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Critical notes on heterogeneous photocatalysis on TiO₂ photocatalysts

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Publications dealing with photocatalytic process with titanium oxide and its modifications have risen over the last few years surpassing a total of 1100 peer-reviewed publications per year! Basic principles of this process are well known. A semiconductor (in this case TiO₂) acts as sensitizer for light induced redox processes. Absorption of a photon of energy greater than the bandgap energy leads to the formation of an electron-hole pair. In the absence of suitable scavengers, the involved energy is dissipated by recombination. If a suitable scavenger (or a surface defect) is available to trap the electron or hole, recombination is prevented and the redox reaction may occur. Numerous titania-based photocatalysts have been described and their photocatalytic activities have been examined with many attempts to generalize the achieved results. These attempts are often reported with azo dyes as model compounds. It is generally stated that in order to obtain an extraordinary photocatalytic material many structural parameters such as particle size, crystal phase, surface morphology, specific surface area, nanostructure order, etc., may contribute. No doubt there are correlations between the structure and the photocatalytic activity, but it cannot simply be explained by crystalline phase, specific surface area, particle size, etc. This is the significant difference from the classical heterogeneous catalysis concept. Besides some general aspects we do not usually know which properties of the photocatalyst are "significant", how many parameters are required, and what kind of combination is indicative. An elegant solution is to "accept" the photocatalytic activity as a relative measure and choose a reference sample for comparison. It could either be an internal standard taken arbitrarily or, as we observe repeatedly, the standard data reported for Evonik's P25. This often exhibits similar or higher activity to in-house samples or other commercial products, but general conclusions on rate data trends cannot be drawn. Endless numbers of papers claim that the extraordinary shape or nanoscopically ordered structure of photocatalyst particles account for the observed activity, which is different from the ordinarily shaped photocatalyst particles. Such materials are usually very nice and often quite active, but there is no proposal as to how the shape of the crystallites is related to the rate expression. The very high nanoscopic uniformity and alignment may even reduce the photocatalytic activity due to increasing the absolute number of inter-particle barriers acting as efficient recombination centers whenever an excited electron passes over. In the current contribution we seek to demonstrate how misleading it could be to draw generally valid conclusions using simple data sets obtained by measuring the kinetics of heterogeneous photocatalytic processes with a series of readily available titania based photocatalysts and three azo dyes as model compounds.