

Supporting information for

Morphology Controlled Self-Assembly and Synthesis of Photocatalytic Nanocrystals

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1. Materials:

Zinc meso-tetra (4-pyridyl) porphyrin (ZnTPP) was purchased from Frontier Scientific, Inc., myristyltrimethylammonium bromide (MTAB), cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were purchased from Aldrich Chemical Co. and used without further purification. Sodium hydroxide (NaOH 1N) standard solution was purchased from Alfa Aesar. Methyl orange (MO, AR) and all other chemicals were used without further purification. All the solutions were prepared in ultrapure water from a Barnstead Nanopure water system, and filtered through a 0.2- μm syringe filter to remove particles.

2. Morphology controlled synthesis:

Typically, 0.5 mL of ZnTPP solution (0.01 M ZnTPP dissolved in 0.2 M HCl solution) was quickly injected into 9.5 mL of aqueous solution containing myristyltrimethylammonium bromide (MTAB) (0.01 M) and NaOH (0.02 M) with continuous stirring, and the mixture was subsequently stirred at room temperature (25 °C) for 48 hours. The tetragonal nanorods was centrifuged at 9500 rpm and washed twice with Millipore water to remove surfactant. The procedures for the other experiments were similar to that for the typical one, but altering either the MTAB concentration, or NaOH concentration (resulting in different pH values after mixing). We can control the morphology and size of these ZnTPP nanocrystals by adjustment of above experiment parameters, and then we can obtain the ZnTPP nanocrystals morphology phase transformation with the MTAB concentration and the pH values.

Photocatalytic Tests: The visible light photo-catalytic performance of ZnTPP nanocrystals was evaluated by the degradation of MO in aqueous solutions under irradiation from a 300 W xenon arc lamp installed in a laboratory lamp housing system (PLS-SXE 300/300UV, Beijing Perfect light Technology Co., Ltd. China). Before entering the photocatalytic reactor, the light passed through a 10 cm water filter and a UV cutoff filter (>400 nm). ZnTPP nanocrystals (1mg) was dispersed in methyl orange (MO) aqueous solution (20 mg/L, 40 mL) in a pyrex beaker made of quartz. After stirring for 30 min in dark to establish an adsorption/desorption equilibrium, then irradiation under visible light. When at designed time intervals, aliquots (4 mL) were taken out from the reaction system and centrifuged to remove the ZnTPP nanocrystals. The concentration of filtrates was monitored using the absorbance value at the maximum peak (464 nm) in the UV-visible spectrum of MO. The degradation efficiency at time t was determined from the value of C/C_0 , where C_0 is the initial concentration before irradiation under visible light and C is the concentration of MO at a certain real-time t . For comparison, blank experiments without catalyst and with 10 mg P25, where no ZnTPP nanocrystals were added, were carried out. Negligible degradation of MO molecules could be observed.^[1]

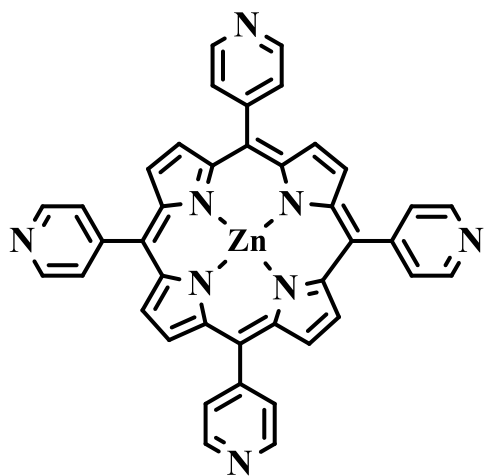
To assess the stability and recyclability of the nanodiscs-based photocatalysts on repeated use, the same catalyst was separated by centrifugation at the end of each run for consecutive photocatalytic experiments. Herein, in order to reduce the loss percentage of the catalyst between consecutive runs, the amount of the employed nanodiscs was 7 times of the above-described photocatalytic experiments where ca.1

mg ZnTPP nanodiscs were used.^[2] Moreover, only the initial concentration (C_0) and the concentration of MO at real-time 2h (C_{2h}) were measured, then the each run degradation efficiency of MO has been calculated applying the following equation:

$$\text{Photodegradation efficiency (\%)} = (C_0 - C_{2h})/C_0 \cdot 100\%.[3]$$

3. Characterizations:

Scanning electron microscopy images were taken using a Hitachi 5200 FEG microscope. Transmission electron microscopy was performed on a JEOL 2010 with 200 kV acceleration voltage, equipped with a Gatan slow scan CCD camera. The absorption spectra were collected on a Hitachi U-4100UV-VIS-NIR Spectrophotometer (Tokyo, Japan) and Fluorescence spectra were obtained from a Hitachi F7000 fluorescence spectrometer (Tokyo, Japan). Photocatalytic activities were performed using PLS-SXE 300/300UV (Beijing Perfect light Technology Co., Ltd. China) as light source. Thermogravimetric analyses were carried on a STD 2960 TA Instruments apparatus.



Zinc meso-tetra (4-pyridyl) porphyrin

$C_{40}H_{24}N_8Zn$

Mol.Wt.:682.06

Figure S1. Zn Porphyrin molecular structure.

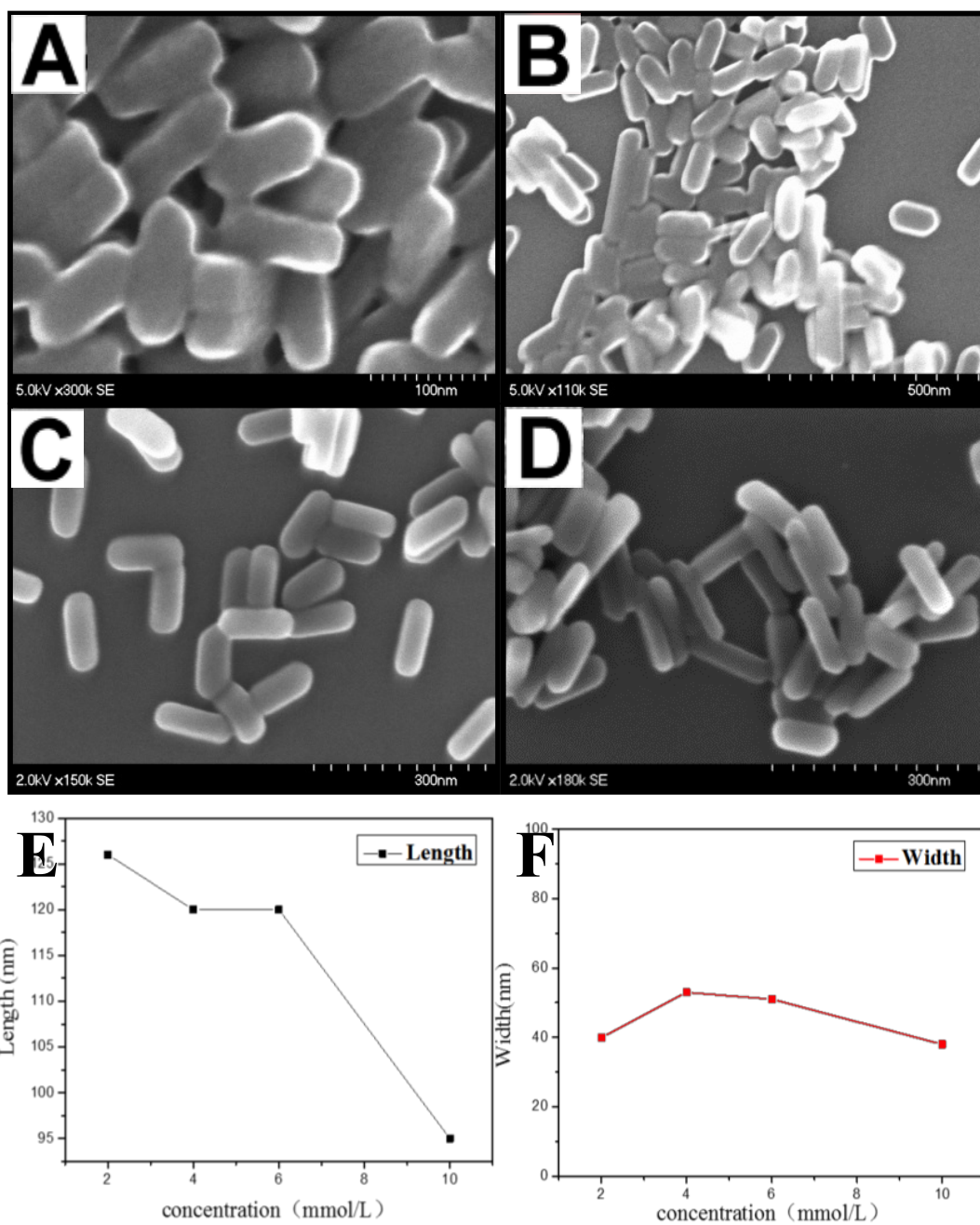


Figure S2. The effects of MTAB concentration on the size of tetragonal rods. Keeping ZnTPP 0.5 mM, pH around 11.5, and tuning MTAB concentration A, 10 mM; B, 6 mM; C, 4 mM; D, 2 mM.

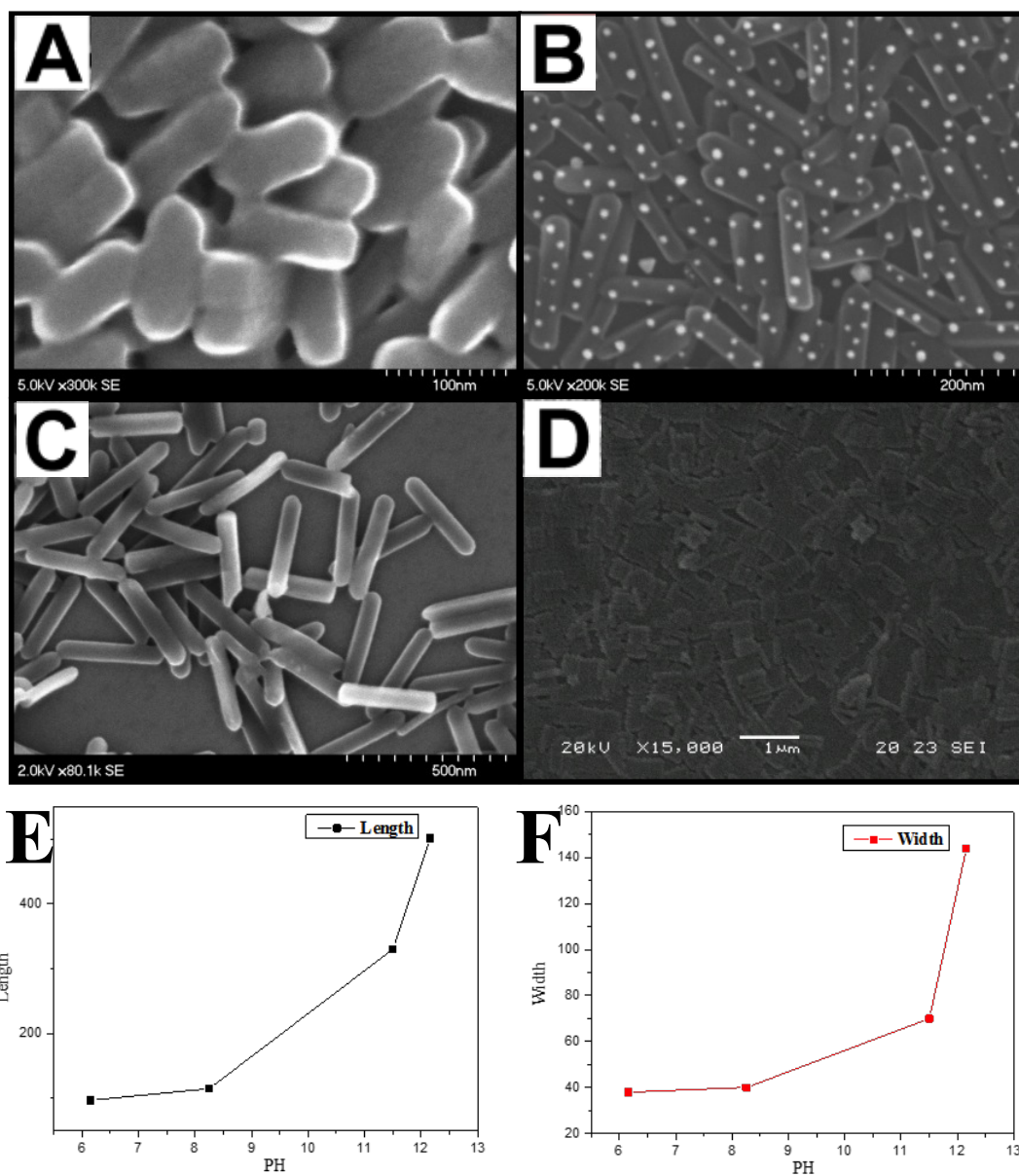


Figure S3. The effects of pH on the size of tetragonal rods. Keeping ZnTPP 0.5 mM, MTAB 10 mM, and tuning pH A, 6.15; B, 8.25; C, 11.5; D, 12.16.

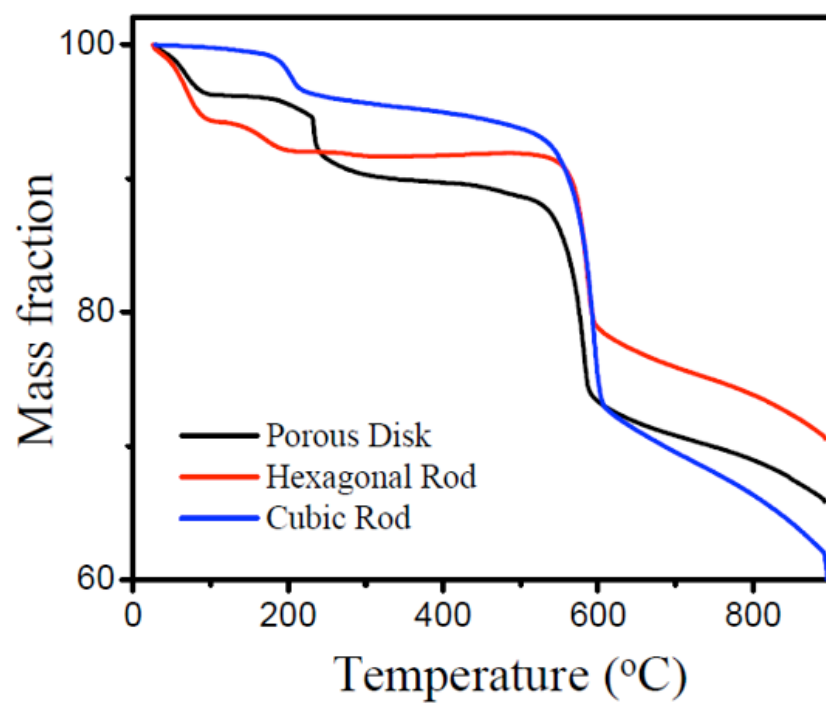


Figure S4. Thermogravimetric Analysis (TGA) curves for different porphyrin nanostructures.

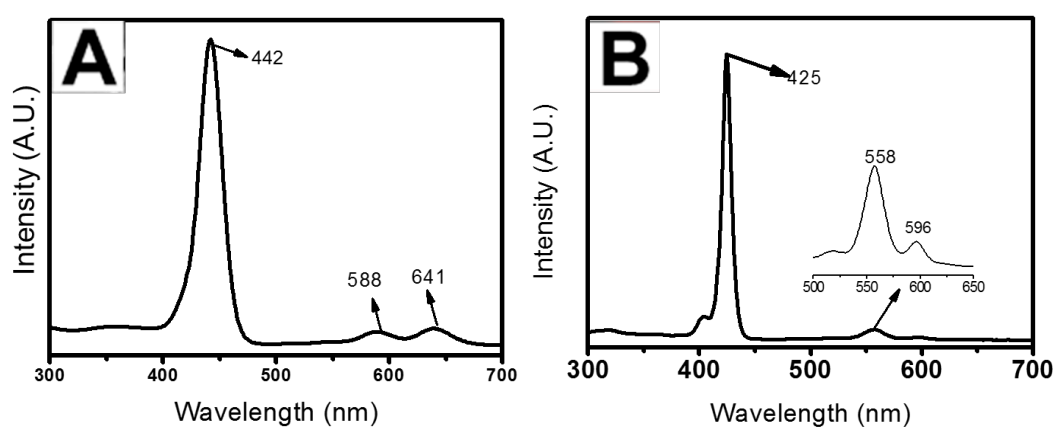


Figure S5. ZnTPP monomer UV-Vis spectra A, in 1 M HCl; B, in DMF.

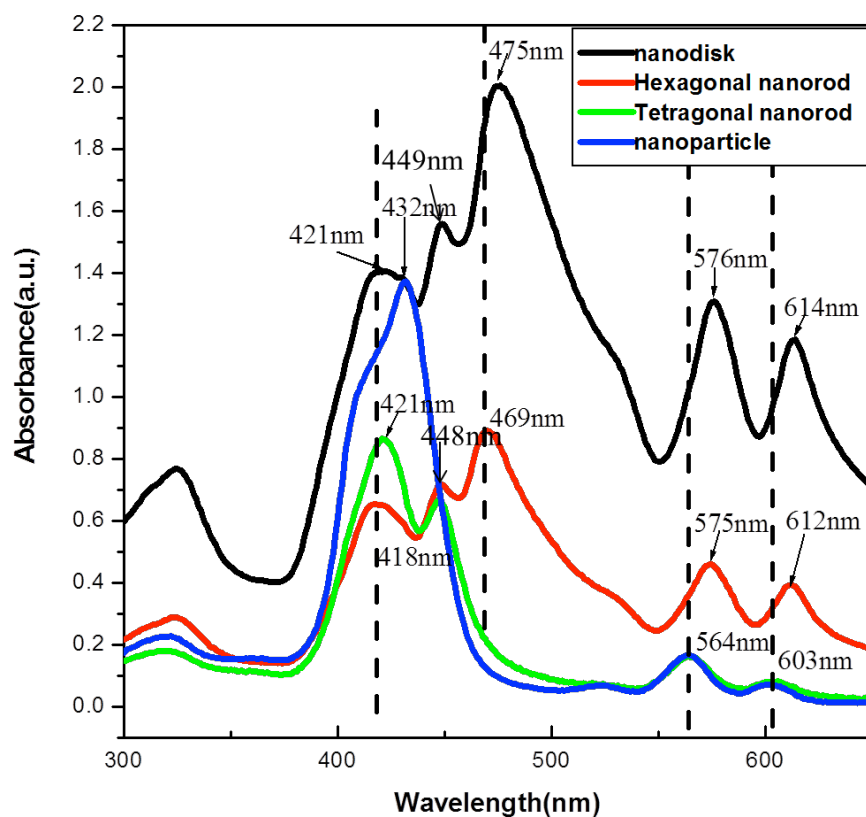


Figure S6. UV-Vis absorptions of ZnTPP nanocrystals with different morphologies.

References:

- [1] Zhong, Y.; Wang, Z.; Zhang, R.; Bai, F.; Wu, H.; Haddad, R.; Fan, H. *ACS nano* **2014**, 8, 827-833.
- [2] Guo, P.; Chen, P.; Ma, W.; Liu, M. *J. Mater. Chem.* **2012**, 22, 20243-20249.
- [3] Mohamed, R. M.; Barakat, M. A. *Int. J. Photoenergy* **2012**, 2012, 1-8.