Supporting information:

Fabrication of Well Ordered Microspheres Film for Efficient Antibacterial Activity

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Contents:

Bacterial Killing Experiments: Monocolony of *E.coli* on the solid Luria-Bertani (LB) agar plate was transferred to 5 mL of liquid LB culture medium in the presence of 50 μg/ml ampicillin and was grown at 37℃ for 12 hours. Bacteria were harvested by centrifuging (4000 rpm for 10 min) at 4 °C and washing by PBS three times. The supernatant was discarded and the deposit was resuspended in PBS. 10 μl bacterial solution was dropped onto the photocatalyst thin film, and the samples were covered with plastic film mulching to prevent medium evaporation. The samples were incubated for 30 min in the dark at 37℃ and then exposed to an optical fiber of 40mW/cm^2 420nm light for 30 min. The treated films were washed by PBS to collect the bacterial cells on the films and the bacterial suspension was diluted for 1.2×10^4 fold in PBS. A 100 L portion of the diluted bacterial *E.coli* was spread on the solid LB agar plate and the colonies formed after 12-16h incubation at 37℃ were counted. The survival fraction was determined by dividing the number of colony forming units (cfu) of the samples incubated with photosensitizers by the number of cfu of the control that was carried out in the absence of photosensitizers for film in the dark.

General Remarks: Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and were used without further purification. Column chromatography (CC): SiO2 (200-300 mesh). TLC glass plates coated with silica (F254) were visualized under UV light. 1H and 13C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25°C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass

spectrometric measurements were performed on a Bruker Biflex III MALDI-TOF instrument. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer, and FTIR spectra were recorded as KBr pellets on a Perkin–Elmer System 2000 spectrometer. Fluorescence excitation and emission spectra were recorded with a Hitachi F-4500 FL fluorimeter at a constant temperature of 25oC. SEM images were taken using a field emission scanning electron microscope (SEM) (Hitachi 4300F and DB-235 FIB), operated at an acceleration voltage of 5-15kV.

Synthesis Process: Synthesis of the porphyrin derivatives TEOP was reported in our previously literature.[1]

UV-vis spectra and Fluorescence spectra: UV-vis spectra and Fluorescence spectra of TEOP was reported in our previously literature. [1]

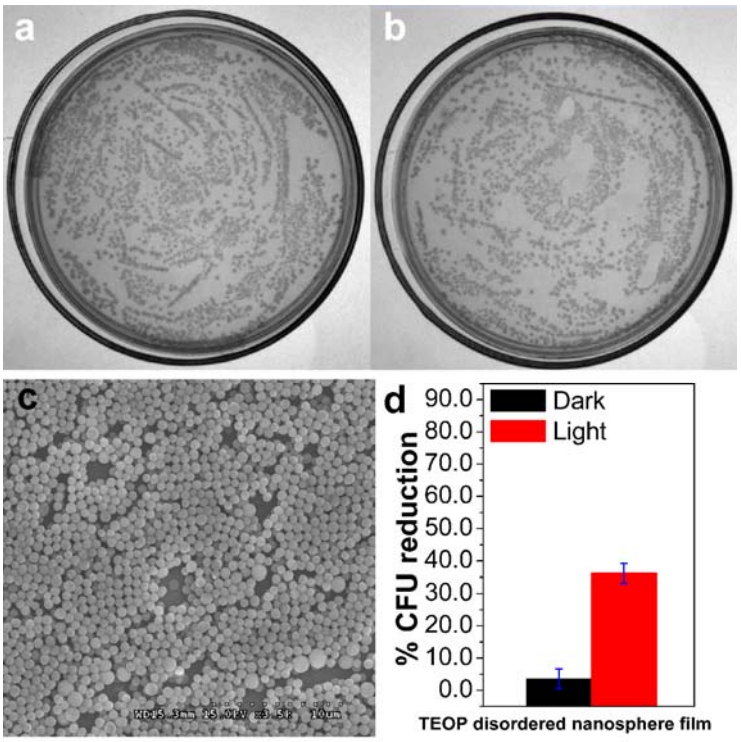

Figure s1. Number of colony forming units (cfu) for E. coli on LB agar plate. (a) Cfu of E. coli suspension incubated with TEOP disordered spheres film in dark, (b) Cfu of E. coli suspension incubated with TEOP disordered film and irradiated with visible light (λ=420nm), (c) TEOP disordered spheres film, (d) Biocidal activity of TEOP toward E. coli in the dark and under light illumination for 30 min.

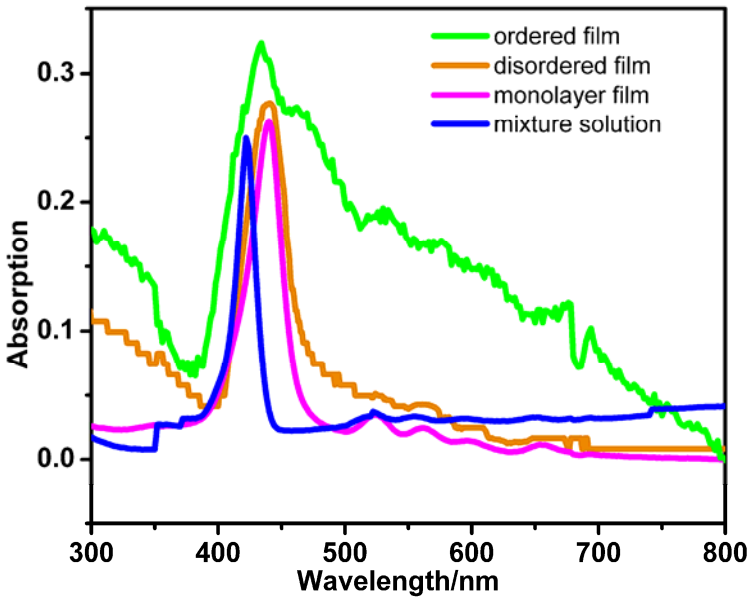

Figure s2. UV-vis spectra of TEOP. **Blue** curve displays the spectra of TEOP in chloroform; **Magenta** curve displays the spectra of monolayer film of TEOP casted directly from the TEOP solution of chloroform on quartz; **Orange** curve displays the spectra of film of disordered TEOP spheres casted from the chloroform/ isopropanol /water (*v*/*v*/*v*, 1/1/0.1) solution of TEOP on quartz; **Green** curve displays the spectra of film of ordered TEOP spheres casted from the chloroform/ isopropanol /water (*v*/*v*/*v*, 1/1/0.1) solution of TEOP on quartz.

As shown in Figure s2, the film of ordered TEOP spheres exhibits much stronger absorption in the region of the window than the reference film of disordered TEOP spheres and monolayer film, which is attributed to the much longer optical path in the well ordered TEOP spheres film as a photonic band gap materials with a periodicity of 560 nm than in the reference films.[2-5] The much greater light harvesting efficiency in the well ordered TEOP spheres film than in the reference films indicates that much more photogenerated singlet oxygen can be produced upon visible irradiation and thus result in the much more antibacterial activity in the former than in the latter.

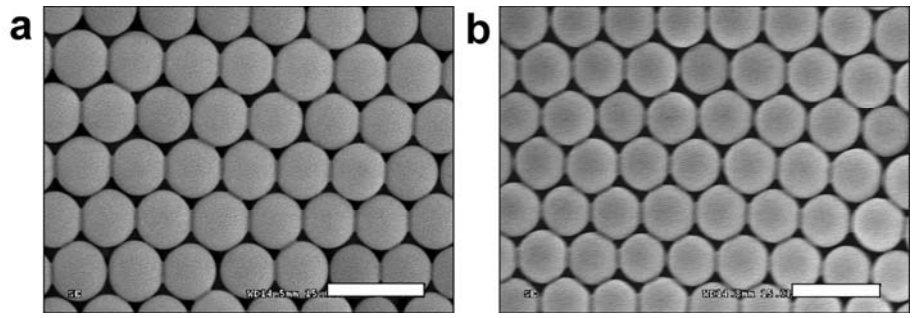

Figure s3. SEM surface images of TEOP ordered pattern film (a) before and (b) after irradiated with visible light (λ=420nm).

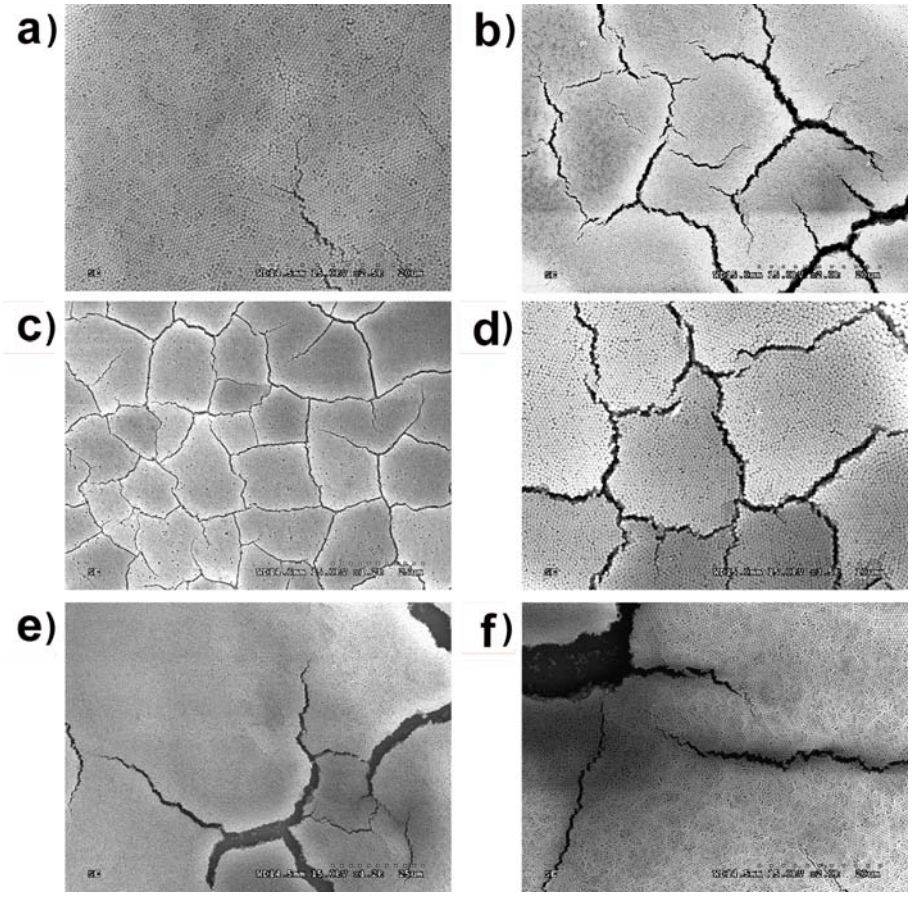

Figure s4. Lower magnification SEM images of large area TEOP ordered film, sphere-like structure with diameters of (a) 345nm, (b) 466nm, (c) 500 nm, (d) 521 nm, (e) 560 nm, (f) 586 nm.

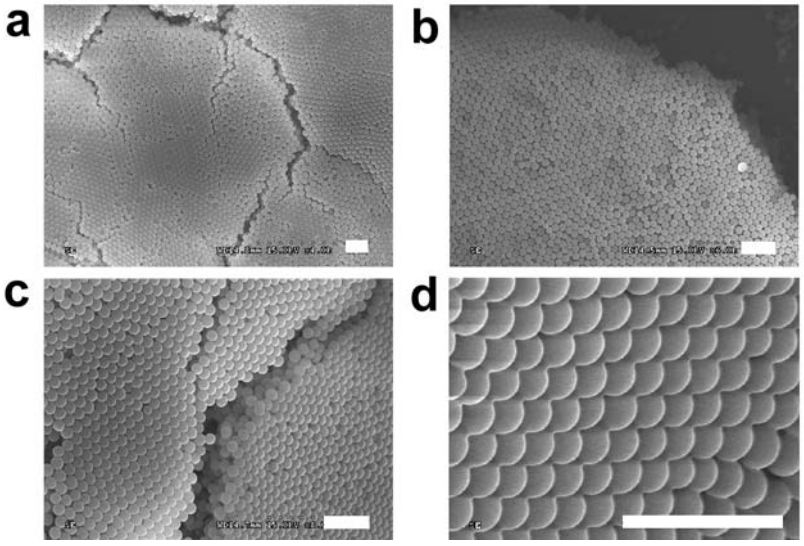

Figure s5. SEM images of large area TEOP ordered film (a) top surface, (b) cleaved edges, (c) oblique view, and (d) cross section of multilayer assembly. Scale bars: 2 μm.

Reference:

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