Electronic Supplementary Information

Cobalt Oxide as a Selective Co-catalyst for Water Oxidation in the Presence of an Organic Dye

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1. *Light source characterization.*

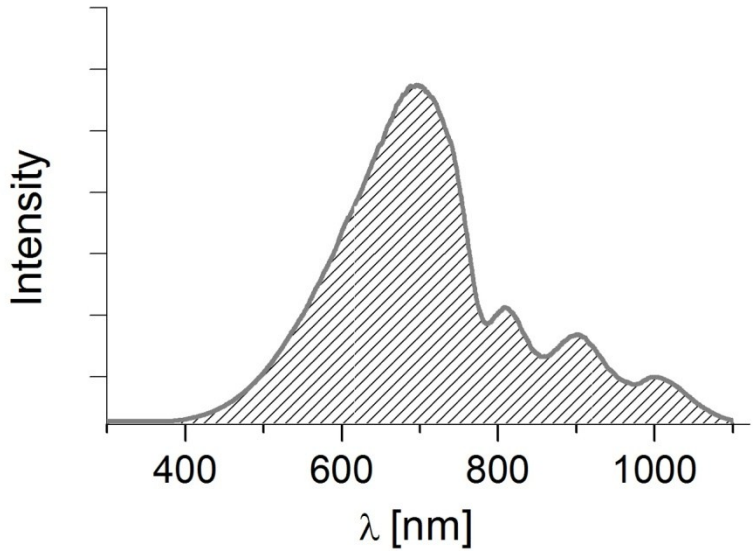

Figure S1. Spectral profile of the applied light source (Fiber-Lite® MI-150™, Dolan-Jenner Industries).

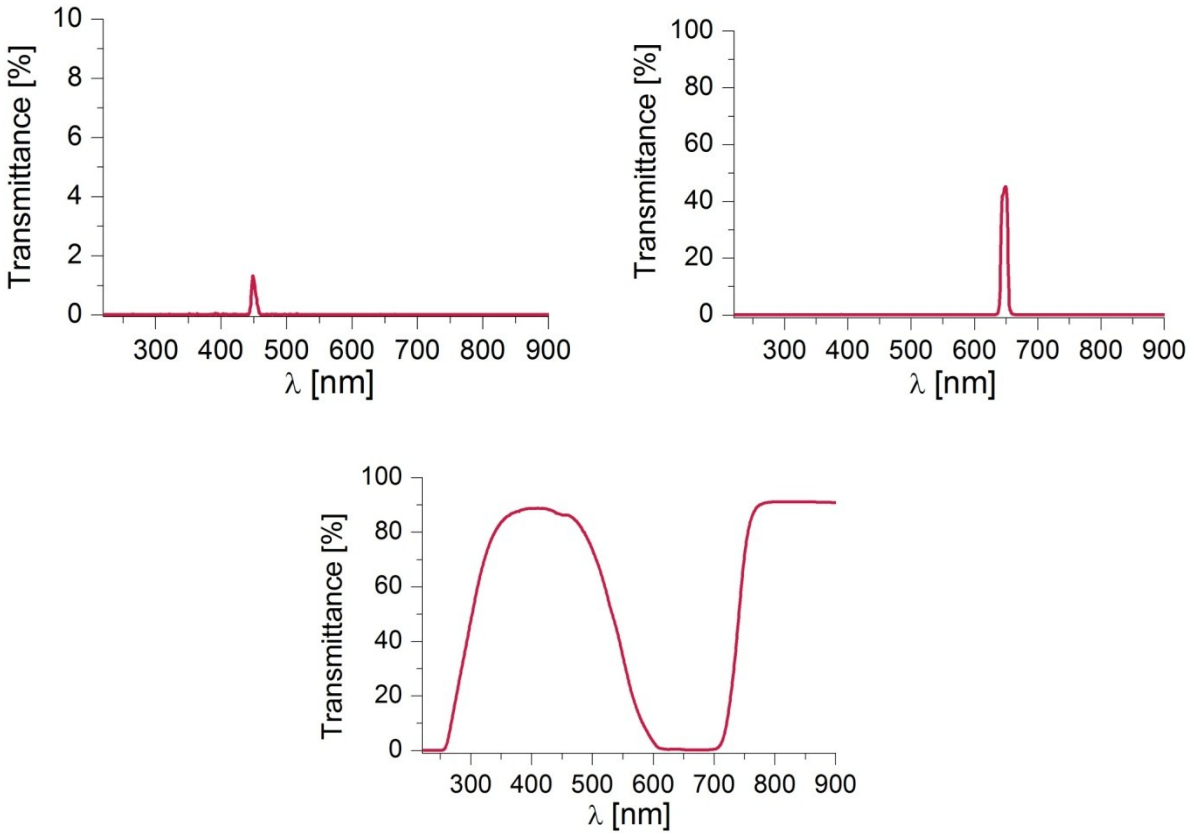

Figure S2. Spectral profiles of applied optical filters. **(upper)** Spectra of band-pass filters used in MB degradation experiment transmitting wavelengths of 450 ± 10 nm and 650 ± 10 nm respectively. (lower) Spectrum of an absorption filter used for NMR samples preparation excluding wavelengths corresponding to MB absorption maximum.

2. Photocatalysts characterization.

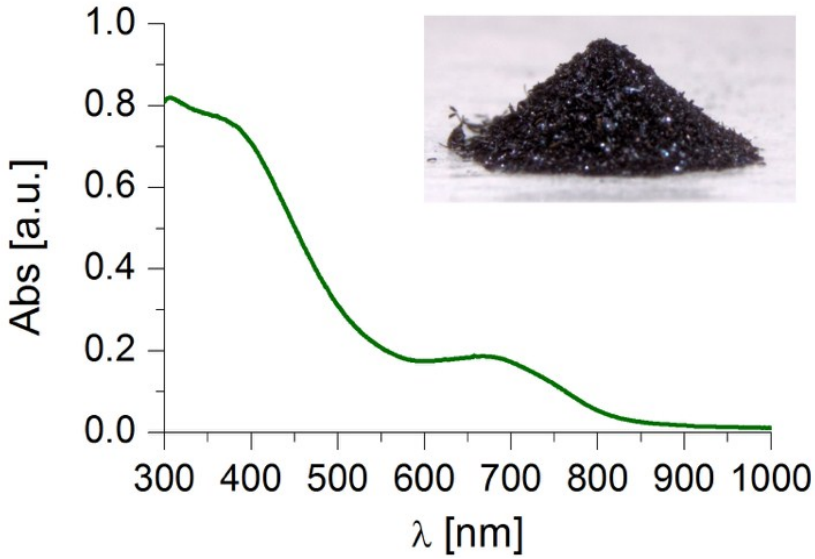

Figure S3. Absorption spectrum of Co_3O_4 NPs showing its visible-light absorption with the maximum located at 670 nm. Insert: Co_3O_4 powder.

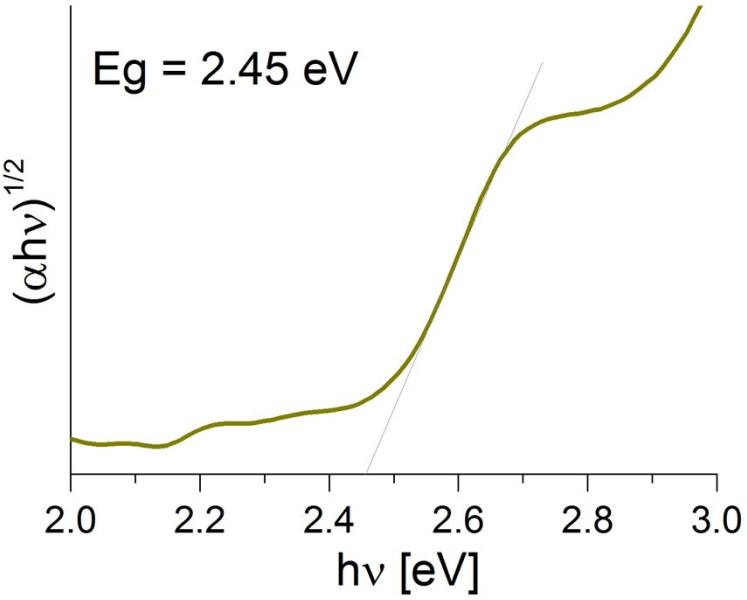

Figure S4. Band gap energy of silver phosphate estimated from the UV-Vis absorption spectrum.

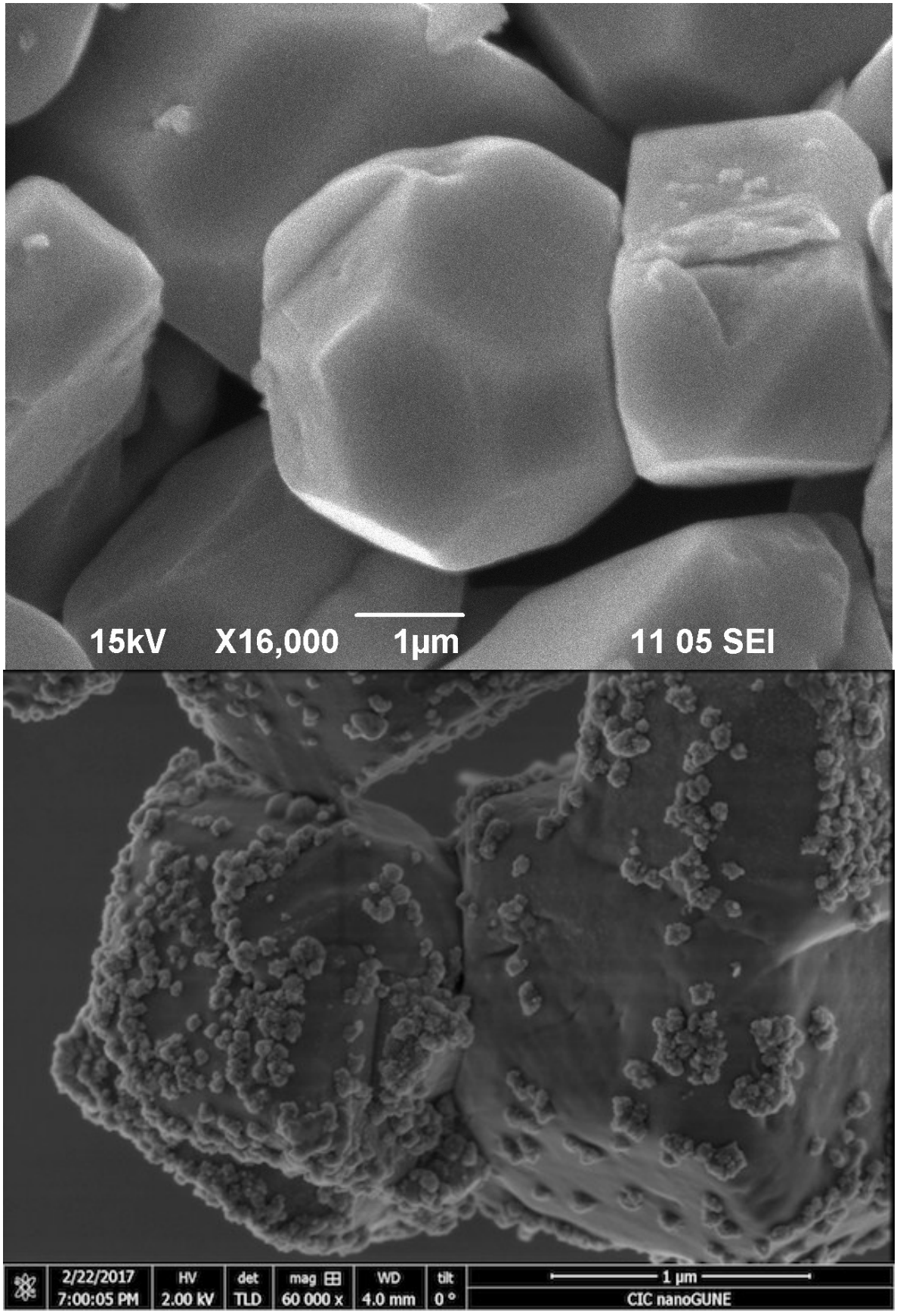

Figure S5. SEM image of initial silver phosphate **(upper)** and functionalized with cobalt oxide **(lower).**

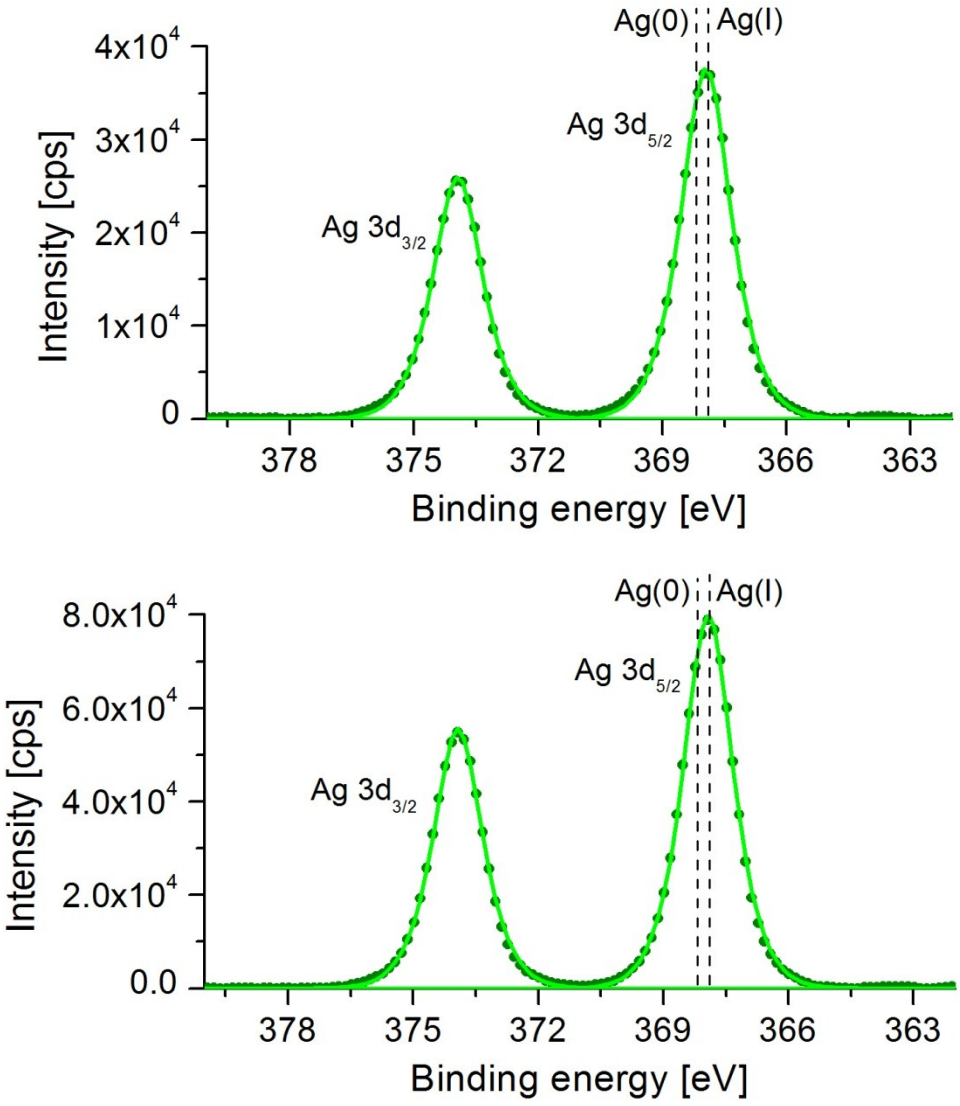

Figure S6. Ag 3d spectra of pure Ag_3PO_4 **(upper)** and Ag_3PO_4/Co_4O_4 0.5 % **(lower)** showing peaks corresponding to Ag(I), both confirming the chemical stability of the sample.

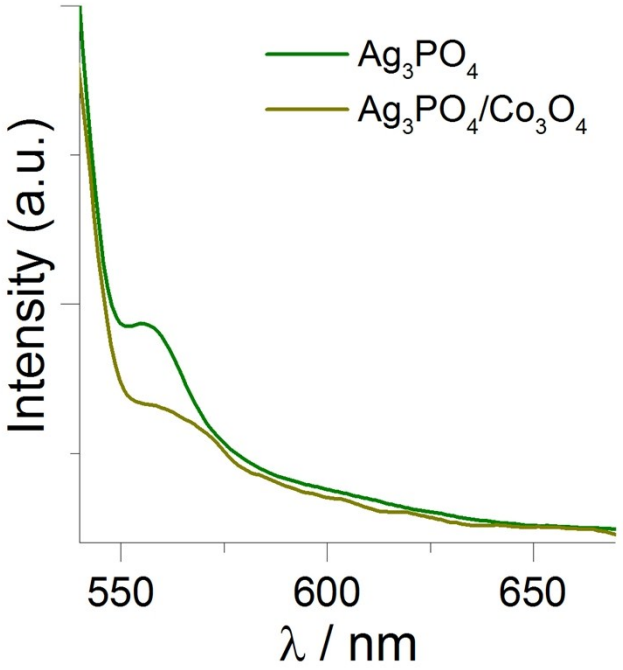

Figure S7. Photoluminescence spectra of Ag3PO4 and Ag3PO4/Co3O4 showing the decrease in the PL intensity in the presence of cobalt oxide. λex = 420 nm.

3. *Photocatalytic reactions.*

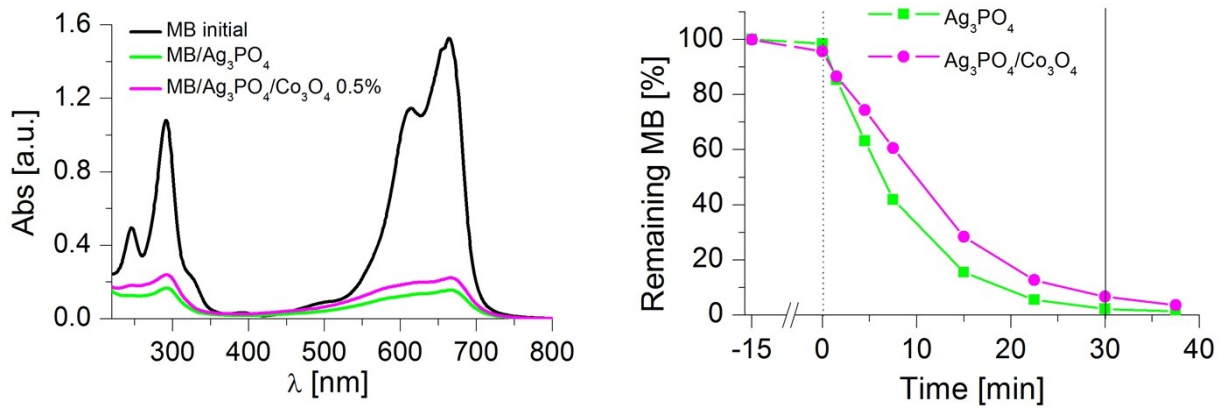

Figure S8. Photocatalyst-driven degradation of MB under visible-light. **(left)** Absorption spectra of MB: initial and irradiated for 30 min in presence of Ag_3PO_4 and Ag_3PO_4/Co_3O_4 0.5 %. **(right)** Percentage of remaining MB as a function of irradiation time showing that the difference in MB degradation degree changes in time. Solid line indicates the time after which reaction was terminated and MB absorption was recorded. Obtained values were recalculated for a percentage of degraded MB presented as purple bars in Fig. 5a.

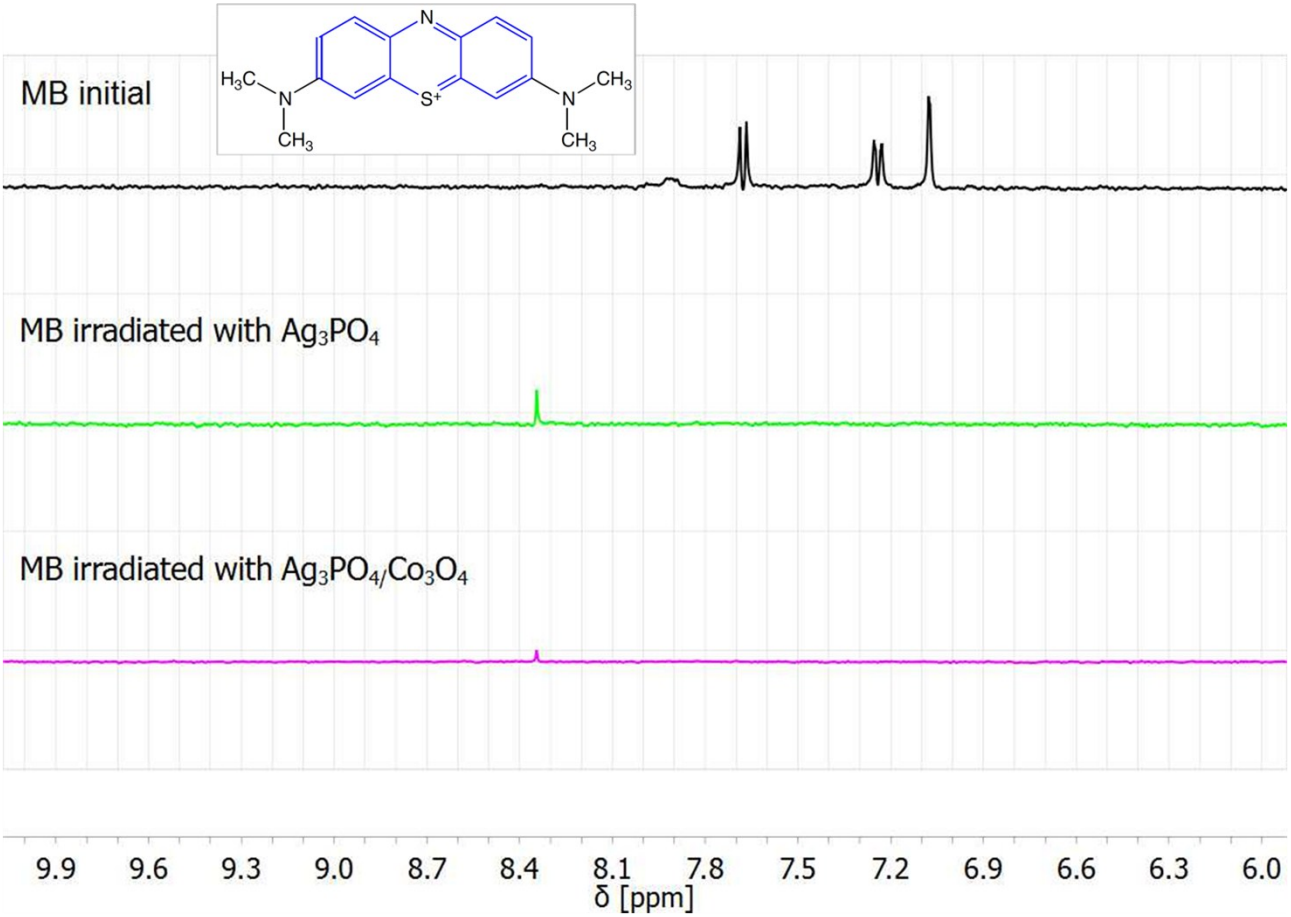

Figure S9. NMR analysis of MB degradation products. **(upper)** NMR spectra of MB: initial solution (black curve), irradiated in presence of Ag_3PO_4 (green curve) and Ag_3PO_4/Co_3O_4 (purple curve). 1H NMR measurements gave us a deeper insight into the structural changes occurring within the MB molecule during the photocatalyzed degradation. Characteristic peaks in the range of 7 - 8 ppm in the

initial MB spectrum correspond to the aromatic rings protons (black curve). The disappearance of these signals after irradiation in presence of both, Ag_3PO_4 and Ag_3PO_4/Co_3O_4, indicates that MB degradation is based on disruption of aromatic rings. Such a chromophore destruction leads to dye color loss and thereby the absorption intensity decrease. On the other hand, an emergence of a new peak located at 8.35 ppm indicates the formation of MB degradation products. It is worth noticing that observed spectral changes are identical for both types of photocatalyst suggesting the same degradation mechanism in the presence and absence of Co_3O_4. **(lower)** Absorption spectra of samples analyzed with NMR technique.

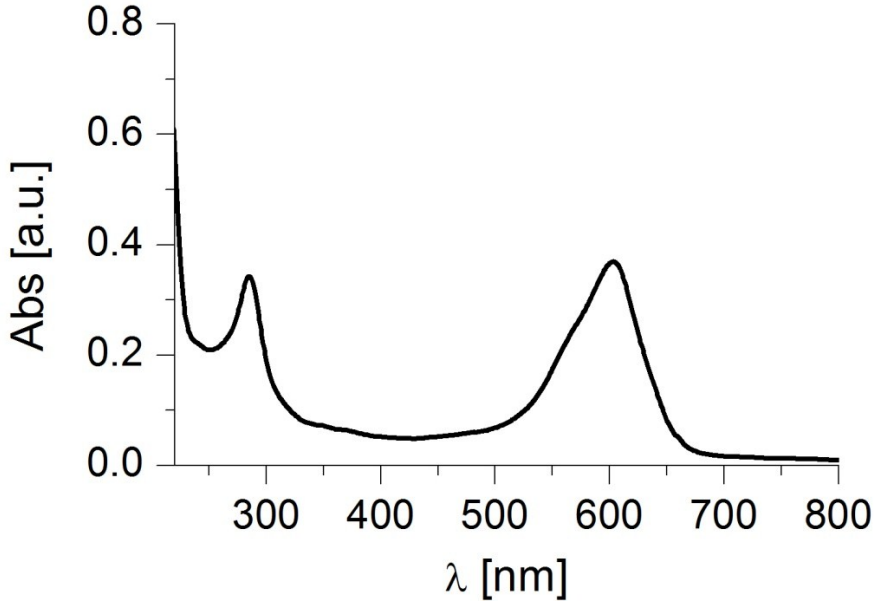

Figure S10. Absorption spectrum of demethylated MB after whole visible range irradiation for 40 min under an argon atmosphere (C_{MB} = 0.024 mM, LPD = 114 mW/cm^2) with the band located at 604 nm matching absorption maximum for thionine.

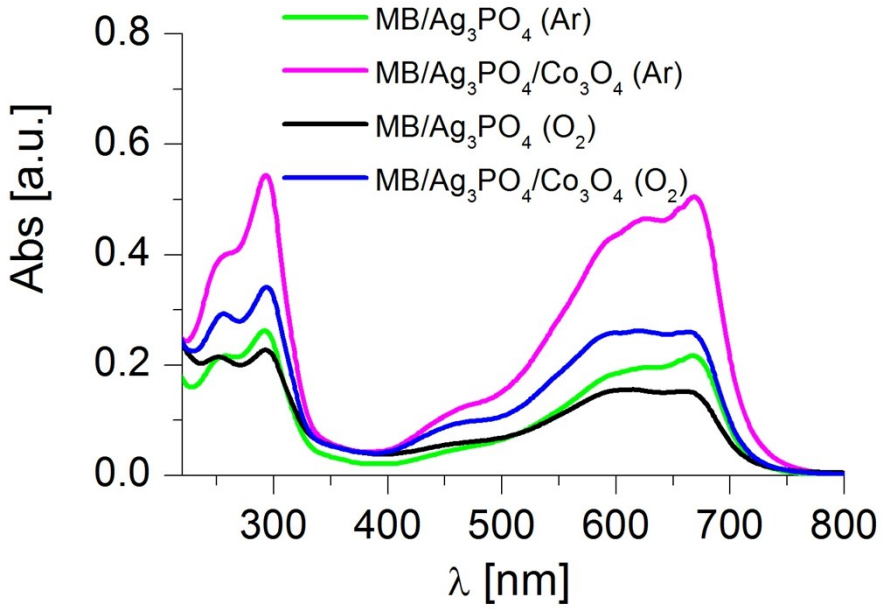

Figure S11. Absorption spectra of MB irradiated in anaerobic (Ar) and aerobic (O_2) conditions in presence of Ag_3PO_4 and Ag_3PO_4/Co_4O_4 0.5 %.

4. Characterization of irradiated Ag_3PO_4.

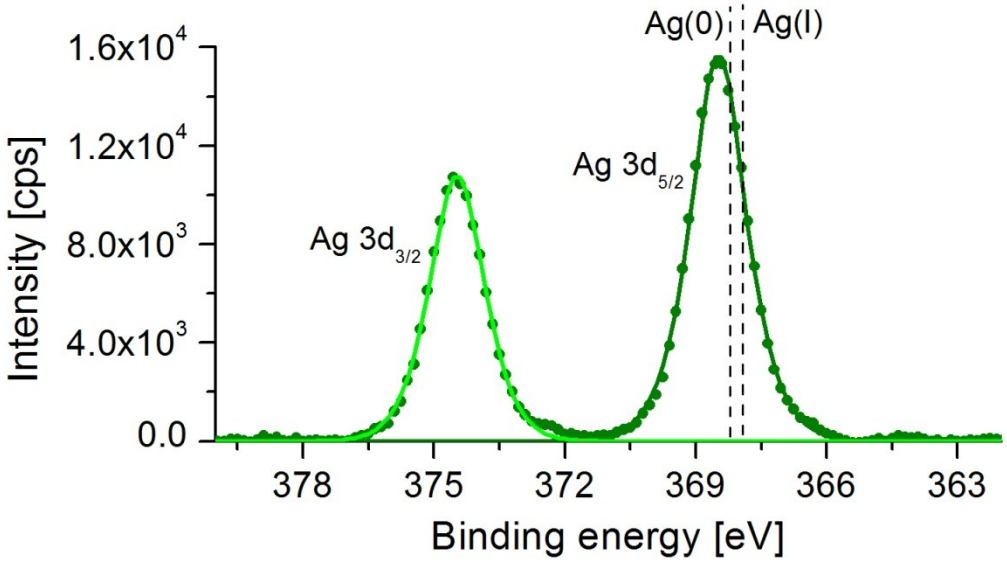

Figure S12. Ag 3d XPS spectrum of Ag_3PO_4 sample irradiated for 2 h confirming the presence of photoreduced silver on the material surface.

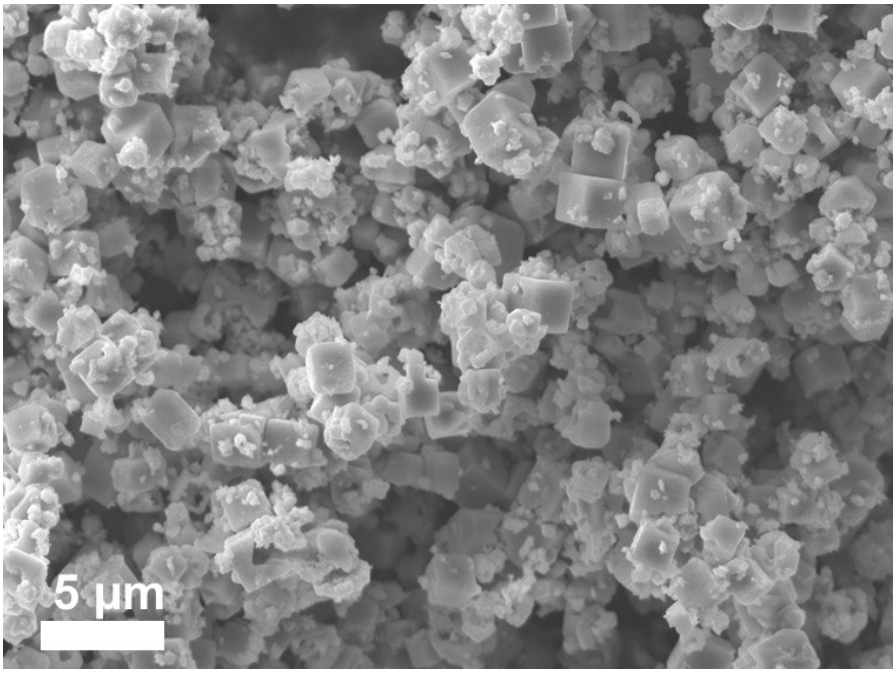

Figure S13. SEI SEM image of Ag_3PO_3 irradiated for 2 h revealing altered crystals appearance caused by silver photoreduction on the material surface.