Supplementary Material (ESI) for *Journal of Materials Chemistry*

Supplementary material
Tuning Hydrogen production during oxide irradiation through surface grafting

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Connection between $G(H_2)_{Ti}$ and TiO_2 band gap values.

We hypothesize that the energy transfer speed k_7 is proportional to the energy overlap between the exciton and the bond to be dissociated.

Assuming a Gaussian shape for the distribution of exciton energy centered a the band gap value $E_{exciton}$ and for the dissociating bond energy E_{bond} centered at 5eV, the overlap integral I can be calculated as :

$$I = cst \times \exp\left(- \frac{(E_{exciton} - E_{bond})^2}{2 \times (\sigma_{exciton}^2 + \sigma_{bond}^2)} \right) \qquad \text{(s1)}$$

where $\sigma_{exciton}$ (respectively σ_{bond}) is the standard deviation of the exciton energy (respectively of the bond to be dissociated). We assumed as a guess value that σ_{bond} could be equalled to the standard deviation of H_2 production with respect to band gap (figure 9 in ref (1) i.e. about 0.5 eV. We used also for E_{bond} the 5 eV value proposed in reference 1. For $\sigma_{exciton}$ we used 0,5 eV, a value derived from emission studies on many types of TiO_2 powders.(2-4) $E_{exciton}$ was equalled to the band gap values measured in figure S3.

Figure S1 shows the variation the overlap integral with respect to the variation of the yield. The correlation is quite good with the value given previously and can be further adjusted by slightly increasing σ_{bond} or $\sigma_{exciton}$ Therefore the overlap model explain quantitatively most of the variation of H_2 production upon titanium grafting

[1] N. G. Petrik, A. B. Alexandrov, A. I. Vall, *J. Phys. Chem. B* **2001**, *105*, 5935.
[2] K. Iijima, M. Goto, S. Enomoto, H. Kunugita, K. Ema, M. Tsukamoto, N. Ichikawa, H. Sakama, *J. Lumin.* **2008**, *128*, 911.
[3] N. Harada, M. Goto, K. Iijima, H. Sakama, N. Ichikawa, H. Kunugita, K. Ema, *Japan. J. Appl. Phys. Part 1* **2007**, *46*, 4170.
[4] A. Riss, T. Berger, H. Grothe, J. Bernardi, O. Diwald, E. Knozinger, *Nano Lett.* **2007**, *7*, 433.

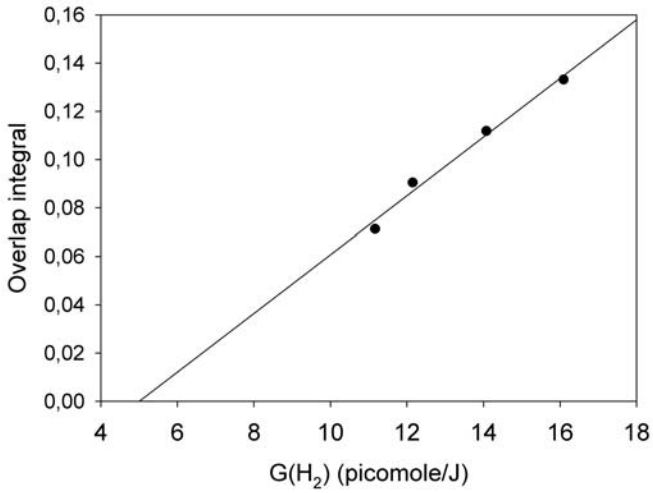

Figure S1. Correlation between the variation of H_2 radiolytic yield and the energy transfer integral I between exciton in TiO2 and water (equation S1)

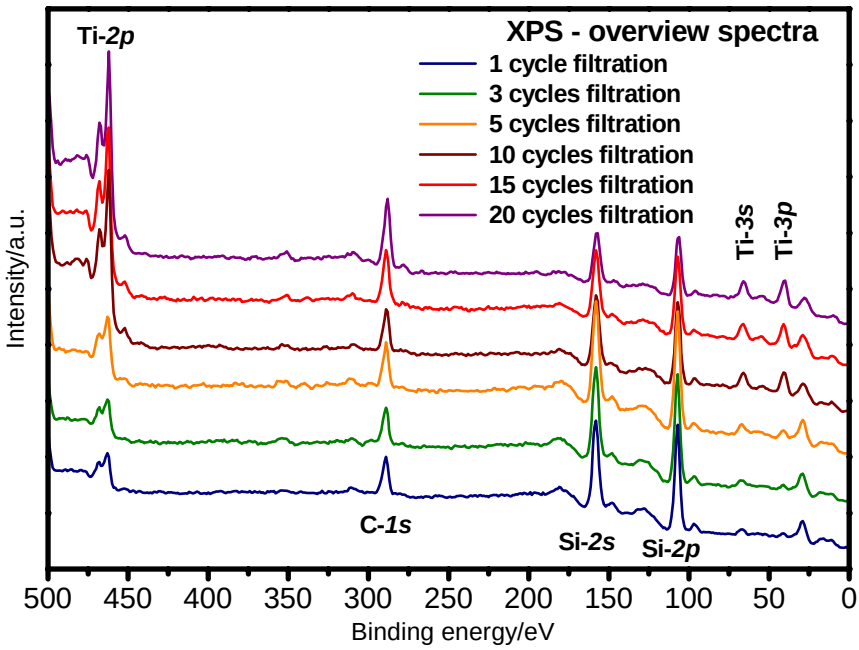

Figure S2. typical XPS spectra of Ti grafted silica fibers.

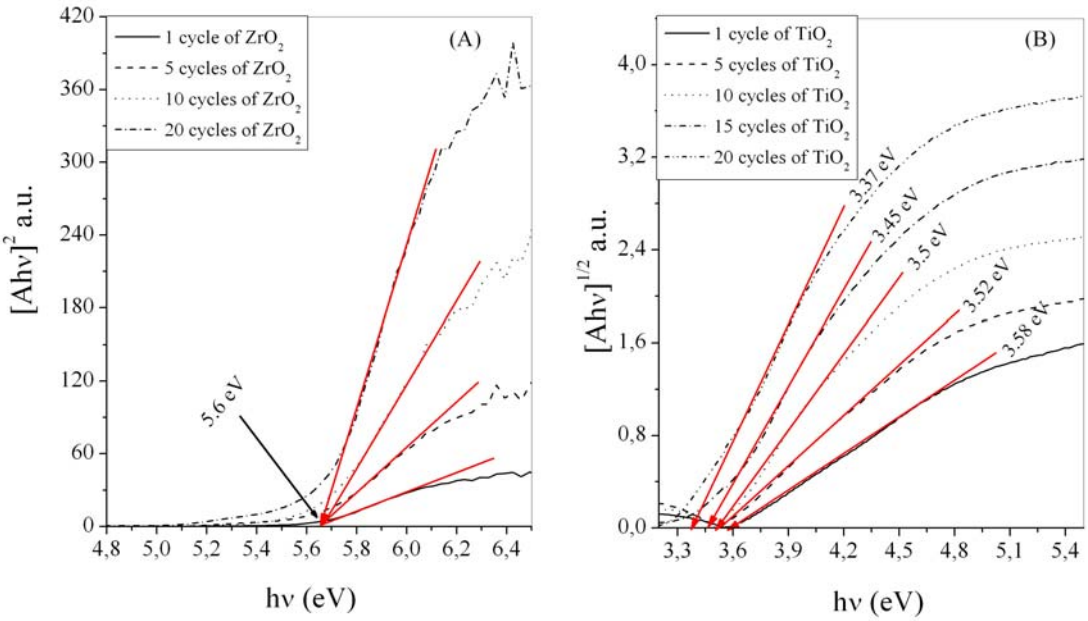

Figure S3 : Plot to determine the band gap

(A) Direct band gap (plot of $(F(R).h\upsilon)^2$ *vs.* hυ) for zirconium grafted silica

(B) Indirect band gap (plot of $(F(R).h\upsilon)^{1/2}$ *vs.* hυ) for titanium grafted silica

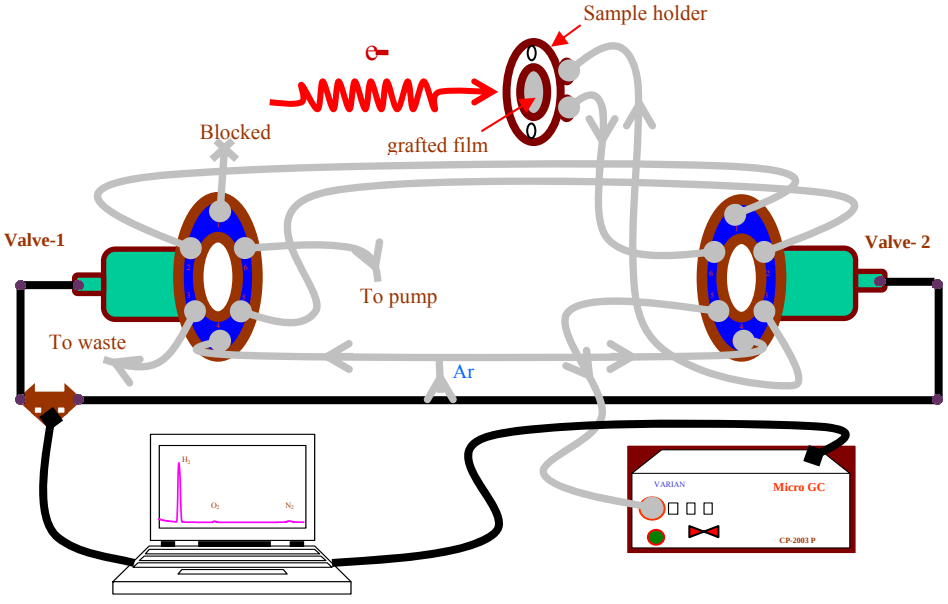

Figure S4. : System for the analysis of the gas produced under irradiation.

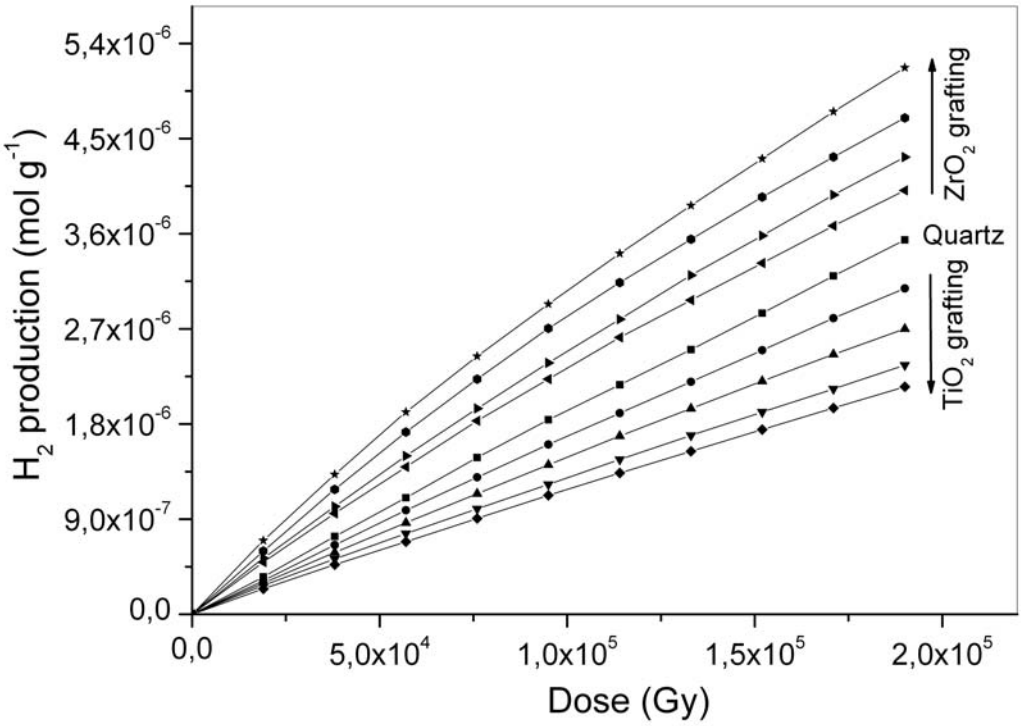

Figure S5: Comparison of dihydrogen production in moles per gram of silica, titanium and zirconium grafted silica samples after irradiation with 10 MeV electrons.