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Sustainable Recovery of CO$_2$ by Using Visible-Light-Responsive Crystal Cuprous Oxide/Reduced Graphene Oxide

Shou-Heng Liu $^{1,*}$, Jun-Sheng Lu $^1$ and Yi-Chiun Chen $^{1,2}$

$^1$ Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan; dalelu4404@gmail.com (J.-S.L.); z10308032@email.ncku.edu.tw (Y.-C.C.)

$^2$ Department of Resources Engineering, National Cheng Kung University, Tainan 701, Taiwan

* Correspondence: shliu@mail.ncku.edu.tw; Tel.: +886-6-2757575 (ext. 65843)

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Abstract: A simple solution-chemistry method has been investigated to prepare crystal cuprous oxide (Cu$_2$O) incorporated with reduced graphene oxide (designated as Cu$_2$O-rGO-x, where x represents the contents of rGO = 1%, 5% and 10%) in this work. These Cu$_2$O-rGO-x composites combine the prospective advantages of rhombic dodecahedra Cu$_2$O together with rGO nanosheets which have been studied as visible-light-sensitive catalysts for the photocatalytic production of methanol from CO$_2$. Among the Cu$_2$O-rGO-x photocatalysts, the methanol yield photocatalyzed by Cu$_2$O-rGO-5% can be observed to be 355.26 µmol g$^{-1}$cat, which is ca. 36 times higher than that of pristine Cu$_2$O nanocrystal in the 20th hour under visible light irradiation. The improved activity may be attributed to the enhanced absorption ability of visible light, the superior separation of electron–hole pairs, well-dispersed Cu$_2$O nanocrystals and the increased photostability of Cu$_2$O, which are evidenced by employing UV-vis diffuse reflection spectroscopy, photoluminescence, scanning electron microscopy/transmission electron microscopy and X-ray photoelectron spectroscopy, respectively. This work demonstrates an easy and cost-effective route to prepare non-noble photocatalysts for efficient CO$_2$ recovery in artificial photosynthesis.

Keywords: cuprous oxide; solar energy; graphene; visible-light-driven; CO$_2$ conversion

1. Introduction

In the past decades, global warming, which is causing serious global climate change problems and ocean acidification, has been becoming more and more severe with the increase of greenhouse gases (e.g., carbon dioxide) [1]. A global agreement to reduce greenhouse gases has been reached on the COP21 in Paris on December 2015. In order to reduce CO$_2$ emissions, technologies developed for carbon capture, storage and utilization (CCSU) have been widely implemented [2,3]. Among these possible technologies, the conversion of CO$_2$ into useful chemicals or fuels is considered as one of the most promising approaches to deal with energy and environmental issues at the same time [4–6]. However, extra energy is required for the transformation of CO$_2$ because it is a stable molecule ($\Delta$G$ = -400$ kJ mol$^{-1}$) value [7]. Therefore, CO$_2$ conversion via photocatalytic reactions, which are involved in the utilization of solar energy, is an eco-friendly attractive route [8–12]. Previous studies [13–16] revealed that photocatalysts consisting of metal oxides are shown to be active in the UV-light region. However, it is difficult to practically use the aforementioned photocatalysts due to the limited fraction of the UV spectrum in natural sunlight [17–19]. Therefore, developments in visible-light-driven photocatalysts for artificial photosynthesis are crucial. To address this issue, many works have focused on enhancing the visible-light-active photocatalysts by using methods.
such as doping the semiconductors with non-metal/metal ions [20–23], engineering semiconductor structures [24], exposing a facet of the semiconductors [21,25–27], and semiconductor coupling [28,29]. As a result, these prepared photocatalysts, by using the above-mentioned routes, possess better charge carrier transfer, hence leading to a notable improvement in the photocatalytic performance under visible light.

Cuprous oxides (Cu$_2$O), which are p-type semiconductors, have been widely investigated for visible-light-responsive photocatalysis in artificial photosynthesis owing to their low cost, small band gap (ca. 2.0–2.2 eV) and suitable energy level of conduction and valence bands [15,30–32]. It is extensively reported that the Cu$_2$O nanocrystals can highly enhance the photocatalytic oxidation of organic pollutants under visible-light irradiation [33–37]. However, the studies on the photocatalytic reduction of CO$_2$ via crystal Cu$_2$O are limited. In the earlier report [38], the different facets of Cu$_2$O were investigated to perform the photocatalytic reduction of CO$_2$, indicating that the low-index facets of Cu$_2$O possessed higher activity than Cu$_2$O with higher index facets. In addition, Cu$_2$O with a stone-like shape exhibited superior activity to that with nanobelt arrays in terms of CO$_2$ photoreduction [39]. Nevertheless, the crystal Cu$_2$O applied in the photocatalytic reactions suffers from the separation of photogenerated electron–hole pairs [31] and long-term stability [40]. Recently, the enhanced durability and activity [41–46] can be achieved by the Cu$_2$O-based photocatalysts. Among them, the incorporation of graphene with the 2D sp$^2$-hybridized carbons has received much attention due to its high electron mobility [47], theoretical surface area [48], and chemical stability [49]. For instance, a microwave-assisted chemical method was proposed to prepare Cu$_2$O/reduced graphene oxide (rGO) nanocomposites which have improved activity and stability toward the photocatalytic reduction of CO$_2$ [50]. Spherical Cu$_2$O nanoparticles were incorporated with rGO by using in-situ reduction method, and their photocatalytic activities toward CO$_2$ reduction were better than that of pristine Cu$_2$O nanoparticles [51]. Although the synthesis of Cu$_2$O–graphene composites with visible-light-active CO$_2$ reduction was proposed previously, the crystal structure of Cu$_2$O decorated with rGO in the photoreduction of CO$_2$ was reported for the first time.

In the present research, the nanocrystal Cu$_2$O possessing facets decorated with various amounts of rGO nanosheets (named as Cu$_2$O-rGO-x, x = amounts of rGO) were synthesized by using a simple solution-chemical method. The resultant Cu$_2$O-rGO-x photocatalysts were thoroughly characterized via a variety of spectroscopic analyses. Also, the tests regarding the photoreduction of CO$_2$ under visible light show that rhombic dodecahedral Cu$_2$O decorated with 5 wt.% of rGO exhibited superior photocatalytic activity to the other Cu$_2$O-rGO-x and pristine Cu$_2$O. The reaction mechanism in the enhancement of CO$_2$ photoreduction by Cu$_2$O-rGO-5% composites is studied and discussed later.

2. Materials and Methods
2.1. Preparation of Crystal Cu$_2$O Decorated with rGO

Graphene oxide (GO) was fabricated by using the modified Hummer’s method based on the earlier work [52]. For the synthesis of crystal Cu$_2$O decorated with rGO, fixed amounts of 0.1 M CuCl$_2$ and sodium dodecyl sulfate (SDS, Sigma, St. Louis, MO, USA, 99%) were added into various weight ratios of GO solution (1–10%) under stirring in a water bath at 34 °C. After 20 min, 1.8 mL of 1 M NaOH solution was added into the mixed solution, and then it was stirred for 20 s. Twenty-four milliliters of 0.1 M NH$_2$OH·HCl (Alfa Aesar, Haverhill, MA, USA, 99%) solution was slowly poured into the mixture. The mixture was stirred for 20 s and kept in the water bath for an hour. Finally, the product was washed and then separated by a centrifuge several times. After that, these precipitates were dried in vacuum at 30 °C for 8 h. The resultant products were symbolized as Cu$_2$O-rGO-x (x represents the amounts of rGO = 1%, 5% and 10%).
2.2. Characterizations

X-ray diffraction (XRD) measurements were carried out by a PANalytical X'Pert PRO diffractometer (Cu Kα, λ = 1.541 Å) at a scan of 3° min⁻¹ from 5 to 80°. The morphologies of samples were identified by scanning electron microscopy (SEM) and transmission electron microscopy on a field-emission scanning electron microscope (JSM-7000F, JEOL, Akishima, Tokyo, Japan) and transmission electron microscope (JEM-1400, JEOL, Akishima, Tokyo, Japan) with respective accelerating voltages of 20 and 200 kV. The rate of the electron–hole recombination of photocatalysts can be determined by photo-luminescence (HR800, HORIBA, Kyoto, Japan) from 450 to 650 nm. X-ray photoelectron spectra (XPS) were recorded via a Kratos AXIS Ultra DLD spectrometer system with an excitation source of Al Kα (1486 eV). The peak of adventitious carbon (284.6 eV) was referenced to calibrate the binding energies of the photoelectrons. The electrons could be excited from the valance band to the conduction band of the sample by excitation light with 325 nm. The spectra of diffuse reflectance ultraviolet/visible (UV/Vis) light were taken on a spectrophotometer (Cary 100, Varian, Palo Alto, CA, USA).

2.3. Photoreduction of CO₂ Experiments

The photocatalytic activity measurements were carried out in a batch reactor (200 mL) equipped with a water-circulation cooling system. About 25 mg of samples and 50 mL of deionized water (DI) water were added into the aforementioned reactor, followed by dispersing homogeneously in water by sonication. Then, pure CO₂ gas (99.995%) was introduced into the reactor for 45 min to keep the solution saturated and ensure adsorption–desorption equilibrium in the dark. After the reactor was sealed, the photocatalytic reaction was performed by using a top-irradiated 300W Xe lamp (Model 66142, Newport, Irvine, CA, USA) with a cut-off filter to remove UV illumination. During the reaction process, the gas (1 mL) and liquid (1 µL) products were withdrawn periodically and examined by gas chromatography (GC, GC-430, Bruker, Billerica, MA, USA) with a thermal conductivity detector (TCD, equipped with molecular sieve 5A column) and a barrier discharge ionization detector (BID, GC-2010 Plus equipped with DB-WAXETR column, Shimadzu, Kyoto, Japan), respectively.

3. Results and Discussion

The X-ray diffraction patterns of GO, crystal Cu₂O and Cu₂O-rGO-x composites (x represents the weight percentage of rGO to Cu₂O) are shown in Figure 1. The results show that all the diffraction features of crystal Cu₂O-rGO-x composites are located at 2θ of 29.6°, 36.4°, 42.3°, 61.4°, 73.6° and 77.5° which can be assigned to (110), (111), (200), (220), (311), and (222), respectively. This indicates the presence of a crystal phase of Cu₂O (JCPDS #78-2076) in the Cu₂O-rGO-x composites. No characteristic peak of GO at 2θ = 10.6° can be observed for all samples, suggesting that the GO may be reduced to rGO. No characteristic peaks of rGO can be found for all Cu₂O-rGO-x samples in the X-ray diffraction patterns, which may be due to the lower contents of rGO and higher intensity of crystal Cu₂O. As reported previously [53], the crystal structure of Cu₂O is a pure rhombic dodecahedron when the intensity ratio of the (220) facet to the (200) facet (I₂₂₀/I₂₀₀) is 0.79. The values of I₂₂₀/I₂₀₀ of Cu₂O and Cu₂O-rGO-x (x = 1%, 5% and 10%) are calculated to be 0.76, 0.72, 0.58, and 0.56, respectively. It can be found that the values of I₂₂₀/I₂₀₀ are decreased when the contents of rGO in the Cu₂O-rGO-x composites are increased. The I₂₂₀/I₂₀₀ of Cu₂O-rGO-10% is decreased to 0.56 while the weight ratio of rGO is increased to 10%. There are two possible reasons which could explain why the crystal structure of rhombic dodecahedral Cu₂O cannot be completely formed. First, the pH of the solution was changed from neutral to acidic by adding GO, which may hinder the formation of a crystal structure of Cu₂O. Second, GO would react with the reductant to form rGO during the synthesis process. This would lead to insufficient amounts of the reductant for the formation of a crystal structure of rhombic dodecahedral Cu₂O [53].
As can be seen from the inset of Figure 2, the corresponding selected-area electron diffraction (SAED) pattern of rhombic dodecahedra can be observed along the [100] direction. The TEM images also show that rGO was decorated onto the surface of Cu2O nanocrystals. This result confirms that rGO is successfully decorated on rhombic dodecahedral Cu2O, as shown in Figure 2.

The transmission electron microscopy (TEM) image of rGO shows a thin sheet with wrinkles, similar to paper, as displayed in Figure 2. The deeper-colored region can be observed in the TEM image of rGO, which may enhance the capacity of CO2 adsorption. Therefore, it is helpful that rGO was decorated onto the surface of Cu2O nanocrystals. The morphological and structural features of Cu2O and Cu2O-rGO-x composites (x = 1%, 5% and 10%) were also studied by TEM and their corresponding images are shown in Figure 2. It can be seen that the morphological features of rhombic dodecahedral Cu2O are similar to a honey-comb shape with a particle size of 400–500 nm. As can be seen from the inset of Figure 2, the corresponding selected-area electron diffraction (SAED) pattern of rhombic dodecahedra can be observed along the [100] direction. The TEM images also show that Cu2O nanocrystals are decorated with thin rGO sheets with some wrinkles. This result confirms that rGO is successfully decorated on rhombic dodecahedral Cu2O.
The elemental compositions and the chemical surface states of GO, rGO, crystal Cu$_2$O and Cu$_2$O-rGO-x composites were examined by XPS. In Figure 3a, the survey scans of the samples suggest the existence of carbon, oxygen and copper. The high-resolution C1s XPS spectra of GO (see Figure 3b) indicate three deconvoluted peaks at 284.6, 286.7, and 289.1 eV, which are ascribed to C–C/C=C, C–O, and C=O/COOH bonds, respectively. The intensities of C–O bindings found for rGO and Cu$_2$O-rGO-x samples are decreased, indicating that GO can be effectively reduced to rGO in the Cu$_2$O-rGO-x. As can be seen from Figure 3c, the Cu2p XPS spectra of Cu$_2$O-rGO-x composites display two major peaks at ca. 932.6 and 952.4 eV corresponding to Cu(I) 2p$_{3/2}$ and Cu(I) 2p$_{1/2}$,
respectively. Moreover, the binding energies of 934.8 and 954.3 eV are attributed to the formation of Cu(II), indicating the presence of Cu(II) on the surface of Cu$_2$O and Cu$_2$O-rGO-x photocatalysts. However, the intensities of aforementioned peaks (i.e., Cu(II)) are obviously reduced for Cu$_2$O-rGO-5% and Cu$_2$O-rGO-10% composites, implying the prevention of surface oxidation of Cu$_2$O. It can be attributed to the enhancement of chemical stability caused by improving the electronic structure of Cu$_2$O nanocrystals in the presence of carbon vacancies and dangling bonds in the rGO [54]. Figure 3d shows high-resolution of O1s XPS spectra of Cu$_2$O and Cu$_2$O-rGO-x. The features at 531.0 and 531.8 eV can be attributed to oxygen vacancy and adsorbed oxygen, respectively [44]. It can be seen that the intensities of two components are increased upon the increased decoration of rGO. As reported earlier [55], the binding of oxygen vacancies in the nanocrystalline Cu$_2$O with bicarbonate ions may be enhanced, which could promote the photoreduction of CO$_2$ discussed below.

The optical absorption of Cu$_2$O and Cu$_2$O-rGO-x composites was investigated by diffuse reflectance ultraviolet/visible (UV/Vis) spectra. The UV/Vis spectra of Cu$_2$O and Cu$_2$O-rGO-x show a wide absorption profile from 300 to 600 nm, as displayed in Figure 4a. In addition, the absorption intensities of Cu$_2$O-rGO-x composites are relatively enhanced in the absorption wavelength >600 nm regions if compared with those of Cu$_2$O. The increased absorption intensity of Cu$_2$O-rGO-x composites depends on the amounts of rGO in the composites; i.e., the intensity is increased with increasing amounts of rGO. Therefore, the rGO could cause a red shift to promote the absorption ability in the visible region of Cu$_2$O. Figure 4b shows that the band gap of Cu$_2$O is reduced as Cu$_2$O combined with rGO. Their corresponding threshold wavelength can be obtained and is shown in Table 1. The band gap of the pure Cu$_2$O nanocrystal is assessed to be 2.18 and those of Cu$_2$O-rGO-x composites are decreased to be 2.16–2.06 with increasing contents of rGO in the Cu$_2$O-rGO-x composites. A red-shift
absorbance and the narrower bad gap of composites means that it can easily absorb the visible light. Therefore, the incorporation of rGO onto the Cu$_2$O is good for the absorption of visible light during photocatalytic reduction.

Figure 4. The photo-luminescence (PL) pattern of Cu$_2$O and Cu$_2$O-rGO-x (x = 1%, 5% and 10%).

Table 1. Energy gaps and threshold wavelength of Cu$_2$O and Cu$_2$O-rGO-x (x = 1%, 5% and 10%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy Gap (eV)</th>
<th>Threshold Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>2.18</td>
<td>570.11</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-1%</td>
<td>2.16</td>
<td>573.01</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-5%</td>
<td>2.16</td>
<td>574.87</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-10%</td>
<td>2.06</td>
<td>603.11</td>
</tr>
</tbody>
</table>

The rates of the electron–hole recombination can be determined by photo-luminescence (PL) with the exited wavelength at 325 nm. The peak position is related to the band gap value of photocatalysts and the intensity of the peak represents the rates of the electron–hole recombination. A higher intensity of peaks indicates a greater rate of electron–hole recombination. On the other hand, a lower intensity of peaks means an inferior rate of electron–hole recombination. As can be seen in Figure 5, the Cu$_2$O-rGO-10% composites have the lowest intensity of PL peaks, which suggests that they have the lowest recombination rates. Accordingly, the rate of electron–hole recombination can be reduced by decorating rGO on Cu$_2$O, and the photo-exited electrons can be effectively transferred from Cu$_2$O to rGO to separate electrons and holes [56–59].
The photoconversion of CO₂ into methanol photocatalyzed by Cu₂O and Cu₂O-rGO-x composites was examined under visible light for 20 h. In this study, the possible products, such as HCHO and HCOOH, which were confirmed by injecting the standard solution of respective compounds, were not detected. Only methanol was observed as the main product. In order to check the formation of methanol during photocatalytic reaction, we performed three blank experiments. It can be seen that no methanol can be obtained without the assistance of photocatalysts, light irradiation and the existence of CO₂ (see Table 2). Moreover, Figure 6 shows that the contents of rGO have a great effect on the photocatalytic activity of Cu₂O nanocrystals. The methanol yields varied with the contents of rGO follow the order Cu₂O-rGO-5% > Cu₂O-rGO-1% > Cu₂O-rGO-10% > Cu₂O. The yields of methanol are 9.76, 47.91, 335.26 and 12.41 μmol g⁻¹-cat, corresponding to Cu₂O, Cu₂O-rGO-1%, Cu₂O-rGO-5% and Cu₂O-rGO-10%, respectively after 20 h of visible-light irradiation. Among these prepared photocatalysts, the Cu₂O-rGO-5% composites possess the best activity for the photoreduction of CO₂. It is concluded that the suitable amounts of rGO which are incorporated onto Cu₂O would have a positive impact on the photocatalytic performance of CO₂ reduction. According to the UV-Vis spectrum, the adsorption intensity of Cu₂O in the visible regions is promoted and the energy gap of Cu₂O is reduced by combining with rGO, indicating that Cu₂O-rGO-x can easily absorb visible light to generate electron–hole pairs which can be utilized to reduce CO₂. The PL patterns indicate that the peak intensities are declined with increasing ratios of rGO to Cu₂O, suggesting that the rGO can effectively prevent the electron–hole pairs from recombination. The SEM/TEM images show that the aggregation of Cu₂O nanocrystals can be suppressed by decorating with rGO, and thus the activity sites are also increased. XPS spectra show that rGO nanosheets served as the protective layers to prevent the photoreduction and oxidation of Cu₂O by photogenerated electrons and water, respectively, which enhance the stability of Cu₂O during the photocatalytic reaction. Consequently, the methanol yield of Cu₂O-rGO-5% composites (355.26 μmol g⁻¹-cat) is ca. 36 times higher than that of pure Cu₂O nanocrystal (9.76 μmol g⁻¹-cat). Additionally, the apparent quantum efficiency (AQE) of Cu₂O-rGO-5% under visible-light illumination was estimated to be 0.724%. However, the photocatalytic activity is observed to be decreased when the ratio (rGO/Cu₂O) is further increased to 10%. This result may be due to the fact that excessive rGO would deteriorate the crystal facet of Cu₂O as well as obstructing light from reaching the surface of Cu₂O nanocrystals which generated fewer electron–hole pairs, thereby decreasing the reduction of CO₂ [52].
Combining the results mentioned above, a possible mechanism of photocatalytic CO$_2$ reduction by Cu$_2$O-rGO-x composites is illustrated in Figure 7. The Cu$_2$O-rGO-x composites possess band gaps of ca. 2.1 eV with more negative reduction potential than that of methanol formation (E = $-0.38$ V vs. NHE at pH = 7) and slightly more positive oxidation potential than that of oxygen evolution (E = 0.81 V vs. NHE at pH = 7) [24]. The photogenerated electrons are transferred to highly conductive rGO to react with CO$_2$ or O$_2$ which have two lone pairs of electrons for the formation of π-electrons bindings on the rGO surface. As such, the recombination of electron–hole pairs would be hindered significantly, which is important for the electron-dominated reduction reaction [50]. More importantly, the removal of electrons from the conduction bands of Cu$_2$O via rGO can prevent the photoreduction of Cu$_2$O and thus enhance the photostability [60]. In addition, the protection of rGO from the oxidation of Cu$_2$O by water may maintain the copper in the Cu(I) state [61]. In Figure S1, the XRD pattern confirms that the crystal phase of Cu$_2$O is intact after 20 h of photocatalytic reaction. It is noteworthy that the dominant product of methanol may be caused by the exposed (110) facets of Cu$_2$O on which hydrogen may perform the addition to the oxygen atom in the bicarbonate rather than a carbon atom. This finding is similar to the pervious study [62]. In terms of photogenerated holes, the evolution of oxygen gas (ca. 4.9 $\mu$mol g$^{-1}$-cat after 20 h of visible-light irradiation) implies that the occurrence of water splitting would serve as the hole scavenger, which hinders the recombination of electron–hole pairs. However, the lower amounts of evolved oxygen after 20 h of photocatalytic reaction may be ascribed to the possibility of carbon corrosion and oxygen reduction.

### Table 2. Conditions for the photocatalytic reduction of CO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Precursor</th>
<th>Visible Light Illumination ($\lambda &gt; 400$ nm)</th>
<th>Methanol Yield ($\mu$mol g$^{-1}$-cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>CO$_2$</td>
<td>O</td>
<td>None</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>CO$_2$</td>
<td>O</td>
<td>9.76</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-1%</td>
<td>CO$_2$</td>
<td>O</td>
<td>47.91</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-5%</td>
<td>CO$_2$</td>
<td>O</td>
<td>355.26</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-5%</td>
<td>CO$_2$</td>
<td>X</td>
<td>None</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-5%</td>
<td>N$_2$</td>
<td>O</td>
<td>None</td>
</tr>
<tr>
<td>Cu$_2$O-rGO-10%</td>
<td>CO$_2$</td>
<td>O</td>
<td>12.41</td>
</tr>
</tbody>
</table>

All experiments were carried out at 27°C with 0.5 mg-cat/mL-solvent.

![Figure 6](image_url)  
**Figure 6.** Photocatalytic methanol formation by Cu$_2$O and Cu$_2$O-rGO-x (x = 1%, 5% and 10%) under visible light irradiation.
Figure 7. A possible mechanism of CO2 photoreduction catalyzed by Cu2O-rGO-x under visible light irradiation.

4. Conclusions

In summary, crystal Cu2O photocatalysts incorporated with various amounts of rGO (1–10%) are prepared via a simple solution-chemistry route. Among the prepared Cu2O-rGO-x composites, we found that the Cu2O-rGO-5% (5 wt.% of rGO) photocatalysts possess the superior photocatalytic performance toward CO2 reduction; i.e., after visible light illumination for 20 h, the methanol yield of Cu2O-rGO-5% composites can reach 355.26 μmol g⁻¹cat, which is about 36 times that of pure Cu2O photocatalysts. This remarkable enhancement in the CO2 photoreduction activity may be due to the increased intensity of visible-light absorption in the Cu2O (identified by UV-VIS), reduced recombination of electron–hole pairs (proven by PL), enhanced dispersion of crystal Cu2O (examined by SEM/TEM) and stabilization of Cu2O (evidenced by XPS). Accordingly, the visible-light-driven photocatalytic reduction of CO2 by Cu2O-rGO-x composites could provide a possible opportunity for CO2 conversion by using sunlight energy.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/10/11/4145/s1, Figure S1: XRD patterns of the fresh and used photocatalysts after 20 h of photocatalytic reaction.

Author Contributions: Designing, writing, review & editing the paper, S.-H.L.; doing the experiments and analyzing the data, J.-S.L. All authors reviewed and approved the manuscript.

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

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