



## Spectroscopic characterization of tetracationic porphyrins and their noncovalent functionalization with graphene

Ting-xiu Ye<sup>a</sup>, Shu-lan Ye<sup>a</sup>, Dong-mei Chen<sup>a</sup>, Qing-ai Chen<sup>c</sup>, Bin Qiu<sup>a,\*</sup>, Xi Chen<sup>a,b,\*\*</sup>

<sup>a</sup> Key Laboratory of Analysis and Detection Technology for Food Safety, Ministry of Education, Department of Chemistry, Fuzhou University, Fuzhou 350002, China

<sup>b</sup> State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China

<sup>c</sup> Fujian Agriculture and Forestry University, College of Food Science, Fuzhou, Fujian 350002, China

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### ABSTRACT

In this study, the noncovalent functionalization of graphene with cationic porphyrins in an aqueous medium was investigated using UV-vis and fluorescence approaches. To characterize the interaction between graphene and cationic porphyrins, 5,10,15,20-tetra (4-pyridyl)-21H,23H-porphine, 5,10,15,20-tetrakis (1-methyl-4-pyridinio) porphyrin tetra (p-toluenesulfonate) and 5,10,15,20-tetrakis (4-trimethylammonio) porphyrin tetra (p-toluenesulfonate) porphyrin were chosen as reagents. The intermolecular interactions were found to occur immediately after mixing the cationic porphyrins with graphene. The absorption spectra of the cationic porphyrins after mixing with graphene showed distinct red shifts of the Soret and Q-bands compared to free cationic porphyrins indicating that interactions occur between the cationic porphyrins and graphene. A strong fluorescence quenching of the cationic porphyrins in the presence of graphene indicated that efficient electron or energy transfer occurred from the excited state of the cationic porphyrins to graphene. Cationic porphyrins were immobilized on the surface of graphene through electrostatic and  $\pi$ - $\pi$  stacking interactions, and the chemical shape of graphene played an important role in the intermolecular interactions and the red shift extent of cationic porphyrins is mostly dependent on the functional groups and charges of the graphene surface. The results show that less functional groups on the graphene's surface and edge would lead to stronger  $\pi$ - $\pi$  stacking interactions between graphene and cationic porphyrins.

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### 1. Introduction

Graphene is a remarkable carbon nanostructure material with an atomically thin two-dimensional lattice of  $sp^2$ -bonded carbon atoms. Due to its unique structure, its unusual electronic and intriguing mechanical and thermal properties, graphene has attracted great attention from both experimental and theoretical scientific communities all over the world [1,2], and it has been exploited in many applications in recent years, such as nanocomposites, Li-ion batteries, supercapacitors and electrochemical biosensors [3]. It is known that graphene has poor processability/compatibility which is mainly caused by the high inter-layer attraction energies. In order to advance its chemical compatibility with different interfaces and media, it is very

important to develop well-dispersed graphene which has tailored functional properties and controlled surface structure [4]. An effective method to improve its processability is through the covalent or noncovalent functionalization of graphene with various molecules and nanomaterials both in water and organic solvents [5–8]. Compared with covalent functionalization, noncovalent functionalization not only preserves the intrinsic properties of graphene [9] but also improves the solubilization of graphene through  $\pi$ - $\pi$  stacking and hydrophobic interactions.

To date, several effective techniques have been developed for producing graphene, and different approaches can provide graphene with different processability and functions. Bulk quantities of graphene were prepared by oxidation of completely insoluble natural graphite powder. Graphene oxide (GO), having abundant functional groups on the graphene sheet including hydroxyl (-OH), aldehyde group (-CHO), carboxyl groups (-COOH) and epoxy [10], is obtained from chemical exfoliation exposing graphite powder to strong oxidant solutions. Chemically converted graphene (CCG) has been prepared by the reduction of GO suspensions which eliminate a majority of the oxygen functional groups and restore the conjugated structure of GO [11]. Carboxylic acid

\* Corresponding author.

\*\* Corresponding author at: State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China. Tel.: +86 592 2184530; fax: +86 592 2184530.

E-mail addresses: [xichen@xmu.edu.cn](mailto:xichen@xmu.edu.cn), [summer328cn@163.com](mailto:summer328cn@163.com) (X. Chen).

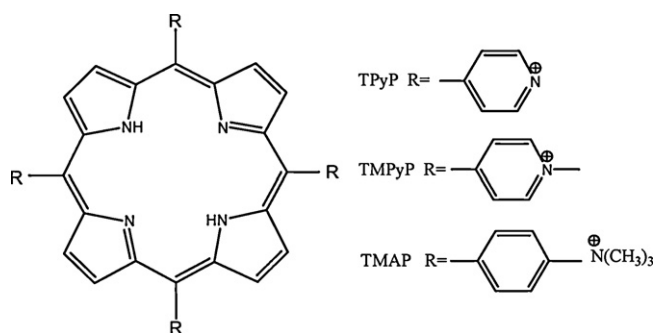


Fig. 1. Molecular structure of meso-substituted cationic porphyrins.

modified GO (CGO) is the final product, selectively reserving the carboxylic acid functional groups prepared from GO as a basic condition [12].

Porphyrins are ‘the pigments of life’, having a 2D 18  $\pi$ -electron structure, and they play an important role in many biological processes such as substrate oxidation reactions, oxygen transport and photosynthesis [13,14]. Porphyrins have predictable rigid structures and prospective photochemical electron-transfer ability. The functionalization of carbon nanotubes (CNTs) with porphyrins has been widely studied on the basis of their  $\pi$ - $\pi$  interactions [15,16]. The functionalization of graphene with porphyrins has attracted significant interest since both graphene and CNTs share the common features of delocalized and conjugated electron structures; Xu [17] and Geng and Jung [18] report the noncovalent functionalization of porphyrins and graphene. Cationic porphyrin derivatives are valuable as probes of nucleic acid structure and dynamics, and could be used in photodynamic therapy and virus control, the photo-physical and electrochemical properties and aggregation behavior of which have been described [14]. In this paper, we attempt to elucidate some aspects of the noncovalent functionalization of cationic porphyrins with graphene, and try to provide supplementary information to understand the molecular behavior of porphyrin in graphene. To characterize these graphene-porphyrin interactions, the interactions between different chemical shapes of graphene with three types of structure related cationic porphyrins, 5,10,15,20-tetra (4-pyridyl)-21H,23H-porphine (TPpP),

5,10,15,20-tetrakis (4-trimethylammoniohenyl) porphyrin tetra (p-toluenesulfonate) porphyrin (TMAP) and 5,10,15,20-tetrakis (1-methyl-4-pyridinio)porphyrin tetra (p-toluenesulfonate) (TMPpP), in aqueous media were studied. The  $\pi$ - $\pi$  interactions were found to occur immediately and without further conditions, and the interactions were dependent on the functional groups and charges on the graphene surface, the less functional groups on the graphene’s surface and edge, and the stronger  $\pi$ - $\pi$  stacking interactions between graphene and cationic porphyrins. The graphene samples with different chemical shape were characterized using IR spectroscopy, and the interplay between graphene and cationic porphyrin molecules was studied using absorption and fluorescence spectroscopy. The molecular structures of cationic porphyrins are shown in Fig. 1.

## 2. Experimental

### 2.1. Materials

TPpP, TMPpP, and TMAP were purchased from Sigma-Aldrich. Natural graphite powder (325 mesh) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. Other reagents were analytical grade and used without further purification. Double distilled water was used throughout the experiments.

**Preparation of GO.** GO was synthesized from natural graphite powder according to a modified Hummers method [19]: 2 g of graphite powder was ground with 100 g NaCl to reduce the particle size. After removing the salt, the ground graphite was added to 80 mL of  $\text{H}_2\text{SO}_4$  (98%) and the mixture was stirred for 2 h. Afterwards, 10 g of  $\text{KMnO}_4$  was added gradually to the mixture under vigorous agitation and the mixture temperature was kept below 20 °C. Next, the mixture was stirred at 35 °C for 2 h, and then diluted with 180 mL of distilled water. The addition of water was carried out in an ice bath to keep the temperature less than 50 °C. The mixture was stirred at room temperature for 2 h, and then an additional 450 mL of distilled water and 20 mL  $\text{H}_2\text{O}_2$  (30%) were added to the mixture. The mixture was repeatedly filtered and washed with 1:10 HCl aqueous solution to remove metal ions, and then washed with distilled water to remove the acid. The resulting solid was dried

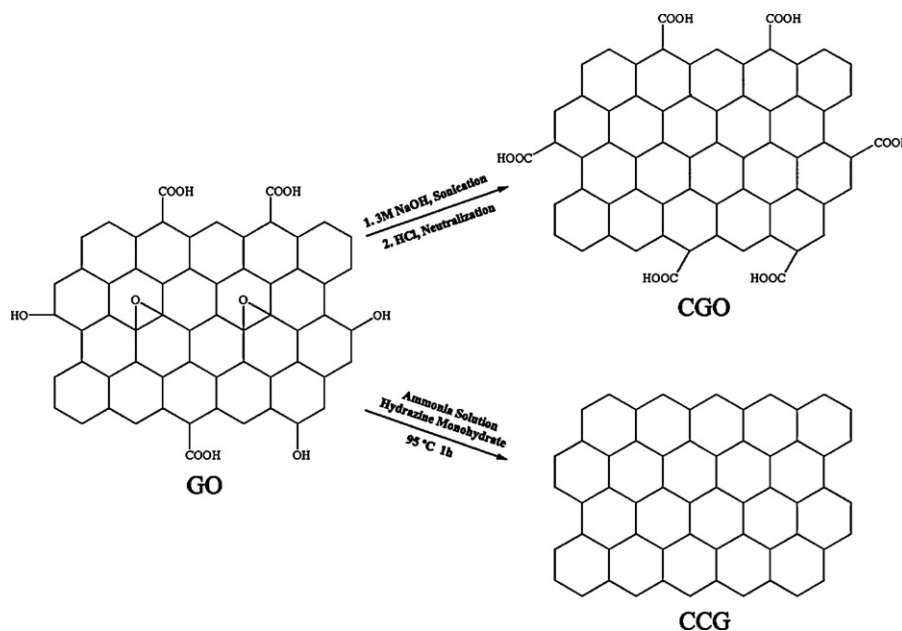


Fig. 2. Transformation scheme of GO, CGO and CCG.

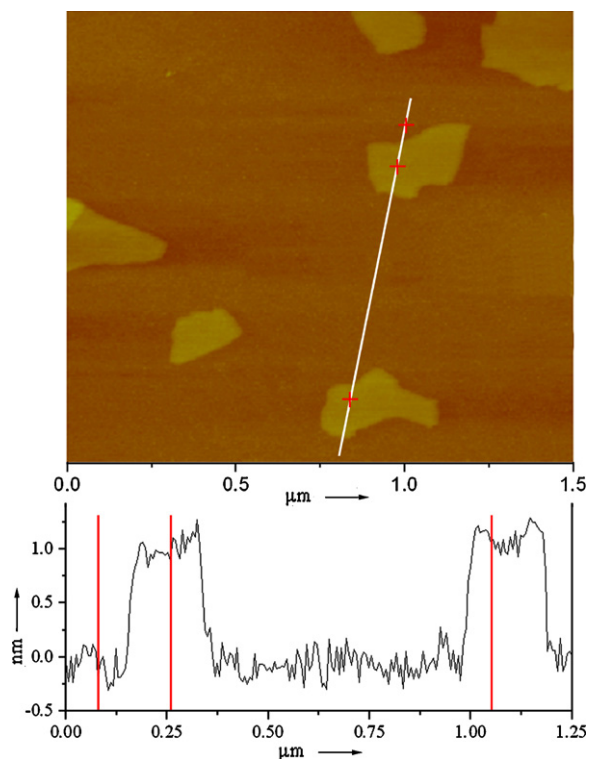


Fig. 3. AFM height image of GO sheets deposited on mica substrates.

in air. Exfoliation was carried out by sonicating the GO (2 mg/mL) dispersion under ambient conditions for 4 h.

**Carboxylic acid modified GO.** CGO was prepared according to the report of Liu et al. [12]: 10 mL of GO solution (2 mg/mL) was mixed with 10 mL of NaOH (3 mol/L) aqueous solution, and the mixture solution was sonicated for 3 h. After sonication, the solution was neutralized with HCl, and the product was filtered and rinsed. Finally, the obtained solid was diluted to make CGO dispersion.

**Chemically converted graphene.** CCG was prepared through the procedures reported by Li et al. [20]. Briefly, a mixture of 25 mL of GO (0.25 mg/mL), 7 μL of hydrazine monohydrate and 75 μL of ammonia solution (28 wt% in water) was prepared in a flask. The mixture was stirred for 1 h at 95 °C. After cooling, a homogeneous black dispersion with a small amount of black precipitate was obtained. Finally, the dispersion was filtered to remove the precipitate to yield a stable black aqueous dispersion of CCG. The scheme of graphene preparation is illustrated in Fig. 2.

## 2.2. Characterization

UV–vis absorption spectra were measured with a Lambda 35 UV–vis spectrometer (Perkin Elmer, USA). Fluorescence spectra were measured with a Hitachi F-4600 fluorometer (Hitachi Co., Ltd., Japan). Atomic force microscope (AFM) images were measured with a Nanoscope IIIa multimode AFM (Veeco Instruments, USA) in tapping mode to simultaneously collect height and phase data. IR spectra were recorded on a SPECTRUM 2000 (Perkin Elmer, USA).

## 3. Results and discussion

### 3.1. Characterization of graphene

The structure and morphology of the resulting GO were characterized using an AFM. Fig. 3 indicates that the prepared GO sheets were almost single-layered and the average thickness was approximately 1.2 nm. This value matched well with those reported [21].

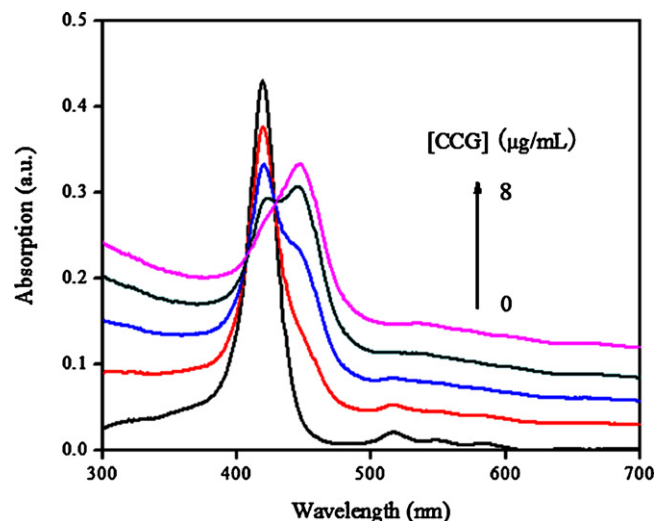


Fig. 4. Absorption spectra of TPyP (2 μM) after addition of CCG at different concentrations (0, 2, 4, 6, and 8 μg/mL).

To further obtain the structural information, IR spectroscopy was carried out. Generally, there were various hydroxyl, epoxy and carboxyl groups on the GO sheets, and the FT-IR spectrum of GO showed the presence of O–H stretching at  $\sim 3300\text{ cm}^{-1}$  and C=O stretching at  $1735\text{ cm}^{-1}$  in the carbonyl groups: skeletal vibration of unoxidized graphitic C–OH stretching at  $1620\text{ cm}^{-1}$  and C–OH stretching at  $1210$  and  $1040\text{ cm}^{-1}$ , which were in good agreement with the literature [7,8]. Similar to that of GO, the FT-IR spectrum of CGO illustrated the characteristic C=O stretching at  $1735\text{ cm}^{-1}$  in carbonyl groups; skeletal vibration of unoxidized graphitic at  $1620\text{ cm}^{-1}$ ; and C–OH stretching at  $1210\text{ cm}^{-1}$ ; whereas the C–OH stretching at  $1040\text{ cm}^{-1}$  disappeared because there is no epoxy on CGO sheets. After reduction with hydrazine, the FT-IR spectrum of CCG was essentially featureless except that the C=C conjugation ( $1570\text{ cm}^{-1}$ ) and C–C bands ( $1190\text{ cm}^{-1}$ ) resembled those of bulk graphite [11] (data not shown).

### 3.2. Absorption spectra measurements

Measurement of the absorption spectra was carried out after mixing 2 μmol/L TPyP with different concentrations of graphene samples at room temperature within 1 min. As shown in Fig. 4, the ground state absorption spectrum of TPyP exhibited a very intense Soret band ( $\lambda_{\text{max}} = 419\text{ nm}$ ) corresponding to the S2 transition, while the weaker Q bands between 500 and 700 were assigned to a pair of vibronic progressions corresponding to S1 transition [22]. With increase of the CCG concentration, the position, width and intensity of the absorption spectra of TPyP were changed. The most obvious change occurred in the Soret band region of the absorption spectrum: the intensity of the original Soret band at 419 nm decreased gradually and a new Soret band appeared at 448 nm. This red shift of 29 nm relative to the Soret band of free TPyP, the occurrence of a new band at 448 nm and the significant decrease of the absorption intensity at 419 nm indicate that  $\pi$ – $\pi$  interactions took place between CCG and TPyP. Figs. 5 and 6 show the absorption spectra of TPyP after mixing with CGO and GO samples. Compared with Fig. 4, there was a bathochromic shift in the Soret band of TPyP after mixing with CGO and GO, but the red shift extent was related to the functional groups on the surface and edge of the graphene: there was a red shift of 22 nm in the TPyP Soret band for CGO, while only a 12 nm shift for GO. These results indicated that the functional groups on the surface and edge of graphene played an important role in the  $\pi$ – $\pi$  interactions between

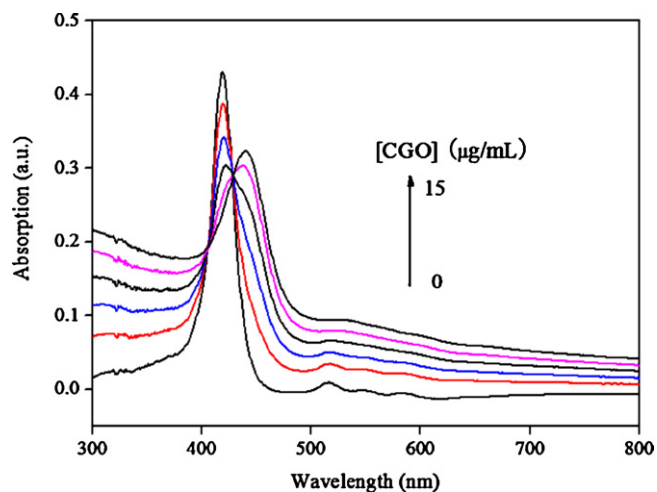


Fig. 5. Absorption spectra of TPyP (2  $\mu$ M) after addition of CGO at different concentrations (0, 3, 6, 9, 12, and 15  $\mu$ g/mL).

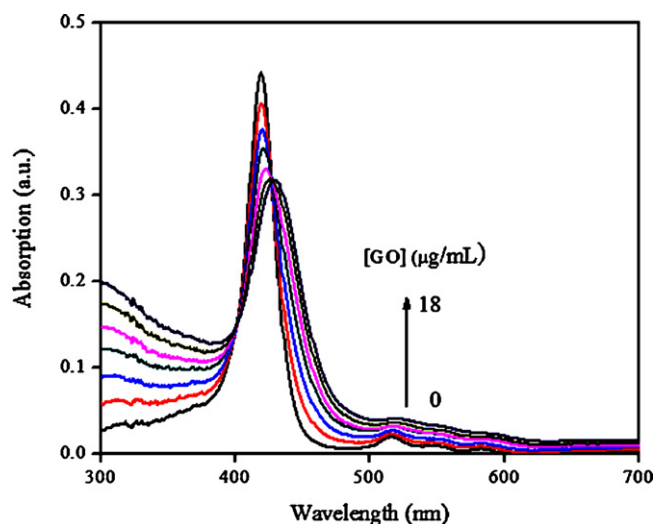


Fig. 6. Absorption spectra of TPyP (2  $\mu$ M) after addition of GO at different concentrations (0, 3, 6, 9, 12, 15, and 18  $\mu$ g/mL).

TPyP and graphene. The  $\pi$ - $\pi$  interactions of TPyP/GO, TPyP/CGO and TPyP/CCG complexes were different, and TPyP molecules had stronger supermolecular interactions with CCG sheets than those with CGO and GO sheets. The noncovalent action of graphene with

**Table 1**

Red shift extent of the Soret band of cationic porphyrins after titration with graphene.

| Graphene | Sample                             |                                     |                                    |
|----------|------------------------------------|-------------------------------------|------------------------------------|
|          | $\Delta\lambda_{\text{TPyP}}$ (nm) | $\Delta\lambda_{\text{TMPyP}}$ (nm) | $\Delta\lambda_{\text{TMAP}}$ (nm) |
| CCG      | 29                                 | 34                                  | 24                                 |
| CGO      | 22                                 | 22                                  | 14                                 |
| GO       | 12                                 | 15                                  | 9                                  |

various molecules through supermolecular interactions such as  $\pi$ - $\pi$  stacking, electrostatic interaction and hydrogen bonding is reported [5]. Since TPyP is positively charged owing to the presence of pyridyl groups, and CCG, CGO and GO sheets in aqueous dispersion are negatively charged, it was expected that the interactions between TPyP and CCG, CGO and GO sheets might have been through electrostatic interaction and  $\pi$ - $\pi$  stacking. Supermolecular interactions between TPyP and graphene restrained the vibrational motion of TPyP's pyridyl groups, and decreased the polarity of TPyP's surrounding environment, further enlarging the  $\pi$  conjugation of the porphyrin system, which resulted in the red shift of the TPyP Soret band. There were no functional groups on the surface and edge of CCG sheets which reduced the distance between the porphyrin planes and CCG sheets and further enhanced  $\pi$ - $\pi$  stacking interaction, leading to a larger extent of red shift in the TPyP Soret band. The red shift extent of CGO was less than that of CCG due to the existence of carboxyl groups at the edge of the sheets. GO has abundant functional groups on the surface and edge of the graphene sheet, and thus the  $\pi$ - $\pi$  stacking interaction between TPyP and GO was weak. These results were in agreement with a report [17] that the  $\pi$ - $\pi$  stacking interactions of TMPyP/CCG and TMPyP/GO are different.

In order to further evaluate the role of functional groups on the surface and edge of graphene in the interactions of cationic porphyrin, the absorption spectra of the structure related cationic porphyrins TMPyP and TMAP were studied. As shown in Fig. 7, the Soret bands of TMAP and TMPyP had a red shift, which demonstrated that both TMAP and TMPyP had interactions with CCG, CGO and GO. Similar to TPyP, CCG had a larger red shift, and the extent of the red shift in the porphyrin Soret band was CCG > CGO > GO. The results are listed in Table 1.

### 3.3. Fluorescence spectrum measurements

To further confirm the differences between the  $\pi$ - $\pi$  interactions of TPyP/GO, TPyP/CGO and TPyP/CCG complexes, the fluorescence spectra of TPyP solutions titrated with graphene were measured.

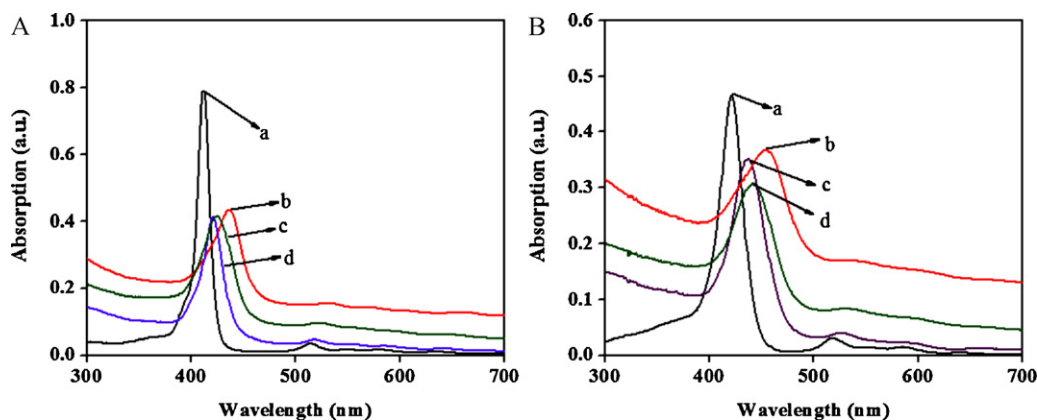
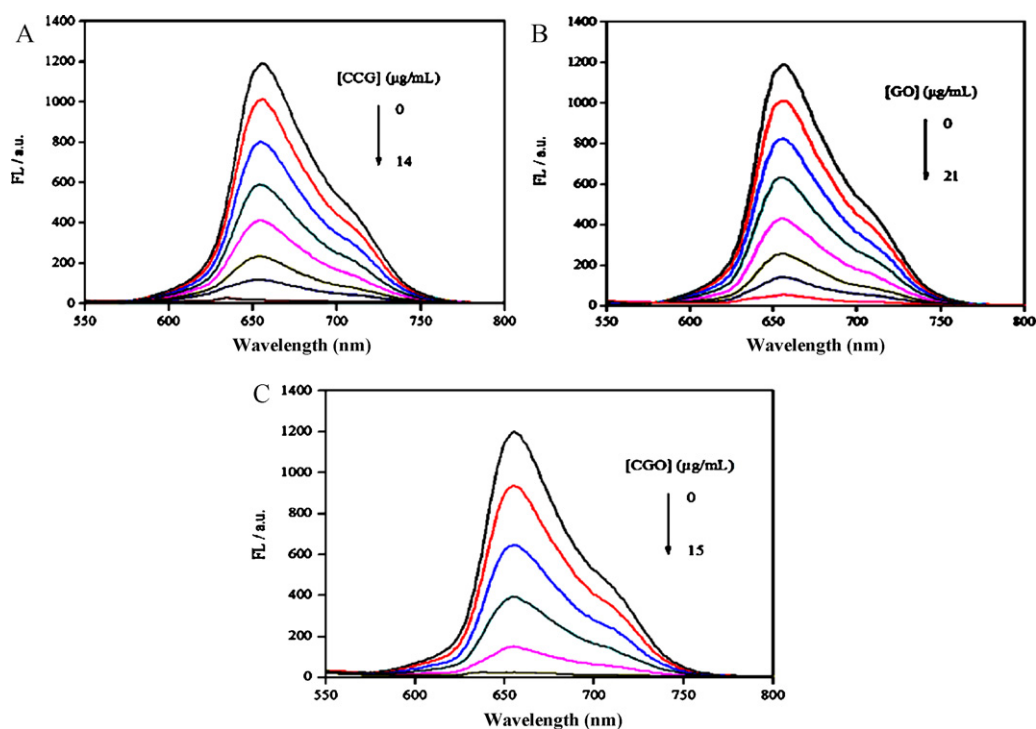


Fig. 7. (A) Absorption spectra of TMAP (2  $\mu$ M) after addition of 12  $\mu$ g/mL CCG, CGO and GO: (a) TMAP; (b) TMAP-CCG; (c) TMAP-CGO; (d) TMAP-GO. (B) Absorption spectra of TMPyP (2  $\mu$ M) after addition of 12  $\mu$ g/mL CCG, CGO and GO: (a) TMPyP; (b) TMPyP-CCG; (c) TMPyP-GO; (d) TMPyP-CGO.





**Fig. 8.** (A) Fluorescence spectra of TPYP (2  $\mu\text{M}$ ) after addition of CCG at different concentrations (0, 2, 4, 6, 8, 10, 12, and 14  $\mu\text{g/mL}$ ). (B) Fluorescence spectra of TPYP (2  $\mu\text{M}$ ) after addition of GO at different concentrations (0, 3, 6, 9, 12, 15, 18, and 21  $\mu\text{g/mL}$ ). (C) Fluorescence spectra of TPYP (2  $\mu\text{M}$ ) after addition of CGO at different concentrations (0, 3, 6, 9, 12, and 15  $\mu\text{g/mL}$ ).

The excitation wavelength was 419 nm which is consistent with the Soret band of UV–vis spectra. As shown in Fig. 8, the main phenomenon found in these assemblies was a strong fluorescence quenching effect with increase of graphene concentration. The fluorescence decays of porphyrin/graphene revealed a large contribution of complex formation. When the concentration of graphene was 12  $\mu\text{g/mL}$ , the quenching efficiency was 90.2% for TPYP/CCG, 87.4% for TPYP/CGO and only 63.8% for TPYP/GO complexes. These results indicated that TPYP molecules had stronger  $\pi$ – $\pi$  stacking interactions with CCG sheets than those with CGO and GO sheets, which was in accordance with previous absorption results. The fluorescence quenching effect could be ascribed to the porphyrin/graphene interactions enlarging the  $\pi$  conjugation of the porphyrin system, which is similar to that of TMPyP [17], or efficient electron or energy transfer from the excited state of the cationic porphyrins to graphene [8]. All results from the absorption and fluorescence spectra measurements demonstrated that the shape of graphene played an important role in its supermolecular interactions with TPYP.

#### 4. Conclusions

A simple method to prepare complexes of cationic porphyrins (TPYP, TMAP and TMPyP)/graphene (CCG, CGO and GO) in aqueous media was developed. The  $\pi$ – $\pi$  stacking interaction of graphene and TPYP was shown in absorption and fluorescence spectrum studies. The strong  $\pi$ – $\pi$  stacking interaction was found to occur immediately after mixing two components, and the functional groups on the surface and edge of the graphene played an important role in their supermolecular interactions.

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