Synthesis and Photoluminescence Study of Reduced Graphene Oxide (rGO)/ZnO for Solar Energy Absorbing Materials

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Abstract. Materials combining reduced graphene oxide (rGO) from coconut shells and commercial ZnO have been synthesized by dry-mixing in weight ratio of 1:2, 2:2, and 3:2. For photoluminescence (PL) characterization, the solutions with concentration of rGO/ZnO in aquadest up to 0.003 mg/mL were prepared. The absorbing photon energy by the samples at wavelength 280-426 nm (ultraviolet-purple) has induced electron transition to conduction band. Further, the returning electron to valence band was followed by photon emission at wavelength of 530-880 nm (green-infrared). The PL intensity was observed to drastically enhance with increasing content of rGO in the solution by 252.5%, 285.0% and 291.3% for the corresponding samples compared to the solution containing pure ZnO. The rGO/ZnO materials exhibit higher absorbance with wider wavelength range, and therefore can potentially be used as solar energy absorbing materials to enhance the efficiency of solar cell.

1. Introduction
A solar cell converts solar energy becomes electricity. The main issue of solar cells up to the present is about the low efficiency. One of the problems may possibly arise from the fact that the low absorption of solar energy in material [1]. ZnO is a semiconductor that has high transparancy and can generally be used as solar energy converter material [2]. It has gap energy about 3.3 eV.

Meanwhile, reduced graphene oxide (rGO) has good characteristics in electrics and can be applied as solar energy absorbing material [3]. The starting material which can be used to produce rGO is old coconut shell which is as a waste, since it contains lignin, hemicellulose, and cellulose which are constituted by carbon elements. As we know that Indonesia as tropical archipelago is a huge habitat of coconut trees as natural resources. Referred to recent research by Nugraheni (2014) and Ananta (2015), the coconut shell has successfully been converted by calcination at 400°C to be material with main molecule bonding like C=C and C-C, and other impurities such as C-H, C-O, C=O and O-H, that indicates rGO phase [4]-[5]. This rGO has an optical bandgap about 0.07 - 1.2 eV, which was measured by Nasrullah (2014) [4].

Photoluminescence (PL) is a phenomenon of light spontaneous emission from a material that is excited by photon energy [7]. The PL spectroscopy, which is a non destructive method, is a selective electrical characterization which is very sensitive for discrete electronic states. Emission spectrum feature can be used to identify surface, interface bonding, and impurity level. According to Chien (2012), if oxygen is reduced in the substance, the PL curve will shift to a lower wavelength [3]. Meanwhile, if ZnO material is added by rGO material, the emission intensity will increase. By receiving photon energy at 426 nm, the electrons inside material can be excited and then return to ground state by emitting electromagnetic wave in range of green-red visible light. This shifting can occur because of oxygen vacancy defect, having energy formation of about 1.7 eV- 2.4 eV [6]. So, if more rGO is added to ZnO, the gap energy will decrease, to be between ZnO and rGO [2]. Thus, the rGO/ZnO can be applied as solar energy absorbing materials (SEAM), which will be studied in this paper.
2. Materials and Experiments

Materials used in this research are old coconut shell waste, ZnO (SAP Chemicals), alcohol, and aquadest. The old coconut shell waste was dried under the sunlight for several days, and then cleaned. To convert it further to carbon compound, it was burned in a carbonization box. It was then crushed by mortar to be granulated shape. Afterwards, it was calcined in a furnace at temperature 400°C for 5 hours. The rGO powder was dissolved in aquadest for ultrasonication for 2 hours, stirring for 1 hour, and centrifugation at 2000 rpm for 30 minutes.

The synthesized rGO was then mixed with ZnO in the weight ratio of 1:2; 2:2; and 3:2, and dissolved in water to be solution, where ZnO 0.002 mg/mL was mixed by each of rGO: 0.001, 0.002, and 0.003 mg/mL for PL (Perkin Elmer LS-55) and particle size (PSA) measurements. Besides, the rGO and ZnO were also characterized by XRD (D8 Advance Bruker) and scanning electron microscopy (SEM) characterizations.

3. Results and Discussions

Presented in Fig. 1 are the XRD patterns of the old coconut shell charcoal powders resulted from the burning process (a), and that after furnace heating at 400°C for 5 hours (b). In Fig. 1 (b), the diffraction angle at 11° decreases, which means that the graphene oxide (GO) phase has partially transformed to rGO. The reduction of GO phase in the sample is caused by heating that makes oxygen atoms release from GO structure. Fig. 2 (a) shows the rGO layers and Fig. 2 (b) shows the ZnO powders with heterogeneous wurtzite structure. Further, characterization by PSA shows the ZnO particle size distribution having two peaks at 685.3 nm and 193.4 nm. It means that the ZnO particle size is heterogeneous. Meanwhile rGO exhibits the particle size average about 300 nm.

![Figure 1. XRD characterization of: (a) old coconut shell charcoal, (d) rGO material.](image1)

![Figure 2. SEM characterization results: (a) rGO, (b) ZnO.](image2)
Figure 3. Emission spectra under excitation wavelength of 341 nm: (a) rGO and ZnO, (b)rGO/ZnO, (c) emission mechanism of red visible light.

The emission spectra with the main peak of about 682 nm resulted by 341 nm excitation wavelength are shown in Fig. 3. Fig. 3 (a) shows that emission spectrum of ZnO which is lower than that of rGO. The higher content of rGO will result in higher intensity of emission. It is seen that samples emit red visible light under the excitation using wavelength at 341 nm. Fig. 3 (b) shows that the emission spectrum of rGO/ZnO having higher intensity than that of pure ZnO. More rGO that was added could increase the emission spectrum of ZnO, as shown in Fig. 3 (b). Fig. 3 (c) shows the process and mechanism of how PL is happened. Excitation spectrum of rGO/ZnO material shifts from 341 nm to 682 nm. Since more oxygen atoms still exist in the samples, so the emission has shifted to higher wavelength. This result is supported by the XRD pattern in Fig. 1 (b), showing that there is still GO phase having peak at diffraction angle of around 11°.

Figure 4. Emission spectrums of some excitation spectrums for rGO/ZnO and ZnO.

In Fig. 4, the emission spectra of the whole sampels using excitation wavelengths of 280 nm, 325 nm, 375 nm, and 426 nm are presented. This figure also shows the same characteristic for 4 samples in the range of 530-590 nm (form green to yellow of the visible light). From these 5 excitation wavelength parameters, it is shown that the emission wavelengths are twice of its excitation wavelength or a half of its excitation energy. The emission spectrum intensity decreases when the excitation wavelength increases because of the decreasing energy given to material. This result is in nice agreement with previous reports [2]-[3]. This composite is a material system consisting of 2 components, rGO and ZnO. This condition makes the light intensity which be
absorbed by this composite system is divided by both of rGO and ZnO. Because of that, the emission intensity of rGO/ZnO is between rGO and ZnO.

4. Summary
The absorbance of ZnO material can be enhanced by introduction of rGO to form a composite. The rGO/ZnO system was able to absorb photon energy of 280–426 nm (ultraviolet-purple visible light) and then emit electromagnetic wave at 530–880 nm (green visible light-infrared). The shift is possible because of energy used by electrons to vibrate as a non-radiative transition. Thus, the rGO/ZnO composite has been developed to have higher absorbance with wider range and higher intensity of light.

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