Electronic Supplementary Information

Improved photocatalytic activity in the first RuO_2/ZnO nanoparticulate heterostructures due to inhomogeneous space charge effects

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XRD characterization of ZnO precipitate before calcination

The XRD pattern of ZnO precipitate before calcination is shown in Fig. S1. It mainly consists of broad bands along with very sharp peaks typical of mixture of amorphous phases and small clusters. As a consequence, crystalline ZnO was not formed just after precipitation.

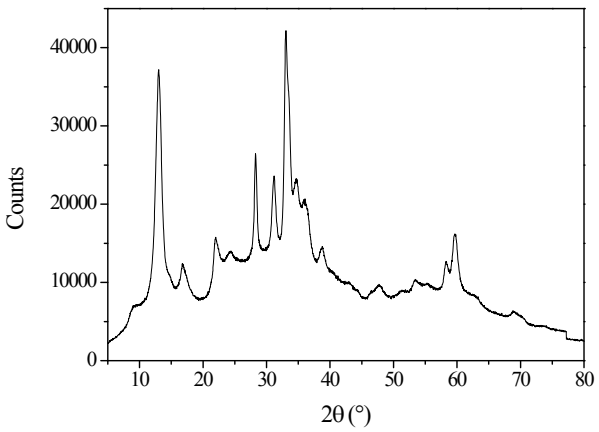

Fig. S1: XRD pattern of ZnO powder before calcination.

Fourier Transform Infrared Spectroscopy

The FITR spectra (KBr pellets) of the various photocatalysts prepared are shown in Fig. S2.

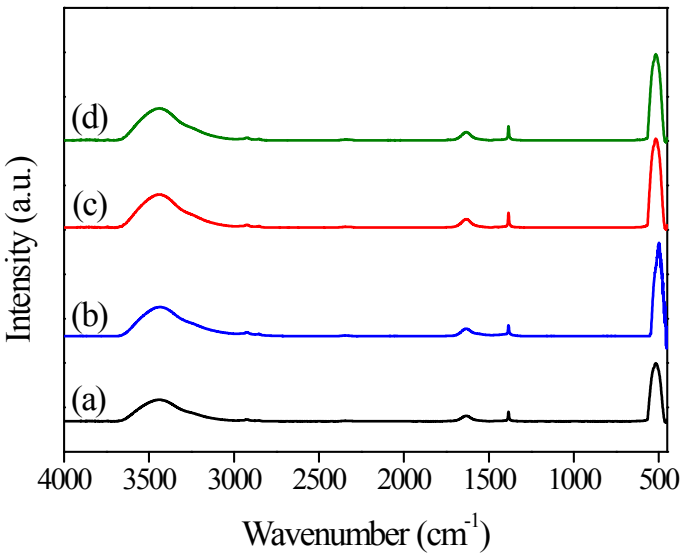

Fig. S2: FTIR spectra of ZnO (a, black), 2wt% RuO_2/ZnO (b, blue), 4wt% RuO_2/ZnO (c, red) and 6wt% RuO_2/ZnO (d, olive) nanomaterials.

EDX analysis

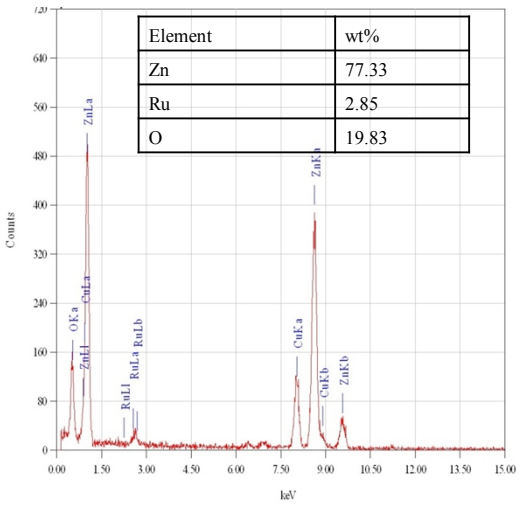

Fig. S3: EDX analysis of the 4wt% RuO_2/ZnO nanocomposite.

N_2 sorption analysis

The N_2 adsorption-desorption of pure ZnO and 4wt% RuO_2/ZnO nanomaterials are shown in Fig. S4.

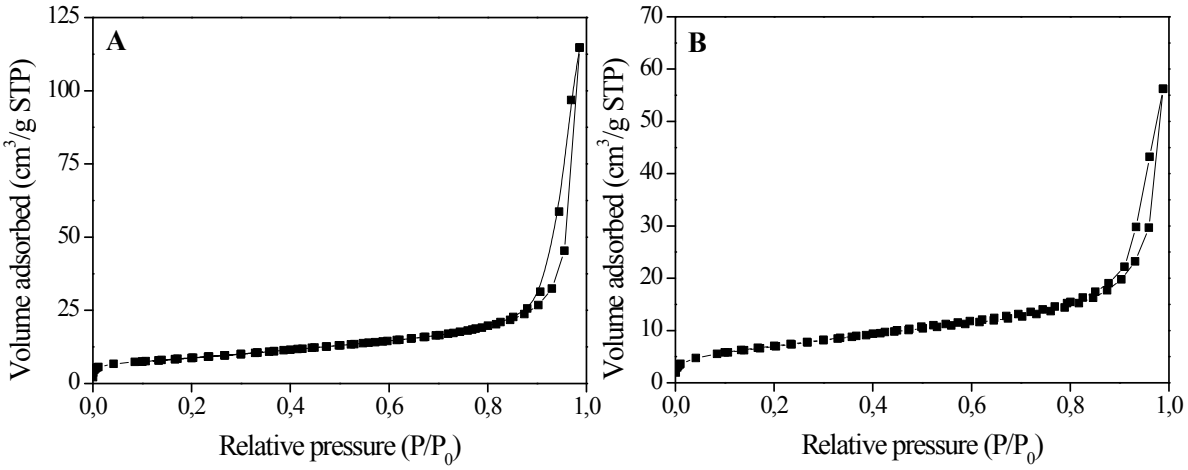

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Fig. S4: N_2 adsorption-desorption of pure ZnO (**A**) and 4wt% RuO_2/ZnO (**B**) nanomaterials.

Interface analysis

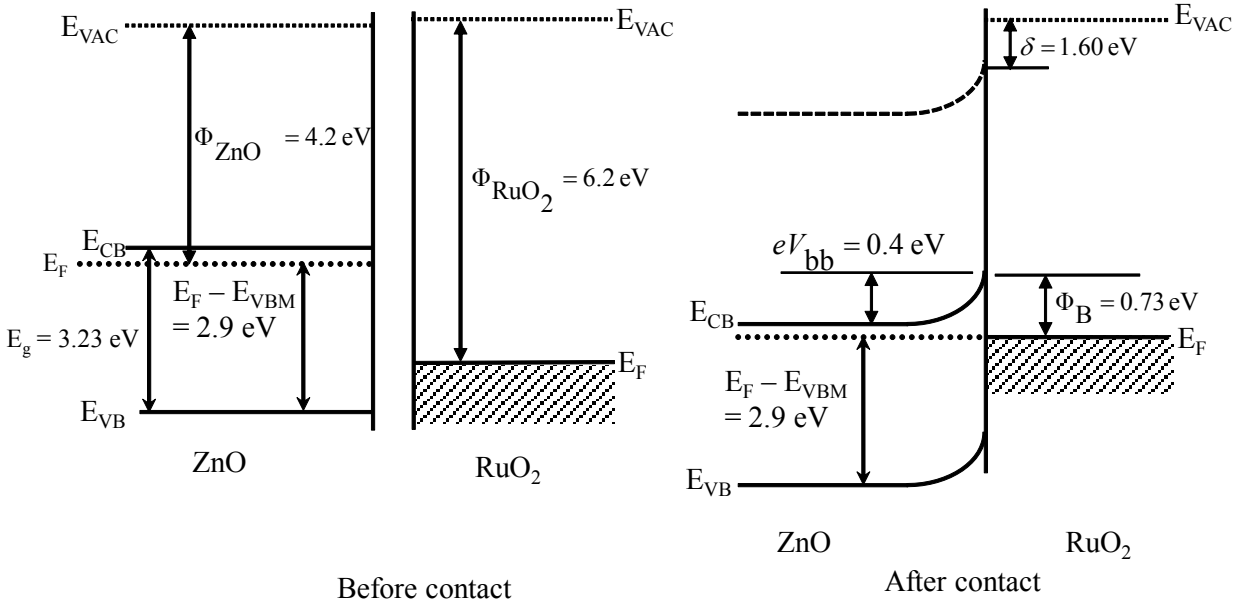
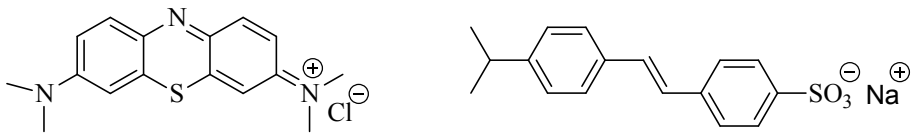


Fig. S5. Schematic band energy alignment at the interface of RuO_2 and ZnO. E_{CB}, E_{VB}, E_F, E_g are conduction band maximum, valence band maximum, Fermi level and energy bandgap, respectively. eV_{bb} refers to band bending at the interface of RuO_2 and ZnO.

Photocatalytic studies

The chemical formula of Methylene Blue (MB) and Methyl Orange (MO) are given in Scheme S1.



MB **MO**

Scheme S1: Chemical formula of Methylene Blue (MB) and Methyl Orange (MO).

To determine the time required to reach the adsorption equilibrium, an experiment was performed in the dark. 0.1 g photocatalyst was dispersed in 100 mL MB solution of initial concentration 10 mg/L. The solution was then vigorously stirred under dark and the concentration of MB was determined at regular time intervals. C/C_0 vs t plot (Fig. S6) clearly shows that there was no significant change in concentration of MB after 30 min.

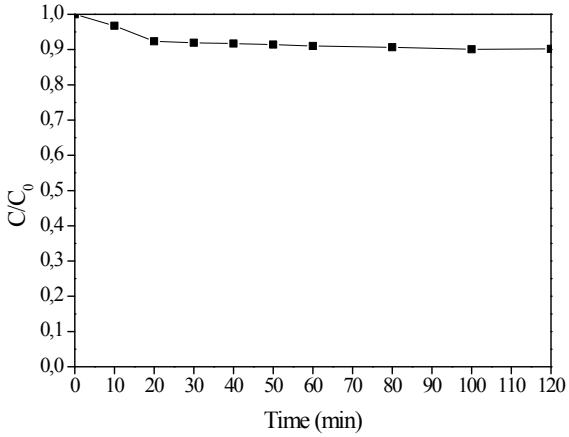


Fig. S6. Changes in the concentration of MB in contact with RuO_2/ZnO photocatalyst as a function of time in the dark.

More quantitatively, the amount of MB adsorbed, q_t (mg/g), at contact time *t* (min) can be calculated according to

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of MB at initial and any time *t*, respectively. *V* (L) is the volume of the solution and *W* (g) is the mass of catalyst used. Once again, the plot of qt as a function of time clearly shows that the amount of adsorbed MB reached a plateau value after 20 minutes and that there no significant change after 30 minutes.

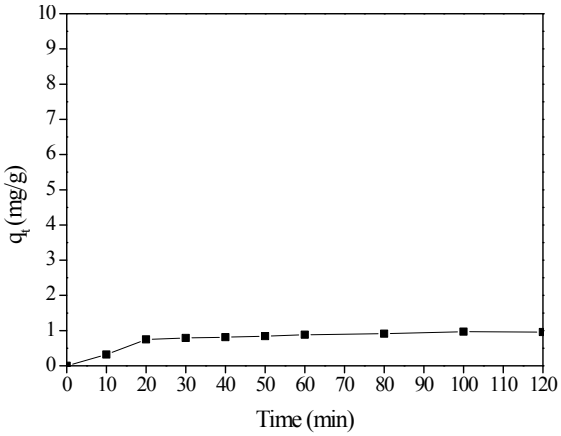


Fig. S7. Changes in amount of MB adsorbed in the dark as a function of.

The photocatalytic activity of the ZnO and 4wt% RuO_2/ZnO photocatalysts in the decomposition of Methyl Orange (MO) has been studied and was compared with that of P25 titania used as a commercial standard. The corresponding data are reported in Fig. S8.

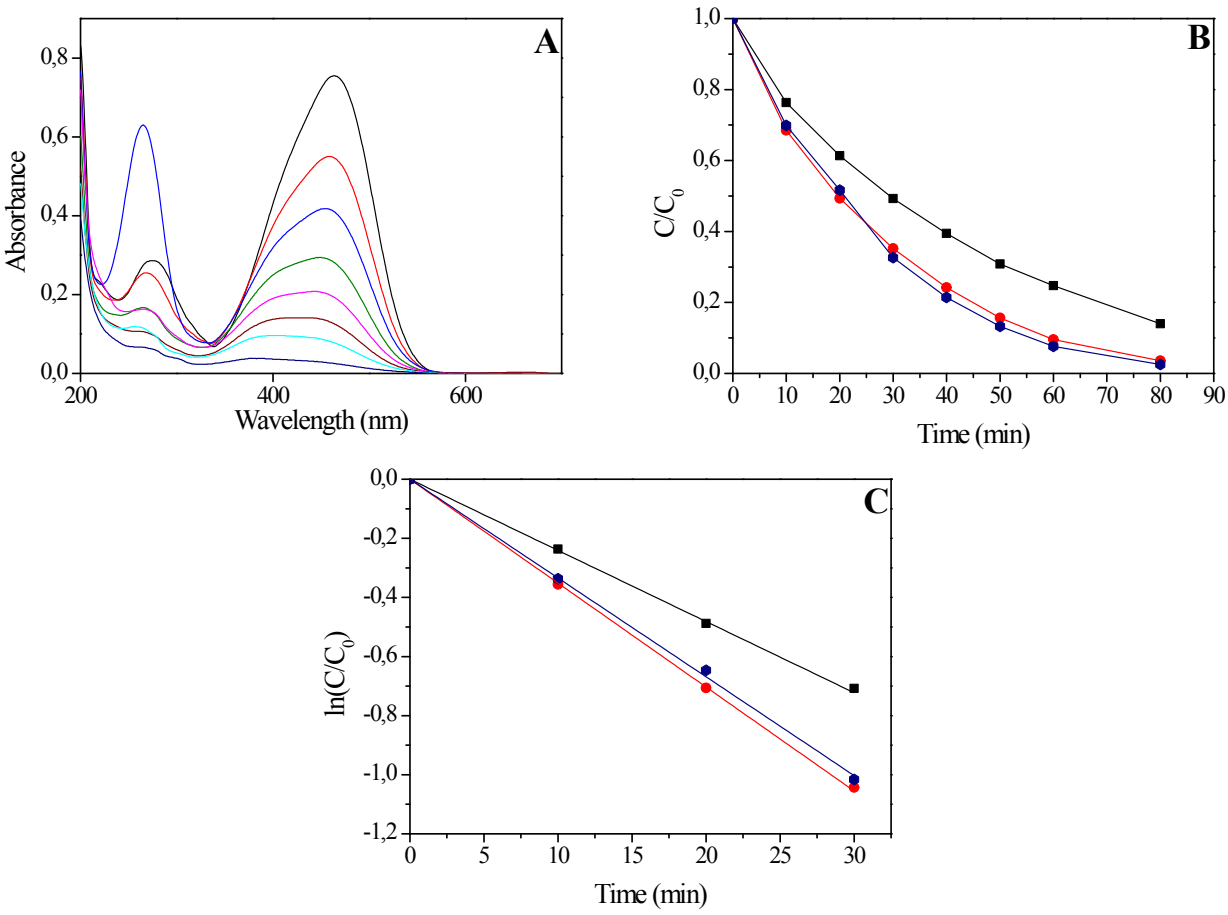


Fig. S8: (A) Absorbance changes of MO solution after different irradiation times in the presence of the 4wt% RuO_2/ZnO sample: equilibrium (black), 10 min (red), 20 min (blue), 30 min (olive), 40 min (magenta), 50 min (wine), 60 min (cyan) and 80 min (navy). (B) Kinetic of the degradation of MO in the presence of ZnO (square, black), 4wt% RuO_2/ZnO (circle, red) and P25 titania (hexagon, navy) photocatalysts. (C) ln[C/C_0] as a function of the irradiation time for ZnO (square, black), 4wt% RuO_2/ZnO (circle, red) and P25 titania (hexagon, navy) photocatalysts.

The XRD patterns of the nanocomposite before and after recycling are shown in Fig. S9.

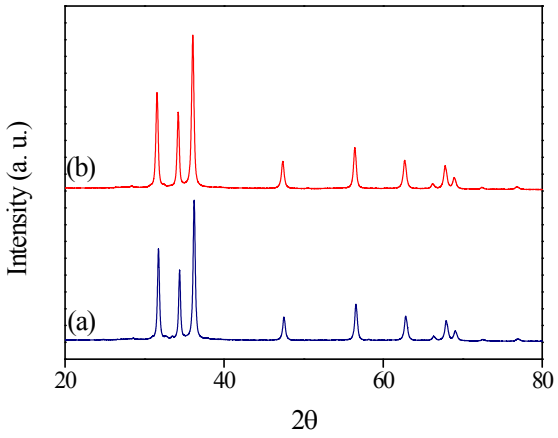


Fig. S9: XRD patterns of the 4wt% RuO_2/ZnO nanocomposite before (a, navy) and after (b, red) cycling photodgardation of MB.

The effect of the pH on the photocatalytic properties of the 4wt% RuO_2/ZnO photocatalyst in the photodegradation of MB is reported in Figure S10.

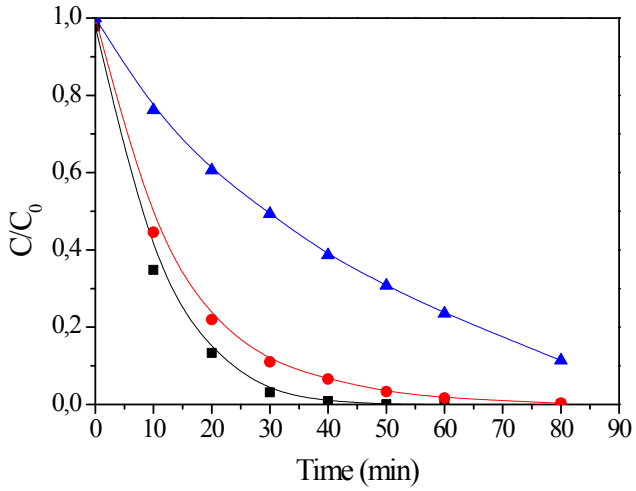


Fig. S10: The pH-effect on the photocatalytic properties of the 4wt% RuO_2/ZnO photocatalyst in the photodegradation of MB: pH = 2.5 (up triangle, blue), pH = 7.5 (circle, red) and pH = 9.9 (square, black).