

Supporting Information

Combinatorial effects of non-thermal plasma oxidation processes and photocatalytic activity on the inactivation of bacteria and degradation of toxic compounds in wastewater

A. Raji ^a, D. Vasu ^a, K. Navaneetha Pandiyaraj ^{b*}, Rouba Ghobeira^c, Nathalie De Geyter^c, Rino Morent^c, Vandana Chaturvedi Misra^d, S. Ghorui^d, M. Pichumani^e, R. R. Deshmukh^f and Mallikarjuna N. Nadagouda^g

^a Research Division of Plasma Processing (RDPP), Department of Physics, Sri Shakthi Institute of Engineering and Technology, Coimbatore, 641062, India.

^b Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641020, India

^cResearch Unit Plasma Technology (RUPT), Department of Applied Physics, Faculty of Engineering and Architecture, Ghent University, Ghent, 9000, Belgium.

^dLaser and Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India.

^eDepartment of Nanoscience and Technology, Sri Ramakrishna Engineering College, Coimbatore-641022, India

^fDepartment of Physics, Institute of Chemical Technology, Matunga, Mumbai, India

^gDepartment of Mechanical and Materials Engineering, Wright State University, Dayton, Ohio 45324, United States.

S1. Materials and Methods

Photoluminescence (PL) spectra of the nanoparticles (NPs) were recorded using a spectrofluorometer (FP8300, JASCO, Japan). The optical properties of TiO₂ and Cu-TiO₂ were examined by ultraviolet-visible diffuse reflection spectroscopy (UV-Vis DRS) using a UV-Visible NIR spectrophotometer (V-770, JASCO, Japan).

S2. Results and Discussion

S2.1. UV-Vis DRS spectral analysis

Figure-S1a shows the UV-Vis absorbance spectra of the synthesized pure TiO₂ and Cu-TiO₂ NPs. The pure TiO₂ displayed an absorbance peak at approximately 365 nm representing a typical bandgap energy of 3.08 eV [1-3]. Doping TiO₂ NPs with Cu generally causes a narrowing band gap, which reduces the rate of electron-hole recombination resulting

in a red shift [4]. Contradictorily, in our case, a shift in the absorbance peak towards lower wavelength of approximately 295 nm (blue shift) was observed. This blue shift might be due to the quantum size effect [4]. Moreover, the increment in particle size of Cu-TiO₂ probably caused a decrement in the absorbance spectrum wavelength (blue shift) [5]. In the absorbance spectrum, the intensity of the absorbance maxima (relative maxima) increased. The addition of metal (i.e. Cu in our case) probably initiated this hyperchromic shift in the absorbance maxima intensity. The DRS peaks of pure TiO₂ and Cu-TiO₂ were observed at 3.08 and 2.88 eV respectively. This is due to the oxygen vacancies and the sub-band states of the Cu dopant [6] (**Figure-S1b**). Hence, the observed bandgap decreased in the Cu-doped TiO₂ NPs. The obtained results also support the hypothesis of the particle size – band gap relation (the band gap decreased when the particle size increased).

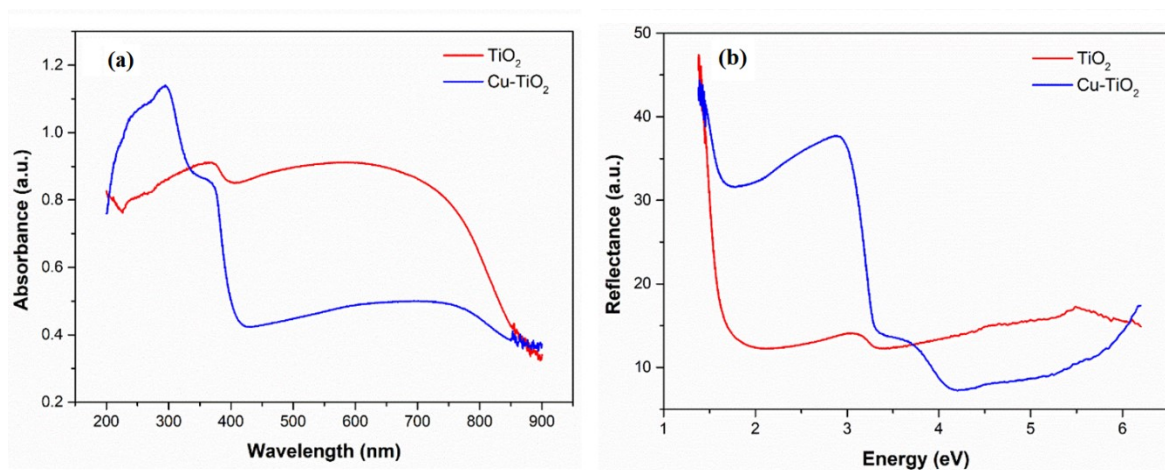


Figure- S1 (a) UV-Vis spectra and (b) diffuse reflection spectra of TiO₂ and Cu-TiO₂ NPs

S2.2. Photoluminescence emission spectral analysis

Figure-S2, depicting the PL spectra of pure TiO₂ and Cu-TiO₂ NPs, shows that the emission intensity of the Cu-TiO₂ NPs is slightly higher than the pure TiO₂ NPs without any shifts in the emission wavelength. Since the size of the Cu-TiO₂ NPs is larger than the pure ones, the surface-to-volume ratio was also decreased. This increased the oxygen defects and vacancies, which further up surged the photoluminescence intensity thus enhancing the photocatalytic activity of the Cu-TiO₂ NPs [7].

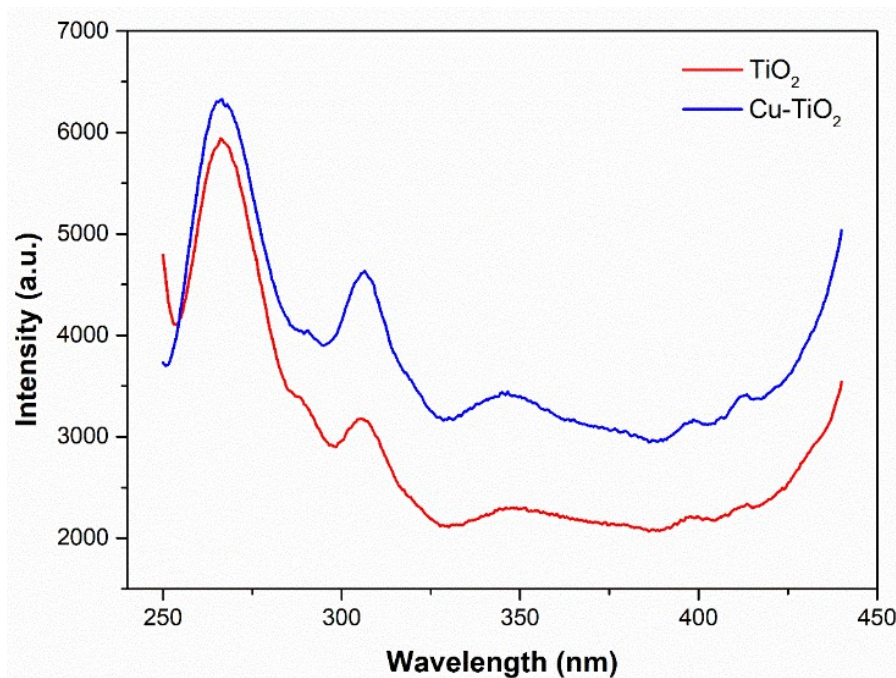


Figure-S2 Photoluminescence (PL) spectra of TiO₂ and Cu-TiO₂ NPs

References

- [1] J. Panda, U.P. Singh, R. Sahu, Synthesis, characterization of TiO₂ nano particles for enhancement of electron transport application in DSSC with Cu-BPCA Dye, IOP Conf. Ser. Mater. Sci. Eng. 410 (2018) 012008.
- [2] N.K. Sethy, Z. Arif, P.K. Mishra, P. Kumar, Green synthesis of TiO₂ nanoparticles from Syzygium cumini extract for photo-catalytic removal of lead (Pb) in explosive industrial wastewater, Green Process. Synth. 9 (2020) 171–181.
- [3] R. Nankya, K.N. Kim, Sol-gel synthesis and characterization of Cu-TiO₂ nanoparticles with enhanced optical and photocatalytic properties, J. Nanosci. Nanotechnol. 16 (2016) 11631–11634.
- [4] C.Y. Tsai, H.C. Hsi, T.H. Kuo, Y.M. Chang, J.H. Liou, Preparation of Cu-doped TiO₂ photocatalyst with thermal plasma torch for low-concentration mercury removal, Aerosol Air Qual. Res. 13 (2013) 639–648.
- [5] E.G. Goh, X. Xu, P.G. McCormick, Effect of particle size on the UV absorbance of zinc oxide nanoparticles, Scr. Mater. 78–79 (2014) 49–52.
- [6] T. Raguram, K.S. Rajni, Synthesis and analysing the structural, optical, morphological, photocatalytic and magnetic properties of TiO₂ and doped (Ni and Cu) TiO₂ nanoparticles by

sol–gel technique, *Appl. Phys. A Mater. Sci. Process.* 125 (2019) 288.

[7] S. Mandal, N. Jain, M.K. Pandey, S.S. Sreejakumari, P. Shukla, A. Chanda, S. Som, S. Das, J. Singh, Ultra-bright emission from Sr doped TiO₂ nanoparticles through r-GO conjugation, *R. Soc. Open Sci.* 6 (2019) 190100.