Transfer Channel of Photoinduced Hole on TiO_2 Surface as Revealed by Solid-state NMR and ESR Spectroscopy

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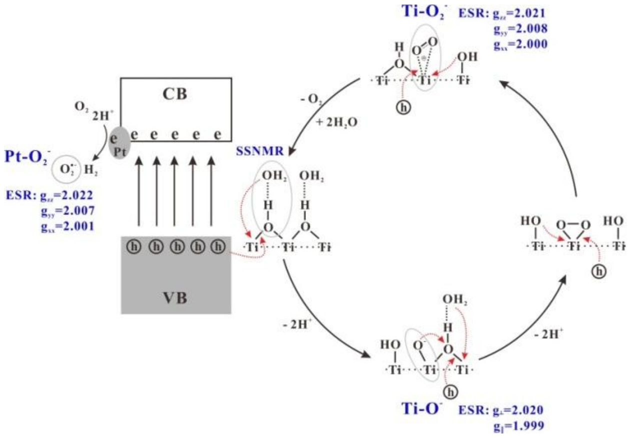
The detailed structure-activity relationship of surface hydroxyl groups (Ti-OH) and adsorbed water (H_2O) on the TiO_2 surface should be the key to clarify the photogenerated hole (h^+) transfer mechanism for photocatalytic water splitting, which however is still not well understood. Herein, one- and two-dimensional ^1H solid-state NMR techniques were employed to identify surface hydroxyl groups, adsorbed water molecules as well as their spatial proximity/interaction in TiO_2 photocatalysts. It was found that although the two different types of Ti-OH (bridging hydroxyl (OH_B) and terminal hydroxyl (OH_T) groups) were present on the TiO_2 surface, only the former is in close spatial proximity to adsorbed H_2O, forming hydrated OH_B. In-situ ^1H and ^{13}C NMR studies of the photocatalytic reaction on TiO_2 with different Ti-OH group and different H_2O loading illustrated that the enhanced activity was closely correlated to the amount of hydrated OH_B groups. To gain insight into the role of hydrated OH_B groups in the h^+ transfer process, in-situ ESR experiments were performed on TiO_2 with variable H_2O loading, which revealed that the hydrated OH_B groups offer a channel for the transfer of photogenerated hole in the photocatalytic reaction, and the adsorbed H_2O could make a synergistic effect with neighboring OH_B group to facilitate the formation and evolution of active paramagnetic intermediates. On the basis of experimental observations, the detailed photocatalytic mechanism of water splitting on the surface of TiO_2 was proposed.



Scheme 1. Proposed hole-transfer mechanism for photocatalytic water splitting on the TiO_2 photocatalyst upon solar-light irradiation.

- Liu, F.; Feng, N. D. ; Wang, Q.; Xu, J.; Qi, G.; Wang, C.; Deng, F. J. Am. Chem. Soc. 2017, 139, 10020.