

ABSTRACT - POSTER

Influence of TiO₂ structure on NaBH₄ reduction and reduction-induced structural changes

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Titanium dioxide (TiO₂) is a widely studied photocatalyst for applications such as the degradation of organic pollutants. However, the photocatalytic efficiency of pristine titania is limited as it utilises only 5% of the solar spectrum and has a relatively low quantum efficiency compared to modified TiO₂ structures. One strategy to improve its properties is the reduction of TiO₂ to black titania, which introduces defects such as Ti³⁺ centres and oxygen vacancies and enhances visible-light absorption.¹ Despite the potential of black titania, contradictory results are frequently reported in the literature.^{2,3} We hypothesize that these differences may partly originate from variations in the initial structure of TiO₂.

In this work, the influence of the TiO₂ structure on NaBH₄ reduction, and conversely the influence of NaBH₄ reduction on the TiO₂ structure, were investigated systematically. Four TiO₂ structural forms, i.e. anatase, rutile, brookite, and amorphous TiO₂, were reduced under identical conditions. The resulting materials were characterised using electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), X-ray diffraction (XRD), Raman spectroscopy, and thermogravimetric analysis – mass spectroscopy (TGA-MS).

Ti³⁺ defects and oxygen vacancies were identified after reduction, although their nature depended on the initial TiO₂ structure. In reduced rutile, clustered Ti³⁺ centres were observed, whereas multiple Ti³⁺ species were detected for anatase, brookite, and amorphous TiO₂. Further, EELS showed that reduced sites in brookite and amorphous TiO₂ still contained a fraction of Ti⁴⁺. UV-Vis DRS measurements showed increased visible-light absorption after reduction. XRD and Raman spectroscopy revealed that only anatase exhibited significant structural changes upon reduction, with Rietveld refinement indicating a decrease in the O/Ti ratio. Furthermore, TGA-MS showed that H₂ evolution differed for anatase and amorphous TiO₂, while rutile and brookite displayed a similar behaviour.

These results show that the initial structure of TiO₂ influences its reduction with NaBH₄, while the reduction itself can also affect the TiO₂ structure, highlighting the importance of the starting material when comparing black TiO₂.

References:

- (1) Rajaraman, T. S.; Parikh, S. P.; Gandhi, V. G. Black TiO₂: A Review of Its Properties and Conflicting Trends. *Chemical Engineering Journal* **2020**, *389*, 123918. <https://doi.org/10.1016/j.cej.2019.123918>
- (2) Rajaraman, T. S.; Gandhi, V. G.; Nguyen, V.-H.; Parikh, S. P. Aluminium Foil-Assisted NaBH₄ Reduced TiO₂ with Surface Defects for Photocatalytic Degradation of Toxic Fuchsin Basic Dye. *Appl Nanosci* **2023**, *13* (6), 3925–3944. <https://doi.org/10.1007/s13204-022-02628-x>
- (3) Ariyanti, D.; Mills, L.; Dong, J.; Yao, Y.; Gao, W. NaBH₄ Modified TiO₂: Defect Site Enhancement Related to Its Photocatalytic Activity. *Materials Chemistry and Physics* **2017**, *199*, 571–576. <https://doi.org/10.1016/j.matchemphys.2017.07.054>