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Optimization the Conditions of Electrophoretic Deposition Fabrication of Graphene-Based Electrode to Consider Applications in Electro-Optical Sensors

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Abstract**—**Graphene has gained much attention owing to its unique optical and electrical properties. Charge carriers in graphene sheets (GS) carry out a linear dispersion relation near the Fermi energy and behave as massless Dirac fermions resulting in unusual attributes such as the quantum Hall effect and ambipolar electric field effect. It also exhibits nondispersive transport characteristics with an extremely high electron mobility (15000 $cm^2/(Vs)$) at room temperature. Recently, several progresses have been achieved in the fabrication of single- or multilayer GS for functional device applications in the fields of optoelectronic such as field-effect transistors ultrasensitive sensors and organic photovoltaic cells. In addition to device applications, graphene also can serve as reinforcement to enhance mechanical, thermal, or electrical properties of composite materials. Electrophoretic deposition (EPD) is an attractive method for development of various coatings and films. It readily applied to any powdered solid that forms a stable suspension. The deposition parameters were controlled in various thicknesses. In this study, the graphene electrodeposition conditions were optimized. The results were obtained from SEM, Ohm resistance measuring technique and AFM characteristic tests. The minimum sheet resistance of electrodeposited reduced graphene oxide layers is achieved at conditions of 2 V in 10 s and it is annealed at 200 °C for 1 minute.

Keywords**—**Electrophoretic deposition, graphene oxide, electrical conductivity, electro-optical devices.

I. INTRODUCTION

GRAPHENE with unique electrical, optical and mechanical properties has been used for many aspects of opto-electronic devices [1], [2]. Depending on the chemical structure and properties of graphene, it is produced in different methods [3], [4]. Graphene has many advantages due to quantum effects of a single atomic layer or few atomic layers [5]. Graphene oxide (GO) can be reduced via using different methods [5], [6]. Due to the difference in the conductivity between reduced GO and GO, an easy and efficient way to deploy reduced GO is required in many applications [7]-[9].

EPD method is used for applying graphene and graphene-based nanomaterials for a wide range of applications, including materials for energy storage [10], fuel cells, solar cells [11], super capacitors and sensors [12]. This type of carbon nanomaterial can be dispersed in organic solvents mainly in water [13], [14]. Most materials are electrophoretically applied under constant electrical potential in different application times [15]. These two parameters (electrical potential and time of application) play an important role in the morphology of created nanomaterial layers [16]. In addition to the simple planar substrates, researches have shown that graphene can interact on the basis of uniform layers on complex three-dimensional substrates, porous, and flexible substrates through EPD method [17]-[19]. In general, the graphene layers applied by EPD show that excellent properties, for example, high electrical conductivity, large surface area, good thermal stability, high optical transparency and appropriate mechanical strength [20]-[23]. Also, the composites contain graphene are applicable very well by EPD, e.g. graphene with metallic nanoparticles or carbon combined with other materials like carbon nanotubes (CNT) [24], [25]. Given the importance of using a highly conductive substrate with a facile manufacturing process in opto-electronic devices, graphene as an appropriate material is known in this field [26]-[29]. In various investigations, formation of graphene layers by EPD method is introduced, but optimization of all parameters involved in the process of electrophoretic depositing of graphene to ensure all electrical and optical properties suitable for opto-electronic applications is not fully performed yet. In this study, we have tried to meet this challenge.

Although several studies have investigated the EPD of GO, the key parameter's effect of EPD process on thickness and conductivity of uniform film has not been investigated completely.

In this research work, anodic electrodeposition of stable GO suspension was done on bare copper foil. The key parameters of EPD process (concentration of GO suspension, electrical potential and application time) due to the better morphology and electrical conductivity and minimum thickness of electrodeposited GO layers were optimized.

II. EXPERIMENTAL

A. Materials

The used materials (with their suppliers) are included of GO nano-platelets (Nanosany Co.), $Mg(NO_3)_2$, NaOH, Methoxy

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ethanol (Merck Co.) and Copper foil #40 microns (SDK-Metal Co.).

B. Equipment

The characteristics of used equipment in this research work are listed in Table I.

TABLE I
THE CHARACTERISTICS OF USED EQUIPMENT

Equipment	**Model**
Digital balance (with accuracy of 0.01 mg)	Sartorius/ CPA 2245
Ultra-sonicator	Bandelin electronic/ 510h
Rectifier	Wachter/ 0-600 V, 0-15 A
Aven	Carbolite/ CSF1100
Ohm meter	Fluke/ 1550B
Scanning electron microscope (SEM)	LEO 1455 VP
Atomic force microscope (AFM)	Micro Photonics Inc/ Dual scope DS 95-200E

C. Process

After stabilization of 0.2 %(w/w) GO in distilled water (@ 35 Hz/40 °C for 2 hours [30]), for anodic EPD process of GO suspension, the copper foil (~40 microns in 2*8 cm diameters and treated with Isopropyl alcohol) and graphite rod were used as anode and cathode, respectively. The distance between anode and cathode was 5.0 cm, and anode to cathode area ratio was 3.3. The temperature of electrophoretic bath was kept at 25 °C for all of the samples. The anodic electrophoretic deposition process of GO is shown in Fig. 1.

Fig. 1 The anodic EPD process of GO on Cu foil

After visually investigating the effects of GO concentration and electrical potential of EPD on deposition behavior of GO on copper foil, the application potentials of 2 and 5 V at application times of 10 and 20 s were selected for two concentrations of the prepared GO suspensions. The characteristics of appropriate samples are introduced in Table II.

TABLE II
THE CHARACTERISTICS OF APPROPRIATE SAMPLES

Sample code	**GO conc.(%w/w)**	**Application voltage (V)**	**Application time (s)**	**Thermal annealing condition**
0.01G-210	0.01	2	10	1 minute @ 200°C
0.01G-220	0.01	2	20	1 minute @ 200°C
0.01G-510	0.01	5	10	1 minute @ 200°C
0.01G-520	0.01	5	20	1 minute @ 200°C
0.2G-210	0.2	2	10	1 minute @ 200°C
0.2G-220	0.2	2	20	1 minute @ 200°C
0.2G-510	0.2	5	10	1 minute @ 200°C
0.2G-520	0.2	5	20	1 minute @ 200°C

III. RESULTS AND DISCUSSION

A. Characterization of Electrodeposited Graphene Films

EPD of dispersed GO on copper substrate was done based on the best conditions of applied potential, time and annealing temperatures (Table V). Images of appropriate samples after thermal annealing are shown in Fig. 2.

a-1 a-2 b-1 b-2 c-1 c-2 d-1 d-2

Fig. 2 Images of prepared samples after thermal annealing (a-1:0.01G-210, a-2:0.01G-510, b-1:0.01G-510, b-2:0.01G-520, c-1:0.2G-210, c-2:0.2G-220, d-1:0.2G-510, d-2:0.2G-520)

Visual results showed a remarkable darkness by increasing the GO concentrations in the same applied potentials (samples of a-1 and c-1 and also b-1 and d-1 from Fig. 2). The effect of higher application time on darkness of films is obvious at samples of c-1 and c-2 and also d-1 and d-2. As the same as GO concentration, applied potential and time of applied EPD were affected on thickness of GO layers certainly.

For evaluation the direct effect of electrical potential on the deposition behavior of GO, the electrical current density was monitored during potential application (at steps of 2, 5, 10, 20, and 30 V). The results of electrical current behavior of electrodeposited samples during potential application is shown in Fig. 3.

According to the results of Fig. 3, during the EPD of GO on the copper foil, because of high conductivity of the copper foil, the changes of electrical current at application potentials of 2, 5, 10, and 20 V are approximately constant. On the other hand, because of very low thickness of copper foil (~40 microns) at application potential of 30 V, the sparkle was seen at the copper substrate in application times of more than 10 s.

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Also, thickness of the GO film got very high, and the electrical current density was increased significantly in this condition. Therefore, electrical potentials of more than 20 V are not suggested for application of GO film on the copper substrate.

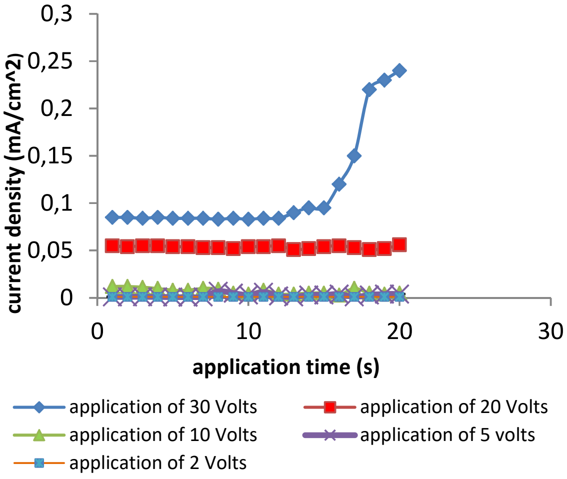
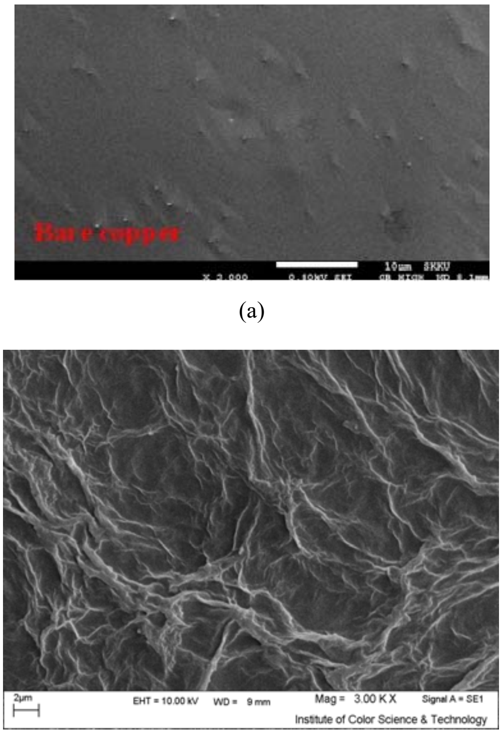


Fig. 3 The results of electrical current behavior of electrodeposited samples during potential application

B. Scanning Electron Microscopy (SEM)

The images of scanning electron microscopy (SEM) of bare copper foil and GO electrocoated sample (0.01G-210) are shown in Fig. 4.



(a)

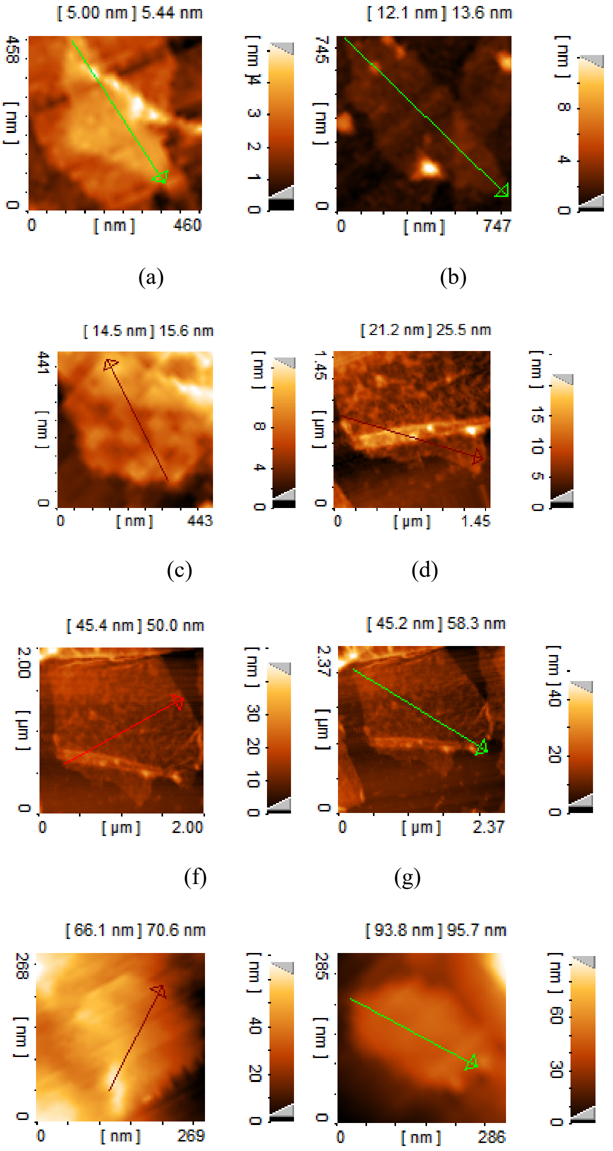
(b)

Fig. 4 The images of SEM of a) bare copper foil and b) GO electrocoated sample (0.01G-210)

As it is seen clearly in Fig. 4, the wrinkled graphene layers are deposited on the copper surface completely uniform.

C. Atomic Force Microscopy (AFM)

The images of atomic force microscopy (AFM) of samples are shown in Fig. 5.



(a) (b)

(c) (d)

(f) (g)

(h) (h)

Fig. 5 Images of AFM of samples (a:0.01G-210, b:0.01G-220, c:0.01G-510, d:0.01G-520, e:0.2G-210, f:0.2G-220, g:0.2G-510, h:0.2G-520)

The average thickness of GO layers that applied on the copper surface is evaluated, and the results are shown in Table III.

The results of AFM showed that the minimum average thickness of electrodeposited graphene film was 5.44 nm (sample#0.01G-210) compared to the maximum average that was 95.7 nm (sample#0.2G-520). The AFM data manifested that, by increasing the key parameters of EPD (GO concentration, electrical potential and application time), the

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average thickness of GO layers deposited on the copper surface is increased continually. Also, by increasing the thickness of GO layers, the coarseness profile of samples is much greater, so it confirms the increase of the wrinkling of GO layers too.

TABLE III
ELECTRODEPOSITION CHARACTERISTICS OF PREPARED SAMPLES

Sample code	Deposition efficiency (mg.cm^{-2})	Sheet resistance (kΩ)/ [sheet resistance of bare copper: 2.40 kΩ]	Average thickness of GO layers (nm)/ [evaluated by AFM method]
0.01G-210	0.11	0.81	5.4
0.01G-220	0.15	0.84	13.6
0.01G-510	0.22	0.91	15.6
0.01G-520	0.26	0.92	25.5
0.2G-210	0.50	2.11	50.0
0.2G-220	0.75	2.20	58.3
0.2G-510	0.91	2.71	70.6
0.2G-520	1.21	2.83	95.7

The results showed that the sheet resistance of the copper substrate with less-layered graphene coating (0.01G-210) is decreased to one over third of initial value of un-coated copper surface sheet resistance. In the other words, the electrical conductivity of electrocoated copper surface after thermal annealing (in accordance with the application conditions of sample# 0.01G-210) is increased three times. According to the results of Table III, by increasing the thickness of RGO coating (by increasing the GO concentration, electrical potential or application time), the sheet resistance of RGO is increased continually so that, by increasing the GO concentration, the rate of sheet resistance increasing trend is much faster. As it is clear from Table III, the minimum sheet resistance of electrodeposited graphene film was 0.8 kΩ (sample#0.01G-210) compared to the maximum one (2.8 kΩ). The reason of this fact is thickness increase of the GO layers deposited on the copper surface and aggregation of graphene sites on the copper surface. In this condition, by significantly increase in thickness of graphene layers, the more resistance barrier is created in the way of electron transfers, so theoretical adaptation of electron mobility within the mono-layer graphene is less according to the Dirac equation.

IV. CONCLUSION

In this research work, anodic electrodeposition of stable GO suspension was done on bare copper foil. The key parameters of EPD process (concentration of GO suspension, electrical potential and application time) due to the better morphology and electrical conductivity and minimum thickness of electrodeposited GO layers were optimized. Electrical current behavior, deposition efficiency, sheet resistance measurement, scanning electron and atomic force microscopy tests were evaluated on the prepared electrocoated GO films applied on copper substrate. All of the carried tests showed that, by increasing the key parameters of EPD, the average thickness of electrodeposited GO layers is increased continually so that the GO concentration effect is the most evident factor. In this study, the minimum sheet resistance and average thickness of electrodeposited RGO layers with uniform wrinkled morphology are achieved at EPD conditions of 2 V in 10 s and annealed at 200 °C for 1 minute. In these conditions, the minimum sheet resistance and average thickness of electrodeposited graphene films which are achieved are 0.8 kΩ and 5.44 nm, respectively. The results of this research manifested that the EPD method is the novel, low cost, and well controllable method to fabricate very conductive electrode base for electro-optical devices. Chemical vapor deposition technique could be replaced by this method to form a low thickness GO film very well.

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