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## COMMUNICATION

# Facile assembly of polystyrene microspheres/graphene oxide/porphyrin composite with core-shell structure

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**5, 10, 15, 20-tetrakis(4-trimethylaminophenyl)porphyrin iodide (TAPPI) was assembled facilely on the surface of graphene oxide (GO) coated polystyrene (PS) microspheres by electrostatic interaction combined with  $\pi$ - $\pi$  interaction. In the monodisperse ternary composite with core-shell structure (PS microspheres/GO/TAPPI), effective electron transfer from excited TAPPI to GO can be achieved as evidenced by fluorescence spectra. Under continuous UV illumination, TAPPI molecules in the ternary composite displayed high UV stability compared with that of pure TAPPI. Furthermore, enhanced thermal stability can also be obtained for the ternary composite. It was possible to enhance the stability of TAPPI molecules through conjugation of delocalized  $\pi$ -electron systems between PS microspheres supported GO and TAPPI.**

## Introduction

Porphyrin derivatives are with a large extinction coefficient in the visible-light region, predictable rigid structure and prospective photochemical electron-transfer ability. As a kind of well-known functional dyes, they have been extensively investigated on sensors, nonlinear optical material and energy conversion.<sup>1-3</sup> Featuring the porphyrin derivatives as electron donor and the carbon materials as electron acceptor to generate charge-separated states have been reported.<sup>4-6</sup> Especially, porphyrins and graphene oxide (GO) have significant  $\pi$ -electron conjugation, and their composites exhibit outstanding photocatalytic, photoelectrochemical and nonlinear optical properties.<sup>7-9</sup>

Nevertheless, porphyrins are easily photobleached. So some of their characteristics disappear. Bonchio et al. found that the introduction of cyclodextrin can partly prohibit the porphyrin moiety from irreversible photobleaching.<sup>10</sup> Compared to cyclodextrin, GO is desirable for use as a two-dimensional functionalized support to provide adsorption and reaction sites due to its extremely high specific surface area, high Young's modulus, high carrier mobility and excellent thermal conductivity.<sup>11</sup> Therefore, it is timely and important to prepare novel porphyrins/graphene composite for stable

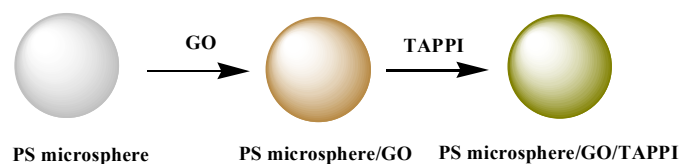
optoelectronic materials. However, the strong van der Waals interactions among reduced GO result in their tendency to aggregate in solution. In addition, porphyrins are also easy to aggregate because of their large aromatic structure.

The composites with core-shell structure are attractive for applications in optical sensors and in optoelectronics.<sup>12</sup> The stability of GO and porphyrin could be improved in a core-shell structure, which is profitable for porphyrins to be applied in photoelectronic devices.

In this paper, with PS microspheres as the core, GO and TAPPI (The structure of TAPPI was shown in Fig. S1) as the shell, a monodisperse ternary composite, PS microspheres/GO/TAPPI is assembled. Furthermore, the thermal stability and UV stability of the PS microspheres/GO/TAPPI is investigated.

## Results and discussion

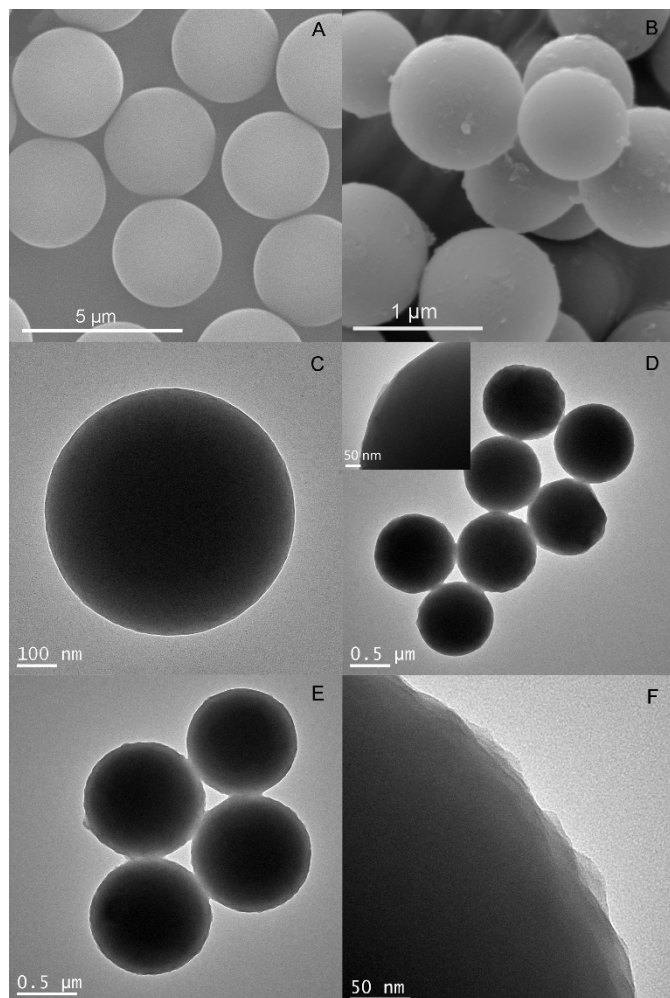
The light green PS microsphere/GO/TAPPI was facilely constructed through simple stirring. As shown in Scheme 1, the brown GO was coated on the surface of white PS microspheres through  $\pi$ - $\pi$  interaction and hydrophobic interaction. The resulting light yellow PS microsphere/GO possesses a negatively-charged surface and a conjugated  $\pi$ -system, which is conducive to the assembly of cationic TAPPI molecules.



**Scheme 1.** Assembly scheme of the PS microsphere/GO/TAPPI.

To observe the morphology of the composite, SEM and TEM images of the samples were taken. Fig. 1A and Fig. 1C show the smoothly spherical outline of the PS microspheres. When the PS microspheres are treated with GO, a rough spherical outline is observed (Fig. 1D). After TAPPI molecules are assembled on the surface of the PS microspheres/GO, the surface roughness of the PS microspheres/GO is changed a little (Figs. 1B, 1E and 1F). In

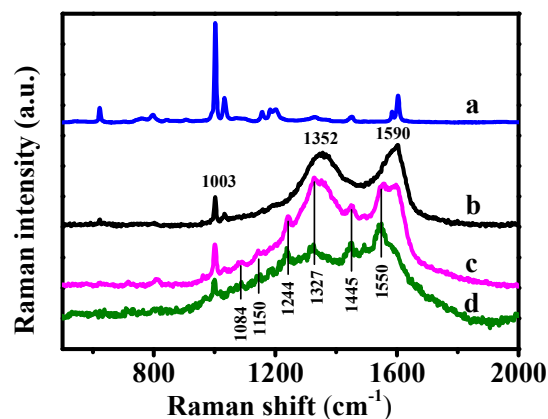
addition, the composite microspheres are monodisperse, and no isolated GO sheets and TAPPI aggregate are found outside of the spheres. It is demonstrated that the GO and TAPPI molecules have been assembled on the surface of PS microspheres. Existence of GO and TAPPI on the PS microspheres will be further characterized by Raman spectra and Solid diffuse reflectance UV-vis spectra followed.



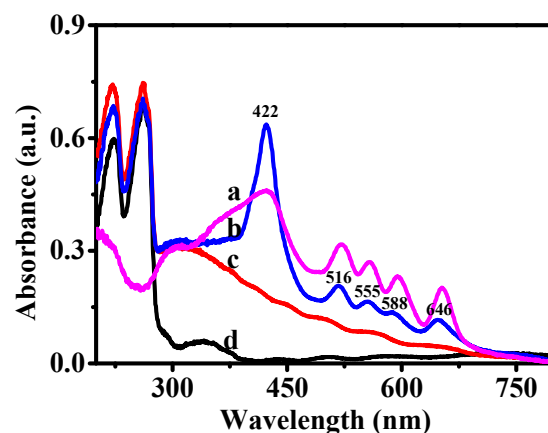
**Fig. 1.** SEM images of (A) PS microspheres and (B) PS microspheres/GO/TAPPI; TEM images of (C) PS microspheres, (D) PS microspheres/GO and (E, F) PS microspheres/GO/TAPPI.

Raman spectroscopy is a versatile and non-destructive characterization technique for obtaining information on the nature of binding of aromatic hydrocarbons. Fig. 2 displays the Raman spectra of the samples. PS microspheres show a very strong peak at about  $1003\text{ cm}^{-1}$ , which is assigned to  $\nu_1$  ring-breathing mode. It dramatically decreases after being coated with GO (Fig. 2 (b)). Meanwhile, D band and G band of the GO can be observed at about  $1352\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$ , respectively. It demonstrates that the GO has coated on the surface of the PS microspheres.<sup>13</sup> Furthermore, in the Raman spectrum of the PS microspheres/GO/TAPPI (Fig. 2 (c)), subtle rather than drastic changes in the D and G bands, the weakened  $\nu_1$  ring-breathing of PS microspheres, and some new peaks are observed. These new peaks are assigned to the characteristics bands of the TAPPI.<sup>14</sup> Namely, the peak at  $1084\text{ cm}^{-1}$  is corresponding to C-H bending vibration, the peaks at  $1150\text{ cm}^{-1}$  and  $1244\text{ cm}^{-1}$  are attributed to the C-C stretching vibration. In addition, the C-N stretching vibration at  $1327\text{ cm}^{-1}$ , the C=C skeletal

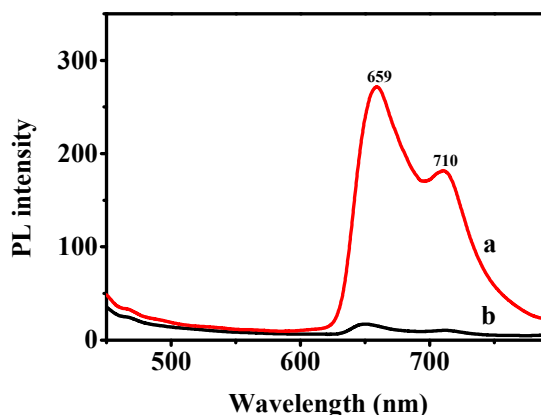
vibration at  $1445\text{ cm}^{-1}$  and N-H bending vibration at  $1550\text{ cm}^{-1}$  are also observed (Fig. 2 (d)). Raman spectral results confirm the presence of GO and TAPPI on the PS microspheres.



**Fig. 2.** Raman spectra of (a) PS microspheres, (b) PS microspheres/GO, (c) PS microspheres/GO/TAPPI and (d) TAPPI.



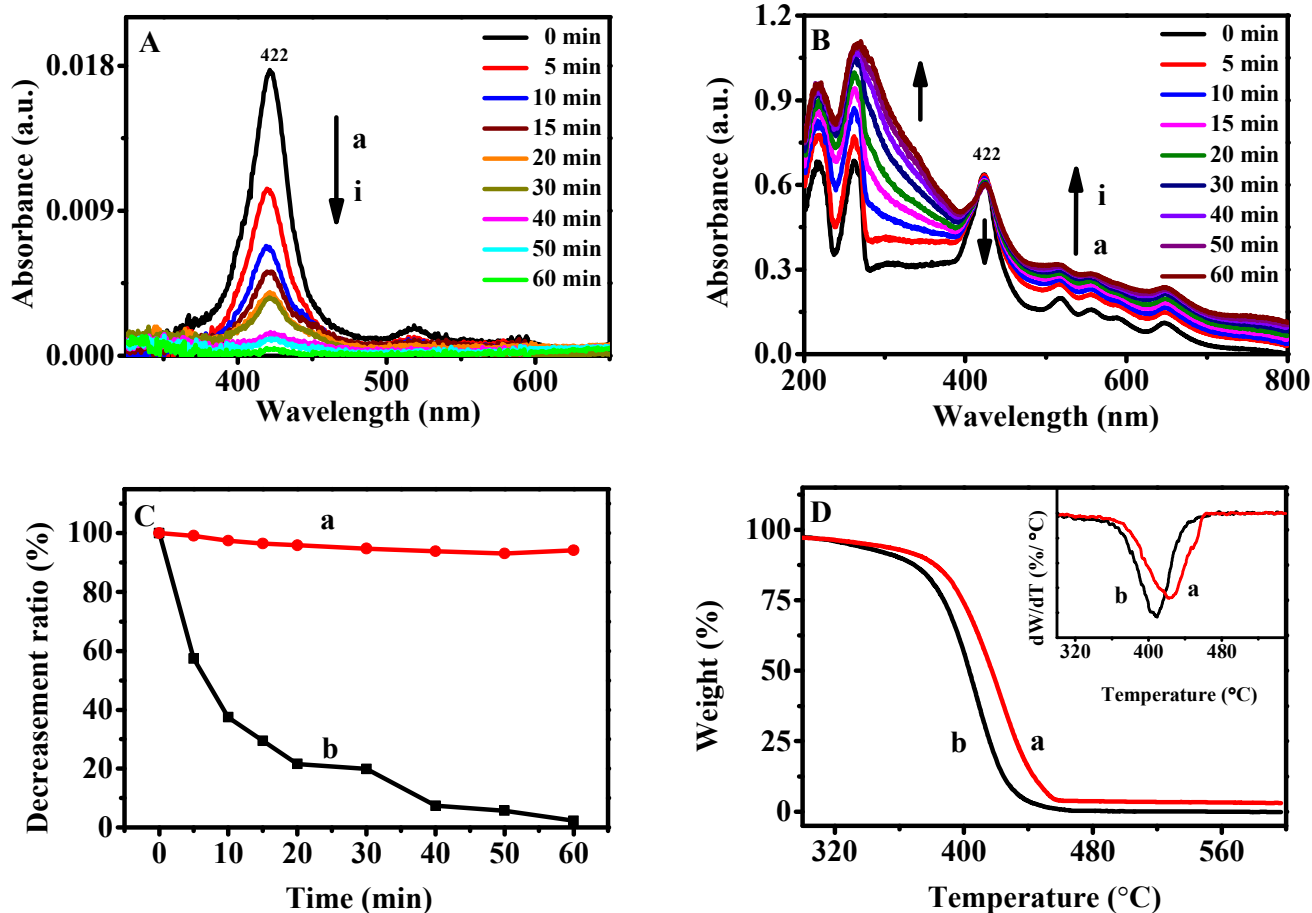
**Fig. 3.** Solid diffuse reflectance UV-vis spectra of (a) TAPPI, (b) PS microspheres/GO/TAPPI, (c) PS microspheres/GO and (d) PS microspheres.



**Fig. 4.** Fluorescence spectra of (a) PS microsphere/TAPPI and (b) PS microspheres/GO/TAPPI. The amount of TAPPI in two samples was same).  $\lambda_{\text{ex}} = 408\text{ nm}$ .

Solid diffuse reflectance UV-vis spectra of the samples are shown in Fig. 3. Two peaks at around 224 nm and 261 nm can be observed (Fig. 3 (d)), which are corresponding to the characteristic  $\pi$ -plasmon absorption of PS microspheres. After being coated with GO (Fig. 3 (c)), a broad band in the range of 282 nm to 800 nm can be observed, which is due to  $n$ - $\pi^*$  transition of the C=O bond. The peak at around 228 nm due to  $\pi$ - $\pi^*$  transition of aromatic C=C bond is overlapped with those of the PS microspheres. In addition, the characteristics bands of TAPPI can be observed in Fig. 3 (b). Namely, a broad Soret band is at about 422 nm, and four Q bands are at about 516, 555, 588 and 646 nm, respectively. The result of solid diffuse reflectance UV-vis spectra is consistent with those of Raman spectra and TEM.

The interaction between TAPPI and GO can be investigated by fluorescence spectra (Fig. 4). When excited at  $\lambda_{\text{ex}} = 408$  nm, no fluorescence is observed for pure PS microspheres and GO (not shown here). Differently, two new emission peaks at 659 nm and 710 nm are displayed for the PS microsphere/TAPPI (Fig. 4a), which are attributed to TAPPI (Fig. S2). The peaks are 94% quenched after introducing the GO (Fig. 4b). It is indicated that there exists strong interaction between TAPPI and GO, which is profitable to transfer the photogenerated electrons from TAPPI to GO. Therefore, recombination of electron/holes pairs in TAPPI is prohibited.<sup>15</sup>



**Fig. 5.** UV-vis absorption spectra of (A) the TAPPI and (B) PS microspheres/GO/TAPPI under UV irradiation for various time intervals: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 30 min, (g) 40 min, (h) 50 min and (i) 60 min from top to bottom, respectively. (C) The dependence of decrement percent of the absorbance at 422 nm on the irradiation time. (a) PS microspheres/GO/TAPPI and (b) TAPPI. (D) TG and DTA (inset) curves of (a) PS microspheres/GO/TAPPI and (b) TAPPI.

The UV stability of the pure TAPPI and the TAPPI on the PS microspheres/GO is investigated. Progressive decay of the pure TAPPI due to absorption of UV light is observed followed by prolonged irradiation time (Fig. 5A). After being irradiated for 60 min, the absorbance at 422 nm decreases about 97.7% (Fig. 5C (b)). Comparatively, for the TAPPI assembled onto the PS microspheres/GO, the absorbance decreases slightly (only about 7.7%, Fig. 5B and Fig. 5C (a)). Obviously, the UV stability of the TAPPI can be improved after it is assembled onto the surface of PS

microspheres/GO. It is known that the GO can be reduced under UV irradiation.<sup>16</sup> In general, the reduction is accompanied by changes in colour and in absorption. Indeed, after UV irradiation, the absorbance of the ternary composite in the range of 263 nm to 392 nm increases, and the colour changes from light yellow green to brownish green.

Due to the strong electrostatic and  $\pi$ - $\pi$  interactions between TAPPI and GO, the reduced GO can stabilize the excited state of the TAPPI. Therefore, the irreversible photo bleaching of TAPPI



molecules can be effectively prohibited. In addition, the direct interaction between PS microspheres and GO hinders the collapse of GO sheets, which is advantageous to keep the interactions between TAPPI and GO.

Furthermore, the thermal stability of the samples is investigated by TG and DTA. It can be seen that (Fig. 5D), the PS microspheres/GO/TAPPI exhibits less weight loss in the range of 330 °C to 460 °C, and decomposition temperature is 423 °C. It increases about 13 °C compared to that of the pure TAPPI. Obviously, the thermal stability of the TAPPI is enhanced after being assembled on the surface of PS microspheres/GO. It could be attributed to that some TAPPI molecules were trapped into the wrinkles of the GO.

## Conclusions

Monodisperse PS microspheres/GO/TAPPI composite was prepared by a facile process. The TAPPI molecules in the ternary composite showed high UV stability and thermostability, which was important to the porphyrin-based optical materials. The PS microspheres/GO/TAPPI composite has a potential in the field of photoelectrochemical sensor. Further efforts are currently being undertaken.

## Experimental

Graphite powder with an average size of 30 µm and purity of >95% was obtained from Shanghai Chemical Reagent Company. PS microspheres (average diameter 1 µm) were purchased from Henghui Yangzhou Chemical Company. TAPPI was synthesized and purified according to the Ref.<sup>17</sup> The other reagents (A.R.) came from Shanghai Chemical Reagent Company and were used as received. Deionized water was used throughout the experiments. The GO was prepared by a modified Hummers method.<sup>18</sup>

PS microspheres/GO/TAPPI was prepared by the following procedure. 5 mL of 5% (w/v) PS microspheres aqueous dispersion was added into 5 mL of 1 mg mL<sup>-1</sup> GO aqueous solution, and stirred overnight at room temperature. The light yellow solid obtained by centrifugation was washed with ethanol and water for three times, respectively. Then, it was re-dispersed into 5 mL of deionized water, and 20 mL of 1×10<sup>-4</sup> mol L<sup>-1</sup> TAPPI aqueous solution was added and stirred for 8 h at room temperature. The light green solid obtained by centrifugation (PS microspheres/GO/TAPPI) was washed thoroughly with water. The morphology of the sample was characterized on a JEM-1400 transmission electron microscope (TEM) (Japan) and Quanta 200FEG scanning electron microscope (SEM) (USA). Raman spectra were measured by the Thermo Scientific DXR Raman microscope with a 532 nm DPSS laser and a 50× objective (NA = 0.42) (USA). The spot is 1.1 µm. The incident laser power is 1 mW and the exposure time is 3 s to avoid laser-induced thermal effects or damage. UV-vis spectra were recorded with a model U-3900/U-3900H spectrophotometer (Japan). Fluorescence spectra were obtained using a Hitachi F-4600 fluorescence spectrophotometer (Japan). The thermo-gravimetric and differential thermal analyzers (TG-DTA) were recorded on a Perkin Elmer TG/DTA-7 instrument (USA). The heating rate was 10 °C per minute under N<sub>2</sub> atmosphere.

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## Notes and references

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