

## Supplementary data Article ID: CE-ART-01-2015-000173

### Structural and optical characterizations of ball milled copper doped bismuth vanadium oxide (BiVO<sub>4</sub>)

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## Photocatalysis experiment

The Photocatalytic activity of Cu doped BiVO<sub>4</sub> powders prepared by high energy ball mill (HEM) technique was investigated on the degradation of methylene blue (MB) dyes. The experiments were carried out in a glass beaker with circulating water jack. The beaker contains 50 ml of an aqueous solution of MB dyes (10<sup>-5</sup> M) and 50 mg of Cu doped BiVO<sub>4</sub> catalyst powders. The photocatalytic reactions were induced with a simulated sunlight based on Hg (Xe) arc lamp (Newport-67005) with 40 W/cm<sup>2</sup> as the illumination power received on the reaction glass beaker. Before illumination, the mixture solution was stirred for 20 min under dark in order to reach the adsorption–desorption equilibrium between catalyst and dye molecules. During the photocatalytic reactions under illumination, 5 mL solution was collected each 20 or 30 minutes and then centrifuged to separate the catalyst powder from the MB dyes. The UV-Vis optical absorption of the centrifuged solution was then recorded and used to monitor the degradation of MB dyes by the photocatalytic process. The time evolution of the optical absorption spectra is reported in the figure S1 (S1A, S1B and S1C) associated respectively to the use of pure, 5 at.% and 10 at.% Cu doped BiVO<sub>4</sub>. A net effect of the Cu doping is clearly traduced through the evolution of the intensity of the absorption spectra during the photocatalytic process where the characteristic  $\lambda_{\text{max}}$  shift is attributed to N-demethylation derivatives of MB dyes [1].

The kinetic reaction rates were calculated from the slope of  $\ln (C_0/C_t)$  plot shown in the Figure S1D (where  $C_0$  is initial concentration of the MB dyes in solution and  $C_t$  is the concentration of the MB dye solution at a given time 't' during the photocatalysis reactions). Indeed, the time evolution of the  $C_t$  parameter follows a pseudo-first-order reaction as  $C_t = C_0 \cdot e^{-kt}$  where k represents the kinetic reaction rate. The final degradation rate (%) derived from  $[(C_0 - C_t) / C_0] \times 100$  and 'k' values are summarized in Table S1 as function of Cu doping rates.

## References:

- [1] H. Xu, H. Li, C. Wu, J. Chu, Y. Yan, H. Shu, et al., Preparation, characterization and photocatalytic properties of Cu-loaded BiVO(4)., J. Hazard. Mater. 153 (2008) 877–84.  
doi:10.1016/j.jhazmat.2007.09.039.