Microscopic and Spectroscopic Understanding of Non-metal Dopants in Photocatalytic Properties of Titania

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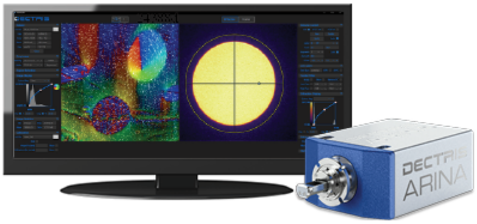

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Meeting-report

Microscopic and Spectroscopic Understanding of Non-metal Dopants in Photocatalytic Properties of Titania

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Research into sustainable renewable energy sources has led to numerous innovative findings in search of a suitable catalyst that will be stable and possess the properties necessary for effective photocatalytic activities. Recently, photocatalysis has been gaining more insight due to the simplicity of setup, low cost, and effectiveness. Improvement of photocatalytic properties of catalyst can be achieved through detailed investigations of parameters required for the fabrication of efficient photocatalyst [1]. Photocatalysis has played a key role in many environmental applications, including water remediation [2], water splitting [3], and battery application [4]. TiO_2, which has a high electron-hole recombination rate, is enhanced photo-catalytically when modified with other elements. Non-metal dopants have played a key role in enhancing light absorption and photocatalytic properties of TiO_2 [5, 6]. The contribution of dopants in modulating the properties and light absorption of TiO_2 is evident in the monitoring of the band gap of TiO_2. Though Li et al. have outlined some advantages and disadvantages of metal and non-metal dopants [7], non-metal dopants have been frequently used due to their greater synergistic effect [8]. Non-metal dopants, such as nitrogen, carbon, phosphorus, selenium, and sulfur, have been reported to introduce orbitals to the oxygen and titanium states in the valence band of titanium dioxide, thereby reducing its band gap. This enhances the light absorption of TiO_2 by reducing its band gap, allowing its photo-absorption to be extended to the visible region. Irfan et al. attributed the shift in the wavelength of absorption band after non-metal doping of TiO_2 to orbital mixing of TiO_2 and the impurity, production of vacancies at O_2 sites as well as raising of valence band of TiO_2. The use of nitrogen dopant results in the interaction of nitrogen 2p and oxygen 2p states which raises the valence band level of TiO_2, while the conduction band remains unchanged [9][10]. The impurity energy levels from the non-metals have also been observed to act as electron traps, reducing recombination of charge carriers [9]. Theoretical studies have been employed to understand the role of non-metal dopants in TiO_2 and has proposed non-metal dopants as promising pathway to enhance the photocatalytic activity of TiO_2 [9][11][12]. Overall, these orbital interactions help to narrow the band gap of TiO_2 for enhanced light absorption for efficient photocatalytic activity.

In this study, a simple, low-cost, and yet effective sol-gel route was employed to synthesize carbon and nitrogen-doped titania (CN-TiO_2) using *titanium (IV) isopropoxide as precursor, p*luronic F-127 block copolymer as surfactant, urea as carbon and nitrogen source, and ethanol as solvent. The composites were collected via an evaporation-induced self-assembly technique. Crystalline CN-TiO_2 was obtained by pyrolyzing the as-formed sample at 800 °C at a ramping rate of 2 $^{o}Cmin^{-1}$ for 3 h in nitrogen condition. Electron microscopy imaging with energy-dispersive x-ray mapping, x-ray diffractometry, x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and N_2 adsorption and desorption analysis confirms successful doping of carbon and nitrogen into porous TiO_2.

SEM images of the synthesized TiO_2 showed well dispersed samples (**Fig. 1a**) with mixed morphologies, predominantly spherical. This dispersion is due to the contribution of the F127 used as surfactant [13][14]. The presence of C, N, Ti and O were observed through EDX analysis and elemental composition was also confirmed through XPS. EDX analysis revealed that CN-TiO_2 contains 36% Ti, 28.7% O, 27.1% C, and 8.2% N by mass when the sample is calcined in N_2 atmosphere at 800 °C. The D and G bands from Raman studies also confirmed the presence of carbon. XRD clearly revealed shifting of peaks, characteristic of doping of TiO_2. Diffusion reflectance spectrophotometer (DRS) was used to study the absorbance spectra for the synthesized samples showed enhanced light absorption across 400 nm to 800 nm wavelength band making it effective for use as photocatalyst both in the UV and visible regions (solar light). Kubelka-Munk function which is used to analyze the scattering and absorption properties of a material employed to determine the band gap energy of semiconductors from diffuse reflectance spectra. From the Tauc equation, $(\alpha h\nu)^{1/n} = A\,(h\nu - E_g)$, where α, h, ν, A, and E_g are respectively the absorption coefficient, Plank's constant, incident light frequency, proportionality constant and band gap, the absorption coefficient is replaced with the Kubelka–Munk function, $F(R_\infty)$, to obtain, $(F(R_\infty)\,h\nu)^{1/n} = A\,(h\nu - E_g)$, since the application of Kubelka–Munk theory revealed that absorption coefficient (α) is proportional to $F(R_\infty)$ [15]. $F(R_\infty) = K/S = (1 - R_\infty)^2/2R_\infty$ where, R_∞ is the percentage reflectance from the DRS data, *K* is the absorption coefficient, *S* is the scattering coefficient and ∞ denotes the thickness of the sample. Plotting $(F(R_\infty)\,h\nu)^{1/n}$ on the y-axis against hν on the x-axis and extrapolating the linear region of the slope gives the band gap of the photocatalyst and the nature of the electron transition is determined as direct transition band gap for n = 1/2 or as indirect for n = 2. Band gap from Tauc plot (**Fig. 2**), showed that synthesized CN-TiO_2 has improved light absorption property as compared to the commercially available TiO_2 (TiO_2 – P25). Amazingly, this enhancement in light absorption of the synthesized TiO_2 as compared to the direct band gap of anatase TiO_2 (3.20 eV) [16][17] was narrowed to 2.67 eV. The band gap CN-TiO_2 is further narrowed down to 2.36 eV which is attributed to the dopant effects. CN-TiO_2 also exhibited good electron transfer property in the transient current switch on and off experiment with a current density of 23 μA/cm^2 at 0 V potential vs Ag/AgCl reference electrode.

CN-TiO_2 samples were successfully synthesized using an evaporation induce self-assembly approach. Doping carbon and nitrogen significantly enhanced light absorption in visible range. Our preliminary study showed that the CN-TiO_2 shows better photocatalytic properties as compared to pure TiO_2 and the commercially available TiO_2. The synthesized material is therefore applicable for use in investigating water splitting activities for hydrogen generation in visible light. The use of urea as nitrogen precursor offered several advantages such ease of handling, and introduction of carbon as co-dopant.

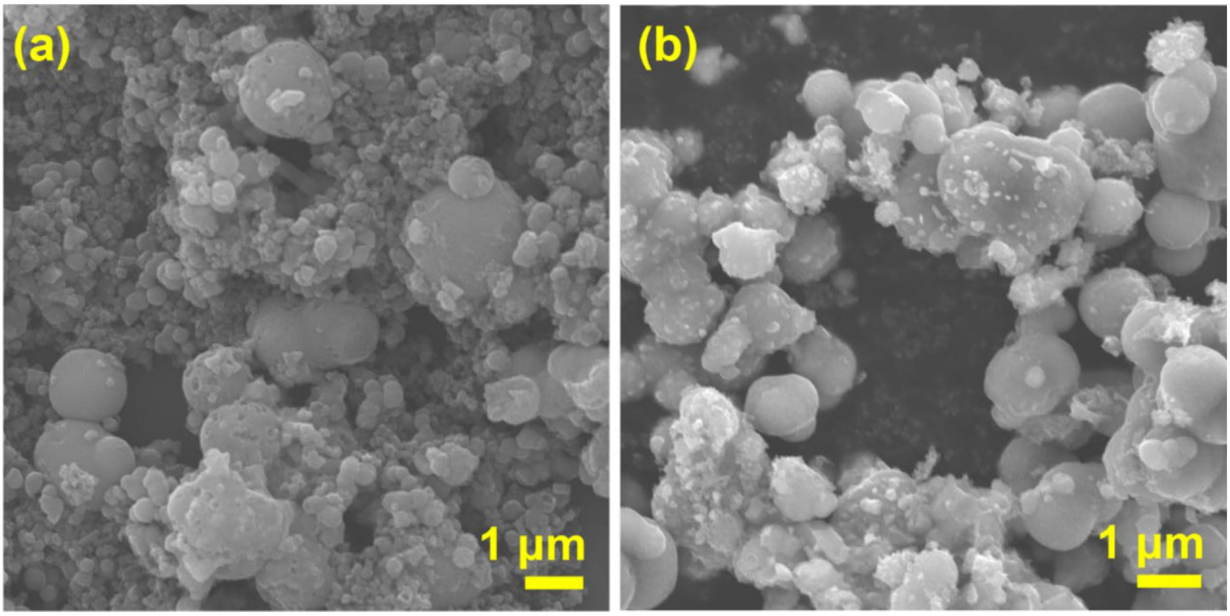

Fig. 1. SEM images of (a)TiO_2 and (b) CN-TiO_2 calcined in nitrogen condition at 800°C.

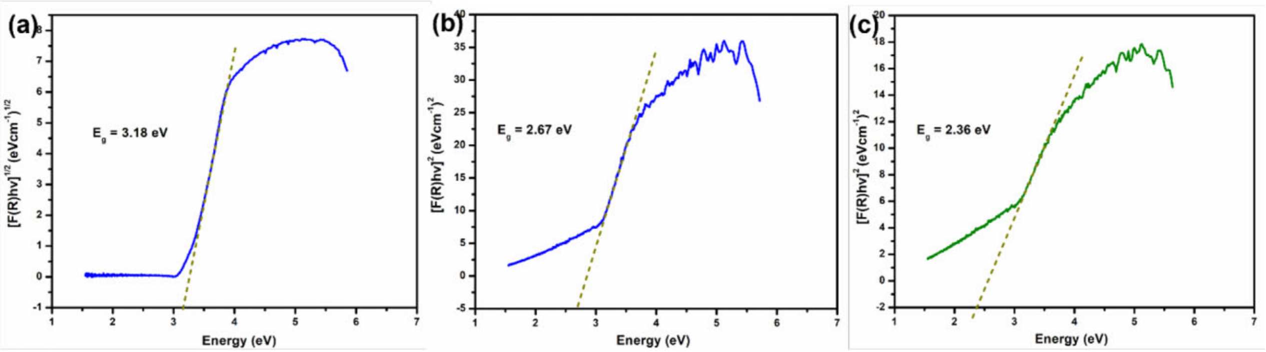

Fig. 2. Tauc plot of optical band gap of (a) Commercial TiO_2-P25, (b) TiO_2 and (c) CN- TiO_2.

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