrial wastes.1,2 Metal oxide semiconductor gas sensors have great promise in scalability. Conjugate polymers embed with metallic, semiconducting, and dielectric nanoparticles.3 Most of the metal oxide sensors operate at high temperatures. At room temperature, conducting polymer sensors have high sensitivities and short response times.3 Mechanical, electrical, and optical properties of nanoparticles, such as nonlinear optical conductance, photoluminescence, electro luminescence, and photoconductivity, can improve by inserting conducting polymers.2,5−8

Among leading polymers, polypyrrole as a p-type semiconductor is often used for the hole-transport layer in OLED and OSC for the framework materials in different sensors.10 Polypyrrole mixed with graphene as a functioning material has been set up for application in gas thin-film sensors. Graphene has numerous excellent electrical properties since it is an allotrope of carbon with a single two-dimensional (2D) layer of sp$^2$-hybridized carbon atoms.11−14 Graphene, graphene oxide (GO), and reduced graphene oxide (rGO) as materials have great application potential for sensing. The two-dimensional structure of graphene has a higher sensing territory for every unit of volume and less noise than other solid-state sensors. There is much literature providing details of the use of graphene and graphene-related materials for observing gases and fumes.14−16 Monitoring and controlling air pollutants have been a huge demand for human health.
because these pollutants cause problems such as chronic lung diseases, which are associated with the inhalation of ammonia, and excessive deposition of ammonia to ecosystems, resulting in nutrient imbalances and eutrophication and causing serious environmental problems. Sulfuric acids are lethal compounds; they harm human health when there is an enormous concentration of them.

In this way, the fabrication of devices (or sensors) to identify ammonia and sulfuric acid is significant. There are many ammonia sensors that have been developed based on SnO$_2$, WO$_x$, or TiO$_2$; they have good sensitivity and response times, but they usually require a vacuum and are very expensive. With the means to lessen these costs, many scientific groups have created gas sensors that are dependent on conducting polymers. The benefits of the polymer-based sensors include simple manufacture, low power usage, and room-temperature activity. PPy has high electrical conductivity, good environmental stability, and simple synthesis; it processes and demonstrates gas-sensing features at room temperature.

We recently announced that graphene/polymer-based sensors can identify both ammonia and CO$_2$. The nanocomposites combine two or several different components to improve the specific surface area of the modified material, resulting in an increase in the number of active sites and a better efficiency for the adsorption rate of gas, thus enhancing gas-sensing properties. In this study, we fabricated a polypyrrole-bonded quaternary semiconductor LiCuMo$_2$O$_{11}$–graphene nanocomposite for gas sensing. We have specifically seen that polypyrrole + GO + LiCuMo$_2$O$_{11}$ sensors are sensitive to NH$_3$ and H$_2$SO$_4$. We need a sensor that is more sensitive to specifically recognize the gas, which would be the LCMGP sensor. Hence, we explored planning of potential LCMGP sensors for specifically recognizing ammonia. In this work, we report the fabrication of graphene–polymer-based nanocomposites, polypyrrole/GO/LiCuMo$_2$O$_{11}$, and LiCuMo$_2$O$_{11}$–GO for H$_2$SO$_4$ and NH$_3$ sensing. We also compare the gas-detecting properties of LCMGP and LiCuMo$_2$O$_{11}$–GO composite films.

2. RESULTS AND DISCUSSION

2.1. Characterization. In Figure 1, the prominent peaks at 20.08, 21.05, 28.36, 30.00, 30.90, 33.92, and 35.51° for both samples indicate the formation of LiCuMo$_2$O$_{11}$ with the crystallographic planes of (002), (211), (220), (131), (113), (312), and (410), respectively. Two smaller peaks at smaller angles of 13.98 and 17.23° with (110) and (021) lattice planes were also observed. However, no observable peak related to the GO was found in the composite X-ray pattern (near ~26°), perhaps because of the less-ordered stacking of the GO sheets.

Figure 2 shows the EDS spectra of the LCM. EDS data indicate the near stoichiometry of Cu and O.

Figure 3a is the SEM image of the as-synthesized pristine LCM (LiCuMo$_2$O$_{11}$) nanoparticles. The nanoparticles with some larger agglomerates are observed in the image. Figure 2b is the image of as-synthesized LCM (LiCu$_{0.5}$Mo$_2$O$_8$). The image of the LCMGP composite sample is in Figure 2c. In this image, the well-incorporated LCM nanoparticles over the GO and polymer are observed. We carried out transmission electron microscopy to confirm the morphology and phase of the composite. Figure 4a,b shows the low-magnification images of the LiCuMo$_2$O$_{11}$ nanoparticles. Figure 4c,d shows the LiCu$_{0.5}$Mo$_2$O$_8$–G–PPy and 4 the LiCu$_{0.5}$Mo$_2$O$_8$–G–PPy embedded in the GO sheets, respectively. The pattern indicates the polycrystalline nature of the nanoparticles.

Raman spectra of the as-prepared graphene oxide (GO)–polymer composite and the LCM samples were carried out in the range of 200–2000 cm$^{-1}$, as shown in Figure 5. For GO, the D and G peaks at 1350 and 1595 cm$^{-1}$ were observed. The G band corresponds to the bond stretching of graphitic sp$^2$ carbon atoms. The D band originates from the lattice defect and lattice distortion, while the D′ band is attributed to intervalley and intravalley scattering processes. For the composite sample along with the D and G bands, additional peaks at 301, 812, and 850 cm$^{-1}$ were recorded. These peaks are related to LiCuMo$_2$O$_{11}$ and similar quaternary materials. However, the D and G bands for the GO and composite had different relative intensity ratios. Graphene-related materials...
usually possess disorders and structure-related defects, which result from the sp³ C atoms incorporated in the lattice. The D band is related to the presence of this disorder, whereas the G band correlates to the sp²-hybridized C atoms in its regular honeycomb lattice. 35 Moreover, hydrothermal reduction affects the incorporation of hydrogen atoms in the composite system, which shrinks the sp² domains; so, it can be inferred that GO has been reduced under the elevated conditions of hydrothermal treatment. 36,37 This result is an indication of the semiconducting LCM–graphene composite phase with the presence of PPy. The LCM–graphene after PPy surface decoration could be a promising approach to LCMGP with good electrical conductivity and mechanical stability due to the presence of graphene, making this material highly effective and selective in gas detection applications.

Values of band gap (E₉) energy of LCM, LCMG, and LCMGP structures were resolved from DRS studies as shown in Figure 6. DRS data were recorded over the absorption
To analyze the electronic structure and oxidation states of the constituent elements present in the LCMGP composite, we recorded the high-resolution X-ray photoelectron spectra, which are depicted in Figure 7. The survey scan of the LCMGP sample is shown in Figure 7a. By deconvolution, one peak is present for Li 1s at 54.68 eV, as seen in Figure 7b. C 1s spectra yield peaks at 284.6, 286.8, and 288.4 eV; these can be ascribed to C−C, C−O, and C==O for the GO counterpart in the composite (Figure 7b). It is evident that, except for the C−C peak, the other two oxygen-containing peaks have relatively low intensities, which indicate the successful hydrothermal reduction of GO, as had already been established by the Raman spectral analysis. Similarly, the N 1s spectrum in Figure 7d has one peak at 398.1 eV. In Figure 7e, the O 1s peak at 530.7 eV strongly indicates the presence of O$^{8-}$. Figure 7f shows the Cu 2p spectrum with two distinct symmetric peaks at 934.3 and 954.08 eV for Cu 2p$_{1/2}$ and 962.08 eV for Cu 2p$_{3/2}$, respectively. Peak splitting of 20.0 eV indicates that Cu is in the +1 state (Figure 7f). In the Mo 3d range, two peaks were detected at 232.28 and 236.08 eV with respect to Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$, which shows that Mo$^{4+}$ has reached a maximum of 3.35 eV (Figure 7f). Thus, all the elements in the composite material have the desired chemical states, validating the formation of a pure phase.

2.2. Sensing Performance. Figure 8 shows outcomes of electrochemical responses of NH$_3$ with LCM, LCMG, and LCMGP electrodes, respectively. To analyze electrical properties (current versus potential curve), when the LCM electrode was introduced with NH$_3$, a significant peak current was found, and then the LCMG electrode was introduced with NH$_3$ gas. The magnitude of the anodic peak current of this electrode increased when the potential increased. Thus, the best consequence of this electrochemical response was delivered by LCMG, which increased the electrochemical current with the expanding potential because of the development of an n-type semiconductor in the p–n junction. This indicated that the electrode occupied a great capacity to transfer electrons efficiently as the combined sample. The results for the measurements of 10 cycles according to the ammonia concentration at 100, 200, 300, 400, and 500–1000 ppm are shown in Figure 9. With ammonia in the chamber, the sensor conductivity increased rapidly, reaching the response value in about 50 s and recovering its initial value in about 45 s, as in Figure 9. The increase in conductivity of the LCMGP sensor is due to the absorbed oxygen species of the gas-sensing material and release of the electrons back to the material, which is an n-type semiconductor in the p–n junction. Meanwhile, NH$_3$ is a highly active and electron-donating free radical; electrons generated by the absorption of ammonia on the surface of the LCMGP film eliminated some of the holes by coupling with each other, resulting in an increase in the LCMGP conductivity. When the LCMGP film was slightly heated, NH$_3$ molecules in LCMGP rapidly evaporated from the film surface, leaving holes along the backbone of the polymer. In such a fashion, the concentration of major charge carriers rapidly increases, whereas the resistance of the sensor decreases. Embedding GO in LCM improved the sensing properties of the LCMGP films. NH$_3$ as a reducing agent, has a lone electron pair that can be easily donated to the n-type GO sheets, thus increasing the conductivity of the GO devices, whereas PPy has helped improve the adsorption efficiency of gas molecules (including...
because of the larger effective surface areas with many sites. Moreover, the addition of both GO and PPy in the LCMGP composite films created not only numerous nanoheterojunctions but also polymer “bridges” for electron transferring. These bridges are clearly revealed by the TEM micrograph, as shown in Figure 3.

Figure 7. (a) XPS spectra of LCMGP, (b) Li 1s, (c) C 1s, (d) N 1s, (e) O 1s, (f) Cu 2p, and (g) Mo 3d.
Figure 10 shows outcomes of electrochemical responses of H$_2$SO$_4$ vapor with LCM, LCMG, and LCMGP electrodes, respectively. It showed that when the LCMGP electrode was introduced with H$_2$SO$_4$ vapor, the anodic peak current of this electrode decreased significantly rather than that of LCM and LCMG. This phenomenon happened when adsorbed oxygen could be on the LCMGP, which traps conduction band electrons and forms a depletion region, and due to the oxidizing agent vapor, the sensor resistivity increases.

From Figure 11, it is shown that the current density linearly decreases with the increased H$_2$SO$_4$ vapor concentration in 100, 200, 300, 400, and 500–1000 ppm within 50 s, and when exposed to air, the LCMGP resistance quickly recovered to the baseline.

Figure 12 shows the long-term stability of the LCMGP sensor with 100 ppm NH$_3$ and H$_2$SO$_4$ vapor. The stability lasted for over 30 days, and the LCMGP sensor has no significant change among the measurements.

Figure 13a,b shows the link between the current density and NH$_3$ and 13H$_2$SO$_4$ concentrations, respectively, shown in the calibration curve, where the linear range and the LOD 50 ppm in the LCMGP sensor are also shown.

Figure 8. NH$_3$ gas-sensing performance based on cyclic voltammograms of (a) LCM, (b) LCMG, and (c) LCMGP samples.

Figure 9. Concentration dependence of NH$_3$ gas detected by the LCMGP sample.

Figure 10. H$_2$SO$_4$ vapor-sensing performance. Sensing performance based on cyclic voltammograms of (a) LCM, (b) LCMG, and (c) LCMGP samples.
Figure 14 shows the temperature dependency of the LCMGP sensor, which shows that it works well in 20−40 °C.

Figure 13. Relationship between the current density and (a) NH$_3$ and (b) H$_2$SO$_4$ concentrations shown in the calibration curve with the LCMGP sensor.

Scheme 1. Synthesis Process of LiCuMo$_2$O$_{11}$/Graphene Oxide/Polypyrrole (LCMGP)

Scheme 2. Formation Mechanism of LiCuMo$_2$O$_{11}$/Graphene Oxide/Polypyrrole (LCMGP)
2.3. Gas-Sensing Mechanism. LCMG shows n-type conductivity, and Ppy shows the p-type conductivity. When LCMG was introduced into Ppy, LCMG electrons and Ppy holes were transported in opposite directions. As a result, a p−n junction was formed. In air, a depletion region formed due to absorbed oxygen on the LCMGP surface and due to captured electrons from its conduction band. Moreover, a new depletion layer between LCMG and Ppy is responsible for the resistance of the LCMGP in air ($R_a$). The electrons return to the LCMGP when NH3 gas molecules react with the absorbed oxygen species. Thus, the depletion layer becomes thin, and the resistance of the LCMGP sensor decreases in the NH3 gas.40 In the case of H2SO4 vapor, the resistance increases in the sensor because of the n-type semiconductor in the p−n junction introduced to the oxidizing agent (Scheme 3).

3. CONCLUSIONS

In conclusion, new, unique quaternary semiconductor nanocrystals of LiCuMo2O11/graphene oxide/polypyrrole, LCMG, and LCM were effectively incorporated by using a simple hydrothermal process, which is cost effective, more environment-friendly, and with less chance for contamination with impurities. At room temperature, it shows the strong interaction between polypyrrole, graphene, LiCuMo2O11, and gas molecules with low energy consumption and simple device formation. The response, sensing performance, and selectivity of LCMGP for NH3 and H2SO4 vapor were significantly improved. These results will lead to meaningful progress in the development of an NH3 sensor with a great performance by showing an improved response time within 50 s and recovering time of about 45 s in LCMGP.

4. EXPERIMENTAL SECTION

4.1. Materials. Copper (II) chloride dihydrate (CuCl2·2H2O, 99%), lithium (II) chloride hexahydrate (LiCl2·6H2O, 99%), polypyrrole (Ppy), and Na2MoO4·2H2O (99%) were purchased from Korea. Only deionized water was used in the synthesis procedure. All the chemicals were analytical grade and used without further purification.

4.2. Synthesis of LCMGP Nanocomposites. First, GO was synthesized by a modified Hummer’s method. Then, 10 mg of GO was ultrasonicated in 40 mL of ultrapure deionized water for 1 h. Then, 1 mmol of copper (II) chloride dihydrate, 0.5 mmol of lithium (II) chloride hexahydrate, and 0.5 mmol of Na2MoO4·2H2O were dissolved in the dispersion and stirred for 30 min. Polypyrrole was dissolved in the NMP (N-methyl-2-pyrrolidione) solution and mixed with the main solution. After being fixed at pH 8.00, the grayish mixture was then transferred into a Teflon-lined stainless-steel autoclave at 180 °C for 10 h. After the autoclave was cooled, the samples were taken out, separated, and washed with deionized water and ethanol. The black product was then dried at 60 °C for 8 h. We carried out a similar experiment without using GO to prepare an LCM (LiCuMo2O11) sample (Scheme 1). Solution intercalation is based on a solvent system in which the polymer is solubilized and graphene can swell. Graphene can be dispersed easily in NMP (N-methyl-2-pyrrolidione), owing to the weak forces that stack the layers together. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form the nanocomposites with graphene and the semiconductive material (Scheme 2).28

4.3. Characterization. We examined the phase structure and purity of as-synthesized products by X-ray diffraction (XRD; Rigaku, X-ray diffractometer) with Cu Kα radiation ($\lambda = 1.5406 \text{ Å}$) at 40 kV, 30 mA over 2θ units for 20–70°. We investigated the morphologies of the obtained samples using field-emission scanning electron microscopy and EDS (energy-dispersive X-ray spectroscopy) analysis provided by an SEM (scanning electron microscope) (JSM-76710F, JEOL, Tokyo, Japan), a transmission electron microscope (TEM) (JEM-4010, JEOL, Tokyo, Japan), and a high-resolution TEM (HRTEM) (JSM-76710F, JEOL, Tokyo, Japan) operated at a 300 kV accelerating voltage. We did X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), and Raman spectroscopy (RAMAN) analyses by using WI Tec Alpha 300 series.

4.4. Gas Sensor Fabrication and Measurements. The fundamental fabrication process is as follows:29 As-acquired
semitecting LCM, LCMG, and LCMGP were slightly ground with ethyl cellulose in a agate mortar to form a gas-sensing paste. The paste was cast on the middle position of a plastic fiber, covered on one side by aluminum foil and on the other side by copper foil, dried for a few minutes in the air, and followed by sintering at 100 °C for 1 h. The paste was coated by using manual physical coating. The dimension of the coating was 5 mm, and the thicknesses of the coating were about 0.1, 0.3, and 0.5 mm. The coatings for all samples had uniform thickness and dimensions. We measured gas-sensing properties by using voltammetry (PG201, potentiotstat, galvanostat, Volta Lab, radiometer, Copenhagen). We estimated the current that flows between working and auxiliary electrodes. Current peaks observed at explicitly connected voltages were direct results of explicit redox responses running on the working electrode surface. Cyclic voltammetry (CV) includes cycling capability of the reference electrode. These were then carefully obtained by an analog-to-digital converter (ADC) transformation organizer. The voltage ramp was intended to have a variable slow rate, ranging from 0.1 up to 10 mV/s. We tested the sensors at different working temperatures between 25 and 40 °C in increments of 2 °C. The temperature was limited by an artistic radiator coupled to a power source that uses a type-K thermocouple located inside the sensor chamber as input for the relevant vital controller (PID). The mechanical grade of NH3 and H2SO4 vapor (>99.999%) was weakened using air in the range of 50–1600 ppm at a gas flow of 200 ppm. The sensor reaction (SRg) was characterized as shown in eq 1:

\[ S_R = \frac{(R_g - R_a)}{R_a} \]  

while the sensitivity (S) of the sensor was characterized as

\[ S = S_R \times 100 \% \]  

where \( R_g \) is the resistance of the sensor in the presence of NH3 and H2SO4 vapor, and \( R_a \) denotes the obstruction of the sensor under dry air.\(^{[14]}\) The response and recuperation times were characterized by the time required to achieve 90% of the obstruction upon exposure to CO2 and air, respectively.\(^{[30]}\)

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**Notes**

The authors declare no competing financial interest.

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