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Additive-free electrophoretic deposition of graphene quantum dots thin films

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Abstract: The electrophoretic deposition (EPD) of graphene-based materials on transparent substrates is highly potential for many applications. Several factors can determine the yield of EPD process, such as applied voltage, deposition time, and particularly the presence of dispersion additives (stabilizers) in the suspension solution. This study presents an additive-free EPD of GQDs thin films on Indium Tin Oxide (ITO) glass substrate and studies the deposition mechanism with the variation of the applied voltage (10 – 50 V) and deposition time (5 – 25 min). It is found that due to the small size (~3.9 nm) and high content of deprotonated carboxylic groups, the GQDs form a stable dispersion (zeta potential of about – 35 mV) without using additives. The GQDs thin films can be deposited onto ITO with optimal surface morphology at 30 V in 5 min (surface roughness of approximately 3.1 (±1.3) nm). In addition, as-fabricated GQDs thin films also possess some interesting physico-optical properties, such as a double-peak photoluminescence at about 417 and 439 nm, with ca. 98% visible transmittance. This low cost and eco-friendly GQDs thin film is a promising material for various applications, e.g. transparent conductors, supercapacitors, and heat conductive film in smart windows.

Introduction

Quantum dots (QD), carbon QDs (CDs, CQDs or C-dots) and graphene QDs (GQDs) have recently emerged as a promising cost-effective alternative to conventional graphene. The advantages of CDs and GQDs over conventional inorganic QDs include their non-toxicity, excellent solubility, stable photoluminescence, better surface grafting and possibility for large-scale industrial production. Many methods have been developed to fabricate GQDs. Previously, GQDs were often obtained from high-cost raw materials such as graphene ^[1] or

photonic crystals ^[2], or prepared by costly and low-effective methods such as laser ablation, ^[3] electron beam lithography, ^[4] electrochemical synthesis, ^[5] or photo-Fenton reaction of graphene oxide (GO). ^[6] In order to reduce production costs, the possibility of fabricating GQDs from inexpensive material sources such as coal or graphite flakes has been investigated. ^[7] Recently, the synthesis of GQDs from citric acid or urea, has been reported, allowing GQDs to be produced at lowered costs and on a larger scale. ^[8]

The processing and application technique plays an important role when exploiting the exceptional properties of graphene-related materials. Amongst which, electrophoretic deposition (EPD) is one of the most attractive methods that could lead to many promising applications of graphene-based materials. ^[9] EPD is described as a compact film deposition process, in which an electric field is used to move charged particles in a suspension towards an oppositely charged electrode. ^[10] Graphene-based thin films prepared by EPD can be used for energy storage applications, ^[11] field emission devices, ^[12] solar cell electrodes, ^[13] transparent conductors, ^[14] electrochemical sensors and biosensors, ^[15] and more. Recently, Yeo et al. also reported the EPD of reduced graphene oxide (rGO) thin film on Fluorine-doped Tin Oxide (FTO) glass, which can be used to manage heat conduction in smart window applications. ^[16]

However, besides the drawbacks in terms of fabrication costs and issues with homogenous, large-area surface grafting, graphene and graphene oxide-based materials also pose several challenges in EPD, particularly the difficulty in obtaining a stable and homogenous suspension solution, the requirement of applying high voltage or long deposition time, and the need of dispersion additives (stabilizers). Moreover, in the applications of transparent conductors or smart windows, the low visible transparency of graphene and graphene oxide is also a serious limitation that needs to be resolved. These drawbacks can be solved by using other graphene-derived materials such as GQDs or graphene nanoplatelets, which have similarly excellent properties as that of graphene or GO, but with significantly improved optical properties. ^[8d,e, 17] In addition, with its smaller size and lighter weight, the use of GQDs may reduce the applied voltage and improve the yield of EPD.

Yet, the EPD of GQDs has not been widely reported to date. Pan et al. and Li et al. reported the EPD of GQDs on TiO₂ nanotubes arrays for photo-electrochemical water splitting applications using NaOH as a dispersion additive. ^[18] 3D nano-arrays of Ag nanoparticles and GQDs were prepared using a photochemical approach and EPD for active surface-enhanced Raman scattering applications. ^[19] Recently, Yan et al. have reported a one-step electrodeposition method to immobilize GQDs on gold electrode for electrochemiluminescent

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applications, in which chitosan was used as a dispersion additive.^[20] The study on EPD of GQDs on transparent conductive glass, e.g. ITO or FTO, is even less common. In general, the use of dispersion additives causes the risk of side reactions during the EPD process, i.e. the electrochemical reaction of additives, which can affect the quality of the final product.^[21]

In this paper, we investigated the formation of GQDs thin film on ITO substrate by additive-free EPD. The GQDs were obtained from the pyrolysis of citric acid and then dispersed in ethanol solution to obtain the suspension for deposition. The mechanism of EPD was investigated, together with the influence of applied voltage and electrodeposition time on the surface morphology and physico-optical properties of the GQDs thin films. It is found that the GQDs dispersion in ethanol is highly stable due to its small size and high content of deprotonated carboxylic groups. In addition, the variation of applied voltage affects significantly the surface roughness and homogeneity of GQDs thin films, while the deposition time has a lesser impact. These fabrication conditions do not change the chemical structures and physico-optical properties of GQDs. The UV-Vis spectra of the as-deposited thin film show absorption peaks at 300 and 380 nm, with approximately 98% visible transmittance. The photoluminescence spectra show a doubled emission peak at ca. 417 and 439 nm. This study serves to provide valuable findings for the additive-free EPD of GQDs on transparent conductive glasses.

Results and Discussion

Electrophoretic deposition mechanism and thin film formation of GQDs: Highly-dispersible GQDs were synthesized by pyrolysis of citric acid at 200 °C. Figure 1 shows the HRTEM images of as-synthesized GQDs dispersed in ethanol. The GQDs observed are small and uniform, with an average diameter of ca. 3.9 (±0.6) nm and a lattice parameter of 0.21 nm (Figure S1). The small size improved the dispersibility of the GQDs in ethanol, enabling a concentrated dispersion of as high as 4% to show a remarkable stability of up to six months.

Figure 1. HRTEM images and SAED pattern of GQDs in dispersion solution.

Figure 2. ζ -potential of GQDs (0.4% wt) dispersion in ethanol and deposited weight of GQDs coating as a function of HCl (1 M) addition.

EPD is a powerful technique for the deposition of various nanomaterials, both organic and inorganic, as a result of their migration based on their surface charges under electric field towards the electrode with the opposite polarity.^[10] Several theories, such as charge neutralization and particles coagulation, have been addressed for a more profound understanding of the deposition mechanism of charged particles at the electrode surface.^[22] Different additives can be utilized in order to charge and control the deposition mechanism. For instance, Lee et al. used Mg^{2+} to positively charge carboxylated GQDs, which enabled their deposition at the cathode surface, to fabricate highly flexible supercapacitors.^[11e] Yan et al. deposited GQDs on gold electrode with the assistance of chitosan additive.^[20] The proposed mechanism was based on charge neutralization of the metal ions by reduction of residual water to form metal hydroxide.^[23] In this work, the set up for depositing GQDs was carried out without any additives, such as metal salts and polymers. Therefore, it is essential to understand the deposition mechanism of carboxylated GQDs on the ITO anode.

Firstly, the dispersion stability was determined by measuring the ζ -potential as a function of acid addition. This was mandatory in order to understand whether the EPD of GQDs is driven by the protonation of the carboxylic acids, which was studied for other carboxylic acid stabilized-nanoparticles.^[24] Figure 2 shows the dependence of the ζ -potential of GQDs in ethanol as a function of HCl (1 M) addition. Since the EPD was conducted in an organic solvent, i.e., ethanol, pH measurements are inaccurate and meaningless. The as-synthesized GQDs are negatively charged in ethanol due to the high content of deprotonated carboxylic acids. Accordingly, the ζ -potential of the dispersed GQD is ca. -35 (±3) mV, which explains its high colloidal stability. Therefore, utilizing electrophoresis as the driving force for the deposition of well-dispersed GQDs onto ITO surface under positive potential could be feasible. It can be observed that the ζ -potential decreased from -35 (±3) to -12 (±3) mV as the amount of HCl added to the dispersion increased from 0 to 1.5 mL. As the ζ -potential decreased (absolute value),

the GQDs were expected to aggregate due to insufficient repulsive forces and favourable van der Waals interactions. Surprisingly, the GQDs remained stable and there was no sign of aggregation as can be observed in Figure S2.

Further insight into the effect of adding HCl on the surface charge of the GQDs was obtained by studying the EPD efficiency, i.e., the amount of deposited GQDs as a function of HCl added. Since EPD is based on the migration of charged particles under an electric field, their surface charge plays a crucial role in determining the quality and amount of deposit at the electrode surface. Figure 2 shows also the dependence of the GQDs deposited weight as a function of HCl addition. It is observed that the addition of HCl, which diminishes the surface charge of the negatively charged GQDs, correlates well with the inferior deposited weight. In other words, reducing the ζ -potential resulted in inadequate electrophoretic mobility under electric field. This is evident by the reduction in deposited weight from ca. 0.33 to 0.12 mg.cm⁻² upon adding 1.5 mL of 1 M HCl.

Even though the addition of HCl indeed reduced the surface charge of the GQDs, no aggregation was observed and the GQDs dispersion remained stable. Therefore, it is reasonable to assume that the driving force of the EPD of GQDs in this system is based on the accumulation of the GQDs on the anode surface, where thinning of the electrical double layer is induced by the electric field, which results in favourable van der Waals attractive forces and subsequent film formation.^[10] As evidence, Figure 3a-e shows the low magnification XHR-SEM images of GQDs coating deposited at different voltages. It can be observed that at low voltages <30 V (Figure 3a-b), a discontinuous film consisting of islands is formed due to insufficient migration and accumulation of GQDs at the anode surface. At stronger electric fields ≥ 30 V, a well-adhered, dense and uniform GQDs film is formed due to fast migration and

enhanced aggregation of GQDs at the anode surface (Figure 3 c-e). Figure 3f-g shows high magnification XHR-SEM images of GQDs film deposited at 10 and 50 V, respectively. These images emphasize that at high voltages, a dense and uniform film is obtained, whereas at low voltages, an irregular and inferior coating is formed. In addition, no significant morphological change is observed as the deposition voltage increased beyond 30 V.

Table 1. Thickness measurement (based on FIB cutting) of GQDs coatings deposited at 30 V for different time (5-25 min).

Time	5	10	15	20	25
Thickness (nm)	24 $\pm$ 1.6	35.4 $\pm$ 1.8	48.7 $\pm$ 2.6	74.4 $\pm$ 5.6	188.2 $\pm$ 2.7

Since a continuous GQDs film was obtained only at voltage ≥ 30 V, we investigated the impact of the deposition duration on the thickness of the film. Table 1 indicates that the thickness of the GQDs film was gradually increased as a function of the deposition time. Specifically, the thickness increased from 24.0 ($\pm$ 1.6) to 188.2 ($\pm$ 2.7) nm as the deposition time increased from 5 to 25 min, respectively. Figure S3 shows XHR-SEM images of the cross-section of GQDs film deposited at 30 V for 5 and 25 min. It can be seen that the conducting glass is composed of a thin layer of ITO (65 $\pm$ 2 nm). Since the electrical conductivity was poor, a few nanometers of Au-Pd layer was sputtered on top of the GQDs film in order to reduce the charging effect during the imaging. In addition, protective films of Pt were sputtered before the FIB cutting to prevent any damage to the carbon layer. These results manifest the controllability of the EPD process in tailoring GQDs coating with a desired morphology and thickness.

Figure 3. Low magnification XHR-SEM images (a-e) of GQDs coatings (deposited at 10, 20, 30, 40, 50 V for 5 min, respectively). High magnification XHR-SEM images of GQDs obtained at voltages of 10 (f) and 50 V (g) for 5 min.

Figure 4. AFM images of ITO substrate (a) and GQDs thin films obtained at 10 (b), 30 (c), 50 (d) V in 5 min, as well as in 15 (e) and 25 (f) min at 30 V.

Surface structure and morphology of GQDs thin films:

Figure 4 presents the AFM images of ITO substrate and several GQDs thin film samples obtained with various applied voltages and deposition times (AFM images of all samples can be found in Figure S5). In comparison with the bare ITO glass surface, the surfaces of electrophoretically deposited GQDs samples are less smooth, especially with higher applied voltage and longer deposition time. Similar to FESEM observation, the thin film deposited at 10 V in 5 min shows a non-uniform surface coverage. At 30 V, the GQDs thin film becomes much more dense and uniform. However, at higher voltages (40, 50 V) and longer deposition times (10 – 25 min), the surface roughness of as-fabricated GQDs thin film seems to dramatically increase. The average surface roughness of all samples is detailed in Figure 5. The left (black) columns represent the surface roughness for GQDs thin film obtained at various applied voltages (in 5 min), while the right (orange) columns indicate the samples obtained with different deposition times (at 30 V). The ITO substrate has a smooth surface, with a surface roughness of approximately 4.4 (± 1.6) nm originally. With an applied voltage of 10 and 20 V, the surface roughness of GQDs thin film increases to about 5.6 (± 1.6) and 10.4 (± 3.8) nm, respectively. The highest surface roughness value is observed for the sample at 40 and 50 V, which is about 13.2 (± 6.7) and 15.1 (± 2.9) nm, respectively. Interestingly, when the applied voltage is 30 V, the smoothest GQDs thin film could be produced with a surface roughness of approximately 3.1 (± 1.3) nm. However, when the deposition time at 30 V increases to 10 and 15 min, the surface roughness of GQDs thin films also increases to about 10.6 (± 1.7) and 13.1 (± 4.5), respectively. It dramatically increases up to 20.7 (± 15.8) and 22.0 (± 10.7) nm for 20 and 25 min deposition, respectively. Overall, both applied voltage and deposition time could affect the surface roughness of the GQDs thin films, with

the sample obtained at 30 V in 5 min, yielding a thin film with the most optimal surface roughness.

Surface chemistry and physico-optical properties of GQDs thin films:

Figure 6 shows the FTIR spectra of GQDs thin films obtained by various deposition conditions. All the typical FTIR absorption peaks for GQDs thin films can be observed, as denoted in this figure. The strong peaks at 1696 and 1206 cm^{-1} are associated with the vibration of C=C and C-OH bonds, respectively. The absorption of carboxyl and hydroxyl groups are also observed, as evidenced by the COO⁻ symmetric stretching vibration at about 1400 cm^{-1} and the COO⁻ antisymmetric stretching vibration at 1571 cm^{-1} . In addition, there are also two small absorption peaks at 1766 and 1025 cm^{-1} , which can be attributed to the vibration of C=O and C-O-C bonds, correspondingly. [1b, 8a, 25] This implies that the GQDs deposited on ITO glass did not see a change in their chemical structures.

Figure 5. Surface roughness of GQDs thin films prepared under various conditions: Left (black) column: various applied voltages in 5 min; Right (orange) column: various deposition times at 30 V.

Figure 6. FTIR spectra of GQDs thin films obtained at different applied voltages in 5 min (a) and deposition times at 30 V (b).

Figure 7 shows the XPS spectra of the as-fabricated GQDs thin film. The wide scan spectra (Fig. 7a-b) show the presence of In3d peak in ITO substrate, and C1s and O1s peaks. As the peak intensity of In3d in all samples is much lower than others, the elemental composition was estimated only for C1s and O1s components from XPS data. The detailed atomic percentage of C1s and O1s in all GQDs thin films is presented in Figure 7c-d. In general, the C/O ratios of all GQDs thin films are ca. 65/35, which are similar to previous reports on GQDs.^[1c] Wang et al. reported that the C/O ratio of GQDs prepared by pyrolysis of citric acid at 180 °C is about 1.8,^[8c] which is in good agreement with the finding in this work (~1.86). For the EPD sample of 10 V for 5 min, the GQDs are only partially deposited on ITO substrate as shown in Figure 3, hence the C/O ratio is estimated to be about 60/40, due to the contribution of O content from ITO glass. At 20 V, with denser GQDs layer, the C/O ratio now increases to about 65/35. Despite further increasing applied voltage, however, the C/O ratios of the samples remain mostly unchanged. When the deposition time was varied, the C/O ratio increases up to 70/30 as the deposition time increases from 5 to 10 min. However, this value starts to decrease with longer deposition times. This may be due to the oxidation of GQDs when subjected to a longer deposition process at 30 V applied voltage.

The fine XPS measurements were used to further analyze the elements in GQDs thin films, as shown in Figure 7e-f. By curve-fitting analysis (Gauss*Lorentz Algorithm), the C1s spectrum indicates that GQDs thin films have 3 main types of C atoms: C-C/C=C, C-O-C, and C=O/COOH, respectively. The highest peak (~285 eV) belongs to C-C/C=C component, which is attributed to the sp² and sp³ hybridization of carbon. The peaks at ~286.9 and ~289.2 eV represent the contributions of hydroxyl/epoxy and carbonyl/quinone/carboxyl groups, which are common in the GQDs structure.^[1c, 7b, 26] The best fitting for O1s indicates that GQDs thin films have two types of O atoms (organic C-O (~532.6 eV) and C=O (~534 eV)), respectively. The deconvolution of C1s and O1s core-level spectra for other GQDs thin films samples shows similar results, which can be

found in Figure S6. It should be noted that in C1s deconvolution, the amount of C=O/COOH component is generally higher than that of C-O-C component, which is in agreement with the study of Yan et al. when depositing GQDs on gold electrode.^[20] The detailed atomic percentage of C1s and O1s components are listed in Table 2. Similar to the C/O ratio observed in Fig. 7c-d, the atomic percentage of each atom of C1s and O1s components does not significantly change with the variation in the applied voltages. However, the increasing deposition time results in the reduction in the C-C amount, thus causing a decrease in overall C content in all samples as seen in Fig. 7c-d. The oxidation of GQDs under long EPD time could also be the reason for such phenomena.

Table 2. Elemental composition of GQDs thin films by XPS analysis.

Samples	C1s			O1s	
	C-C	C-O-C	O-C=O	C-O	C=O
5 min					
10 V	31.4±0.8	8.5±0.7	20.2±0.7	19.4±0.5	20.6±0.6
20 V	32.4±0.9	11.2±0.8	21.2±0.8	18.2±0.5	16.9±0.5
30 V	33.8±0.9	9.0±0.8	19.8±0.8	19.1±0.5	18.4±0.6
40 V	36.2±0.9	9.9±0.8	18.4±0.8	16.6±0.6	18.9±0.6
50 V	34.5±0.9	9.8±0.8	19.4±0.7	18.5±0.5	17.9±0.6
30 V					
10 min	40.3±1.0	14.3±0.9	15.1±0.8	17.6±0.6	12.8±0.5
15 min	34.0±0.9	14.9±1.0	17.8±0.8	10.9±0.5	22.4±0.7
20 min	33.0±0.9	12.3±0.9	19.4±0.7	18.6±0.5	16.7±0.5
25 min	31.6±0.9	13.4±0.9	18.6±0.8	20.5±0.6	15.9±0.5

Figure 7. XPS spectra (a-b, elemental composition (c-d), and deconvolution of C1s and O1s core-level XPS spectra (e-f) of different GQDs thin films.

The physico-optical properties of as-fabricated GQDs thin films were characterized by UV-Vis and PL measurements. Figure 8 shows the UV-Vis absorbance spectrum of GQDs thin films for 200 – 800 nm. Two absorption peaks are observed for the samples with different applied voltages and deposition times. The first absorption peak is at approximately 300 nm, which is similar to the UV-Vis absorption behaviour of GQDs solution prepared by cutting graphene [1a, c] or carbon fibre [27], by electrochemical synthesis of graphene [5] or from the pyrolysis of citric acid. [8b] The GQDs electrodeposited on gold electrode also demonstrate a similar absorption peak at ca. 300 nm. [20] The second, more obvious absorption peak is located at ca. 380 nm, which also matches the samples fabricated by pyrolysis of citric acid in previous reports. [8a, c, 25b] The appearance of two absorption peaks in the UV-Vis spectra of as-fabricated GQDs

thin films can be attributed to the formation of a graphene-like component by the assembly of GQDs on ITO surface. The size of GQDs cut from graphene source is generally larger, ca. 8 – 10 nm, than by other methods. Comparatively, the GQDs fabricated in this work is significantly smaller, ca. 3.9 nm. [1a, c] Most importantly, the GQDs thin films obtained by EPD in this study demonstrate excellent visible transparency. The visible transparency of the film can be confirmed in Figure S7, where even the thickest film (25 min, 30 V) could barely be observed by the naked eye. The UV-Vis measurement within the range of 300 – 800 nm reveals that as-fabricated GQDs thin films allow an average of more than 98% visible light transmittance for all synthesis conditions (Figure S8 and Table S1). This value is

Figure 8. UV-Vis spectra of GQDs thin films obtained at different applied voltages in 5 min (a) and deposition times at 30 V (b).

Figure 9. PL spectra of GQDs thin films prepared by various fabrication conditions excited at 330 nm (a-b). Emission spectra of different GQDs thin films with excitation at different wavelengths (c-f).

much higher than that reported by Choi et al. in their work on electrophoretic deposition of graphene film on FTO glass, which resulted in 80% transmittance for samples deposited for 5 s. [13a] Ishikawa et al. reported on graphene films deposited on glass substrate (with a back electrode) by EPD with only 83.8% visible transmittance. [14b]

Figure 9 shows the photoluminescence (PL) spectra of as-fabricated GQDs thin films under various deposition conditions. When excited by UV at 330 nm, all GQDs thin film samples emit two bands at ca. 417 (indigo) and 439 (blue) nm, with the latter having a higher intensity (Fig. 9a-b). The indigo light emission was similarly observed for the carbon dots obtained by the pyrolysis of epoxy-enriched polystyrene (PS) photonic crystals at 300 °C. [2] Moreover, Chhabra et al. also reported the preparation of indigo emitting GQDs by citric acid pyrolysis. [7d] The reports on blue emission of GQDs are more common, and have been observed for the GQDs obtained from graphene, graphite and carbon fibre sources, [1a, 7b, 27] or by photo-Fenton reaction of graphene oxide. [6] The pyrolysis of citric acid at 160 °C is also able to produce blue emission GQDs. [8b] With the excitation at different wavelengths ranging from 300 to 340 nm, the emission wavelength of all GQDs thin films is found almost independent of the excitation wavelength (Fig. 9c-f and Fig. S9). The PL intensity of all samples, however, increases proportionally with the increasing excitation wavelength. The excitation-independent PL spectra of as-fabricated GQDs thin films are in agreement with many other studies on GQDs. [6b, 7a, 8a-c, 25b] Particularly, this emission feature of GQDs thin films is very similar to that of the carbon dots prepared by pyrolysis of citric acid and urea mixture at 160 °C, in terms of both excitation wavelength (~440 nm) and their excitation-independent property. [8b] This observation reveals that the EPD process causes a minor effect on the PL properties of GQDs thin film, while the

nature of the GQDs remaining mostly unchanged. Nevertheless, a stable and intensity-variable emission light can be achieved with the GQDs thin film obtained by EPD method.

Conclusions

In this study, a highly transparent GQDs thin film has been successfully fabricated on ITO substrate by electrophoresis without using any additives. Due to the small size and high content of deprotonated carboxylic groups, the GQDs dispersion solution is sufficiently stable for electrophoretic deposition. The optimal surface morphological properties of as-fabricated GQDs thin film can be achieved by varying the applied voltage and deposition time, and was found to be at 30 V and 5 min. Such thin films also possess many excellent physico-optical properties of the original GQDs, e.g. a double-peak photoluminescence and excitation-independent emission. Moreover, the deposited films provide as high as 98% visible transparency. The low-cost and eco-friendly GQDs thin films are likely to make electrophoresis an appealing approach and the films a promising material for various applications such as transparent conductors, supercapacitors and smart windows.

Experimental Section

Electrophoretic deposition of GQDs thin film: The fabrication of GQDs thin films was conducted in two steps and is presented in Scheme S1. For the synthesis of GQDs, 4 g of citric acid (ACS reagent, Sigma) in a glass beaker (100 mL) was placed inside an oven. The oven was heated and maintained at 200 °C for 40 min. Subsequently, the dark orange liquid formed was cooled down to room temperature and 100 mL of ethanol (EMSURE® ACS, Merck) was added. A stable dispersion was

obtained after 20 min of sonication using a standard ultrasonic bath. After sonication, the dispersion solution was centrifuged at 10000 rpm for 10 min to discard any aggregates.

EPD was conducted by using a DC power supply (Major Science, Mini 300) in a conventional two-electrode cell. Prior to EPD, ITO was ultrasonically cleaned in acetone, ethanol and water for 10 min, each. Cleaned ITO substrate (with a rectangular size of 4 × 5 cm²) was used as the anode, while stainless steel 316L with the same dimensions was used as the cathode. The two electrodes were placed in parallel and the distance between them was approximately 1 cm. For each experiment, a fresh 10 mL dispersion solution was used on a deposited area of 4 × 4 cm². The EPD was carried out either by applying different voltages (10–50 V) for 5 min, or under a constant voltage of 30 V for different deposition time (5–25 min). After deposition, the coated ITO was gently washed in ethanol and dried at ambient temperature.

Characterization: The geometrical feature of GQDs in dispersion was characterized by a JEOL 2010 high-resolution transmission electron microscope (HRTEM). The stability of GQDs suspension was determined by a Malvern ZS Zeta Potential-Zetasizer machine. The surface morphology and deposited thickness of GQDs thin film were measured by an extreme high-resolution scanning electron microscope (XHR-SEM, FEI MagellanTM 400L) and a focus ion beam-SEM (FIB-SEM, FIB-460F1 Dual Beam). The amount of GQDs deposition was estimated by measuring the weight of ITO substrate before and after EPD using a microanalytical balance (Mettler Toledo, XP26). The surface roughness of GQDs thin films were characterized by an atomic force microscope (AFM) (Asylum Research Cypher S) via the AC Air Topography mode.

A Perkin Elmer Frontier spectrophotometer was used to measure the Fourier-transform infrared (FTIR) spectra of as-fabricated GQDs thin films. The surface chemistry of GQDs thin films was characterized by a Kratos AXIS Supra X-ray photoelectron spectrometer (XPS). The ultraviolet-visible (UV-Vis) spectra were measured on a Cary 500 UV-Vis-NIR spectrophotometer. The photoluminescence (PL) of GQDs thin films was measured by a Cary Eclipse spectrofluorometer. Experimental Details.

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Keywords: electrophoretic deposition • additive free • graphene quantum dots • thin film • visible transparency

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