Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2020

## **Supplementary material**

Figures



**Fig. s1** XRPD patterns of pure and boron doped ZnO nanoparticles (A) Pseudohexagonal and (B) elongated spindle-like particles having different mol fraction x of boron at levels a) 0.000, b) 0.005, c) 0.010, d) 0.050, e) 0.100, f) 0.150, g) 0.200 in Zn<sub>1-x</sub>B<sub>x</sub>O were studied.



**Fig. s2** FTIR spectra of pure and boron doped ZnO nanoparticles measured in KBr after 48 h of drying at 130° C. (A) Pseudohexagonal and (B) elongated spindle-like particles having different mol fraction x of boron at levels a) 0.000, b) 0.005, c) 0.010, d) 0.050, e) 0.100, f) 0.150, g) 0.200 in Zn<sub>1-x</sub>B<sub>x</sub>O were studied.



**Fig. s3** Absorption spectra of dyes used as a model of catalytic photodegradation on pure and variously doped ZnO nanoparticles. The narrow spectral bandwidth of the UV-LED with a wavelength of  $365 \pm 5$  nm employed in the photoreactor is also shown.



**Fig. s4** Molecular structures of: A) Phloxine B containing a xanthene ring and four chlorine atoms in a carboxyphenly ring; B) Oxazine 170 in a form of perchlorate composed of phenoxazine; and C) Rhodamine 123 containing a xanthene ring attached to the benzoic acid methyl ester. These organic dyes were used to simulate various organic pollutants.



**Fig. s5** Calibration curves for the (a) Phloxine B, (b) Oxazine 170 and (c) Rhodamine 123 water solutions within the concentration interval 0  $\mu$ mol / L – 4  $\mu$ mol / L measured by a UV-VIS spectrometer (Agilent 8453). Obtained dependencies were linear over the entire measured concentration range. Low concentrations of calibration solutions for the study of photolysis were chosen due to the strong absorption by the dyes even at low concentrations.

## Photolysis of Phloxine B on pure and boron doped ZnO nanoparticles with different morphology



**Fig. s6** Photolysis of Phloxine B on pure ZnO nanoparticles with different morphology. A shift of  $A_{max}$  from 542 nm to 532 nm and 540 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s7** Photolysis of Phloxine B on ZnO nanoparticles with different morphology doped with boron at a level of 1 mol %. A shift of  $A_{max}$  from 542 nm to 525 nm and 528 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles, indicating more intense decomposition. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s8** Photolysis of Phloxine B on ZnO nanoparticles with different morphology doped with boron at a level of 20 mol %. A shift of  $A_{max}$  from 542 nm to 523 nm and 525 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles and nanoparticles doped with boron at a level of 1 mol %. This finding indicates more intense degradation than in ZnO systems with lower boron content. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.

Photolysis of Oxazine 170 on pure and boron doped ZnO nanoparticles with different morphology



**Fig. s9** Photolysis of Oxazine 170 on pure ZnO nanoparticles with different morphology. A shift of  $A_{max}$  from 616 nm to 607 nm and 611 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s10** Photolysis of Oxazine 170 on ZnO nanoparticles with different morphology doped with boron at a level of 1 mol %. A shift of A<sub>max</sub> from 616 nm to 605 nm and 608 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles, indicating more intense decomposition. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s11** Photolysis of Oxazine 170 on ZnO nanoparticles with different morphology doped with boron at a level of 20 mol %. A shift of  $A_{max}$  from 616 nm to 602 nm and 606 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles and nanoparticles doped with boron at a level of 1 mol %. This finding indicates more intense degradation than in ZnO systems with lower boron content. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.

Photolysis of Rhodamine 123 on pure and boron doped ZnO nanoparticles with different morphology



**Fig. 12** Photolysis of Rhodamine 123 on pure ZnO nanoparticles with different morphology. A shift of  $A_{max}$  from 554 nm to 535 nm and 544 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s13** Photolysis of Rhodamine 123 on ZnO nanoparticles with different morphology doped with boron at a level of 1 mol %. A shift of  $A_{max}$  from 554 nm to 528 nm and 533 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles, indicating more intense decomposition. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.



**Fig. s14** Photolysis of Rhodamine 123 on ZnO nanoparticles with different morphology doped with boron at a level of 20 mol %. A shift of  $A_{max}$  from 554 nm to 525 nm and 529 nm was observed for pseudohexagonal and elongated spindle-like morphology respectively. The shift is more pronounced than in the case of pure nanoparticles and nanoparticles doped with boron at a level of 1 mol %. This finding indicates more intense degradation than in ZnO systems with lower boron content. The spectra were measured using a UV-VIS spectrometer (Agilent 8453). The spectra are shown after subtracting non-catalytic reductions in concentrations.

## Kubelka-Munk Method for the diffuse reflectance spectra estimation

A model describing the behaviour of light passing through a strongly scattering sample, and the use of DRS spectra for determining the optical  $E_g$  was designed by Kubelka and Munk [46, 47]. The central assumption in this model is that the medium to be measured is a flat layer with a finite thickness and an infinite surface, with no binding interactions. Therefore the only light interactions present are absorption and scattering. Spontaneous emission is neglected by the model [48]. The light source is assumed to be perfectly homogeneous and diffuse. The final assumption is that the S and K parameters (defined below)) must be constant at all points of the medium through which the diffuse light penetrates [49, 48]. The infinite surface model simplifies the solution with respect to the sample thickness, and the incident perpendicular luminous flux incident on the surface can be transferred from upper to lower layers (Fig. 1).



**Fig. s15** The luminous flux paths in the Kubelka – Munk model showing the geometry of the medium with scattering, where I and J describe the penetrated and reflected luminous flux, Rg is reflection from the support base, L is the thickness of the layer, and x is the depth coordinate.

In the absence of scattering, the downward change in the irradiance of the flux of light would be defined in terms of the Beer–Lambert–Bouguer law as dI = -Kdx. The constant K represents the absorption coefficient, and the greater its value, the greater is the probability of a photon being absorbed. As we include scattering, the downward light flow will decrease, with Kubelka and Munk predicting that, like absorption, this is a first order phenomenon [49, 50]. The coefficient S is known as the Kubelka-Munk scattering coefficient, and its units are the same as those of the absorption coefficient K. The downward flow of light *I* has a positive value only if the light penetrates downwards perpendicular to the sample surface. The upward light flux, marked by Kubelka-Munk as *J*, is only positive if the light penetrates upwards. It must be noted that the upward light flux is also scattered, as described by the term + SJd [49, 51]. By combining the terms described above, and taking into account light propagation scattering, we obtain two differential equations describing the opposing directions of light propagation in the sample (Eq. 2, Eq. 3)

$$dI = -KIdx - Sidx + SJdx$$
(Eq. 2)

$$dJ = -KJdx - SJdx + SIdx$$
(Eq. 3)

A part of the penetrating radiation is absorbed, and a part of the dispersed light changes its vector of incidence to the opposite direction, so it is necessary to keep separate the coefficients K and S. Transmission of incident flux and reflection of back-reflected flux are defined by

 $T = I / I_0$  and  $R = J / I_0$  respectively. Kubelka-Munk solved these differential equations to obtain an analytical expression of R and T at the appropriate wavelength. In the analytical expression, the reflection of the underlying area located under the sample is defined as  $R_g$ , (Eq. 4).

$$R(\lambda) = \frac{\frac{R_g - R_{\infty}}{R_{\infty}} - R_{\infty} \left(R_g - \frac{1}{R_{\infty}}\right) \exp\left[SL\left(\frac{1}{R_{\infty}} - R_{\infty}\right)\right]}{\left(R_g - R_{\infty}\right) - \left(R_g - \frac{1}{R_{\infty}}\right) \exp\left[SL\left(\frac{1}{R_{\infty}} - R_{\infty}\right)\right]}$$
(Eq. 4)

Where  $R_{\infty}$  is reflection by a layer that completely obscures the underlying surface. The Kubelka-Munk method has some limitations. First, is the assumption that the absorption and scattering coefficients are constant throughout the sample thickness [48]. Reflection at the air-surface interface is not included. Surface reflection can be neglected, because it is only significant for shiny materials [52] which do not include ZnO powder. In contrast, in the case of very dark samples, the use of the Kubelka-Munk method is less useful because the light is absorbed rather than scattered [53].

## Difference between optical and electronic bandgap energy

There is a slight difference between the electronic band gap and the optical band gap [58, 59, 60] (Fig. 2). The term electronic band gap refers to the gap between the valence band maximum and the conduction band minimum; whereas the optical band gap  $E_g$  is often somewhat wider. The reason for this difference can be explained by the fundamental properties of photon wave vector k, which represents its energy and direction of propagation. Visible light photons have values of k such that they excite electrons mainly from the highest energy level of the valence band to the lowest energy level of the conduction band (Fig. 2). In a lossless isotropic medium (gas, liquid, amorphous solids and cubic crystals) the direction of the wavevector is coincident with the direction of the wave propagation [61]; whereas in an anisotropic medium, such as asymmetric crystals, the wavevector may diverge from the wave [62].



Fig. s16 Schematic diagram of the difference between electronic bandgap and optical bandgap.