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Enhanced Photocatalytic Degradation of 2-Butanone Using Hybrid Nanostructures of Gallium Oxide and Reduced Graphene Oxide Under Ultraviolet-C Irradiation

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Received: 20 April 2019; Accepted: 10 May 2019; Published: 15 May 2019

Abstract: Hybrid nanostructures made of gallium oxide (Ga_2O_3) and reduced graphene oxide (rGO) are synthesized using a facile hydrothermal process method, where the Ga_2O_3 nanostructures are well dispersed on the rGO surface. The formed Ga_2O_3 -rGO hybrids are characterized via Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), a diffuse reflectance Ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer, Brunauer–Emmett–Teller (BET), and photoluminescence (PL). Gas chromatography mass spectrometry (GC-MS) was used for analyzing volatile organic compounds (VOCs). The photocatalytic activity of the hybrid nanostructures is evaluated via the degradation of the 2-butanone, representing the VOCs under 254-nm radiation in the atmosphere. That activity is then compared to that of the Ga_2O_3 and commercial TiO_2 -P25. The Ga_2O_3 -rGO hybrid shows enhanced photocatalytic degradation of 2-butanone compared to Ga_2O_3 and TiO_2 -P25, which is attributed to the enhanced specific surface area. The results indicate that the Ga_2O_3 -rGO hybrid could be a promising method of enhancing photocatalytic activity and thereby effectively degrading VOCs, including the 2-butanone.

Keywords: gallium oxide (Ga_2O_3); reduced graphene oxide (rGO); 2-butanone; volatile organic compounds (VOCs); photocatalytic oxidation (PCO); hydrothermal process; ultraviolet C (UVC) irradiation

1. Introduction

Volatile organic compounds (VOCs) with high vapor pressures at room temperature are everywhere because they are emitted from a wide range of consumer products, building materials and adhesives. Many VOCs are toxic and adversely affect the human body in both indoor and outdoor environments [1–3]. As human beings spend more time at home and in the work place, the control of VOCs in indoor environments is a critical concern [4]. While absorption and incineration methods have traditionally been used to remove VOCs, photocatalytic oxidation (PCO) using metal oxide semiconductors has emerged as an attractive alternative due to their low cost and non-toxicity [5]. The photo-induced generation of electron-hole pairs promotes reduction and oxidation upon the surface of the semiconducting transition metal oxides [6,7]. Among various semiconductors, TiO_2 is preferred in terms of its photocatalytic activity under UV light absorption [8]. It has been widely applied to

photocatalysts due to its nontoxicity, low cost and high reactivity. Nevertheless, its long-term instability greatly limits the practical applications, due to the deactivation of the photocatalytic sites resulting from the accumulation of a stable intermediate on the TiO_2 surface from the oxidation of aromatics in a dry atmosphere [9,10]. Recently, interest has increased in Ga_2O_3 ($E_g = 4.8$ eV) as a wide band gap semiconductor with its high redox ability and long-term stability, compared to commercial TiO_2 ($E_g = 3.2$ eV), for the degradation of aromatic pollutants, such as the benzene series and toluene [11–15]. In addition to its strong redox ability, due to a higher conduction band ($E_{cb} = -1.55$ eV) and lower valence band ($E_{vb} = 3.25$ eV) than TiO_2 ($E_{cb} = -0.5$ eV, $E_{vb} = 2.7$ eV) [16], Ga_2O_3 is composed of a valence band of O 2p orbitals and a dispersive conduction band of s and p orbitals from the p-block metal oxide atom, which promotes the mobility of photo-induced electrons in the Ga_2O_3 [13,17,18]. This improves the separation efficiency of the photo-induced electrons and holes, resulting in an increase in photocatalytic activity. Advanced strategies to enhance photocatalytic activity have been reported via the formation of a heterogeneous structure with noble metals, semiconductors and/or graphene allotropes [19–22]. Among these materials, the addition of graphene oxide has been demonstrated to be an effective method due to its large specific surface area and excellent charge carrier mobility [5,21–26]. However, to the best of our knowledge, few studies thus far have looked at the photocatalytic degradation of gas-phase contaminants for the purification of enclosed atmospheres with the use of Ga_2O_3 -reduced graphene oxide (rGO) hybrids under ultraviolet C (UVC) irradiation. The present study focuses on the photocatalytic degradation of 2-butanone, which is used in adhesives and cleaning agents, as an indoor VOC source [27,28]. Herein, we report on the synthesis of the Ga_2O_3 -rGO hybrids formed using the hydrothermal method, and the photocatalytic degradation of 2-butanone is discussed as compared to TiO_2 and Ga_2O_3 .

2. Results and Discussion

Figure 1a shows the Field emission scanning electron microscope (FESEM) images of the rGO, Ga_2O_3 -rGO hybrids and Ga_2O_3 . The results showed that the rGO flakes were wrinkled, partially folded and stacked. This was attributed to the weakening of the hydrogen bonding network between the flakes and the generation of various structural defects during the hydrothermal process [29,30]. The images of the Ga_2O_3 -rGO hybrids showed that the Ga_2O_3 nanorods were well dispersed and uniformly anchored on the rGO. The chemical bonds between the Ga_2O_3 and rGO were discussed via the Fourier transform infrared spectra (FTIR) analysis, thereby promoting the charge transfer of photo-excited carriers from the Ga_2O_3 to rGO and eventually enhancing the photocatalytic activity. The magnified image (inset of Figure 1a) of the Ga_2O_3 revealed that the Ga_2O_3 possessed a mesoporous surface that could contribute to the improvement of photocatalytic performance [31,32]. Figure 1b shows the X-ray diffraction (XRD) patterns of the pristine GO, rGO, Ga_2O_3 -rGO hybrids and Ga_2O_3 nanorods. The pristine GO showed a very strong intensity at $2\theta = 10.55^\circ$, representing a typical inter-planar d-spacing (0.84 nm) of the GO stacks [33]. After the GO was reduced to rGO via the hydrothermal process, the peaks originating from the GO d-spacing diminished, but the broad peak at $2\theta = 24^\circ$ appeared, corresponding to the inter-planar d-spacing (0.37 nm) of the rGO [34]. The decreased d-spacing in the rGO compared to the GO was attributed to the removal of oxygen-containing functional groups, which also indicated the reestablishment of the sp^2 carbon network in the rGO [35]. The results also revealed that the hydrothermal process was an effective method for the reduction of a GO without strong acidic conditions [25,36]. For Hybrid-2, the most noticeable peaks were indexed to the β - Ga_2O_3 with a broad rGO peak. As the ratio of Ga_2O_3 over rGO increased, the peaks representing Ga_2O_3 increased while the broad peak representing rGO diminished, as shown with Hybrid-1. These results showed that the Ga_2O_3 retained its crystal structure even after the hydrothermal process and dispersion on the rGO.

Figure 2 shows the FTIR spectra in the wavenumber range from 4000 to 650 cm^{-1} , along with a schematic drawing representing the responsible chemical bonds of the pristine GO, rGO, Ga_2O_3 -rGO hybrids and Ga_2O_3 . The spectrum of the pristine GO showed typical transmittance peaks. The bands in the range of 1700 to 1000 cm^{-1} were associated with oxygen functional groups such as the carboxyl

groups, hydroxyl groups and epoxy groups on both sides of the GO surface [24,36,37]. These bands of oxygen functional groups in the GO significantly decreased after the formation of rGO via the hydrothermal process [34,38]. This revealed that most oxygen functional groups had been removed from the GO surface while the GO was reduced [29]. These eliminated peaks associated with the oxygen functional group were recovered in the spectra of the Ga_2O_3 -rGO hybrids. The presence of these oxygen functional groups indicated the formation of the chemical bonds between the Ga_2O_3 nanorods and the rGO, which allowed the carrier transfer from the Ga_2O_3 to rGO, and thereby enhanced the photocatalytic activity.

Figure 1. (a) FESEM images of rGO, Hybrid-2, Hybrid-1 and Ga_2O_3 (the scale bar is 3 μm); the scale bar of the inset is 1 μm), and (b) XRD patterns of the pristine GO, rGO, Hybrid-2, Hybrid-1 and Ga_2O_3 with the reference from Joint Committee on Powder Diffraction Standards (JCPDS) card no. 760573 (monoclinic Ga_2O_3 phase).

Figure 2. FTIR spectra of pristine GO, rGO, Hybrid-2, Hybrid-1 and Ga_2O_3 , along with schematic chemical structure of GO, rGO and Ga_2O_3 -rGO hybrids.

The Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption of the Ga₂O₃ and hybrids were characterized in the wavelength range of 240 to 1000 nm, and the results are shown in Figure 3a. These results showed that the Ga₂O₃ was transparent in the visible light and ultraviolet C. As the ratio of the rGO over Ga₂O₃ increased, the overall absorption from the visible and near infrared (400–1000 nm) into the UV wavelength regions (260 nm ~) increased. In detail, a red shift in the absorption edge was observed in Hybrid-1 compared with Ga₂O₃, indicating a narrowing of the Ga₂O₃ band gap due to the coupling in the Ga₂O₃-rGO hybrids. The inset in Figure 3a shows the Tauc plot for the Ga₂O₃ and Ga₂O₃-rGO hybrids, where $(ah\nu)^2$ was plotted against the photo energy ($h\nu$), and the band gap energies were calculated from the extrapolated lines as shown. The optical energy band gap of the Ga₂O₃ and Hybrid-1 was calculated as 4.63 and 4.25 eV, respectively. However, it was difficult to calculate the exact optical energy band gap for Hybrid-2 because the large amount of rGO induced a very significant background absorption in the range of 400 to 800 nm. Also, while the absorption of Hybrid-1 around 254 nm was comparable to that of Ga₂O₃, the absorption of Hybrid-2 (a greater rGO ratio) was greatly reduced. This indicated that the photogenerated electrons from the Ga₂O₃ in Hybrid-1 were able to move along the rGO and then interact with the absorbed O₂ to produce OH[•], which facilitated the strong oxidative ability to degrade the organic pollutants. In this process, the rGO acted as an electron collector and transporter to effectively interfere with the electron-hole recombination and extend the lifetime of the photogenerated charge carriers formed by Ga₂O₃, leading to the higher photocatalytic efficiency in Hybrid-1. However, with the excessive addition of rGO (Hybrid-2), the rGO nanosheets blocked the UVC light from reaching the surface of the Ga₂O₃, resulting in the lower generation rate of the charge carriers. Figure 3b shows the PL emission spectra of the Ga₂O₃, Hybrid-1 and -2 when excited at 260 nm. A broad emission band ranging from 300 to 500 nm was observed in the Ga₂O₃ spectrum, while considerable PL quenching was observed in the hybrids with higher ratios of rGO over Ga₂O₃. The decreased intensity of the PL emission might have been due to the reduction in the recombination process of electrons and holes because of the charge carrier transfer from the excited Ga₂O₃ to the rGO [23,39,40]. To further discuss the charge carrier transfer from the excited Ga₂O₃ to the rGO, the PL decay characteristics of the Ga₂O₃ and hybrids were investigated, as shown in the inset of Figure 3b. The results were fitted to multi-exponential curves to derive the PL decay parameters that were obtained using Equations (1) and (2) [41]. The lifetime, pre-exponential factors and average lifetime of the Ga₂O₃ and hybrids are summarized in Table 1.

$$f(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}} + A_4 e^{-\frac{t}{\tau_4}} \quad (1)$$

$$\langle \tau \rangle = \sum_{i=1}^n \frac{A_i \tau_i^2}{A_i \tau_i} \quad (2)$$

where A_i denotes the pre-exponential factor, τ_i is the lifetime decay constant, and $\langle \tau \rangle$ is the average lifetime.

For the Ga₂O₃, the fast and slow component of the PL decay had a lifetime of 2.5 ns and 2876 ns, respectively. As the ratio of the rGO over Ga₂O₃ increased, the fast lifetime and average lifetime decreased, but the slow lifetime increased. The analysis revealed that the charge carrier transfer between the excited Ga₂O₃ and rGO was dominated by the fast component. Furthermore, from the fast decay component, the electron-transfer rate could be estimated using Equation (3).

$$k_{et} = \frac{1}{\tau} (Ga_2O_3 - rGO) - \frac{1}{\tau} (Ga_2O_3) \quad (3)$$

The electron-transfer rate of Hybrid-1 was $0.017 \times 10^9 \text{ s}^{-1}$, while that of Hybrid-2 was $0.225 \times 10^9 \text{ s}^{-1}$. This showed that the electron-transfer rate of Hybrid-2 was 13.5 times higher than that of Hybrid-1, while the number of electron-hole pairs was lower in Hybrid-2. Based on this analysis, it was concluded that the chemical bonds between the Ga₂O₃ and rGO were very effective in transferring the photo-excited electrons before the recombination process.

Figure 3. (a) UV-Vis-NIR spectroscopy and (b) PL spectroscopy of Ga_2O_3 and Ga_2O_3 -rGO hybrids at room temperature. The inset in Figure 3a shows a Tauc plot, which is one method of extracting an optical energy bandgap in semiconductors. The inset in Figure 3b shows the normalized PL decay of the Ga_2O_3 and Ga_2O_3 -rGO hybrids, which was measured at the emission wavelengths of 455 nm and 459 nm, respectively.

Table 1. Summary of the fitting parameters for the PL decay components of the Ga_2O_3 and hybrids.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	A_4	τ_4 (ns)	$\langle\tau\rangle$ (ns)
Ga_2O_3	8973	2.5	0		603	110	201	2876	68.3
Hybrid-1	9538	2.4	0		236	126	81	3081	30.7
Hybrid-2	9597	1.6	186	43.6	59	419	49	4171	25.7

The identification of the adhesive component was measured with a GC-MS analysis, which was identified by comparing retention times and mass spectra with library spectra. Figure 4a shows that air, water and 2-butanone were detected before the photodegradation. After UVC irradiation of the 2-butanone for 30 min using a Ga_2O_3 -rGO hybrid (Figure 4b), it was found that air and water were the main by-products. Figure 4c shows the degradation of 2-butanone as a function of exposure time under the 254 nm UVC irradiation time, at intervals of 30 min when different catalysts were used. The TiO_2 -P25, which is known to be a good photocatalyst, was also compared with its counterparts under the identical reaction conditions. With conventional TiO_2 -25, the 2-butanone degraded to 62% within 1 h. On the other hand, the 2-butanone degraded to 93% within 1 h when Ga_2O_3 was used as a catalyst. The hybrids showed a much-enhanced photodegradation efficiency compared to the Ga_2O_3 and TiO_2 . The 2-butanone degraded to 99.9% and 98.2% under the identical conditions when Hybrid-1 and Hybrid-2 were used, respectively. The additional rGO in the Ga_2O_3 played a role as a transfer pathway of the photo-generated carriers. In addition, the rGO provided a much higher specific surface area, improving the photocatalytic performance of the Ga_2O_3 . It was found that Hybrid-1 had a higher specific surface area ($S_{\text{BET}} = 149 \text{ m}^2\cdot\text{g}^{-1}$) than the pure Ga_2O_3 ($S_{\text{BET}} = 3.4 \text{ m}^2\cdot\text{g}^{-1}$) and Hybrid-2 ($S_{\text{BET}} = 36 \text{ m}^2\cdot\text{g}^{-1}$), using the Brunauer–Emmett–Teller (BET) surface area measurement [42,43]. While the additional rGO in the Ga_2O_3 improved the photocatalytic performance via the reasons above mentioned, it adversely degraded the photocatalytic performance due to the lower UVC absorption blocked by excessive rGO [20,34], which could be observed in Figure 3a. This explained the experimental results; the degradation performance of different catalysts was in the order of Hybrid-1 (1 wt. % of rGO) > Hybrid-2 (5 wt. % of rGO) > Ga_2O_3 > TiO_2 -P25. In addition to the photocatalytic activity, the stability and repeatability of the 2-butanone degradation was investigated using Hybrid-1, with the results shown in Figure 4d. The results showed that Hybrid-1 retained its photocatalytic activity even after prolonged operation.

Figure 5 shows the optical transmittance of Hybrid-1 before and after 2-butanone degradation. The transmittance decreased after 2-butanone degradation particularly around 1710 cm^{-1} and 1560 cm^{-1} ,

representing C=O bonding [12] and C=C bonding [44], respectively. This indicated that the decomposed residue of the 2-butanone remained on the Hybrid-1 surface. These residual byproducts on the surface need to be investigated further.

Figure 4. Gas chromatography graph (a) before and (b) after photodegradation under 254 nm UVC irradiation for 30 min. (The inset in (a) is the mass spectrum of 2-butanone, and the inset in (b) is the mass spectra of H₂O and air), (c) photodegradation of 2-butanone under 254 nm UVC irradiation with different catalysts such as TiO₂-P25, Ga₂O₃ and Ga₂O₃-rGO hybrids. TVOC refers to the total volatile organic compounds and a group of a wide range of organic chemical compounds. The guideline below 0.3 mg/m³ provides practical guidance to manage health and safety risks, which are regulated under Health and Safety, and subject to change (inset: Schematic drawing of the photocatalytic reactor), and (d) repeatability test of photocatalytic degradation of Hybrid-1 under 254 nm UVC irradiation at intervals of 15 min.

Figure 5. Optical transmittance of fresh Hybrid-1 and used Hybrid-1 as a function of wavelength.

3. Materials and Methods

3.1. Synthesis of Hybrids

The GO was prepared using a modified Hummers' method [45], and the Ga₂O₃ powder (particle diameter 2.5–6 µm, 99.999%) was purchased from Taewon Scientific Co., Ltd. (Republic of Korea). Ga₂O₃-rGO hybrids were synthesized via a conventional hydrothermal method. First, a GO solution in which the GO (lateral size > 3 µm, 99%) was dispersed in distilled water (DI water, 50 mL) was ultrasonicated for 3 h to obtain uniform dispersions of exfoliated GO. Next, Ga₂O₃ powders were added into the prepared GO solutions. After being vigorously stirred for 2 h, the mixture of Ga₂O₃ and GO solutions was transferred to a Teflon-lined autoclave for the hydrothermal process. The mixed solution was heated in an oven at 150 °C for 6 h (6 °C min⁻¹) and cooled at room temperature. The unreacted solvent and the resulting precipitate were separated by centrifugal force at 4000 rpm for 30 min. The collected precipitate was washed and rinsed with DI water and ethanol several times and then dried at 60 °C for 12 h (6 °C min⁻¹). Finally, two Ga₂O₃-rGO hybrids with 1 wt. % and 5 wt. % of rGO were formed, which were called Hybrid-1 and Hybrid-2, respectively. It was noted that the GO was successfully converted into rGO without strong acidic conditions via the hydrothermal process.

3.2. Materials Characterization

The microstructures of the synthesized Ga₂O₃-rGO hybrids were observed using a field emission scanning electron microscope (FESEM, JEOL JSM-7100F, Japan) at 15 kV acceleration voltage; the samples were distributed on the sticky-carbon tape followed by a Pt coating. The crystallographic structures of the synthesized hybrids were determined using a powder X-ray diffraction system (XRD, Rigaku Ultima IV XRD, Japan) over the 2θ range of 5–80° with Cu Kα radiation (λ = 0.15405 nm). Middle-infrared (4000–650 cm⁻¹) transmission spectra were collected with a Fourier-transform infrared spectra (FTIR, Agilent Cary 670, U.S.A.) spectrometer with an ATR accessory (ZnSe and Ze crystal). UV-Vis-NIR spectroscopy (DRS, Shimadzu SolidSpec-3700, Japan) was measured in the range from 240 to 1000 nm using BaSO₄ as a reference. Photoluminescence (PL) spectra were recorded under 260 nm UV laser excitation (PL, HORIBA LabRAM HR-800, Japan). Furthermore, Time-resolved PL measurements were performed on a HORIBA Fluorolog-3 via a time-correlated single photon counting (TCSPC) spectrometer equipped with a Pulsed Nano LED 260-nm excitation source. The specific surface area of the product was measured using a nitrogen adsorption-desorption isotherm on a BELSORP-max instrument and calculated via the Brunauer–Emmett–Teller (BET) method. Prior to measurement, the samples were degassed at 473 K for 4 h.

3.3. Photocatalytic Activity

The photocatalytic performance of the Ga₂O₃-rGO hybrids with different rGO wt. % were evaluated via the photodegradation of 2-butanone using a commercial VOC air detector (KHALDER: KD-001) with TVOC values ranging between 0.00 to 9.99 mg/m³. For every experiment, 200 mg of the photocatalyst powder and 18.2 mg of a commercial adhesive (as a 2-butanone source) were used with a UVC source (λ = 254 nm, 4W, irradiance of 340 µW·cm⁻² with a distance of 15 cm, Model: LF-104.S). No noticeable degradation of the 2-butanone was observed in the absence of a photocatalyst under the UVC irradiation. In the presence of a photocatalyst under UVC exposure, the photodegradation efficiency was calculated using Equation (4):

$$\text{Degradation efficiency (\%)} = (C_0 - C)/C_0 \times 100 \quad (4)$$

where C₀ is the initial concentration and C is the final concentration of the 2-butanone. Changes in the 2-butanone concentration were measured at intervals of 30 min. For comparison, photodegradation efficiency of Ga₂O₃ and TiO₂-P25 was also carried out. To further explore the long-term stability of the Ga₂O₃-rGO hybrids, repeated recycling experiments were carried out using Hybrid-1 under

identical conditions. The gaseous products generated before and after the photocatalytic degradation were collected and analyzed with a gas chromatograph (GC, Agilent 5975C, U.S.A.) equipped with a HP-5 MS column (with dimensions of 60 m $\times$ 0.25 μ m $\times$ 0.25 mm). A product sample was injected into the GC column with a split ratio 20:1. Helium was used as the carrier gas at a flow rate of 1.0 mL·min^{−1}. The column temperature program was as follows: 50 °C for 10 min, increasing at a rate of 10 °C min^{−1} to 300 °C. The product identification was confirmed with a gas chromatograph-mass spectrometer. Major reaction products were identified by comparing retention times and mass spectra with reference compounds.

4. Conclusions

Ga₂O₃-rGO hybrids were synthesized using a facile hydrothermal process method without using any additives or surfactants. The Ga₂O₃ nanorods were well dispersed on the surface of the rGO nanosheet through strong coupling between the Ga₂O₃ and rGO. Compared with the pure Ga₂O₃ and conventional TiO₂-P25, the photocatalytic activity of the hybrids was significantly enhanced. The enhanced photocatalytic activity of the hybrids was attributed to the effective carrier transfer from the Ga₂O₃ to rGO and enhanced specified surface area. The best photocatalytic activity was observed with Hybrid-1 (1 wt. % rGO) instead of Hybrid-2 (5 wt. % rGO), indicating that the presence of rGO with Ga₂O₃ can also degrade the photocatalytic performance via the lower absorption of UVC light blocked by the excessive rGO. The Ga₂O₃-rGO hybrid offers a promising method of enhancing photocatalytic activity and thereby effectively degrading 2-butanone.

Author Contributions: Conceptualization, B.J.C., W.S.H.; formal analysis, H.J.B., T.H.Y., S.K., W.C.; methodology and resources, Y.S.S., D.-K.K., B.J.C., W.S.H.; writing, review and editing, H.J.B., T.H.Y., S.K., W.C., Y.S.S., D.-K.K., B.J.C., W.S.H.

Funding: This work was funded by the National Research Foundation of Korea (NRF) through the Basic Science Research Program (2017R1A2B4012278), and by the Center for Advanced Soft-Electronics that is funded by the Ministry of Science, ICT and Future Planning, through the Global Frontier Project (CASE-2011-0031638).

Acknowledgments: Gas chromatography mass spectrometry (GC-MS) analysis was conducted at Korea Basic Science Institute (Busan Center).

Conflicts of Interest: The authors declare no conflict of interest.

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