

- Electronic Supplementary Information -

A General Approach for Encapsulating Organic Crystals in Polyaniline

Shell

Miao Yan, Neng Wang, Bingju Zhong, Xuejun Cheng, Hong Wang and Hongyu Chen**

Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu Nation Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China.

Email: ias_hwang@njtech.edu.cn; iashychen@njtech.edu.cn

Materials

All chemical reagents were used in experiments without further purification. All kinds of organic crystals, 98%, were purchased from Alfa Aesar; Tetramethylene (THF, 99.8%) and *N,N*-dimethylformamide (DMF, 99.8%) were purchased from Tedia; Isopropanol and *m*-xylene were purchased from Beijing Chemical Reagent Corp, China; Cetyltrimethyl ammonium bromide (CTAB) was purchased from Aldrich Chemical Co, USA; Hydrochloric acid (HCl, Qrec Chemical 37%) was purchased from P. P. Chemicals Sdn Bhd, Aniline (99%, Alfa Aesar) was fractionally distilled under reduced pressure and stored at 4 °C; Sodium dodecyl sulfate (SDS, 99%) and (NH₄)₂S₂O₈ (98%) were purchased from Alfa Aesar. Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing Zhongjingkeyi Technology Co.

Methods

Characterization. TEM images were collected from a HT7700 Transmission Electron Microscopy operated at 100 kV and a Talos L120C model operated at 120 kV. Fluorescence spectra were measured from a PerkinElmer LS 55. The emission intensity at 460 nm was recorded. The excitation wavelength was at 385 nm; all measurements were carried out in a cuvette of 1 cm pathlength; and the excitation and emission slits were kept at 2.5 nm.

Synthesis of organic crystals. In a typical synthesis process, tetraphenylethylene (TPE) organic crystals were synthesized by a precipitation method. Organic crystal (2 mM in THF, 50 μL) was quickly added to an SDS aqueous solution (3.6 mM, 300 μL) with vigorous stirring (< 5 s), and the mixture was aged for 30 min to ensure the formation of organic crystals.

For other organic crystals, the synthetic method is similar to the TPE. Different molecular crystals have different optimal solvents: molecule 3, 4, 8, 9, 12, and 14 were dissolved in THF; molecule 2, 5, 6, 7, 11, 13, 15, 16, 17, and 18 were dissolved in DMF.

Synthesis of C₆₀ rod. In a typical preparation procedure for single-crystal nanorod,¹ 1.5 mL of C₆₀/*m*-xylene stock solution (1.2 mg/mL) was injected vigorously into stirred 1.5 mL of CTAB (5 mM) isopropanol solution at the room temperature. The mixed solution immediately turned to clear mauve from colorless. After 30 s, the solution became turbid lemon-yellow. After continuous

stirring 10 min, C₆₀ nanometer rod was synthesized. The solid samples were obtained by centrifugation at 3000 rpm for 10 min.

Polyaniline encapsulation of organic crystals. Solutions of aniline (5 mM, 1000 μ L), SDS (40 mM, 200 μ L), and acidic (NH₄)₂S₂O₈ (5 mM in 10 mM HCl, 1000 μ L) were added into 300 μ L organic crystal solution, and the mixture was vortexed for 10 s. The mixture was then incubated at room temperature for 4 h for the polymerization. The colour of the mixture is emerald. Finally, they were purified by centrifugation at 3000 rpm for 10 min.

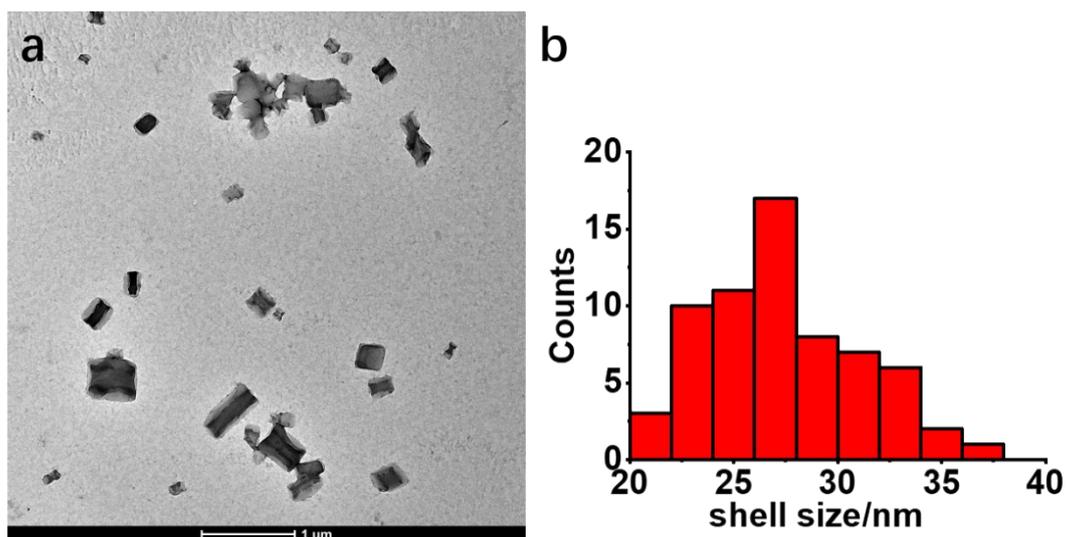


Figure S1. (a) TEM image of TPE@PANI, where partial TPE sublimated under irradiation of electron beam of TEM. (b) Size distribution of PANI shell, the average thickness is 28 nm \pm 1.6 nm.

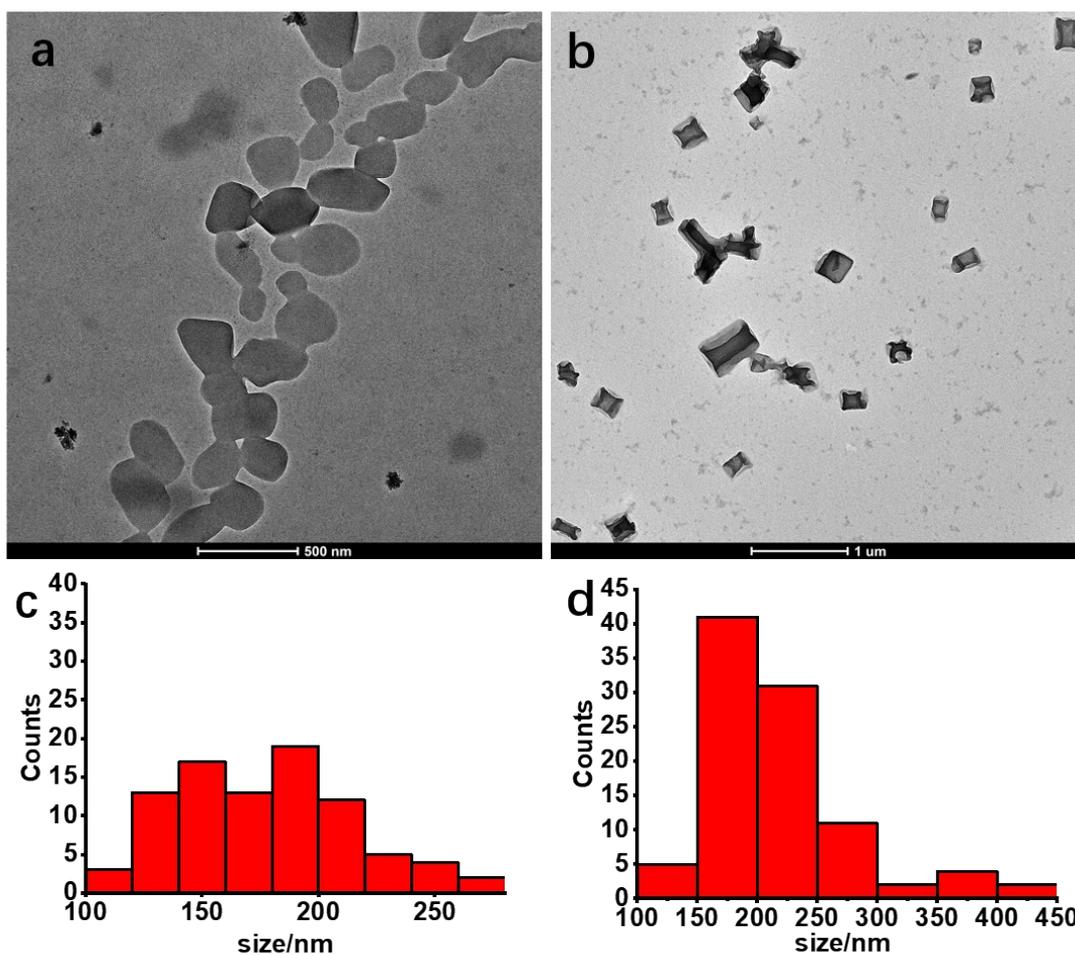


Figure S2. TEM images of (a) TPE crystals, and (b) TPE@PANI nanoparticles; (c) Size distributions of TPE crystals, the average size is $190 \text{ nm} \pm 2.5 \text{ nm}$; (d) Size distributions of TPE@PANI nanoparticles, the average size is $220 \text{ nm} \pm 1.8 \text{ nm}$.

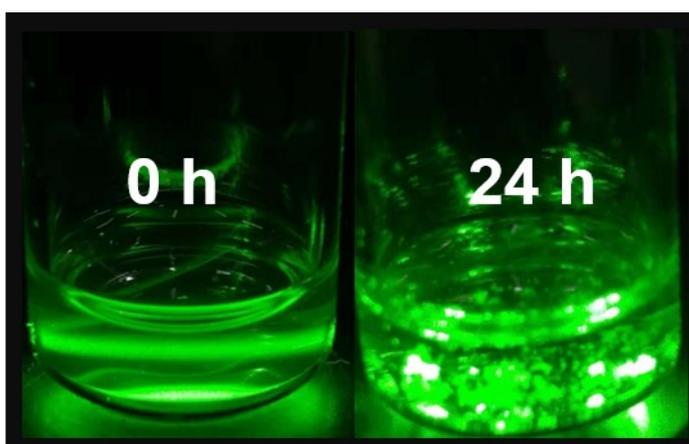


Figure S3. Tyndall effect of TPE crystals.

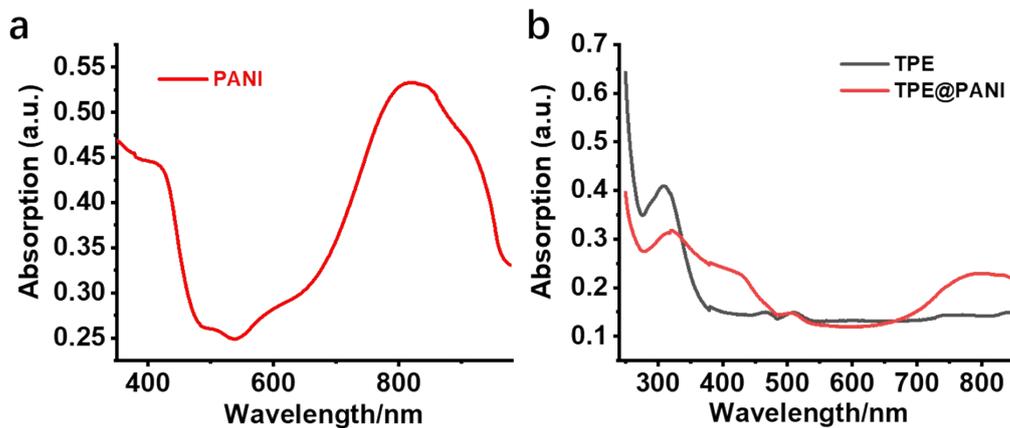


Figure S4. The UV-vis spectra of (a) polyaniline; (b) TPE crystals and purified TPE@PANI nanoparticles.

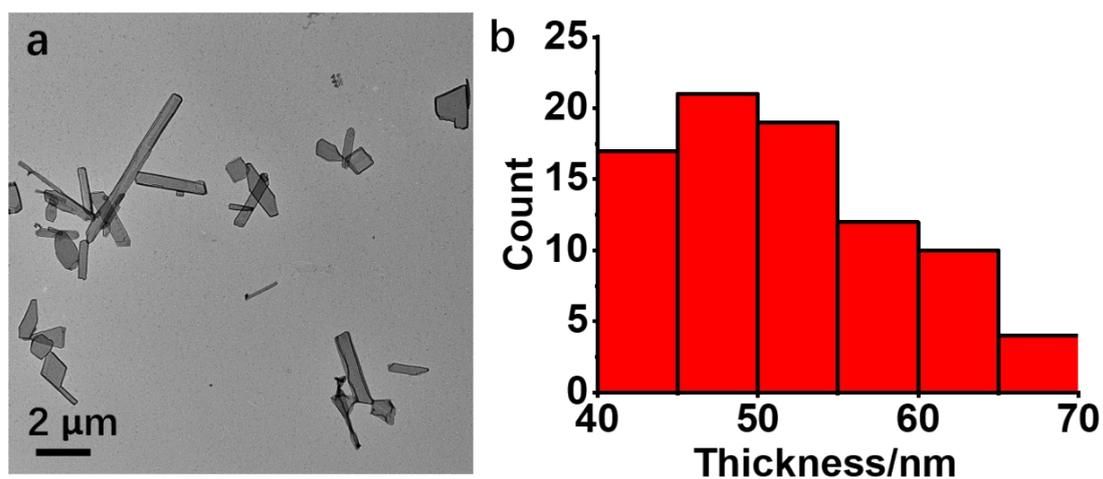


Figure S5. (a) TEM image shows the TBB@PANI nanoparticles synthesized when the concentration of organic crystals is 0.4 mM; (b) Size distribution of PANI shell thickness in Figure S5a, the average thickness is $52 \text{ nm} \pm 0.6 \text{ nm}$.

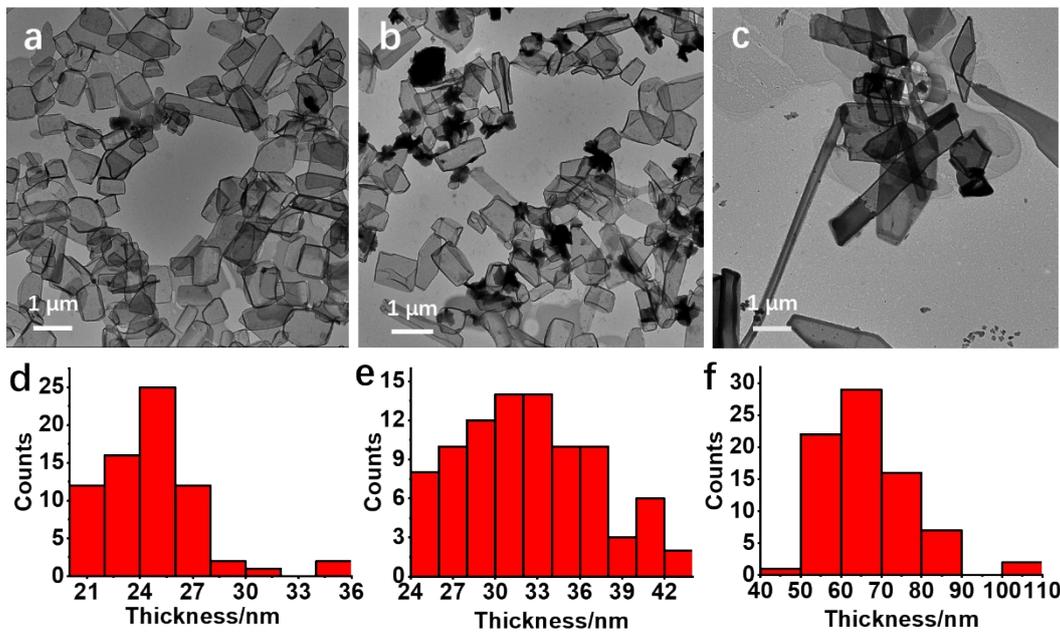


Figure S6. TEM images of TBB@PANI nanocomposites synthesized with: (a) 80 mM SDS; (b) 100 mM SDS; and (C) 120 mM SDS, respectively; (d-f) Size distributions of PANI shell thickness (d) in Figure S6a, the average thickness is $25 \text{ nm} \pm 0.8 \text{ nm}$; (e) in Figure S6b, the average thickness is $30 \text{ nm} \pm 1.1 \text{ nm}$; (f) in Figure S6c, the average thickness is $65 \text{ nm} \pm 1.8 \text{ nm}$.

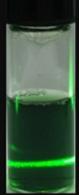
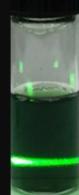
Organic crystals	TPE-2OH		Anthracene		Hexacosanoic acid	
Time (day)	0	180	0	180	0	180
Top						
Middle						
Bottom						

Figure S7. Tyndall effect of TPE-2OH@PANI, anthracene@PANI, and Hexacosanoic acid@PANI nanocomposite.

References:

1. H.-X. Ji, J.-S. Hu, Q.-X. Tang, W.-G. Song, C.-R. Wang, W.-P. Hu, L.-J. Wan and S.-T. Lee, *The Journal of Physical Chemistry C*, 2007, **111**, 10498-10502.