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Tunable doping sites and the impacts in photocatalysis of W–N codoped anatase TiO_2

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Tungsten-nitrogen (W-N) co-doping has been known to enhance the photocatalytic activity of anatase titania nanoparticles by utilizing visible light. The doping effects are, however, largely dependent on calcination or annealing conditions, and thus, the massive production of quality-controlled photocatalysts still remains a challenge. Using density functional theory (DFT) thermodynamics and time-dependent DFT (TDDFT) computations, we investigate the atomic structures of N doping and W-N co-doping in anatase titania, as well as the effect of the thermal processing conditions. We find that W and N dopants predominantly constitute two complex structures: an N interstitial site near a Ti vacancy in the triple charge state and the simultaneous substitutions of Ti by W and the nearest O by N. The latter case induces highly localized shallow in-gap levels near the conduction band minimum (CBM) and the valence band maximum (VBM), whereas the defect complex yielded deep levels (1.9 eV above the VBM). Electronic structures suggest that substitutions of Ti by W and the nearest O by N improves the photocatalytic activity of anatase by band gap narrowing, while defective structure degrades the activity by an in-gap state-assisted electron-hole recombination, which explains the experimentally observed deep level-related photon absorption. Through the real-time propagation of TDDFT (rtp-TDDFT), we demonstrate that the presence of defective structure attracts excited electrons from the conduction band to a localized in-gap state within a much shorter time than the flat band lifetime of titania. Based on these results, we suggest that calcination under N-rich and O-poor conditions is desirable to eliminate the deep-level states to improve photocatalysis.

Keywords: DFT, Titania, Photocatalyst, Codoping, TDDFT