Supporting Information for:

Three-Dimensional Cuprous Oxide Microtube Lattices with High Catalytic Activity Templated by Bacterial Cellulose Nanofibers†

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Experimental section:

Oxidation of bacterial cellulose (BC)

All chemicals used were of analytical grade and purchased from Chinese domestic suppliers. The original BC membranes were produced by *Acetobacter xylinum* and purified using previously described methods.[1] The oxidation of BC involved two steps.[2] Firstly, BC was immersed in an H_2SO_4 solution (pH=1.0) for 48 h. Then $NaIO_4$ was added to the solution to reach a final concentration of 0.20 M and start the modification. After stirring the mixture at 50 °C for 3 h in the dark, the reaction was quenched by addition of ethylene glycol. The modification BC was washed thoroughly with deionized water. Secondly, the modified BC prepared was immersed in a $NaClO_2$ solution (0.20 M) for 48 h at room temperature, followed by washing in deionized water. Then the oxidized-BC was obtained.

Synthesis of three-dimensional (3D) Cu_2O microtube lattices (Cu_2O-MTLs)

To reach equilibrium ion absorption, the oxidized-BC pellicles were immersed in cupric nitrate solution (0.17 M) for 48 h, followed by thorough rinsing with water. Then the reduction of Cu^{2+} was carried out under constant stirring at room temperature for 2 h in a hydroquinone solution (0.17 M, 150 mL). During reaction, triethylamine ($N(Et)_3$) was added to adjust pH (pH=9.0) of the solution. The final products (Cu_2O-MTLs) were washed with distilled water. Additionally, the Cu_2O was also deposited on original BC under the same conditions as a control experiment.

Synthesis of Cu_2O particles

In a typical procedure, 1.208 g $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in deionized water (100 mL) in a round-bottomed glass flask at room temperature, and triethylamine was added to adjust the pH=9. After stirring for 10 min, a hydroquinone solution (2.76 g, 50 mL H_2O) was added dropwise to the $Cu(NO_3)_2$ solution, and the mixture was maintained at 25 °C in a water bath for 2 h with continuous stirring. The red products collected was washed several times with distilled water and absolute alcohol, and then dried at 40 °C for 8 h.

Catalytic degradation of methylene blue

Catalytic activity of the Cu_2O-MTLs was evaluated by degradation of methylene blue in the presence of hydrogen dioxide (H_2O_2) in the dark. The reaction was carried out at 35 °C in a 30 mL brown glass bottle wrapped with the tinfoil. Typically, 0.020 g of Cu_2O-MTLs was dispersed in 20.0 mL of methylene blue solution (10 mg/L), followed by addition of the H_2O_2 solution (400 uL, 30 wt%). Then the suspension was vigorously stirred in the dark at 35 °C for degradation reaction. At given reaction time intervals 650 uL of the reaction suspension was sampled and separated by centrifugation (10,000 rpm for 1 min). The concentration of methylene blue was monitored by using a TU1810PC model UV-vis spectrophotometer. For comparison, the catalytic ability of quasi-cubic Cu_2O particles (see Figure S4 (a) for their morphology) and commercial P25 TiO_2 (Degussa, Germany; Figure S5) were also investigated as references under identical conditions.

To study the stability of the Cu_2O-MTL catalyst, repeat experiments on methylene blue decomposition were conducted in the presence of H_2O_2 in the dark. For the first cycle, the mixture was reacted for 40 min, resulting in total decomposition of methylene blue. The resultant suspension was protected from light for a further 320 min, and then the Cu_2O-MTLs were separated by centrifugation (10000 rpm, 1 min). The the second degradation cycle was performed for 360 min (with complete degradation after 70 min (Figure 7) and further reaction for 290 min) after freshly adding 20.0 mL of methylene blue solution (10 mg/L). This process was repeated in successive cycles, giving the degradation data shown in Figure 7.

The degradation rate of methylene blue was calculated according to the initial and final absorbance (λ= 665 nm) of methylene blue in the solution:[3]

$$D\% = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where $D\%$ is the degradation rate, and A_0 and A_t are the initial and final absorbance of methylene blue solution, respectively.

Characterization:

X-ray diffraction was conducted on a Rigaku D/max 2500v/pc X-ray diffractometer at a scanning rate of 8 °/min. Field-emission scanning electron microscopy (FESEM) was performed on a Hitachi S-4800 microscope and a Philips XL-30 microscope. The elemental composition of products was analyzed with an EDAX Genesis XM2 attached to the S-4800 SEM. Their morphology was determined by using an FEI Technai G2 F20 TEM with accelerating voltage of 200 kV. Chemical bonding information for original BC and oxidized-BC was studied with an attenuated total reflection Fourier transform infrared (FTIR) Nicolet 470 spectrometer. UV-vis absorption spectra were recorded using a TU1810PC spectrophotometer (Beijing Purkinje General Instrument Co.). N_2 adsorption-desorption experiments were carried out at 77 K to examine the Brunauer-Emmett-Teller surface area and micropore volume (BJH method).

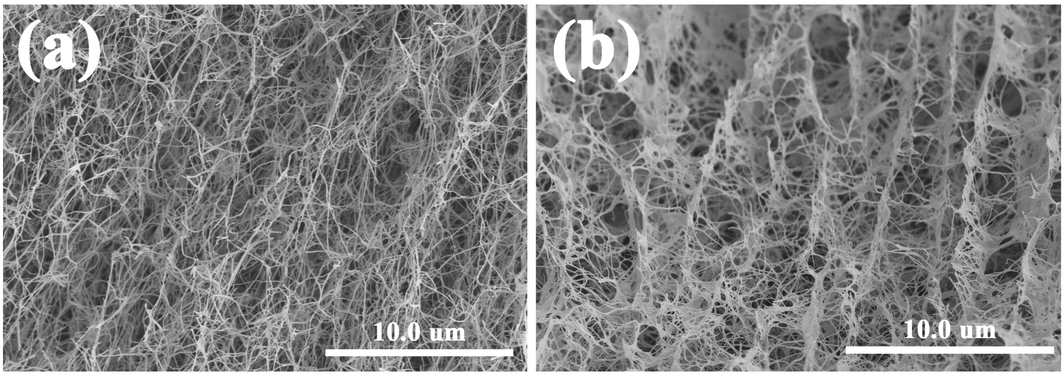

Figure S1. SEM images of (a) original BC, and (b) oxidized-BC.

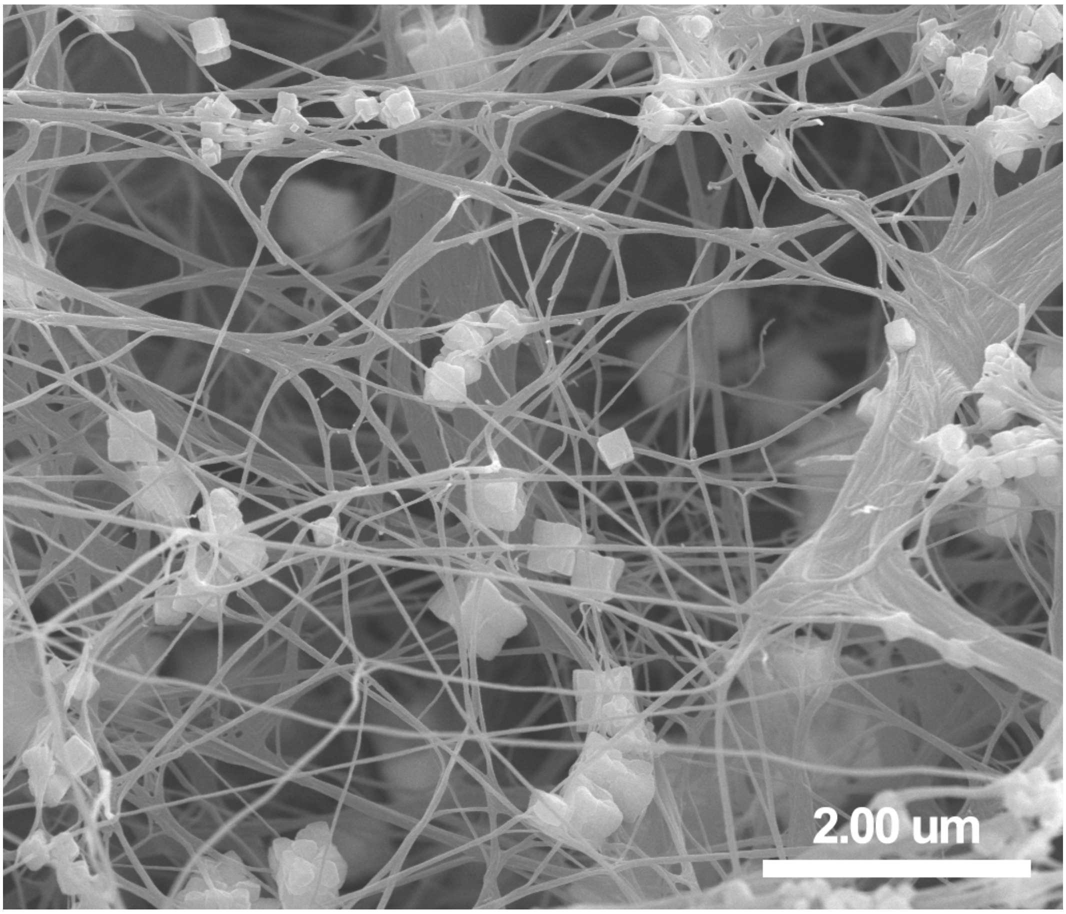

Figure S2. SEM image of Cu_2O particles deposited on original BC

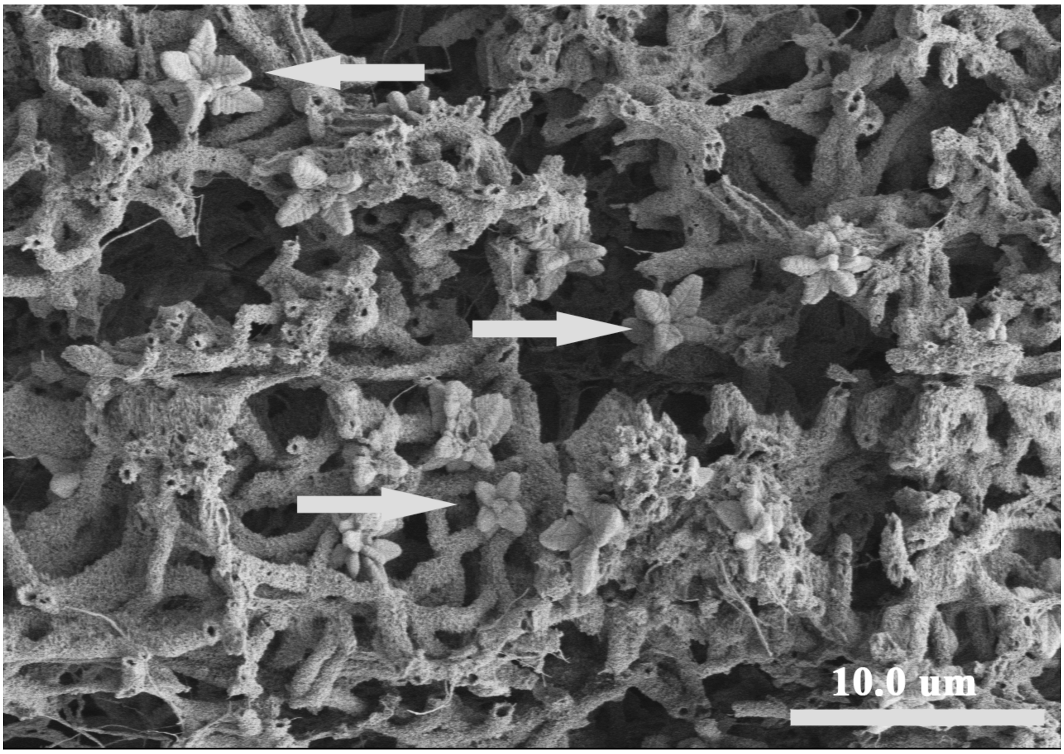

Figure S3. SEM image of Cu_2O-MTLs. The arrows indicate flowerlike Cu_2O crystals.

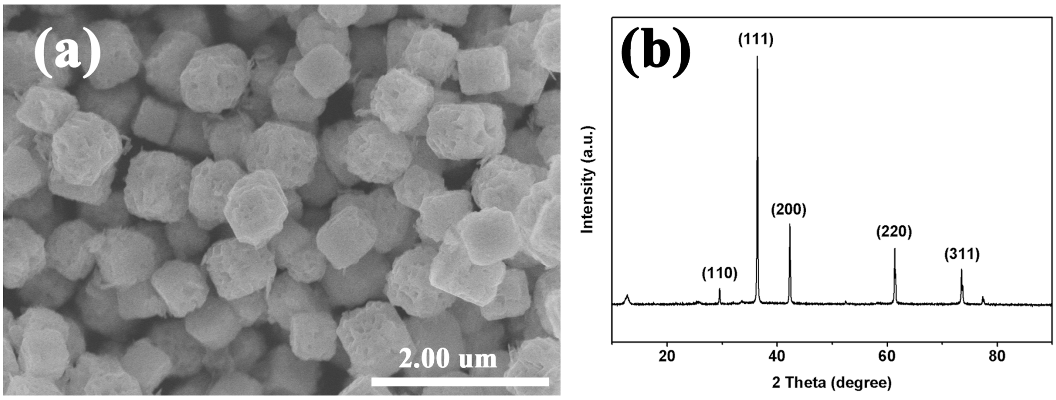

Figure S4. (a) SEM image, and (b) XRD pattern of quasi-cubic Cu_2O particles.

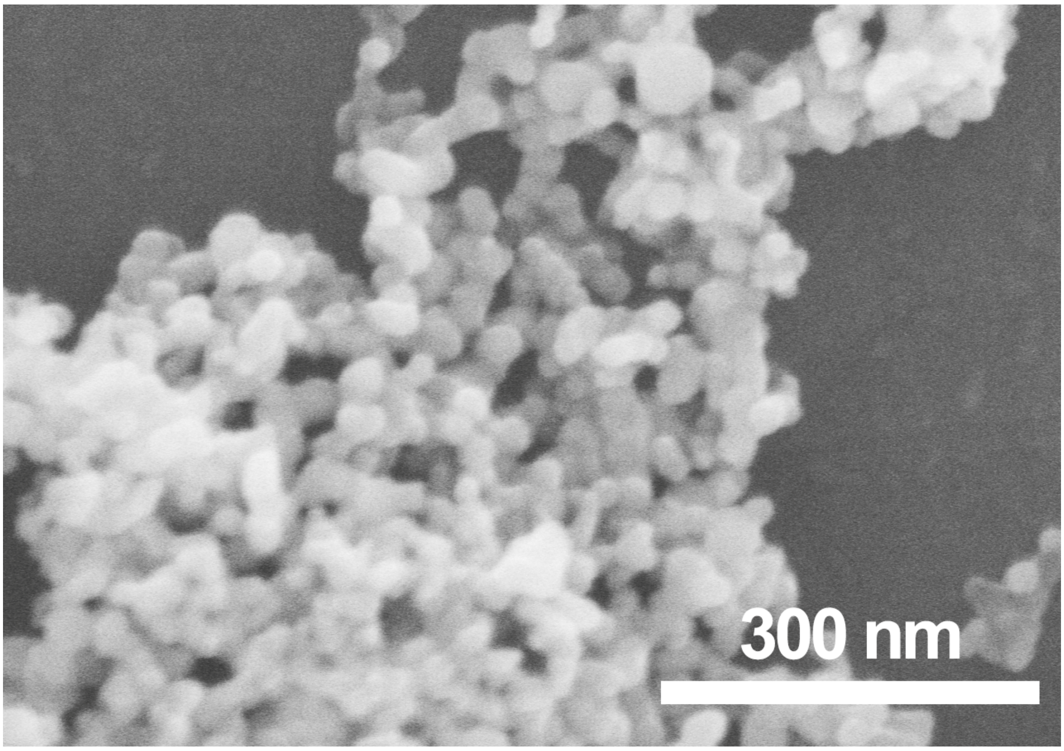

Figure S5. SEM image of P25 TiO_2 particles which show an average particle size of 30 nm.

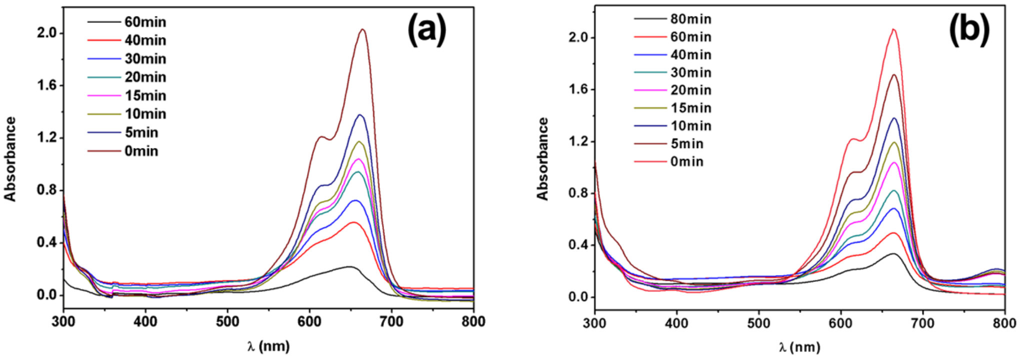

Figure S6. Time-dependent absorption spectra of methylene blue solution in the presence of H_2O_2 and catalysts (a) quasi-cubic Cu_2O, and (b) P25 TiO_2.

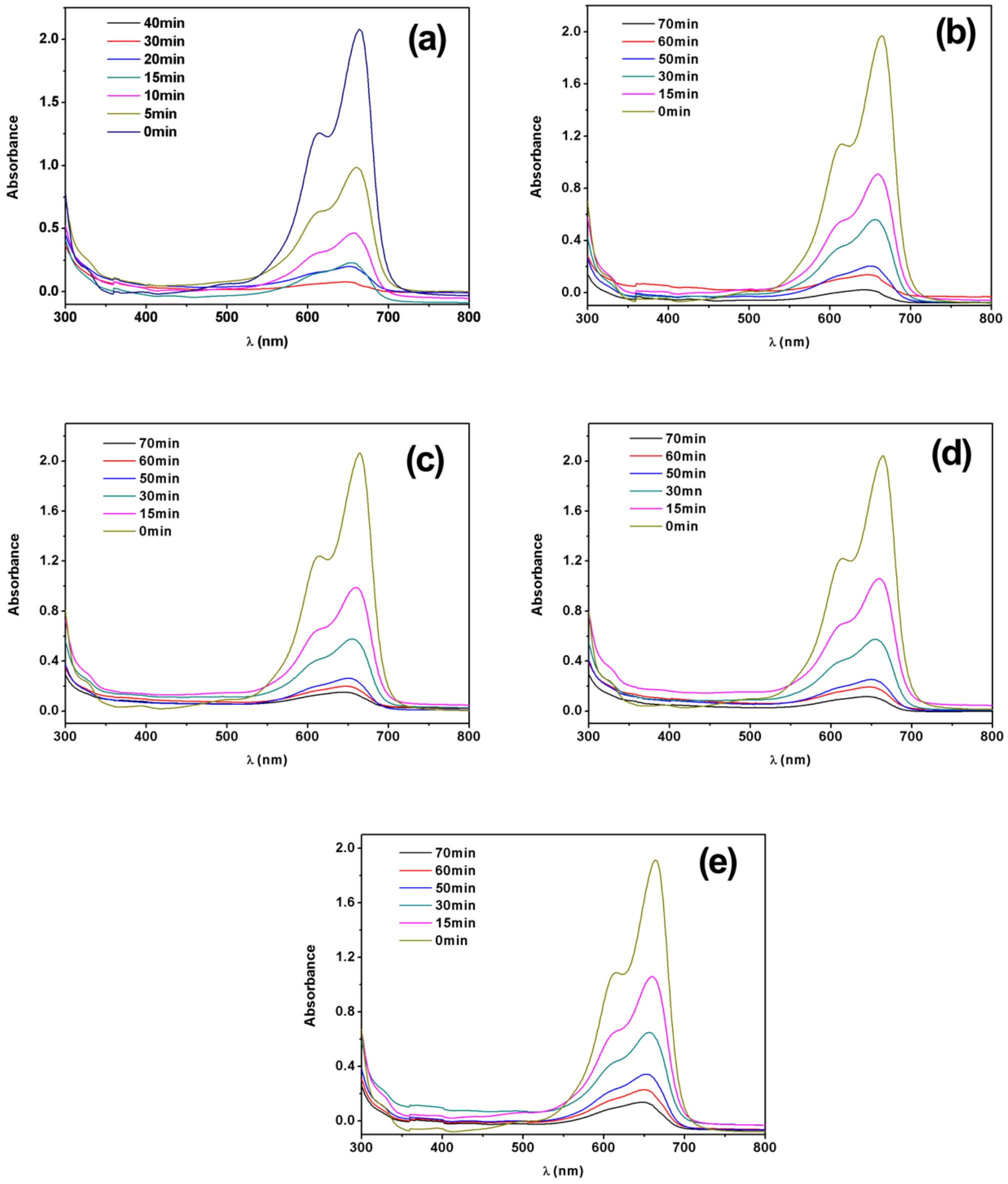

Figure S7. Time-dependent absorption spectra of methylene blue solution degraded by recycled Cu_2O-MTLs. (a), (b), (c), (d) and (e) represent cycles 1, 2, 3, 4 and 5, respectively.

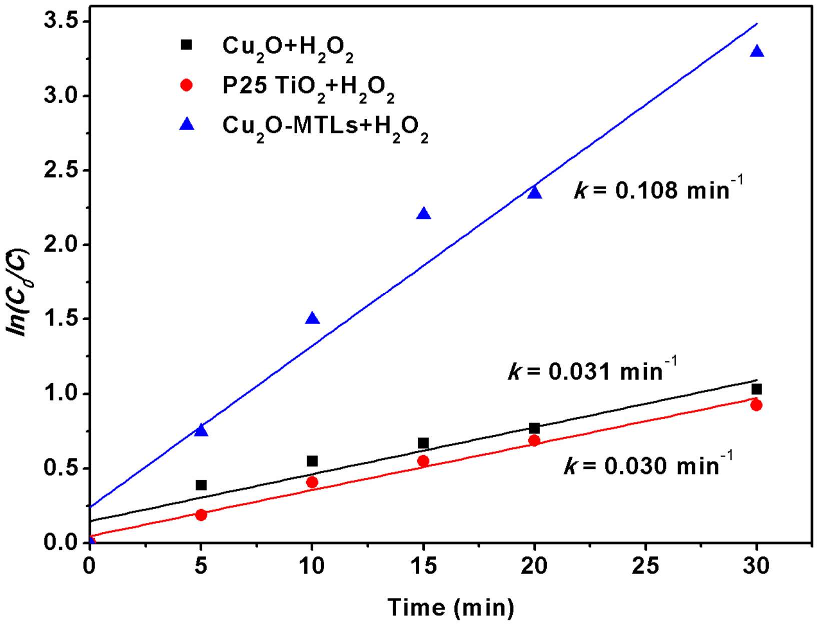

Figure S8. The fit lines of degradation data. The degradation reaction follows the equation: $ln(C_0/C)=kt$, where C_0 is the initial concentration of methylene blue, C is the concentration of methylene blue after catalytic reaction for t min, and k is the apparent rate constant. The reaction shows pseudo-first order reaction kinetics.

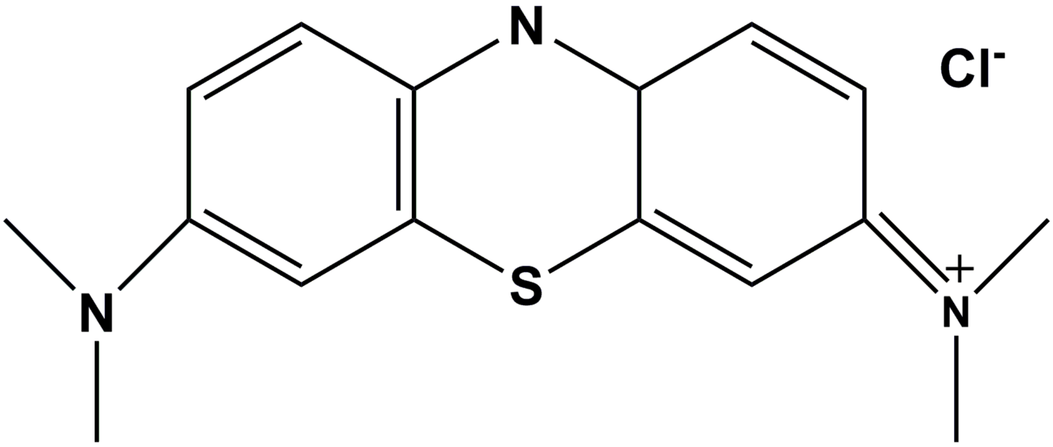

Figure S9. Molecular structure of methylene blue.

REFERENCES

(1) Wan, Y. Z.; Hong, L.; Jia, S. R.; Huang, Y.; Zhu, Y.; Wang, Y. L.; Jiang, H. J. *Compos. Sci. Technol.* **2006**, *66*, 1825.

(2) Kim, U. J.; Kuga, S.; Wada, M.; Okano, T.; Kondo, T. *Biomacromolecules* **2000**, *1*, 488.

(3) Xu, C.; Cao, L.; Su, G.; Liu, W.; Liu, H.; Yu, Y.; Qu, X. *J. Hazard. Mater.* **2010**, *176*, 807.