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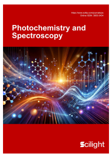

Supplementary Materials

Does the Catalyst Always Assist the Methylene Blue Photodegradation or does It Sometimes Hinder It?

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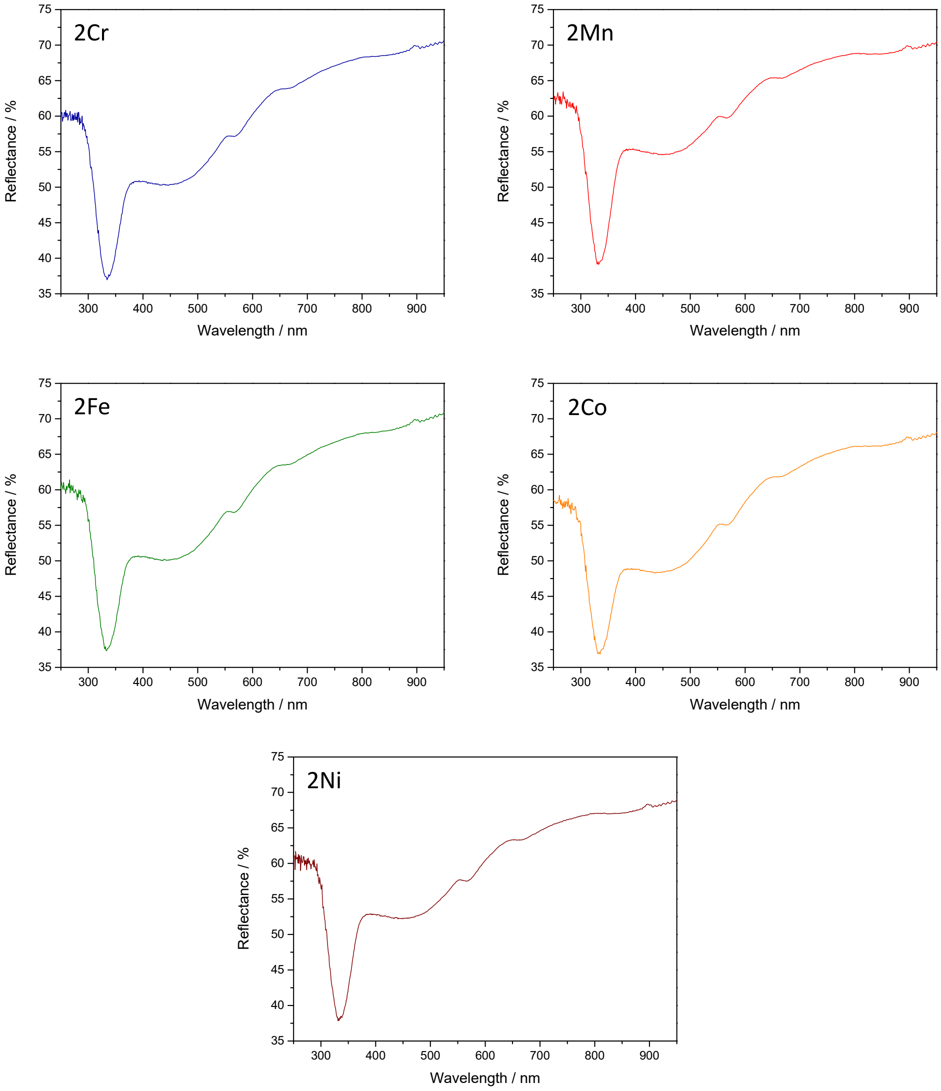

Figure S1. Reflectance spectra of investigated HEOs.

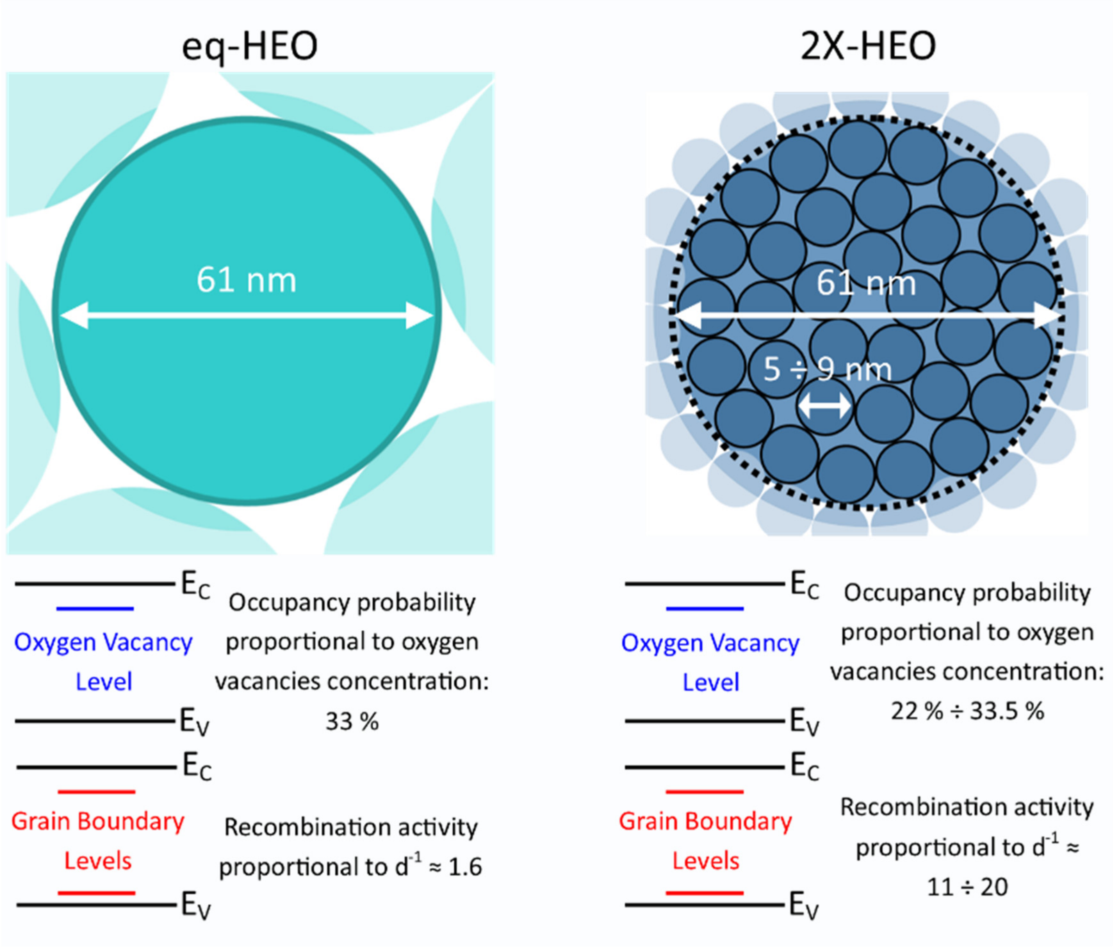

Figure S2. GB density as a function of size of HEO nanoparticles.

The oxygen vacancy concentration is not the primary factor governing the photocatalytic performance in MB degradation in the investigated HEOs. The key factor is the defect density: when defects are sparsely distributed, trapped electrons must migrate over long distances via sequential hopping and tunneling mechanism before recombining with holes, which slows down recombination. Conversely, in the case of densely distributed defects, the probability of hopping and tunneling processes increases and the trapped electrons can easily transfer between nearby trap states, thereby facilitating recombination. Moreover, distinguishing between bulk and surface defects is crucial, as surface defects not only promote photocarrier separation, but also provide readily accessible active adsorption sites. In the investigated HEO photocatalysts, the post-deposition thermal treatment determines both the crystalline phase formation and the morphological features, which in turn strongly influence the defect density associated with the grain boundaries. Here, the trap generation is due to dangling bonds caused by the sudden discontinuation of the crystal. These defects promote trap-assisted recombination processes, the extent of which depends on the surface defect density. In 2X HEOs, the low calcination temperature limits the growth of grains (<10 nm) and results in a very high density of grain boundary defects, which can be considered as surface defects (since the bulk contribution can be neglected owing to the grain size). All active sites are readily available; however, an excess of grain-boundary defects favors recombination. This imbalance between beneficial defects (i.e., oxygen vacancy mainly) and grain boundary defects accounts for the poor photocatalytic performance of 2X HEOs in methylene blue degradation. Conversely, in eq-HEOs, the higher calcination temperature leads to larger grains and improved crystallinity, which reduces the density of grain-boundary defects. This creates a more favorable balance between grain-boundary defects and oxygen vacancies, enabling more efficient photocarrier separation and ultimately enhancing the methylene blue degradation efficiency.

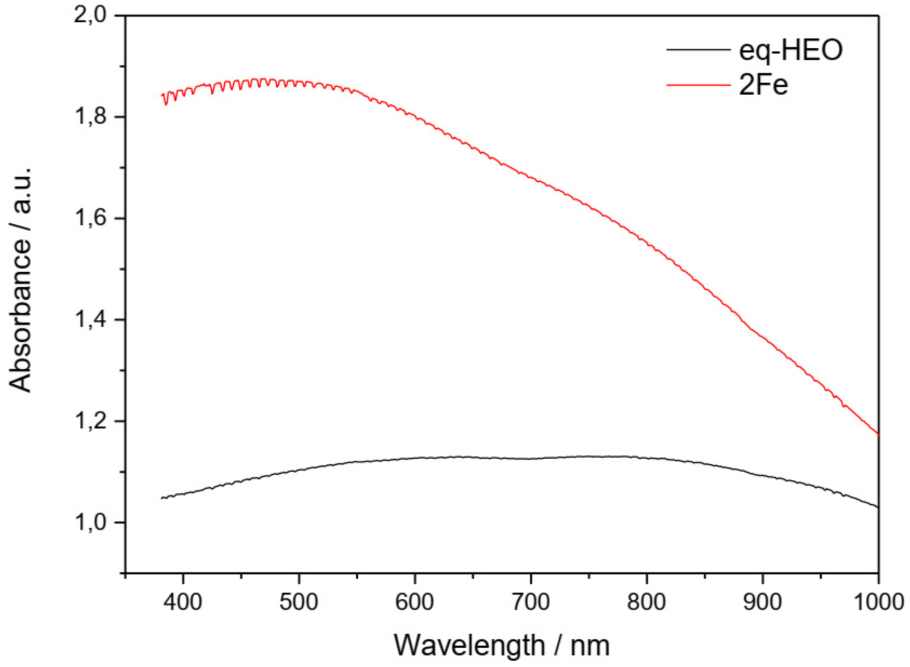

Figure S3. UV-Vis absorbance spectra measured on two aqueous solutions with the same load (0.235 g L^{-1}) of 2Fe and eq-HEO PCs.

Both absorbance spectra are characterized by a broad band that extends across the entire visible region. This demonstrates that dispersion of PC, regardless its nature, makes the solution turbid. Nonetheless, the turbidity of the solution containing 2Fe is higher than that containing eq-HEO, which suggests an inverse dependence on the PC particle size. It is noteworthy that the PC concentration used for the above absorbance measurements (0.235 g L^{-1}) is lower than that used for photodegradation measurements (0.30–90 g L^{-1}); for higher PC loads, the high turbidity of the solution led to saturation of the absorbance signal.

The above shown results confirm that the worse degradation efficiency obtained with PC eq-HEO and 3% diluted H_2O_2 compared to that with H_2O_2 alone is due to the turbidity of the solution in the presence of the catalyst, which hinders the penetration of light and, consequently, reduces the photoexcitation rate.