

Role of Fe doping in tuning the band gap of TiO₂ for photo-oxidation induced cytotoxicity paradigm

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Supporting Information

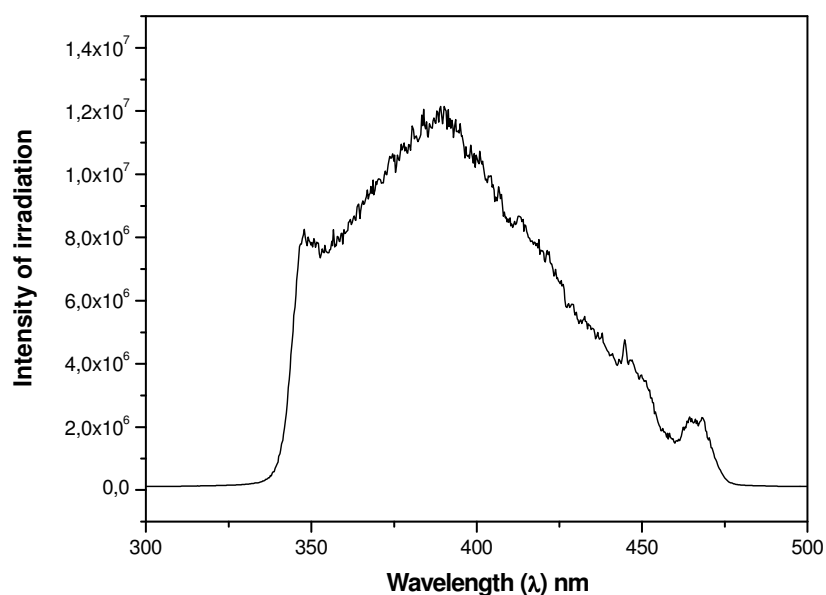


Figure S1. Near-visible spectrum ($\lambda=350-450$ nm) of light (light filter) used for photoactivation of nanoparticle.

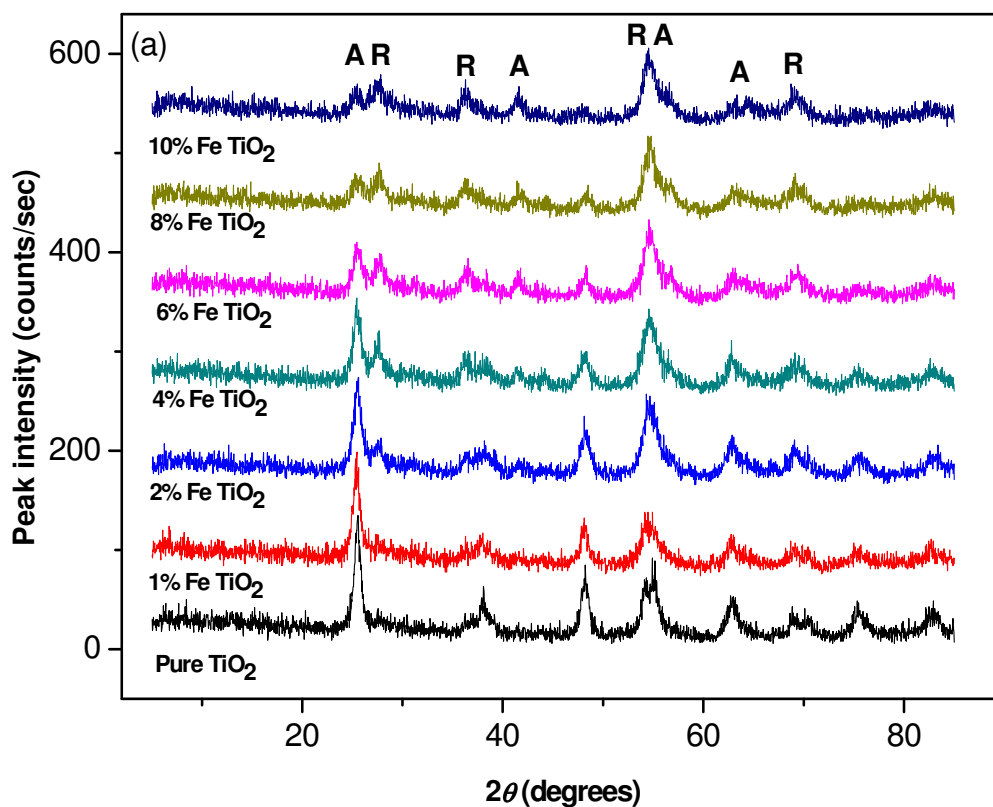


Figure S2: XRD Characterization of pure and Fe doped TiO₂ nanoparticles. The XRD patterns were recorded using PANalytical X'Pert MPD PRO diffracting system, equipped with Ni-filtered CuK α ($\lambda=0.154$ nm) radiation within the range of 5-85° 2 theta. The anatase (A) and rutile (R) phases have been identified using PDF database No. 00-021-1272 for anatase and 00-021-1276 for rutile phase. The anatase phase dominates at lower iron loadings while rutile phase increases with increasing Fe loading.

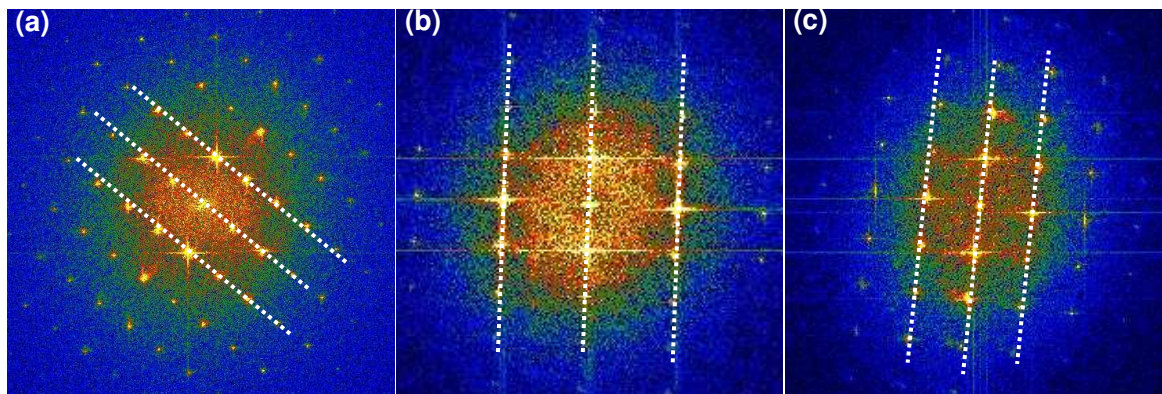


Figure S3: The Fourier Filtered HRTEM images of nanoparticles. The High resolution images were filtered by applying masks using the offline GATAN imaging technique. Noise reduction was applied to the wide spots of the FFT power spectrum. (a), (b), and (c) are the resulting images after performing an inverse FFT on the High resolution TEM images shown in Figure 2 (A) third row. The images show the highly crystalline nature of both anatase and rutile phases.

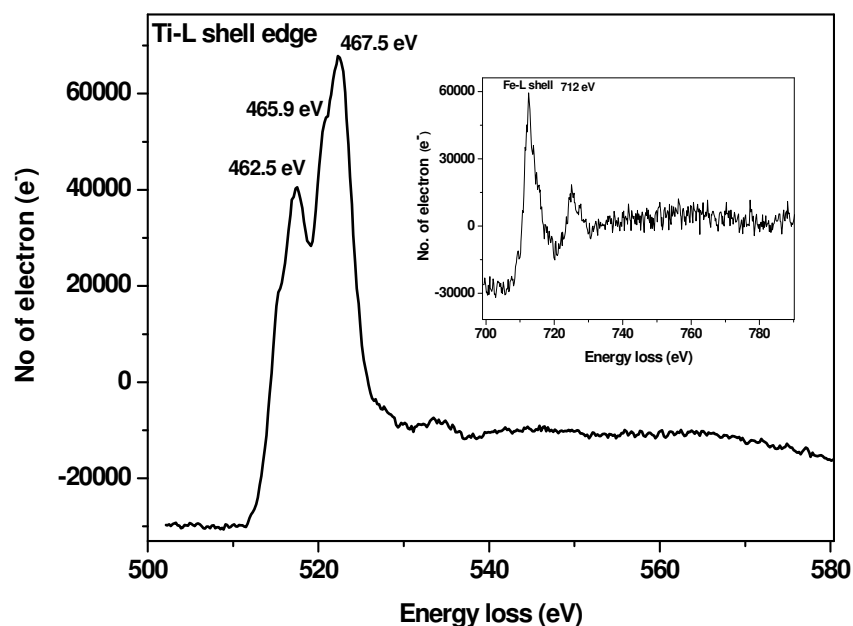


Figure S4. Electron Energy Loss Spectroscopy (EELS) spectrum of 10.2% Fe doped TiO₂ nanoparticles. EELS were obtained with a FEI Titan 80/300 microscope equipped with the GATAN parallel EELS spectrometer operated at 0.2 eV per channel as an energy dispersive detector. Electron Energy Loss Spectroscopy (EELS) spectrum of 10 % Fe doped TiO₂ nanoparticles after zero loss correction. The spectrum shows the Ti-L shell structure and the inset shows the Fe-L shell in the TiO₂ matrix. The energy loss values of 712 and 724 eV from the L-shell of Fe show clear indication of the homogeneous distribution of Fe in TiO₂.

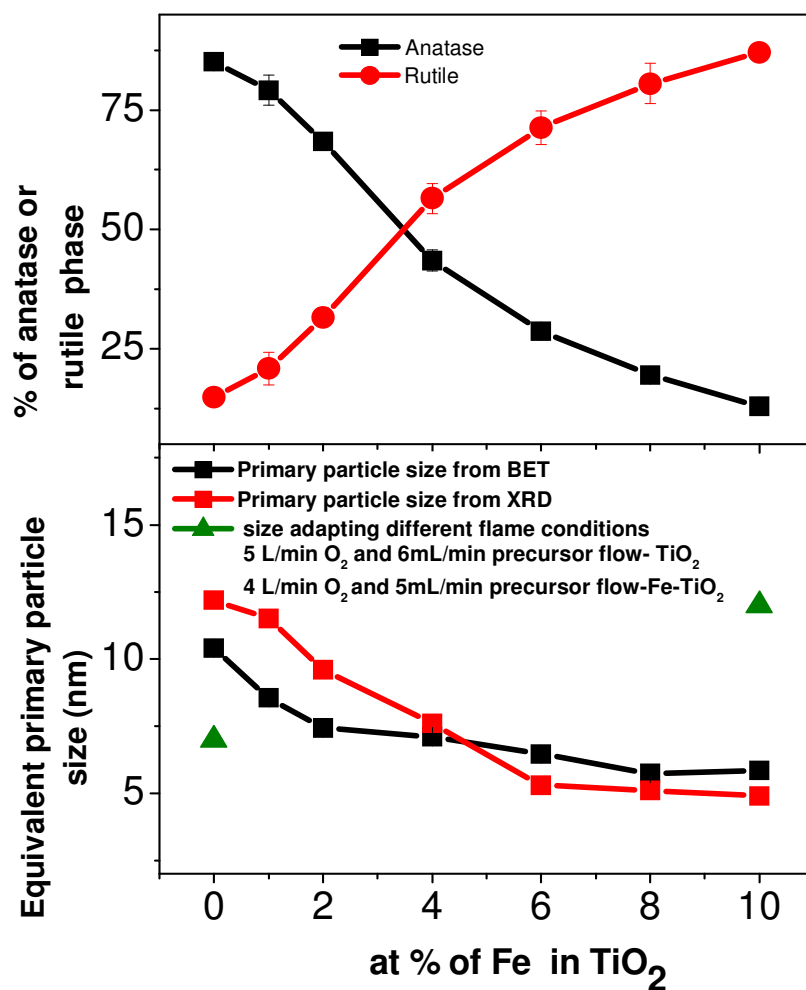


Figure S5. The crystalline phase and primary particle size of undoped and doped TiO₂. From the X-ray diffraction analysis (a) rutile phase was found to increase with increased Fe content in TiO₂ (b) The particle sizes obtained from two different techniques (XRD and BET). The green triangle points denote the particle sizes (d_{BET}) of TiO₂ or Fe doped TiO₂ at adapted flame parameters.

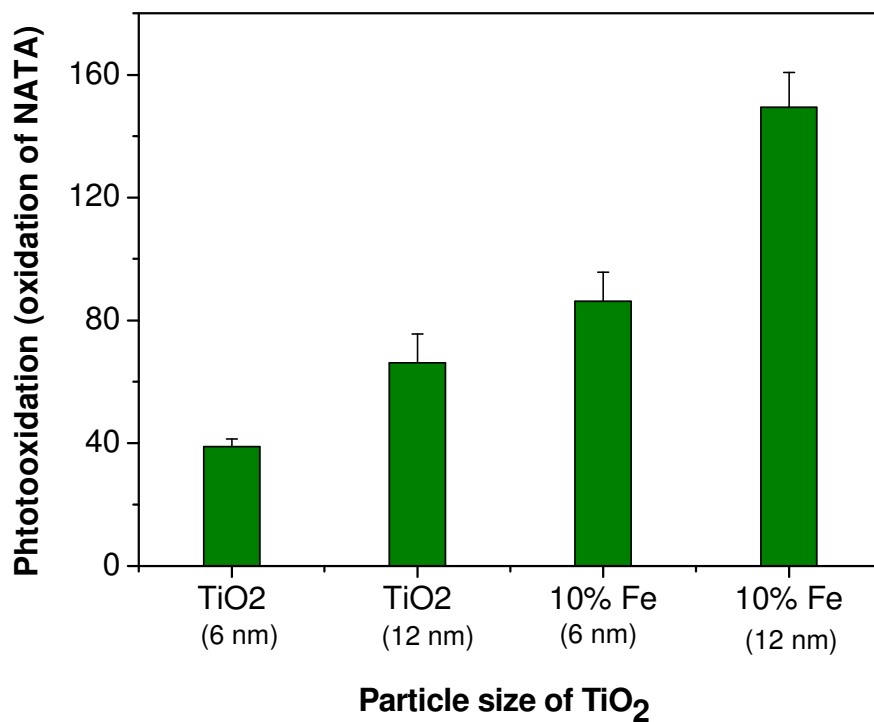


Figure S6: Photooxidation capacity of TiO₂ nanoparticles of varying sizes. The photooxidation capacity significantly decreased in the of pure TiO₂ and band gap tuned TiO₂ when the size was decreased from 12 nm to 6 nm. The particle sizes are presented in the brackets.

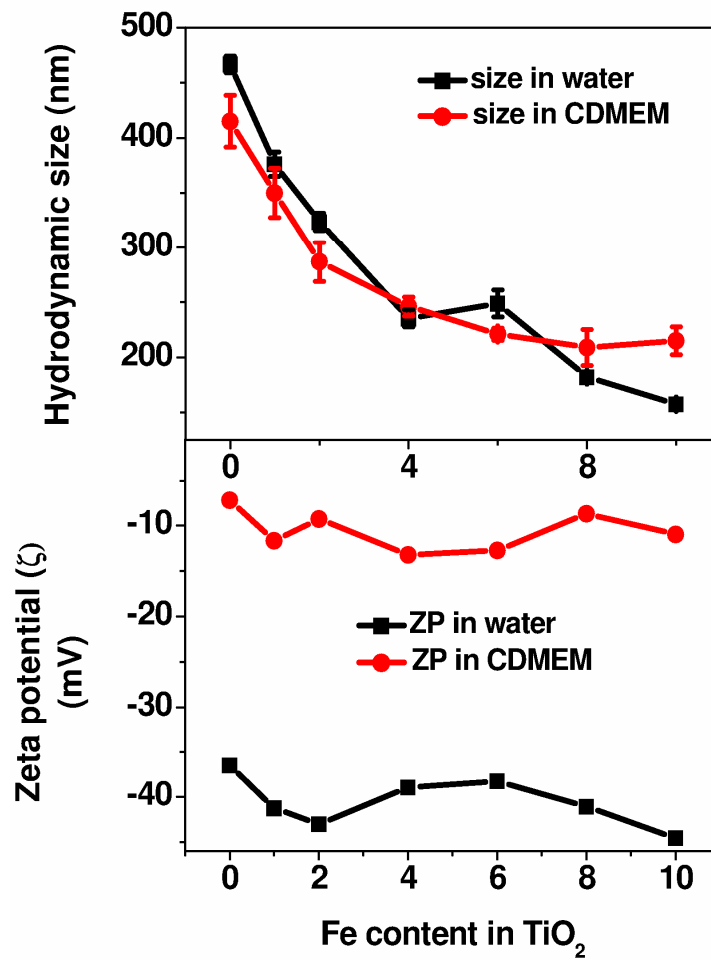


Figure S7: The hydrodynamic size and zeta potential of NPs suspended in water and CDMEM medium.

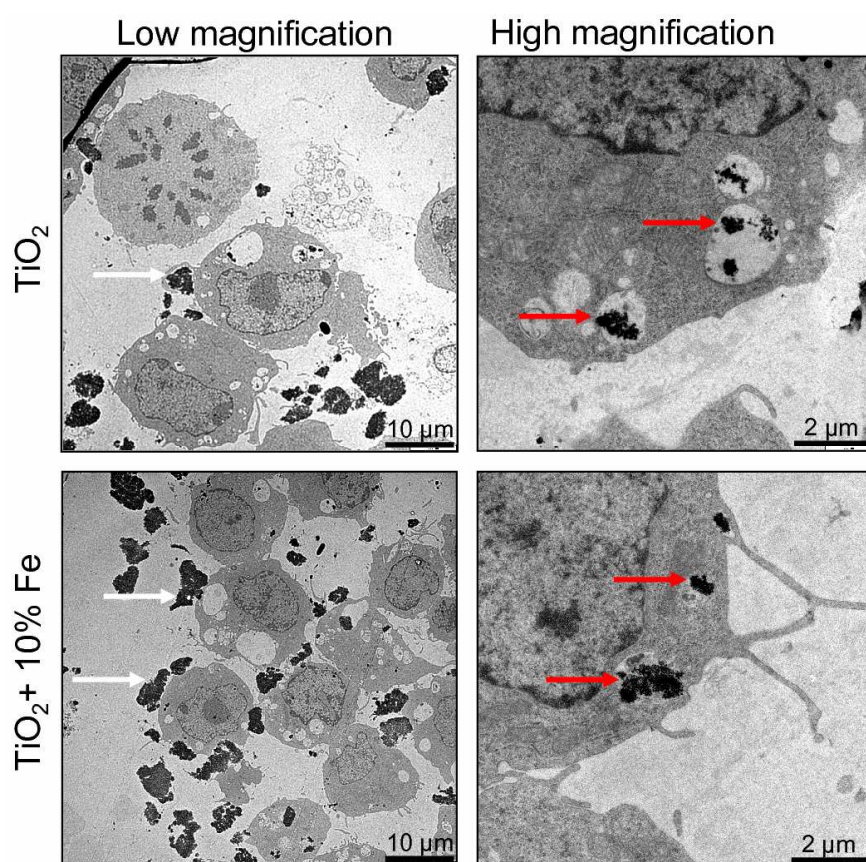


Figure S8. TEM images of nanoparticles treated RAW 264.7 cells. TiO₂ and TiO₂-10%Fe associated with the cells (outside-white arrow and inside-red arrow) showed comparable agglomeration sizes.

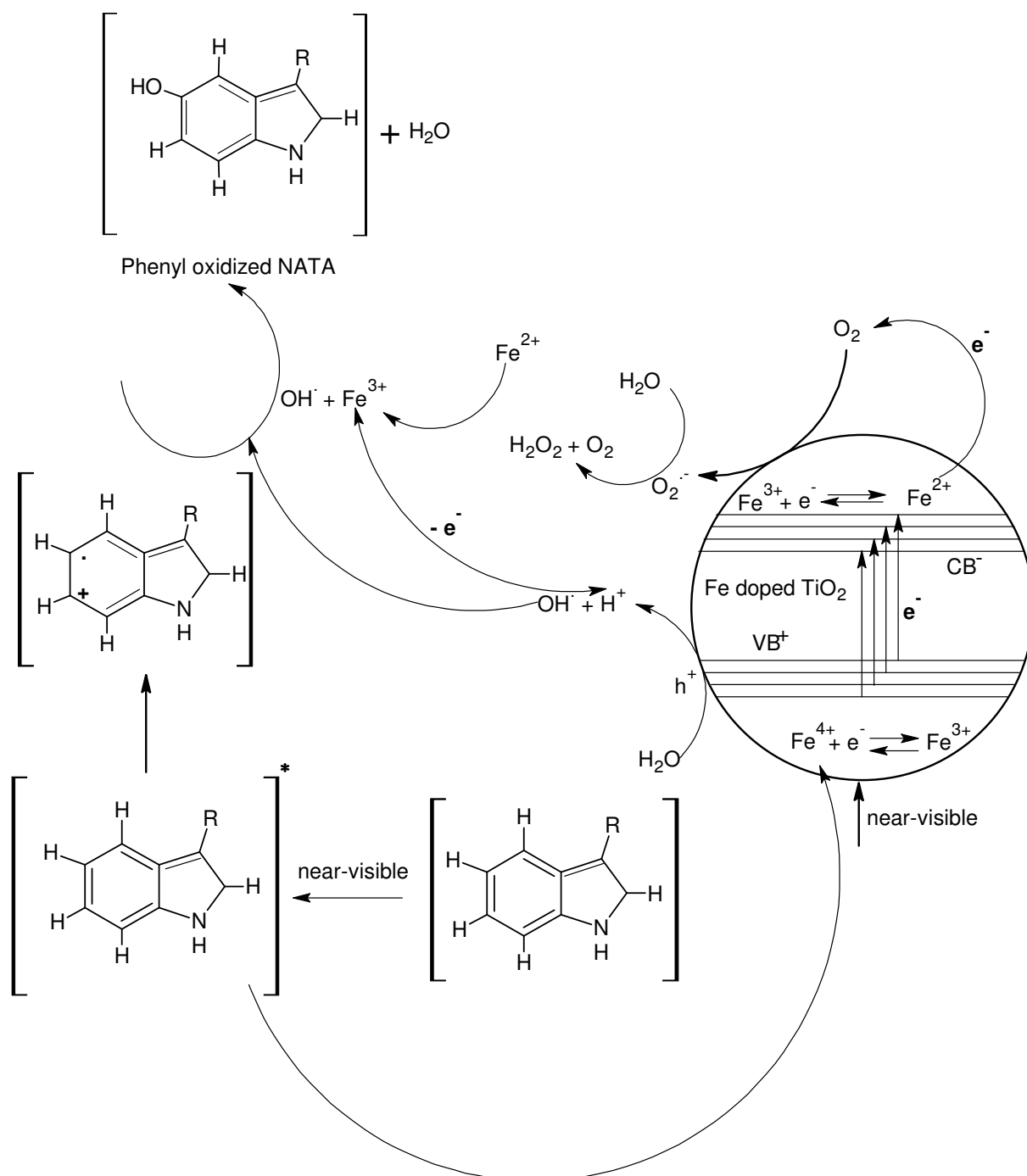


Figure S9. The oxidation of *N*-acetyl-L-tryptophanamide and hydroxyl radical generation due to near-visible light illumination to the undoped and Fe doped TiO₂ nanoparticles. During photo-oxidation of NATA in presence of doped TiO₂ nanoparticles, the electron excited to the conduction band is taken up by Fe³⁺ and reduces superoxide generation as well as the recombination of e⁻/h⁺ pair. Holes (h⁺) in the valence band abstract an electron from surface associated NATA, leading to NATA oxidation. The simultaneous redox process of trapping electrons in the Fe³⁺ states is enhanced by surface molecular dioxygen to produce ROS. These species react with charged NATA molecules to form phenyl oxidized NATA. The subsequent

oxidized and unstable Fe^{4+} species are immediately reduced to Fe^{3+} by electron transfer from the excited NATA molecule during light illumination.