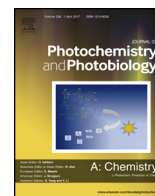




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)



Invited feature article

## Supramolecular self-assembly of layer-by-layer graphene film driven by the synergism of $\pi$ – $\pi$ and hydrogen bonding interaction

Sumin Wang, Lei Yang, Qiguan Wang\*, Yaru Fan, Jiayin Shang, Shenbao Qiu, Jinhua Li, Wenzhi Zhang, Xinming Wu

Shaanxi Key Laboratory of Photoelectric Functional Materials and Devices, School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021, China

### ARTICLE INFO

#### Article history:

Received 30 June 2017  
Received in revised form 15 August 2017  
Accepted 11 September 2017  
Available online xxx

#### Keywords:

Graphene  
LBL film  
Self-assembly  
Quadruple hydrogen bonds  
 $\pi$ – $\pi$  interactions  
Electrochemistry

### ABSTRACT

In this paper an organic molecule labeled as UPPY with both  $\pi$ – $\pi$  interaction unit of pyrene (PY) and hydrogen bonding unit of ureidopyrimidinone (UP) was employed as binding module to link the layer-by-layer graphene film. Firstly, UPPY was anchored on the surface of thermal reduced graphene (trGO) with the aids of  $\pi$ – $\pi$  interactions forming trGO-UPPY. The trGO-UPPY showed different morphology in  $\text{CHCl}_3$  and *N,N*-dimethylformamide (DMF) due to the different hydrogen binding mode. Then by the synergism of hydrogen bonding and  $\pi$ – $\pi$  interactions offered by UPPY, multilayer film of trGO-UPPY was prepared through layer-by-layer technique. The electron-transfer resistance (Ret) of trGO-UPPY/ITO decreased from  $53\ \Omega$  of bare ITO to  $27\ \Omega$ . In addition, trGO-UPPY/ITO electrodes exhibited enhanced electrochemical activity toward dopamine (DA). Compared with bare ITO, the oxidation peak current of DA on rGO-UPPY/ITO can be enhanced about 100 times than that of bare ITO.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

The supramolecular self-assembly afford researchers ideal bottom-up approaches for fabricating novel functional materials and devices with desirable architectures and properties. Design of novel building blocks and assembly strategies is of great importance for materials to self-assembly at nanometer scale. As the zero-dimensional (0D) and one dimensional (1D) functional units, dendrimers [1,2], nanoparticles [3,4], fullerenes [5,6], carbon nanotubes [7,8] have been widely used as the favorite nanoscale building blocks in the supramolecular chemistry. By means of its single-atom thickness and unprecedentedly large lateral surface, graphene has recently become a novel kind of two-dimensional (2D) building blocks [9,10]. By using supramolecular self-assembly methods, not only the solubility and conductivity of the graphene have been enhanced, but also complicated graphene based structures such as 2D multilayer film [11,12], three-dimensional (3D) ball [13,14] and hydrogels [15,16] exhibiting novel collective physiochemical properties have also been realized, which significantly expands the practical applications of graphene.

Molecular recognition through noncovalent interactions is the fundamental of supramolecular self-assembly. Because graphene

has the large lateral dimension, for the achievement of stable graphene assemblies, those noncovalent interactions with high binding strength are usually needed to overcome the stacking of graphene sheets. Pyrene (PY) derivatives based  $\pi$ – $\pi$  interactions which have strong affinity with the graphene layer by physical adsorption on the conjugate structure of graphene, would be a potential driving force for graphene assembly [17–19]. In addition, ureidopyrimidinone (UP) quadruple AADD (A: hydrogen bond acceptor, D: hydrogen bond donor) hydrogen bonding unit possessing very strong binding strength ( $10^7\ \text{M}^{-1}$  in  $\text{CHCl}_3$  or toluene) [20], is also a good candidate in the self-assembly of graphene [21].

Cooperation of noncovalent multi-interactions would be an effective way to fabricate graphene assemblies with desirable architecture and functionality [22–24]. Through hydrogen bonding and  $\pi$ – $\pi$  interactions, Cheng et al. prepared graphene oxide (GO) hydrogels and organogels by supramolecular self-assembly from an amphiphilic molecule, which has a polarcarbohydrate head group attached to a pyrene group [25]. In our previous work, by designing and employing a self-assembly precursor of UP terminated pyrene derivatives (labeled as UPPY) (Fig. 1a), a novel hybrid showing graphene-wrapped MWNT morphology with enhanced electrochemical sensitivity was fabricated thanks to the cooperation of the hydrogen bonding and  $\pi$ – $\pi$  interaction. Benefiting from the quadruple AADD hydrogen bonding arrays of

\* Corresponding author.

E-mail address: [qgwang@xatu.edu.cn](mailto:qgwang@xatu.edu.cn) (Q. Wang).

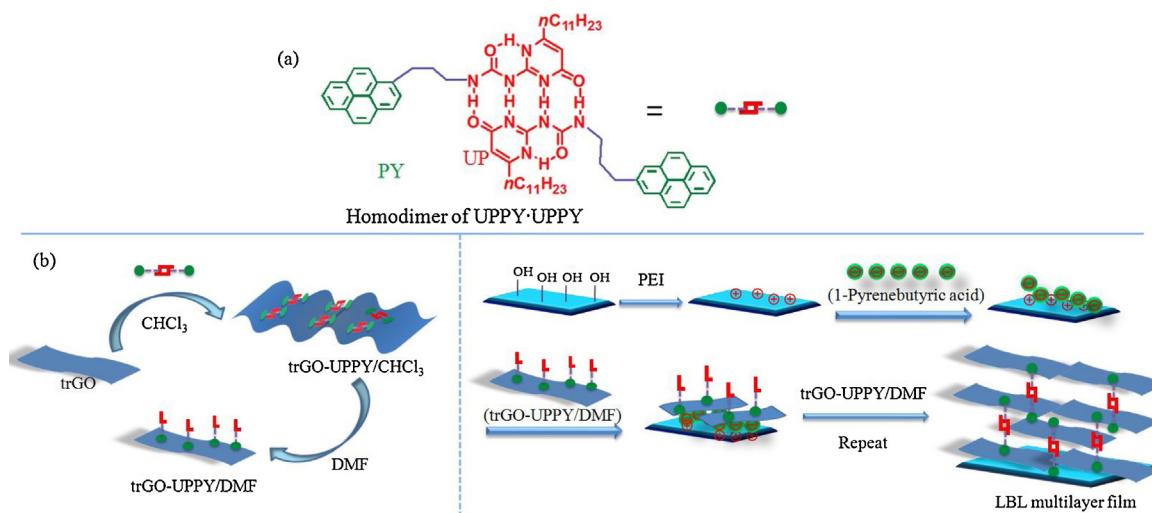


Fig. 1. Supramolecular self-assembly scheme of trGO-UPPY LBL multilayer film from the module of UPPY.

UP, UPPY·UPPY homodimer could be formed (Fig. 1a). Simultaneously, the PY unit could also form strong  $\pi$ - $\pi$  interaction with nano-carbon material. In this article we want to show that as a binding module, UPPY has universal adaptability to the self-assembly of nano-carbon material due to the contained  $\pi$ - $\pi$  and hydrogen bonding unit [26].

The Layer-by-Layer (LBL) self-assembly method, initially reported by Decher and Hong is one of the most convenient techniques for fabricating films with finely controlled [27]. LBL films of graphene linked by noncovalent interactions such as electrostatic, hydrogen bonding supplied by the polymer for instance poly (vinyl alcohol), polyacrylic acid and ionic liquid modified on the graphene layer have been prepared [28–34]. Herein, UPPY unit was further employed to drive the supramolecular self-assembly of graphene film by LBL technique. Firstly, the UPPY was anchored on the surface of thermal reduced graphene (trGO) with the aids of  $\pi$ - $\pi$  interactions forming trGO-UPPY (Fig. 1b left). Then by the layer-by-layer technique, a 2D graphene multilayer film of trGO-UPPY showing enhanced electrocatalytic properties to the oxidation of dopamine was self-assembled by the synergism of hydrogen bonding and  $\pi$ - $\pi$  interactions offered by UPPY (Fig. 1b, right).

## 2. Experimental section

### 2.1. Regents

Graphene oxide (GO) was prepared from natural graphite by the modified Hummers procedure [35,36]. Thermal reduced graphene oxide (trGO) was prepared by thermal reduction of GO under the Ar atmosphere at 600 °C for 2 h [37]. UPPY (Fig. 1a) was prepared according to our previous reported methods [26]. Poly(ethyleneimine) (PEI) with the average molecular weight of 50,000 by GPC was purchased from Aldrich. During electrochemical experimental process, Milli-Q water (18 M $\Omega$ /cm) was used. *N,N*-Dimethylformamide (DMF) of HPLC grade was used for self-assembly process. All other reagents and chemicals were used as received unless otherwise noted.

### 2.2. Synthesis of trGO-UPPY

Mixture of trGO (2 mg) and UPPY (6 mg) in CHCl<sub>3</sub> (20 mL) was subjected to ultrasonication, and then it was allowed to stir for 6 h

at room temperature affording a stable black dispersion. After filtrated and thoroughly washed with CHCl<sub>3</sub>, black powder of trGO-UPPY was prepared.

### 2.3. Preparation of trGO-UPPY LBL Films

Firstly, a cleaned quartz or ITO slide that had been ultrasonicated in a piranha solution (mixture of 98% H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub>, v/v 7:3) for 30 min was dipped in the PEI solution of H<sub>2</sub>O (1.5 mg/mL) at pH = 7.0 for 1 h. After it was rinsed with water and dried with nitrogen flow, the PEI modified substrate was dipped into the 1-pyrenebutyric acid solution of DMF for 15 min, rinsed and dried, leading to the modification of the substrate by 1-pyrenebutyric acid. Then the 1-pyrenebutyric acid modified substrate was immersed in the suspension of trGO-UPPY in DMF (0.1 mg/mL) for 15 min. After dried by N<sub>2</sub>, the substrates adsorbed by one layer of trGO-UPPY were dipped again into the trGO-UPPY dispersion to obtain the second trGO-UPPY layer. The LBL multilayer films of (trGO-UPPY)<sub>n</sub> with desirable layer number (n) could be prepared by repetition of such steps (Fig. 1b, right).

### 2.4. Instrumentation

UV-vis spectra were measured by a Shimadzu 1901 UV-vis spectrophotometer. Transmission electron microscope (TEM) images were recorded from a JEM2010 instrument. Scanning electron microscope (SEM) images were collected by an S4800 instrument. X-ray photoelectron spectra (XPS) were measured using a PHI 5400 X-ray photoelectron spectrometer. All spectra were calibrated with the C 1s photoemission peak for sp<sup>2</sup> hybridized carbons at 284.5 eV. The X-ray diffraction (XRD) patterns of the samples were recorded with a Shimadzu XRD-6000 X-ray diffractometer. The Cu K $\alpha$  line ( $\lambda$  = 1.5451 nm) from a sealed tube with a copper anode was used as a source of radiation. Cyclic Voltammetry (CV) was carried out in a conventional three-electrode system with the LBL trGO-UPPY multilayer films assembled on ITO glass as working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt wire as the counter electrode, using a 0.1 M phosphate buffer solution (PBS, pH = 7.0) containing 0.1 M KCl as electrolyte solution. The working electrode area is 0.25 cm<sup>2</sup>, which was always kept immersed in the electrolyte solution during the data collection.

Download English Version:

<https://daneshyari.com/en/article/6492746>

Download Persian Version:

<https://daneshyari.com/article/6492746>

[Daneshyari.com](https://daneshyari.com)