

**NOVEL/GREEN SYNTHESIS AND CHARACTERIZATION OF  
HYBRID TITANIUM DIOXIDE PHOTOCATALYSTS FOR  
VISIBLE LIGHT PHOTODEGRADATION OF POLLUTANTS  
AND THE REACTIVE OXYGEN SPECIES INVOLVED**

*A Thesis submitted  
in partial fulfillment for the Degree of*

**Doctor of Philosophy**

*by*

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## ABSTRACT

TiO<sub>2</sub> based visible light photodegradation is one of the amenable solution to the environmental problems especially the water pollution. However, various surface modifications has to done to make them visible light responsive. The reaction course and reactivity of these modified surfaces differ significantly from unmodified TiO<sub>2</sub>. Deep insights and the photodegradation mechanistic views of these new systems are highly essential in designing an efficient visible light photocatalytic materials.

This thesis mainly focuses on the preparation methods of various TiO<sub>2</sub> modified composites, its characterization, to study its photodegradation properties and also to examine the reactive oxygen species (ROS) involvement in the photodegradation of rhodamine B (RhB) under visible light. In the (001) exposed facet TiO<sub>2</sub>-graphene composite, the composite is prepared using photochemical reduction method using UV light. The composite is showing excellent selectivity towards the photodegradation of positive dyes and •OH and <sup>1</sup>O<sub>2</sub> are the dominant ROS species (This work was published in Solar Energy Materials and Solar Cells, 2016).

Nitrogen doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) and TiO<sub>2</sub>-MoS<sub>2</sub> (TMS) photocatalysts are prepared using one step solvothermal method lead and exhibit excellent visible light photodegradation properties. ROS O<sub>2</sub>•- plays dominant role in the visible light photodegradation of RhB by N-TiO<sub>2</sub> and TMS photocatalysts (N-TiO<sub>2</sub> work was published in RSC Advances, 2016 and TMS photocatalyst work was published in New Journal of Chemistry, 2016). In N-TiO<sub>2</sub> photocatalyst, intra-band gap states is for visible light enhancement while in TMS composites few layered MoS<sub>2</sub> sensitized TiO<sub>2</sub> mechanism is the reason.

Modification of commercial P25 with carbon dot (C-dot) lead to the improved visible light absorption and the photodegradation properties. Here the composite is prepared from the physical mixing of P25 and C-dot. Up-converted photoluminescence is responsible for the dominant •OH ROS production. Scavenging studies reveal how ROS contributions alters the reaction pathway of the resulting intermediate especially the importance of •OH ROS in the mineralization of RhB dye.

Similarly the photochemical reduction is employed in the preparation of TiO<sub>2</sub>-C<sub>60</sub> (This work was published in Carbon, 2014) or TiO<sub>2</sub>-reduced graphene oxide (rGO) (This work was published in Environmental Progress and Sustainable Energy, 2016) composites using cyclcodextrin as a linker molecule. Visible light absorption is achieved by ligand to metal charge transfer (LMCT) mechanism. ROS O<sub>2</sub>•- and <sup>1</sup>O<sub>2</sub> are dominant with TiO<sub>2</sub>-CD-C<sub>60</sub> and TiO<sub>2</sub>-CD-rGO composites respectively.

In conclusion, this thesis presents an understanding of, how the various surface modifications of TiO<sub>2</sub> and the resulting photodegradation mechanism affects the contribution of ROS in the visible light photodegradation.