Preparation of graphene oxide thin films using voltage cyclic electrochemical deposition method and its characterization

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Abstract. Graphene oxide (GO) is frequently used as a precursor to obtain ‘graphene like’ materials. We study preparation of GO thin film using voltage cyclic electrochemical deposition. GO thin films were obtained from 0.5 mg/ml GO-water dispersion on ITO glass substrate in the range of -1.6 to 0 V at scan rate of 75 mV/s. The electrochemical deposited GO thin films were characterized using UV-Vis spectroscopy, the GO morphology and oxygen containing groups were obtained by using SEM, EDX and FTIR, respectively. Cyclic voltammetry (CV) was employed to measure its capacitive characteristic. We obtain that thickness of GO thin films can be controlled by number of voltage cycles applied during deposition. From cyclic voltammetry measurements, we obtained hysteresis curve that imply its potential application as supercapacitor electrode.

1. Introduction
Graphene is one atom-thick layered crystalline with a honeycomb structure of sp²-bonded carbon. Because of its excellent properties, graphene has been widely studied for many applications [1]. Graphene oxide (GO) has received a lot of attention due to its role as a precursor for cost-effective and mass production of graphene-based materials. Hydrophilic property of GO makes this material easily dispersed in water and deposited on substrates [2]. The most attractive property of GO is that the material can be (partly) reduced to graphene-like sheets by removing its oxygen-containing groups and recovery its conjugated structure [3].

Various coating methods have been used for GO depositions, such as spin coating, solution casting, dip coating and electro-deposition. Previously we prepared thin films of GO from GO dispersion in water using spin coating [4, 5] and drop casting [6] methods. It was reported one-step electrodeposition of GO in glassy carbon which the film deposited and reduced electrochemically [7, 8]. In this paper, we report preparation of GO film from GO that dispersed in water using voltage cyclic electrochemical deposition on indium tin oxide (ITO) substrate and its characterization.
2. Experimental
2.1 Preparation of Samples
For GO film preparation, we employed a commercial GO suspension (Graphenea SA ES A75022608) with concentration of 0.5 mg/ml that dispersed in water. Prior to use, GO dispersion was sonicated for 1 h at room temperature. Indium Tin Oxide (ITO) glass with size of 2.5 cm x 1.25 cm that used as conductive substrate was cleaned with teepol and then rinsed respectively with aquades, ethanol and isopropanol using ultrasonication for 15 minute at 50°C and dried before used.

The GO samples were electrochemically deposited in three-electrodes electrochemical cell contained GO/milliQ water dispersion with a clean ITO glass substrate as a working electrode, a platinum plate as a counter electrode, an Ag/AgCl as a reference electrode, and was carried out by different number of voltage cycles deposition. The GO films were deposited on the ITO glass substrates in the voltage range of -1.6 to 0 V at scan rate of 75 mV/s. The voltage range was setting in respect to the reference electrode.

2.2 Sample Characterizations
Electrochemically prepared GO films were characterized using UV-Vis spectroscopy (T70+ UV-Vis Spectrometer) in the wavelength range of 200 nm to 700 nm and FTIR in order to inspect deposited GO in the substrates. Scanning electron microscope (SEM) and EDX of GO samples were measured using HITACHI SUE3500. Cyclic voltammetry (CV) measurements of samples were carried out using a MetrOhm Autolab potentiostat in 1 M KCl.

3. Results and Discussion
3.1. Electrochemical Deposited GO Films
Visually we can observe a color change of ITO substrate after one cycle of voltage scanning with a scan rate of 75 mV/s in range of -1.6 V–0 V. It indicates a deposition of GO on ITO substrate has been taken place. In order to follow a deposition process, we run an in-situ current-voltage (CV) measurement in the GO/milliQ water dispersion. Figure 1 shows the current change during voltage scanning of GO films deposition in ITO glass substrate, from one cycle until six cycles. We found that a shape of CVs changed with increasing number of cycle. The change of peak currents with increasing number of voltage scans confirm that the deposition of GO on ITO substrate has taken place during the cycle.

![Figure 1](image-url)

Figure 1. Current-Voltage change on 0.5 mg/ml GO-milliQ water during GO deposited on ITO substrate at varied number of cycles.
Quantitatively an increasing of GO films thickness with increasing number of deposited cycles were characterized by using UV-Vis spectroscopy at range wave length 200 – 700 nm. We observed an increasing of absorbance of GO films with increasing number of voltage cycles applied during the deposition. Figure 2 shows the change of absorbance of samples that deposited at certain number of voltage cycles evaluated at several wavelengths. Figure 2 also shows that the absorbance change at higher wavelength is more pronounced than at shorter wavelength. It is obvious that the absorbance increased with increasing number of deposition cycles. The change of absorbance confirmed that number of voltage cycles applied during a deposition process influenced the film thickness. We found that until six cycles, the GO films deposited using higher number of deposition cycle will produce thicker GO films.

![Absorbance of GO films that deposited at varied number of voltage cycles.](image)

**Figure 2.** Absorbance of GO films that deposited at varied number of voltage cycles.

From EDX analysis GO samples on ITO substrate have 49.34 C atomic percentage and 50.66 O atomic percentages. The oxygen contain in the EDX result are contributed by GO and ITO substrate. The morphology of GO as shown by SEM images in figure 3 has wrinkled paper-like sheets. These geometric wrinkling is caused by nanoscale interlocking of GO sheets, providing enhanced mechanical properties, reduced surface energy, increased surface roughness and area [1, 2].

![SEM Image of electrochemical GO film on ITO glass substrate.](image)

**Figure 3.** SEM Image of electrochemical GO film on ITO glass substrate.

The FTIR spectrum of the GO film that prepared using six voltage-cycles deposition is shown in figure 4. The GO spectrum has peaks at 3400 cm\(^{-1}\) that corresponding to O-H stretching, at 1630 cm\(^{-1}\) related to C-C vibration, 1575 cm\(^{-1}\) related to C=C, 1382 cm\(^{-1}\) related to C-O carboxyl, and 1090 cm\(^{-1}\) related to C-O stretching. This spectrum is slightly different compare to the spectrum of GO film that prepared using drop casting [6] and spin coating [9]. The IR spectrum of the electrochemical deposited
GO film has no peak at 1735 cm\(^{-1}\) that related to carbonyl and carboxyl C=O group. Also the spectra of electrochemical sample have a weak peak at 1575 cm\(^{-1}\) that related to C=C. It is slightly similar to IR spectra of rGO film prepared using casting technique that has peak at 1575 cm\(^{-1}\) but no peak at 1735 cm\(^{-1}\) [6, 9]. This result shows that in electrochemical deposition technique, beside deposition of GO, the reduction process also slightly taken place.

![FTIR Spectra of electrochemical deposited GO film](image)

**Figure 4.** FTIR Spectra of electrochemical deposited GO film.

### 3.2. Electrochemically Prepared GO Films

The electrochemical measurement of GO film were carried out using cyclic voltammetry measurement with three electrode configuration, that RGO film on ITO as working electrode, a platinum as counter and Ag/AgCl as a reference electrode and 1 M KCl as electrolyte medium. Measurement were performed in voltage range of 0 V to 0.9 V at varied scan rate from 25 mV/s to 125 mV/s.

![Cyclic voltammograms of GO films prepared using 6 cycle Deposition at varied scan rate in 1 M KCl](image)

**Figure 5.** Cyclic voltammograms of GO films prepared using 6 cycle Deposition at varied scan rate in 1 M KCl.

As shown in figure 5, cyclic voltammograms of GO film that prepared using six voltage-cycles has a rectangular-like shape. It is indicated an electrochemical double-layer capacitance characteristics of the sample [10]. It is also obvious that the voltammograms in figure 5 do not have any peaks indicated the supercapacitive behavior of the electrochemical GO film. It is clearly that electrochemical GO film free from redox reactions or purely based on the electrostatic mechanism [11]. CV hysteresis area of these samples increases at the higher scan rates. CV hysteresis area are calculated according to equation (1) [12], where \( P \) is CV hysteresis area or power (\( \mu \)Watt), \( i \) is current respond and \( dV \) is step potential (which is 0.00244 V). The specific capacitance of RGO electrode obtained by CV measurements is calculated according to equation (2) [12], where, \( C \) is specific capacitance of RGO.
(F/g), m is mass of electroactive materials (g), $\Delta V$ is potential window (V), s is scan rate (mV/s) and i is current response in a given potential V.

$$P = \left( \int_{-0.2}^{0.8} i \, dV + \int_{0.8}^{-0.2} i \, dV \right)$$

$$C = \frac{1}{2m \cdot \Delta V \cdot s} \left( \int_{-0.2}^{0.8} i \, dV + \int_{0.8}^{-0.2} i \, dV \right)$$

We can see that the CV hysteresis area is increasing as the scan rate increased (figure 6(a)). It relates to current response of GO electrode, which at the higher scan rate the GO electrode can give the higher current response [13]. The calculation result of specific capacitance of GO electrodes at varied scan rates is shown in figure 6(b). The specific capacitance of GO is decreased at higher scan rate. It is well known that at very low scan rates, capacitance are higher because the ions have much longer time to penetrate and reside in the electrode pores and form electric double layers, which are needed to generate higher capacitance [11].

![Graph showing CV hysteresis area vs scan rate](image)

![Graph showing capacitance vs scan rate](image)

**Figure 6.** Hysteresis area (a) and capacitance of electrochemical deposited GO film at varied scan rate.

**4. Conclusion**

Graphene oxide (GO) can be deposited on ITO glass substrate using voltage-cyclic electrochemical deposition using voltage in range of -1.6 V to 0 V using scan rate of 75 mV/s. Thickness of GO film can be controlled by number of voltage cycle applied during deposition. The prepared GO film has lower oxygen contain compared to film prepared using casting. The voltammogram shows that the prepared GO has reduced electrochemical double-layer capacitance characteristic.

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