Supporting information for Characteristics of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> catalyst and its catalytic wet oxidation (CWO) of dye wastewater under extremely mild condition

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Table S1

Color removal at different pH and time

t (min) -	Color removal		
	pH = 5	pH = 7	pH = 9
5	96.96%	82.26%	30.44%
10	99.26%	87.94%	82.64%



Figure S1. Color removal of MB on different catalysts



Figure S2. UV-Vis spectral of MB over CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>

**Infrared spectroscopy.** Figure S3 shows the infrared spectrum of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>. The broad band at 3444 cm<sup>-1</sup> was ascribed to stretching vibrations of H<sub>2</sub>O molecules (free OH group). The absorption at 1625 cm<sup>-1</sup> resulted from the stretching vibration of the bound hydroxyl group. Bands at 1160 and 1066 cm<sup>-1</sup> corresponding to symmetric and

asymmetric vibration modes of terminal  $(PO_3)^{2-}$  groups show that copper introduction favor pyrophosphate group formation. The major absorptions at 1065, 965, 865 and 785 cm<sup>-1</sup> assigned to stretching vibrations of P-O, Mo=O, Mo-O-Mo bonds and P-O bond of P-O-Mo group, respectively (1), indicating combination of MoO<sub>3</sub> and  $(PO_3)^{2-}$ . Bands for P-O stretching frequency at 1066 cm<sup>-1</sup> and Mo-O stretching frequencies at 963 865 and 816 cm<sup>-1</sup> in Figure S3 shifted a little due to the copper introduction, indicating the influence of copper on the bond of P-O and Mo-O. The absorption at 965 cm<sup>-1</sup>, maybe assigned to Mo–O asymmetric stretching vibration of the terminal oxygen. The absorption at 865 cm<sup>-1</sup> was attributed to the bridged oxygen (Mo-O-Mo).



Figure S3. Infrared spectra of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>

**SEM and EDXS analysis.** Figure S4a and 4b magnified to 5000 times to their original size were  $CuO-MoO_3-P_2O_5$  SEM images of before and after reaction, respectively. There were significant differences in two pictures. In Figure S4a, the surface of sword-shaped catalyst was almost alabastrine except for some smaller dispersed crystal grains. In

Figure S4b, rod-like structure of CuO-MoO<sub>3</sub>- $P_2O_5$  after reaction was not changed, however the scraggly surface with sheet material can be observed in Figure S4b compared with Figure S4a, which maybe due to that some changes happened to the appearance of catalyst during catalytic oxidation process.

Figure S5 gives EDXS (energy dispersion X-ray Spectroscopy) elemental composition signals associated with the total image in Figure S4a and one region (point 1) as indicated in Figure S4a. Strong signals in the total image corresponded to O, P and Mo, while, Cu signal was very faint in Figure S5. Point 1 shows nearly the same element signals as the total image, indicating that the elemental compositions of the dispersed crystal grains on the surface were consistent with that of the rod-like catalyst.



Figure S4. SEM images of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> before (a) and after (b) reaction



Figure S5. EDXS spectrum for the total image in Figure S4a and point 1 indicated in Figure S4a.

**Ordered Array of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>.** The selected area electron diffraction (SAED) of the catalyst was excellent and it shows that the composite has a face-centered cubic structure (Figure S6). The nearest transverse distance between two spots was equal to the nearest lengthways distance between two spots, indicating unit lattice constant a = b. (001) can be obtained from this pattern, which agreed with the XRD analysis. Ordered array shows that growing of crystal depends on grain-oriented property.



Figure S6. SAED image of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>

Effect of treated wastewater on soil and plants growth. Many papers have studied environmental effect of the discharged pollutants from the pulp and paper industry, such as water, air and land (2,3). Less information is available today concerning the effect of irrigation of secondary treated swage water on ecologies. In the present study, we investigated the effect of irrigation of catalytic wet oxidation of methylene blue wastewater on the soil TOC/TIC changes and the amount of chlorophyll changes of clover, which can be regarded as the influences on sentimental system.

The experiment was conducted in laboratory, in a climate controlled model greenhouse using a heating system and an evaporative cooling system. The set point

minimum and maximum temperatures in the greenhouse were 15 and 20 °C night/ day. The minimum day and maximum night relative humidities were 60% and 90%, respectively. The plants were planted 2 cm apart and the irrigation was supplied once a day at 8:00 am. Samples were collected fifth per two hours a day from 8:00 am to 16:00 pm, including the soil and leaf blade. Determination of chlorophyll a and b was using a spectrophotometer Micronal with wavelengths of 645 and 663 nm, according to Mackinney's equation (4). The results are shown in Figure S7.

It can be seen from Figure S7 that the treated wastewater has little effect on the content of chlorophyll, the overall chlorophyll content gradually increased when the treated wastewater was irrigated into the soil, and then the chlorophyll content reduced rapidly from 10:00 am to 13:00 pm, the overall content of chlorophyll varied from 24.62 to 17.32 mg L<sup>-1</sup>, however, it was interesting to find its content gradually recovered to normal level at 16:00 pm, which indicated that the treated wastewater could totally apply to irrigate. The TOC and TIC of soil was also studied. As the figure depicted, when the treated water was irrigated into the soil, the TOC and TIC increased at the beginning and decreased to average level gradually with the time gone, which was probably attributed to the absorption effect of plants' root.



FigureS7. Changes of TOC, TIC and chlorophyll concentration of clover as the function of time

**COD and TOC removal during the degradation.** Figure S8 presents color, COD and TOC removal during the degradation of 0.3 g L<sup>-1</sup>MB at initial pH = 3, and T = 35 °C. The complete removal of color was achieved within a short period of time (10 min). 92.86 % COD removal and 87.5 % TOC removal efficiency can be achieved at 50 min.



Figure S8. Removal efficiency of 0.3 g L<sup>-1</sup> MB. (a) Decolorization removal (b) COD removal (c) TOC removal

**Effect of reaction temperature.** Figure S9 presents the color removal at different operating temperatures. It was clear that the color removal increased with the temperature increasing. The higher the temperature, the higher the color removal percent can be achieved. And 35 °C was chosen as the suitable temperature.



Figure S9. Effect of reaction temperature on the catalytic degradation of MB  $(pH:7.0; MB: 0.3 \text{ g L}^{-1})$ 

**Degradation pathway of MB.** The intermediates and products generated during the degradation process were analysed by LC-MS. And a possible degradation pathway was proposed: (i) cleavage of C-N bond of heteropolyaromatic; (ii) cleavage of C-S bond of heteropolyaromatic; (iii) cleavage of C-N bond of the substituting group of the heteropolyaromatic; (iv) cleavage of C-S bond of the substituting group of the benzene; (v) small molecules formed. The main steps of MB degradation were listed in Scheme S1.



Scheme S1. The basic degradation pathway of MB

## Literature cited

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