Supporting Informations

Structural and Functional Behaviour of Ce-doped Wide-Bandgap Semiconductors for Photo-Catalytic Applications

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Figure S1 shows the photocatalytic tests for CO_2 reduction. The O_2 released by CZ20, CCZ20 and CT20 during the reaction, was attributed to the possible photo-driven reduction of Ce^{4+} into Ce^{3+} acting as electron sink. Only bare ZnO and TiO_2 resulted able to photo-convert CO_2 into methane.

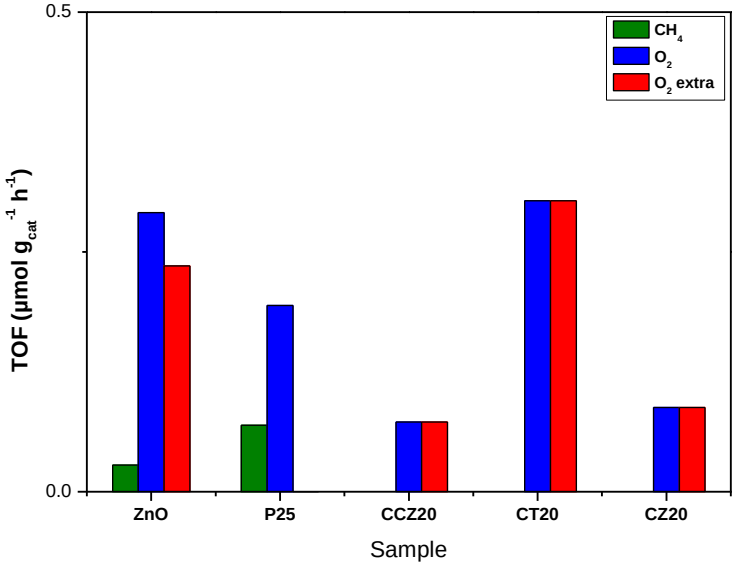

Figure S1 *Calculated TOF of ZnO- and TiO_2-based materials exposed to 6 h UV illumination in presence of gaseous CO_2 and H_2O.*

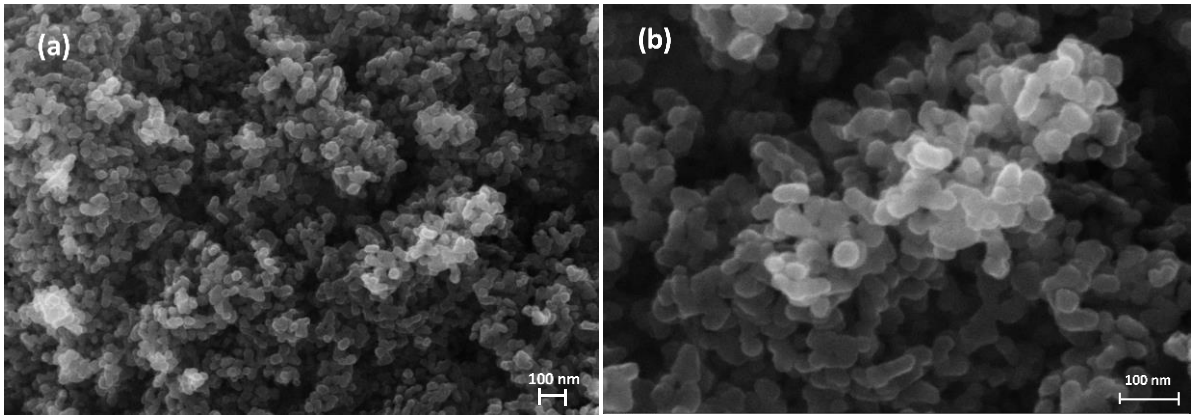

Figure S2 *SEM of bare ZnO showing aggregates at (a) 100 kx and (b) 250 kx magnification.*

Figure S3 shows the BJH pore distribution with an average pore diameter of ~18 nm.

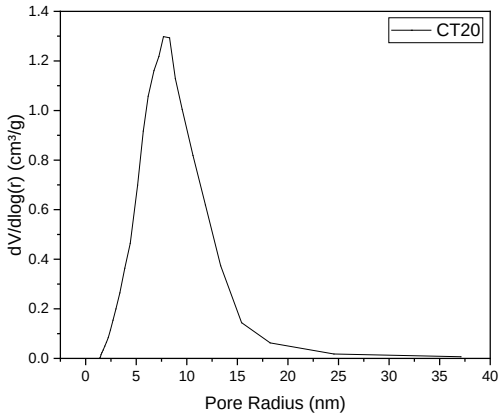

Figure S3 *Pore distribution of CT20ù*

In line with DRS and XRD data, results showed that the bandgap of CZ20 and CCZ20, evaluated as $E_g \cong 3.25\ eV$ (figure S4), was not considerably affected by the presence of cerium. However, a red shift in the absorption was still detected as possible consequence of defects content and of the presence of Ce^{3+} centres on the surface.

Conversely, in CT20 the presence of cerium modified the value of the bandgap energy E_g for indirect type of transitions when compared to bare TiO_2 (P25, Evonik). The Tauc plots suggested a bandgap shift from $3.26\ eV$ to $E_g = 2.39\ eV$ when TiO_2 was treated as indirect bandgap semiconductor (figure S4). Therefore, the bandgap modification was more pronounced for CT20 with respect to CCZ20 and CZ20, also as the possible effect of the as well remarked structural modifications.

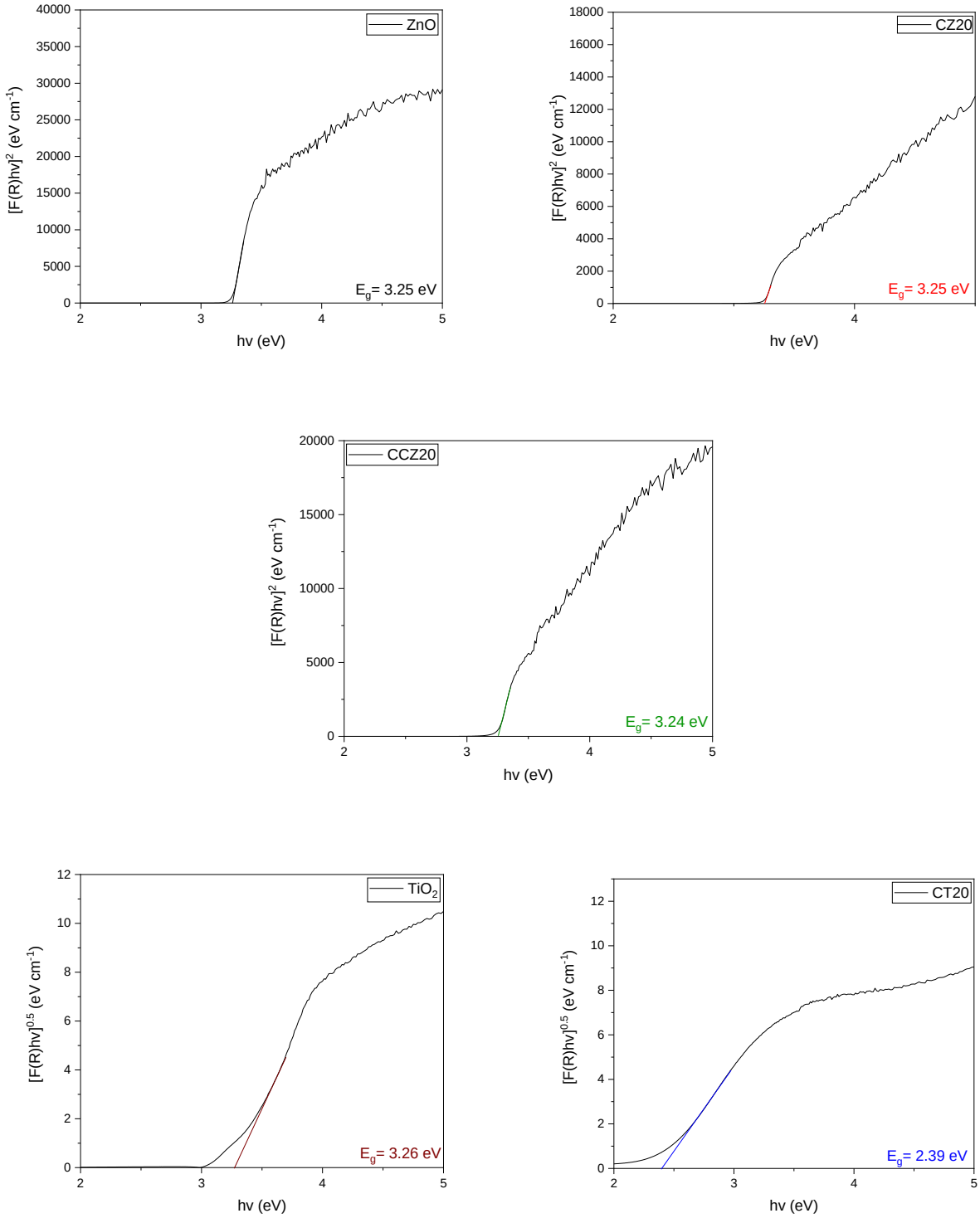

Figure S4 *Tauc plots of (up) ZnO and ZnO-based composites calculated with m=1/2 as and TiO_2-based samples calculated using m=2 considered as indirect bandgap semiconductor.*

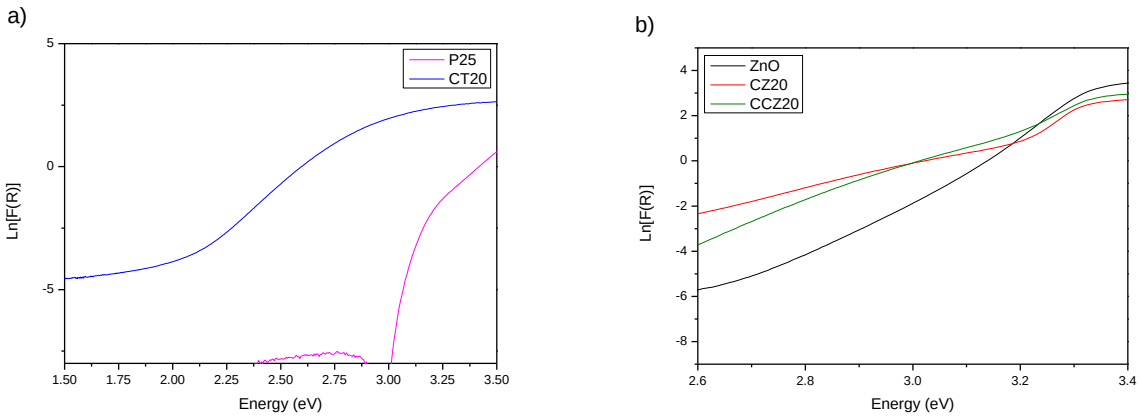

Figure S5 *Urbach plot of a) TiO_2-based and b) ZnO-based materials.*