SUPPORTING INFORMATION

Alkaline treatment as a means to boost activity of TiO₂ in selective photocatalytic processes

Sedat Yurdakal,^{*a}, Sıdıka Çetinkaya^a, Vincenzo Augugliaro^{*b}, Giovanni Palmisano^{c,d}, Javier Soria^e, Jesus Sanz^f, Maria Jose Torralvo^g, Stefano Livraghi^h, Elio Giamello^h, Corrado Garlisi^c

^aKimya Bölümü, Fen-Edebiyat Fakültesi, Afyon Kocatepe Üniversitesi, Ahmet Necdet Sezer Kampüsü, 03200 Afyonkarahisar, Turkey. E-mail: sedatyurdakal@gmail.com

^{b.}"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), Università degli Studi di Palermo, Viale delle Scienze (ed. 6), 90128 Palermo, Italy. E-mail: vincenzo.augugliaro@unipa.it

^{c.}Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates.

^dResearch and Innovation on CO2 and H2 (RICH) Center, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates

^eInstituto de Ciencia de Materiales, CSIC, C/Sor Juana Inés de la Cruz, Cantoblanco, 28049 Madrid, Spain.

^{f.}Instituto de Catálisis y Petroleoquímica, CSIC, C/ Marie Curie 2, Cantoblanco, 28049 Madrid, Spain.

^g Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain.

^h Dipartimento di Chimica and NIS, University of Torino, Via P. Giuria 7, 10125 Torino, Italy.

Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

*Corresponding authors



(a)

Fig. S1 Digital images of the used setup for catalyst refluxing (a) and dialysis (b).



(a)

Fig. S2 Digital image of the used photocatalytic UV system and the emission spectrum of used lamps.

Commander Sample ID (Coupled TwoTheta/Theta)



Commander Sample ID (Coupled TwoTheta/Theta)



Fig. S3 XRD diffractograms of a mechanical mixture of TiO_2 (BDH (up) or Merck (down) and CaF₂ (50%, w/w), recorded for the estimation of crystallinity. A: Anatase.



BDH-1M-24h-25

BDH-1M-24h-100



BDH-1M-24h-100

BDH-12M-24h-25



Merck-NaOH-25



Merck-NaOH-100 <u>5 mm</u>

Fig. S4 TEM micrographs of modified BDH and Merck TiO₂ samples.



Fig. S5 TGA analysis of a pristine and a select alkaline-treated BDH and Merck TiO₂ catalyst.





Fig. S6 UV-Vis diffuse reflectance spectra reported in absorption of BDH, BDH-1M-24h-100, Merck and Merck-1M-24h-100 samples in different visualization.



Fig. S7 Raman spectra of pristine and selected Merck TiO₂ catalysts.





Fig. S8 Photoluminescence emission spectra of NaOH treated BDH (up) and Merck (down) samples.



Fig. S9 DRIFT spectra of selected BDH and Merck in the range of 4000-500 cm⁻¹.

- $TiO_2 + h\upsilon \rightarrow e^- + h^+$ (S1)
- $O_2 + e^- \rightarrow {}^{\bullet}O_2^-$ (S2)
- ${}^{\bullet}\text{O}_2{}^- + \text{H}^+ \longrightarrow \text{HO}_2{}^{\bullet} \tag{S3}$

$$2\mathrm{HO}_2^{\bullet} \to \mathrm{O}_2 + \mathrm{H}_2\mathrm{O}_2 \tag{S4}$$

 $H_2O + h^+ \rightarrow H^+ + {}^{\bullet}OH \tag{S5}$



Scheme S1. The proposed mechanism for photocatalytic oxidation of 3-pyridinemethanol to 3-pyridinemethanal and vitamin $B_{3.}^{1,2}$

References

1. S. Yurdakal, Ş. Ö. Yanar, S. Çetinkaya, O. Alagöz, P. Yalçın and L. Özcan, *Appl. Catal. B*, 2017, **202**, 500-508.

2. S. Yurdakal, S. Çetinkaya, M.B. Şarlak, L. Özcan, V. Loddo, L. Palmisano, *Catal. Sci. Technol.*, 2020, 10, 124-137.