

Design, Preparation and Characterization of Solid Photocatalyst Materials Based on Energy-resolved Distribution of Electron Traps

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How can we design solid photocatalysts? What is the decisive factor controlling photocatalytic activities? So-called band-structure model (BSM), electrons in a valence band (VB) of a photocatalyst is photoexcited into a conduction band (CB), leaving positive holes in VB, and electrons and holes reduce and oxidize, respectively, substrates adsorbed on the surface of the photocatalyst, does suggest preferable band positions for redox reaction uniquely decided only by crystalline structure. The other possible factors, e.g., particle size and surface structure, cannot be discussed within BSM.

Recently, we have developed reversed double-beam photoacoustic spectroscopy (RDB-PAS) which enables measure energy-resolved density of electron traps (ERDT). Those electron traps (ETs) seem to be predominantly located on the surface of almost all the metal oxide particles and therefore they reflect macroscopic surface structure in ERDT patterns [1,2]. Using ERDT pattern along with the data of CB-bottom position (CBB), i.e., ERDT/CBB patterns, it has been shown that metal oxide powders and the other semiconducting materials such as carbon nitrides can be identified without using the other analytical data such as X-ray diffraction patterns or specific surface area, and similarity/differentness of a pair of metal-oxide samples can be quantitatively evaluated as a parameter, ζ , degree of coincidence of ERDT/CBB patterns [3].

Three representative photocatalytic reactions, (a) hydrogen (H_2) evolution from deaerated aqueous methanol (H_2 system), (b) carbon-dioxide (CO_2) evolution from aqueous acetic acid under aerobic conditions (CO_2 system) and (c) oxygen (O_2) evolution from aqueous silver fluoride (O_2 system), were carried out with those titania samples, and the ratios of evaluated photocatalytic activities for pairs of titania samples ($0 < \zeta_{pc} < 1$) were compared with ζ . It was observed that the higher the value of ζ at > 0.6 is, the higher becomes ζ_{pc} , i.e., the ERDT/CBB patterns reflect bulk/surface structures which govern overall photocatalytic activities of titania samples; ERDT/CBB patterns can identify these titania samples and this can be extended to the other metal oxides and semiconducting materials such as carbon nitride (C_3N_4).

Then, reversed analysis has been made, i.e., those ERDT/CBB patterns were arranged in the order of photocatalytic activity from higher side to lower side. Interestingly, for CO_2 and O_2 systems, highest activity titania samples exhibited similar patterns in each system, while middle or low-activity samples did no similarity. One of the possible reasons is that photocatalytic activities are governed by many independent factors, which are all optimized in the highest activity samples, though activities can be much reduced only by one unfavorable factor. In the other words, we cannot expect to find titania samples of activity higher than those titania samples in CO_2 and O_2 systems. This assumption, however, may suggest that titania samples exhibiting superior photocatalytic activity in H_2 system may be discovered, because they seem not to be optimized.

[1] *Chem. Commun.*, **2016**, 52, 12096–12099. [2] *Electrochim. Acta*, **2018**, 264, 83–90. [3] *Catal. Today*, **2019**, 321–322, 2–8.