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Synthesis of Graphene/g-C_3N_4 Composite Photo-Electrodes for Li – Ion – Oxygen Battery

Nilay KACAR
Eskisehir Osmangazi University

Ersu LOKCU
Eskisehir Osmangazi University

R. Can OZDEN
Eskisehir Osmangazi University

Mustafa ANIK
Eskisehir Osmangazi University

Abstract: Graphene was synthesized by the chemical vapor deposition (CVD). Initially ratios of Ar, H_2 and CH_4 gases were optimized to get a single layer graphene by CVD. Raman characterizations showed that the optimized synthesis conditions provided I_{2D}/I_G ratio as 3 that this ratio indicated the formation of the single layer graphene. The synthesized single layer graphene was mixed with melamine at the certain ratios to obtain the graphene/graphitic-C_3N_4 (g-C_3N_4) semiconductor composites. All the synthesized composites were prepared as the photo-electrode to be used in the photo-assisted charging of the lithium-ion oxygen battery. The photo-current levels produced by the photo-electrodes were determined by the linear sweep voltammetry technique.

Keywords: Graphene, Lithium oxygen battery, Chemical vapor deposition, g-C_3N_4

Introduction

The extraordinary properties (conductivity, transmittance, flexibility, strength) of graphene enable its use in critical applications such as electronics, composites, membranes and renewable energy technologies. There are numerous studies on the synthesis of graphene that mechanical exfoliation, liquid-phase exfoliation and chemical vapor deposition (CVD) can be counted as the main synthesis techniques. Among these techniques CVD is relatively inexpensive and the most promising method to get the monolayer graphene on the large areas (Li et al., 2016).

Graphitic carbon nitride (g-C_3N_4) can be simply synthesized from a convenient precursor via series of poly-condensation reactions and it can be used as effective photo-electrode semiconductor or electro-catalyst for the Li ion oxygen battery cathodes since it catalyzes both the oxygen reduction and oxygen evolution reactions (Niu et al., 2012). In this work the CVD graphene was chemically mixed with g-C_3N_4 to get the efficient composite photo-electrode. g-C_3N_4 has approximately 2.7 eV band gap and this value makes it attractive visible light photocatalyst (Wang et al., 2008). The chemically mixed CVD graphene is expected to increase the conductivity and decrease the band gap of g-C_3N_4 to make g-C_3N_4 excellent sunlight harvesting semiconductor.

Method

Graphene was synthesized with a prescription provided in Figure 1 on 2x2 cm Cu substrates. After synthesis, Cu substrates were dissolved in 0.5 M $FeCl_3$ + %50 HCl solution and then cleaned with distilled water (Figure 2). The synthesized graphene was kept in methanol until starting to the synthesis process. If graphene was needed for the characterization, then the Cu substrate was coated with PMMA solution on the spin coater and then they dried at 140°C for 30 min. The graphene/PMMA film was cleaned with distilled water after the Cu substrates were dissolved and dried at 60°C for 30 minutes. For the characterizations the cleaned graphene/PMMA film was transferred either onto wafer (for Raman) or onto TEM grit (for SEM). The transferred graphene/PMMA film was cleaned with acetone and isopropanol to remove PMMA.

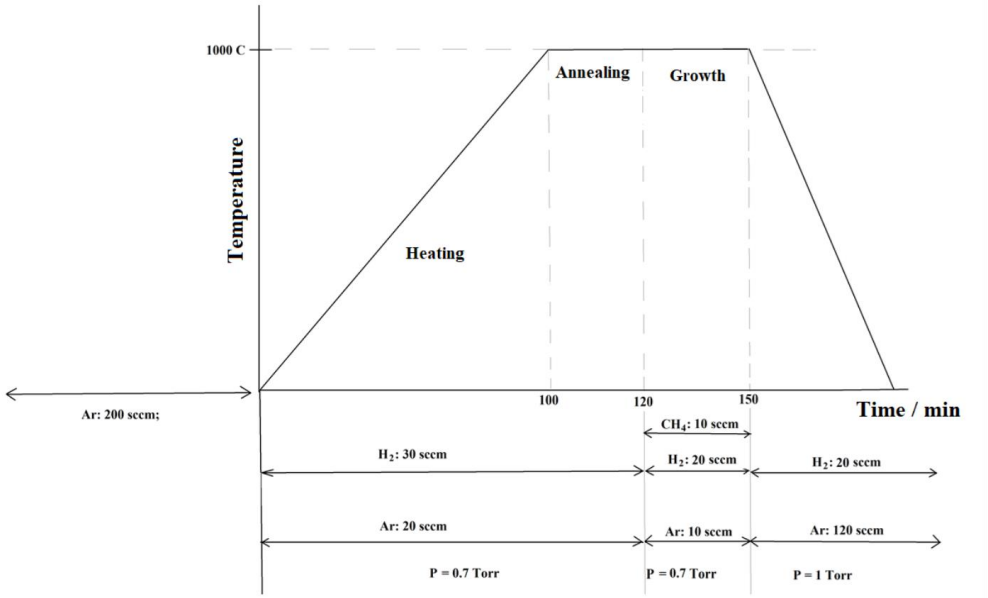

Figure 1. CVD graphene synthesis.

Figure 2. Cleaning and transfer processes of graphene after synthesis by CVD.

For the photo-electrode synthesis, melamine ($C_3H_6N_6$) and graphene were mixed in methanol in an alumina crucible at 50°C for several h until all methanol volatilized. After drying completely, the mixture heated at a rate of 3°C/min up to 550°C and it kept at this temperature for 3 h under continuous Ar flow in a fully sealed crucible. Then it left to cool down to RT inside the furnace to get g-C_3N_4 - graphene composite.

The composite photo-catalyst was coated on the conductive surface of ITO (8 mm x 6 cm) with 0.1 mg cm^{-2} loading by spin coater for the photo-current experiments and then the ITO specimens were dried at 100°C for overnight in a vacuum oven. The photo-currents were measured by lineer sweep voltammetry technique by using Gamry Reference 3000 potentiostat in 0.1 M KCl / 0.1 M H_2PO_4 (pH 7) solution in a spectral cuvette as in Figure 3. During the experiments light was sent by solar simulator (A-type 150 W, 1-3 SUN, Xenon lamb, 1.5 AM Filter: 400 nm - 700 nm visible light).

X-ray diffraction (XRD) analyses were performed on a PANalytical Empyrean diffractometer with Cu K-alpha radiation at a scanning rate of 2° min^{-1}. The morphologies of the electrodes were examined with a ZEISS Ultraplus scanning electron microscope (SEM). Raman spectra was obtained using a RENISHAW RAMAN inVia Microscope with 532 nm wavelength laser.

Figure 3. The photo-current measurements of CVD graphene - g-C_3N_4 composites.

Results and Discussion

Characterization

Raman spectra of synthesized graphene according to the prescription provided in Figure 2 is shown in Figure 4. In general, there are three main peaks of graphene in Raman spectra that they are labeled as G (~1580 cm^{-1}), D (~1360 cm^{-1}) and 2D (~2700 cm^{-1}) bands. The intensities (I) and the relative intensity ratios of these peaks provide the information about the quality and the layer numbers of graphene. As the layer number of graphene increases, the intensity of G band increases and that of 2D band decreases. D band represents the disorder and if this band disappears completely then the synthesized graphene is accepted as flawless. In Figure 4, there is no D band peak and the ratio of the 2D band intensity to G band intensity (I_{2D}/I_G) is approximately 3. This ratio indicates that the synthesized graphene according to the prescription provided in Figure 2 is single layer graphene.

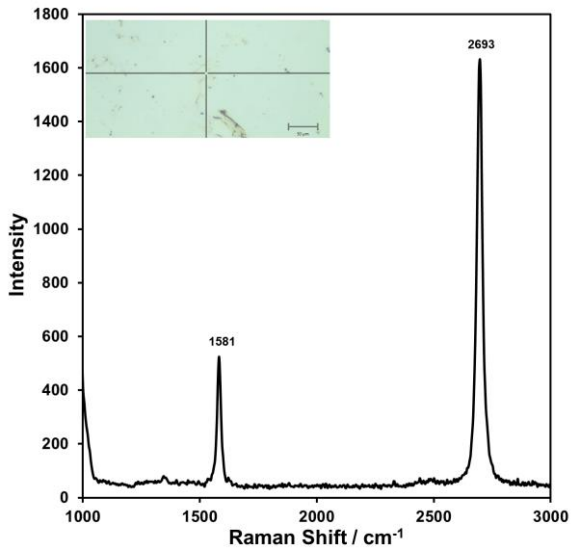

Figure 4. 532 nm Raman spectra of synthesized graphene.

Photo-Current Measurement

CVD graphene - g-C_3N_4 composite photo-electrodes were synthesized based on the graphene area ratio (cm^2) to g-C_3N_4 weight (mg). The obtained chopped photo-currents (on-off) depending on the potential is depicted in Figure 5. Obviously as the CVD graphene ratio increases in the composite, the photo-catalytic efficiency of the of the composite electrode increases. Graphene shows the dual action that firstly it increases conductivity and thus decelerates the rate of the hole – electron re-combinations in g-C_3N_4 semiconductor. Secondly graphene

decreases band gap of g-C_3N_4 since it is defined as zero band gab semiconductor. Both actions of graphene increase the sunlight harvesting capacity of g-C_3N_4.

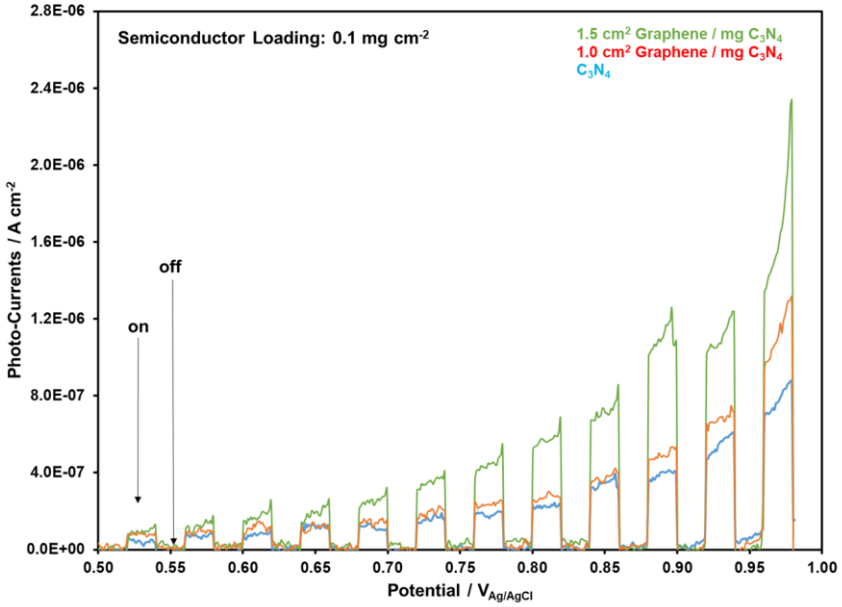

Figure 5. Photo-currents of CVD graphene - g-C_3N_4 composites.

Conclusion

Initially single layer graphene was synthesized by chemical vapor deposition (CVD) and then CVD graphene - g-C_3N_4 composite photo-electrodes were synthesized. Photo-current measurements showed that graphene improved the photo-catalyst efficiency of g-C_3N_4 significantly.

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Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Author Information

Nilay KACAR
Metallurgical and Materials Engineering
Eskisehir Osmangazi University
Contact e-mail: *nilaykacar032@gmail.com*

Ersu LOKCU
Metallurgical and Materials Engineering
Eskisehir Osmangazi University

R. Can OZDEN
Metallurgical and Materials Engineering
Eskisehir Osmangazi University

Mustafa ANIK
Metallurgical and Materials Engineering
Eskisehir Osmangazi University

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