

# Photoelectrochemical properties of electrostatically self-assembled multilayer films formed by a cobalt complex and graphene oxide

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## ABSTRACT

The multilayer films consisting of graphene oxide and a cobalt complex were fabricated through electrostatic layer-by-layer self-assembly technique and characterized by UV–Vis absorption spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and cyclic voltammetry. The results demonstrated that the hybrid films were successfully prepared and exhibited good electrochemical activity. The film was also subjected to photoelectrochemical studies and were found to exhibit large cathodic photocurrent density of  $6.1 \mu\text{A}/\text{cm}^2$  while irradiated with  $100 \text{ mW}/\text{cm}^2$  polychromatic light ( $730 \text{ nm} > \lambda > 325 \text{ nm}$ ) at an applied potential of  $-0.4 \text{ V}$  versus saturated calomel electrode.

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## 1. Introduction

As a novel carbon material discovered in 2004 [1], two-dimensional (2D) graphene with only a single layer of carbon atoms has received great attention owing to its extraordinary properties including high charge-carrier mobility and optical transparency [2], flexibility, robustness [3], and environmental stability [4]. Its atomically thin plane geometry, unusual band structure, and unique transport properties make it a promising candidate for the application in nano-electronics, catalysis, energy storage, and photovoltaics [5–7]. However, the applications of graphene have been hindered by its poor processability which is mainly caused by the high interlayer attraction energies. This problem can be solved by the modification on the sheet surface through either a covalent or a noncovalent method [8]. Solution-processable graphene can be derived from an aqueous suspension of graphene oxide (GO) that could be obtained by reacting with strong oxidants. The sheet surface of the GO can thus carry hydroxyl, epoxy, and carboxyl groups [9,10]. The presence of oxygen functionalities on the surface of GO not only make GO become active and easily absorbed by polar molecules [11–13] and polymers [14,15], forming different composites, but also provide the reactive sites for chemical modification or functionalization [16].

Besides covalent functionalization, some simple and versatile noncovalent methods through supramolecular interactions such as  $\pi$ – $\pi$  stacking, electrostatic interaction, and hydrogen bonding have the advantage of preserving the unique electronic properties

of GO without serious damage [8]. In recent years, as one of the simplest and versatile methods in constructing molecular assemblies on a surface, electrostatic layer-by-layer (LBL) self-assembly technique initially introduced by Decher [17] has been applied to fabricate GO-based multilayer films by taking advantage of GO's negatively charged surface in aqueous solution [18–25]. The LBL films based on polyelectrolytes and GO have been reported for electrochemical and Li ion battery applications [19,20]. GO nanosheets and polyoxometalate clusters have been co-assembled into the LBL multilayer films, which showed excellent electronics properties [21]. The multilayer hybrid films based on graphene oxide and titania nanosheets have been reported and found to exhibit ultrafast electron transfer and photoconversion properties [22,23]. A ruthenium tris(bipyridyl) polymer has been successfully alternately adsorbed by GO, and the electroactivity of the junction has been observed at a positive bias [24]. Recently, we have reported monolayer GO film assembled onto protonated indium-tin oxide (ITO) coated glass electrode by LBL technique, which exhibited a large photocurrent density of  $3.72 \mu\text{A}/\text{cm}^2$  [25].

Among the species used for preparing GO-based hybrid materials, cobalt oxides and nitrogen-coordinated cobalt complexes have attracted considerable interest due to their low cost, simple preparation, high stability, and environmentally benign and electrocatalytic properties [26] and well-defined electrochemical redox activity [27]. For example, cobalt oxide nanowall arrays on reduced GO has been investigated as electrode materials for Li-ion batteries [28,29]. A manganese-cobalt spinel  $\text{MnCo}_2\text{O}_4$ /graphene hybrid has been developed as a highly efficient electrocatalyst for oxygen reduction reaction in alkaline conditions [30]. Herein, we report preparation and interesting electrochemical and photoelectric

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conversion properties of electrostatic LBL self-assembled multilayer films based on GO and a cobalt complex of CoTPPCl<sub>2</sub> {where TPP = 4'-(thiophen-2-yl)-2,2':6',2''-terpyridine} (see Scheme 1 for molecular structure).

## 2. Experimental

### 2.1. Materials

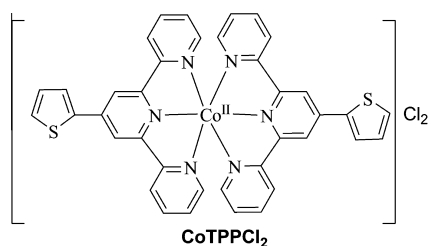
(3-Aminopropyl)trimethoxysilane (99%) was used as received from Acros. Ethyl viologen dibromide was prepared according to the previously reported method [31].

**Synthesis of CoTPPCl<sub>2</sub>·2CH<sub>3</sub>OH·H<sub>2</sub>O:** This was synthesized according to a slightly modified literature method described for synthesis of the nitrate salt of the same complex cation [32]. Briefly, to a solution of TPP (0.2 g, 0.64 mmol), 5 mL CHCl<sub>3</sub> was added CoCl<sub>2</sub>·6H<sub>2</sub>O (7.3 mg, 0.32 mmol) in methanol (10 mL) under constant stirring. The resulting brown–red solution was subjected to slow evaporation at the room temperature to afford brown–red crystals (0.15 g, 56% yield). Anal. Calcd. for C<sub>38</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>6</sub>S<sub>2</sub>Co·2CH<sub>3</sub>OH·H<sub>2</sub>O: C, 57.01; H, 4.31; N, 9.97. Found: C, 56.99; H, 4.33; N, 9.91. IR (KBr):  $\nu/\text{cm}^{-1}$ : ~3411 s, ~3053 m, 2891 w, 1610 s, 1566 w, 1542 m, 1525 m, 1472 s, 1428vs, 1370 w, 1334 w, 1305 w, 1247 m, 1118 w, 1094 w, 1050 w, 1009 m, 868 w, 857 w, 840 w, 790 s, 749 m, 708 s, 655 m, 561 w, 507 w, 463 w, 417 w.

**Preparation of GO:** GO was prepared from natural graphite by a modified Hummers' method [33]. Briefly, natural graphite (0.5 g) and concentrated H<sub>2</sub>SO<sub>4</sub> (11.5 mL) were added into a 100 mL flask and stirred in an ice bath uniformly. KMnO<sub>4</sub> (1.5 g) was added gradually with stirring and cooling in order to keep the temperature below 5 °C for 2 h. Then, the ice bath was removed and the solution kept stirring at 35 °C for 8 h. After that, distilled water (23 mL) was slowly added and this reaction was transferred to a 98 °C water bath and stirred for 0.5 h. After the suspension was diluted to ~45 mL by distilled water, 30% H<sub>2</sub>O<sub>2</sub> solution (5 mL) was added and kept stirring for 1 h. The mixture was centrifuged and washed with distilled water several times. The as-synthesized GO was suspended in water to give a brown dispersion, which was subjected to dialysis for one week to completely remove residual salts and acids.

### 2.2. Instrumentation

Elemental analysis was performed with a FLASH EA1112 elemental analyzer. Infrared spectrum was recorded on a Nicolet Avtar 360FT-IR spectrometer as KBr disk. X-ray photoelectron spectra (XPS) were measured on an Axis Ultra X-ray photoelectron spectrometer of Phermo Fisher, using an Al K $\alpha$  irradiation on an ESCA-250 system. For calibration, C1s line was set at 284.6 eV as standard. The surface morphologies of the deposited films were studied using scanning electron microscopy (SEM; Hitachi S-4800-II). Ultraviolet–Visible absorption spectra were recorded on a Cintra 10 e UV–Vis spectrophotometer. Cyclic voltammograms



Scheme 1. Molecular structure of CoTPPCl<sub>2</sub>.

of the films were recorded in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution on a CHI electrochemical analyzer, by using indium-tin oxide (ITO) coated glass substrate modified with the self-assembled films with an effective area of 1.5 cm<sup>2</sup>, saturated calomel electrode (SCE) and Pt wire as the working, reference and counter electrodes, respectively. Oxygen was removed from the electrolyte solution by bubbling N<sub>2</sub> for 15 min before every measurement. All the photoelectrochemical measurements were also carried out on a CHI electrochemical analyzer at room temperature in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution by using ITO modified with the self-assembled films with an effective area of 0.28 cm<sup>2</sup>, a platinum wire and a saturated calomel electrode (SCE) as working, counter and reference electrodes, respectively. The light source (730 nm >  $\lambda$  > 325 nm) used for photoelectrochemical studies was a 500 W xenon lamp. The light beam was passed through an infrared cutoff filter. In order to obtain the photocurrent action spectra, a monochromatic light was acquired from a 500 W xenon lamp fitted with optical interference filters. The light intensities at each wavelength were measured by a model ST-900 M photometer. The distance between the lamp and the electrode was about 15 cm.

### 2.3. Preparation of the multilayer films

The schematic illustration for the fabrication procedure of LBL self-assembled multilayer films is shown in Scheme 2. The quartz or ITO substrates were precleaned as previously described [34,35] and then silanized in a 3-aminopropyltriethoxysilane/ethanol (1:20, v/v) solution for 30 min at 70 °C to create the amino groups covered with the surface of the ITO substrate. The amino groups on the surface were protonated by immersing the silanized sheets in an aqueous HCl solution (pH  $\approx$  3) for 10 min. The quartz or ITO substrates were then immersed into a 1 mg/mL GO aqueous solution for 10 min and a 1 mM CoTPPCl<sub>2</sub> aqueous solution for 50 min in sequence, rinsed with deionized water copiously, and dried with air every time when taken out from GO or CoTPPCl<sub>2</sub> solution. The multilayered films of quartz or ITO/(GO/CoTTP)<sub>m</sub> were obtained by repeating the above-mentioned two steps alternatively (*m* stands for the number of layer on both sides of the substrate).

## 3. Results and discussion

### 3.1. Synthesis and characterization of the Co(II) complex

The Co(II) complex used in this study, CoTPPCl<sub>2</sub>, was synthesized according to a modified procedure previously reported for [Co(TPP)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH·H<sub>2</sub>O [32]. Elemental analysis results are consistent with the theoretical values for the presence of one solvent H<sub>2</sub>O molecule and two solvent CH<sub>3</sub>OH molecules, which well coincides with previously reported results for [Co(TPP)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH·H<sub>2</sub>O that was structurally characterized by single-crystal X-ray diffraction [32]. IR spectrum of [Co(TPP)<sub>2</sub>]Cl<sub>2</sub>·2CH<sub>3</sub>OH·H<sub>2</sub>O showed a strong and very broad hydroxyl group (OH) stretching band peaking at ~3411 cm<sup>-1</sup> as well as a sharper C–H stretching band in the range 2946–3113 cm<sup>-1</sup>, which is due to presence of the solvents of water and methanol, and is in agreement with the published works [36,37]. In addition, there are bands at 1000–1150 and 1600–1607 cm<sup>-1</sup>, which are associated with C=C and C=N stretches of the terpyridine moiety, respectively. The band in the 835–844 cm<sup>-1</sup> region is attributed to C–S stretching [38]. Also, the Co–N bond stretching vibration was seen at 463 cm<sup>-1</sup> for the cobaltous complexes [38].

### 3.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectrum of an ITO/(GO/CoTTP)<sub>4</sub> film is shown in Fig. 1. As shown in Fig. 1a, chloride ion characteristic

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