Supplementary information

Effect of synthesis method on reaction mechanism for hydrogen evolution over Cu_xO_y/TiO_2 photocatalysts: a kinetic analysis

Laura Clarizia [1,*], Giuseppe Vitiello [1,2,*], Robert Bericat Vadell [3], Jacinto Sá [3,4], Raffaele Marotta [1], Ilaria Di Somma [5], Roberto Andreozzi [1] and Giuseppina Luciani [1]

[1] Department of Chemical, Materials and Industrial Production Engineering, University of Naples "Federico II", p.le V. Tecchio 80, 80125 Napoli, Italy
[2] CSGI, Center for Colloid and Interface Science, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
[3] Department of Chemistry-Ångström, Physical Chemistry Division, Uppsala University, P.O. Box 532, 751 20 Uppsala, Sweden
[4] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[5] Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS)-Consiglio Nazionale delle Ricerche, p.le V. Tecchio 80, 80125 Napoli, Italy
* Correspondence: laura.clarizia2@unina.it (L.C.); giuseppe.vitiello@unina.it (G.V.)

Table S1. Effective radiative powers of the medium-pressure mercury lamp (Helios Italquartz).

λ (nm)	Effective radiative power (Ein/s)
305	2,23E-06
313	2,76E-06
366	3,37E-06
404,7	8,88E-07
407,8	2,01E-07
435,8	1,47E-06
546,1	1,65E-06

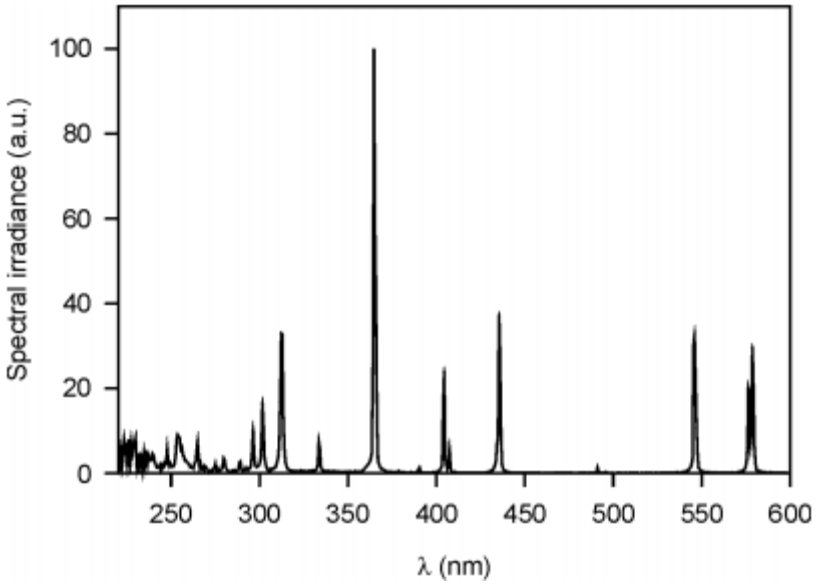

Figure S1. The emission spectrum of a medium-pressure mercury lamp Helios Italquartz 125W.

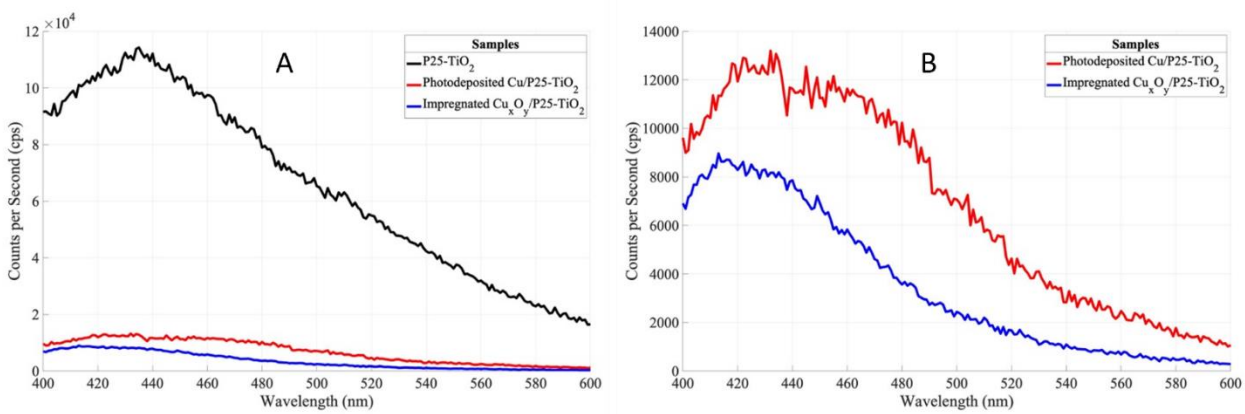

Figure S2. PL spectra were measured in degassed pH 4 aqueous solution. P25-TiO_2_NPs (black trace). Cu_xO_y/TiO_2-P25_NPs (blue trace) and Cu/TiO_2-P25_NPs (red trace).
(A) all the samples; and (**B**) only copper-modified samples.

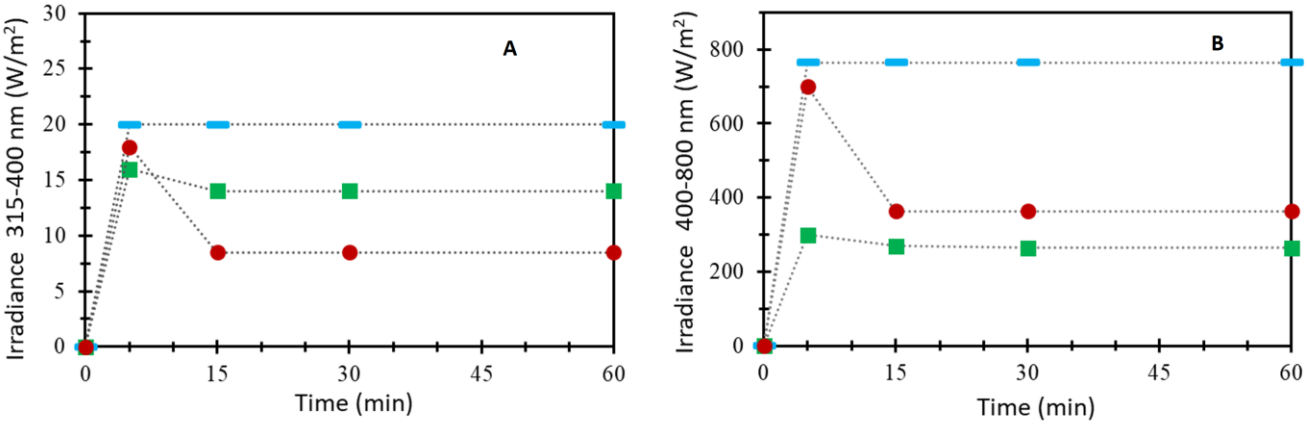

Figure S3. Irradiance values measured between **(A)** 315–400 nm and **(B)** 400–800 nm for during methanol photoreforming under de-aerated conditions in the presence of Cu/TiO_2_NPs prepared via photodeposition (●), Cu_xO_y/TiO_2_NPs prepared via impregnation method (■), and bare P25-TiO_2(—).
Copper/TiO_2 weight ratio=3%; $[CH_3OH]_0$= 2.47 M; photocatalyst load= 150 mg·L^{-1}; T=25 °C; P=1 atm.

Information on the iterative optimisation procedure developed

Values for the unknown parameters (k_r, N, and Φ_{UV}) were estimated by an iterative optimisation procedure (Marquardt approach) that minimised the square of the differences between calculated and measured data for hydrogen generation rate (i.e., objective function)[Reklaitis GV, Ravindran A, Regsdell KM. Engineering Optimization. Wiley, New York, 1983]:

$$\phi = \sum_{l=1}^{m}\sum_{j=1}^{n}\sum_{i=1}^{h}\left(y_{i,j,l} - c_{ijl}\right)^2$$

in which the terms y and c are the calculated and experimental concentrations, where m, n, and h are the number of experimental data recorded in each experiment, the number of the involved species and the number of experiments used in the optimisation procedure, respectively.