

## Full Length Article

# Room temperature Zinc-metallation of cationic porphyrin at graphene surface and enhanced photoelectrocatalytic activity



Rongjin Zeng\*, Guoliang Chen, Chungang Xiong, Gengxian Li, Yinzhi Zheng, Jian Chen, Yunfei Long, Shu Chen\*

Key Laboratory of Theoretical Organic Chemistry and Function Molecule of Ministry of Education, Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, China

## ARTICLE INFO

## Article history:

Received 18 June 2017

Received in revised form 12 October 2017

Accepted 29 October 2017

## Keywords:

Porphyrin

Graphene

Zinc-metallation

Photoelectrocatalytic activity

CO<sub>2</sub> reduction

## ABSTRACT

A stable zincporphyrin functionalized graphene nanocomposite was prepared by using positively charged cationic porphyrin (5,10,15,20-tetra(4-propyl pyridinio) porphyrin, TPPyP) and successive reduced graphene oxide (rGO) with tuned negative charge. The nanocomposite preparation was accompanied first by distinct electrostatic interactions and  $\pi$ - $\pi$  stacking between TPPyP and rGO, and followed by fast Zinc-metallation at room temperature. In contrast to free TPPyP with Zn<sup>2+</sup>, the incorporation reaction is very slow at room temperature and heating or reflux conditions are required to increase the metallation rate. While at the surface of rGO nanosheet, the Zinc-metallation of TPPyP was greatly accelerated to 30 min at 25 °C in aqueous solution. The interaction process and composites formation were fully revealed by significant variations in UV-vis absorption spectra, X-ray photoelectron spectra (XPS) measurements, atomic force microscope (AFM) images, and fluorescence spectra. Furthermore, photoelectrochemical activity of resultant rGO/TPPyP-Zn nanocomposites was evaluated under visible-light irradiation, and enhancement of the photoelectrocatalytic reduction of CO<sub>2</sub> was achieved.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

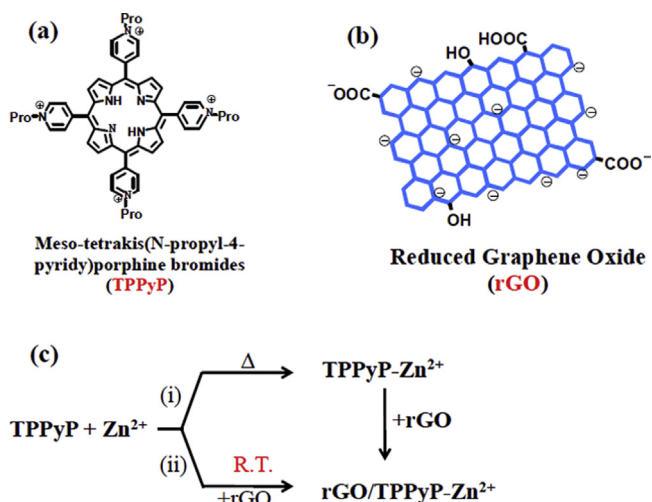
Porphyrins and metalloporphyrins derivatives have been widely regarded as excellent light harvesting materials [1,2]. Their unique photophysical and electrochemical properties including various electron transfer and catalytic reactions are tunable by varying the meso-functional groups and central metal ions [3–5]. For example, there are iron porphyrin in heme for oxygen transport in the bloodstream of mammals and magnesium chlorin in chlorophyll as a light driven proton pump [6]. The crucial central metal in metalloporphyrins is closely related to their versatile functionalities such as photosynthesis, photodynamic therapy, photoelectrical devices and etc [7,8]. However, the metallation of free base porphyrin at room temperature is very slow, e.g. their complex rate is several orders of magnitude lower than open-chain ligand o-phenathroline with bivalent metal ions [9]. In order to avoid heating or reflux at high temperature, several attempts have been made to accelerate the formation of met-

alloporphyrins, such as enzymes-catalyzed metal ions insertion [10], cyclodextrin/porphyrin inclusion complex with Zn<sup>2+</sup> ion [11], graphene/porphyrin supermolecular assembly with Cd<sup>2+</sup> ion [12], surface chemical reaction at the solid-vacuum interface around room temperature [13,14]. Therefore, numerous artificial assemblies and sensors based on porphyrins have been designed under mild conditions.

Graphene, a monolayer of carbon atoms in 2-D honeycomb lattice, is regarded as one of the most promising catalyst support due to its huge specific surface area and remarkable electron transfer ability [15,16]. Especially, the organization of porphyrins onto graphene surface via covalent or noncovalent interaction has attracted significant interest recently [17]. It was found that the formation of porphyrin-graphene nanohybrids to yield donor-acceptor system could create synergistic effect and provide more efficient photoinduced electron transfer, which significantly enhances the photo/electro-catalytic activity [18,19]. Chen's group first prepared an organic soluble graphene hybrid material with excellent optical limiting property, in which porphyrin was covalently bonded to graphene oxide by the amide linkage [20]. Xu and Geng et al. reported the noncovalent functionalization of graphene with free-based porphyrins and metalloporphyrins [12,21]. Porphyrins were found to be noncovalently assembled onto the surface

\* Corresponding authors.

E-mail addresses: [zengrj1963@126.com](mailto:zengrj1963@126.com) (R. Zeng), [chenshumail@gmail.com](mailto:chenshumail@gmail.com) (S. Chen).



**Scheme 1.** Building bricks (a, b) and synthesis routes (c) for rGO/TPPyP-Zn nanocomposites.

of graphene nanosheets through  $\pi$ - $\pi$  stacking, van der Waals and electrostatic interactions [22]. Arramel et al. showed that noncovalent interaction with metalloporphyrins can cause a band gap opening in graphene, which could be further tuned by the metal cation of the porphyrin [23]. Nevertheless, to design stable and efficient metalloporphyrin-based photoelectrocatalysts that can be prepared in a facile and rich manner is still a significant challenge.

In this work we provide a new route to prepare metalloporphyrin/graphene nanocomposites in aqueous media at room temperature. Noncovalent assembly of the free-based porphyrin (TPPyP) onto the surface of reduced graphene oxide with proper negative charge can enable the incorporation of  $\text{Zn}^{2+}$  into TPPyP more efficiently. The formation of rGO/TPPyP-Zn nanocomposite causes a red shift at the Soret band of TPPyP in UV-vis spectroscopy, morphological change in AFM images, remarkable fluorescence emission quenching in fluorescence spectra, and enhanced activity for the application in photoelectrocatalytic reduction of  $\text{CO}_2$ .

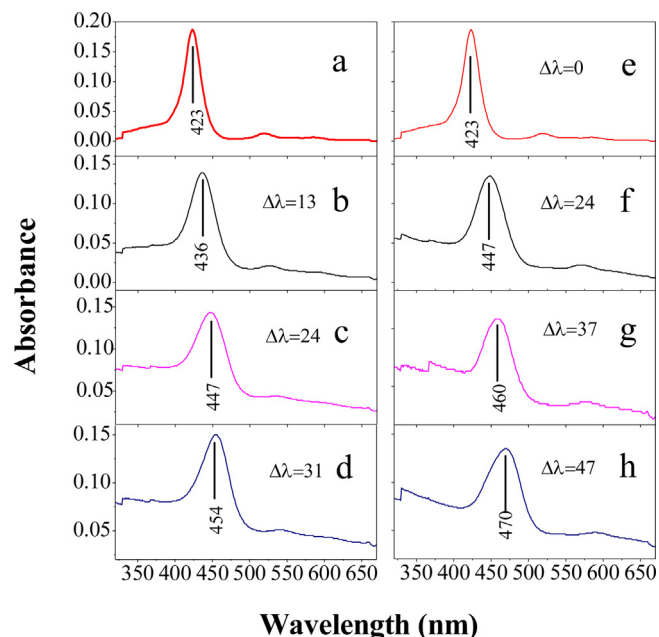
## 2. Experimental

### 2.1. Chemicals and solutions

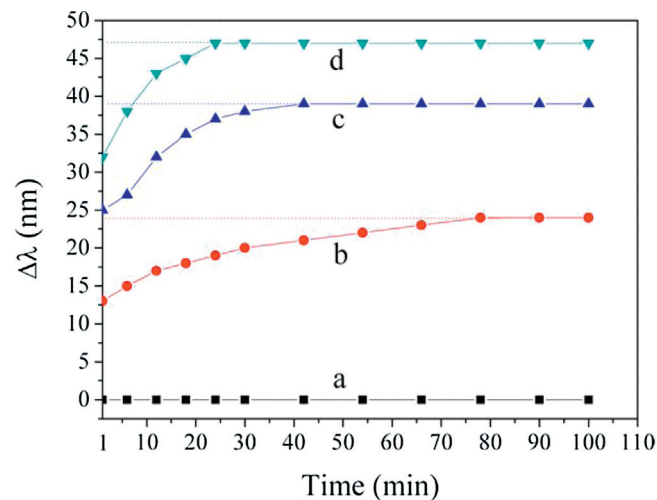
Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. The cationic porphyrin (5,10,15,20-tetra(4-propyl pyridinio) porphyrin (TPPyP, shown in Scheme 1), were synthesized and purified in our laboratory according to the literature procedures [24,25]. Its zinc complex (TPPyP-Zn) was obtained from 1  $\mu\text{M}$  TPPyP and 2.5  $\mu\text{M}$  ZnAc at 80 °C reflux for 4 h in aqueous solution (Scheme 1c, route (i)). Double-distilled water was used throughout the experiments. All chemicals were of analytical grade and were used without further purification.

### 2.2. Preparations of GO and rGO

Graphene Oxide (GO) was prepared from graphite according to the modified Hummer's method [26]. The resultant GO was dried at 60 °C for 24 h and then dispersed in water, ultrasonic produce a homogeneous dispersion of the GO with concentration of 0.15 mg/mL. In order to prepare rGO with different reduction degree, we used a given mass of hydrazine hydrate (7.5 mL into 40 mL GO colloid) as reducing agent at 95 °C, by changing the time of reducing from 0 to 90 min. Depending on the time of reduction, the products successively named GO, rGO-1 and rGO-2. The rGO-2



**Fig. 1.** UV-vis absorption spectra of (a) TPPyP, (b) GO/TPPyP, (c) rGO-1/TPPyP, (d) rGO-2/TPPyP and (e-h) with the addition of  $\text{Zn}^{2+}$  into (a-d) after 30 mins under room temperature. All  $\Delta\lambda$  are relative to (a).



**Fig. 2.** Time-dependent advancement of the Zinc-metallation of (a) TPPyP, (b) GO/TPPyP, (c) rGO-1/TPPyP, (d) rGO-2/TPPyP after addition of  $\text{Zn}^{2+}$  at room temperature.  $\Delta\lambda$  are relative to the maximum band of TPPyP.

is the highest reduction degree we can get from chemical reduction method (Zeta potential series was shown in Fig. S1).

### 2.3. Preparations of rGO/TPPyP and rGO/TPPyP-Zn nanocomposites

The prepared rGO was dispersed in water, producing a homogeneous dispersion with concentration of 0.15 mg/mL. To prepare rGO/TPPyP, a 3 mL 1 mM ( $M = \text{mol/L}$ ) aqueous solution of TPPyP was titrated with 0.15 mg/mL of rGO dispersion (0 ~ 80 mL) at room temperature. Then, 0.1 mM  $\text{Zn}^{2+}$  (zinc acetate) solution was added to rGO/TPPyP dispersion drop-by-drop (0 ~ 80 mL). The mixture solution was ultrasonicated for 30 s and standing several minutes before test. All of these processes were conducted under room temperature (R.T., 25 °C) as shown in Scheme 1c, route (ii).

Download English Version:

<https://daneshyari.com/en/article/7836474>

Download Persian Version:

<https://daneshyari.com/article/7836474>

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