

Supporting Information

Facile synthesis of novel nitrogen-doped carbon dots adorned zinc oxide composite for photodegradation of methylene blue

Raji Atchudan^{a,1,*}, Thomas Nesakumar Jebakumar Immanuel Edison^{a,1}, Mani Shanmugam^{c,1},
Suguna Perumal^{b,1}, Rajangam Vinodh^{d,1}, Thirunavukkarasu Somanathan^{e,1}, Yong Rok Lee^{a,*}

^aSchool of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

^bDepartment of Applied Chemistry, Kyungpook National University, Daegu 41566, Republic of Korea

*^cDepartment of Science and Humanities, Institute of Aeronautical Engineering,
Dundigal, Hyderabad 500043, India.*

^dSchool of Electrical and Computer Engineering, Pusan National University, Busan 46241, Republic of Korea

*^eDepartment of Chemistry, School of Basic Sciences, Vels Institute of Science, Technology &
Advanced Studies (VISTAS), Chennai - 600117, India*

¹Authors contributed equally to this work.

*Corresponding authors.

E-mail addresses: atchudanr@yu.ac.kr (R. Atchudan); yrlee@yu.ac.kr (Y. R. Lee)

Photocatalytic degradation measurements

The photocatalytic degradation was examined using methylene blue (MB) as an organic dye, degradation measurements were carried out in the neutral aqueous medium at room temperature under UV-light irradiation. For this experiment, the absorbance intensity of organic dyes was fixed around 1.7 counts. Typically, 20 mg of the synthesized nitrogen-doped carbon dots decorated zinc oxide nanoparticle (N-CDs@ZnO composite) was mixed into 50 mL of aqueous MB dye in a glass beaker. The suspension was placed at a 100 mm distance from the UV-light source (365 nm) and was irradiated with mild stirring until the decoloration of aqueous MB dye. A 2 mL of suspensions were collected for every 10 min time intervals and absorbance was measured until near-zero value attained by the UV-vis spectrophotometer. A similar procedure was adopted for the MB dye degradation in presence of synthesized bare zinc oxide (ZnO) nanoparticles. The percentage and rate constant (k) of MB dye degradation were calculated in the presence of synthesized bare ZnO nanoparticles and N-CDs@ZnO composite. The N-CDs@ZnO composite was recovered after the photocatalytic degradation of neutral aqueous MB dye under UV-light irradiation. Typically, the degraded mixture of MB solution was centrifuged, and then received residue was dried at 70 °C overnight in a hot air oven under atmospheric condition. The dried N-CDs@ZnO composite was again used for the photocatalytic degradation of neutral aqueous MB dye under UV-light irradiation up to three cycles (in each cycle, the same sample was placed into a fresh aqueous solution of MB for 60 min under UV-light irradiation). N-CDs@ZnO composite was recovered after three cycles and characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to determine the stability of the recycled materials as well as complete degradation of adsorbed MB dye on the N-CDs@ZnO composite.

Instrumentation Methods

Nitrogen-doped carbon dots decorated zinc oxide nanoparticle (N-CDs@ZnO composite) was successfully fabricated by a simple and direct wet-impregnation method and was characterized by various physicochemical techniques such as field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). FESEM with EDS analysis was carried out on a Hitachi S-4800 equipped with EDX at an accelerating voltage of 4 kV. XRD measurements were carried out using a PANalytical X'Pert³ MRD diffractometer with monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 30 mA and were recorded in the range from 10 to 90° (2θ). ATR-FTIR spectra were recorded in transmittance mode on a Perkin Elmer Spectrum100 in the wavenumber range from 400 to 4000 cm^{-1} by the addition of 8 scans at a resolution of 8 cm^{-1} at the core research support center for natural products and medical materials of Yeungnam University. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS System, Thermo Fisher Scientific, U.K.) was conducted using the following X-ray source: monochromated Al K α radiation ($h\nu = 1486.6 \text{ eV}$, X-ray energy = 15 kV and 150 W, spot size = 500 μm , take-off angle = 90, pass energy = 20 eV, and binding energy resolution = 0.6 eV (calibrated using Ag 3d_{5/2}). CasaXPS software was used for the deconvolution of the high-resolution XPS spectra and the binding energies were calibrated using C 1s = 284.8 eV. The C 1s, N 1s, and O 1s levels were deconvoluted by fixing full width at half maximum (FWHM) as 1.48, 1.58, and 1.22, respectively. The photodegradation measurements of MB dye were carried out in the neutral aqueous medium at room temperature under UV-light irradiation by Ultraviolet-visible (UV-vis) UV-vis absorbance. The UV-vis absorption spectra were recorded from 300 to 800 nm using an

OPTIZEN 3220UV spectrophotometer. The UV-vis diffuse reflection spectra (UV-DRS) were obtained using an ultraviolet-visible-near infrared (UV-VIS-NIR) double beam spectrophotometer (Neosys-2000, Scinco Co., Korea) equipped with a diffuse reflectance accessory. An appropriate amount of the sample was pressed uniformly in the sample holder, which was then placed at the integrating sphere for the absorbance/reflectance measurements. The range of wavelengths from 200 to 1100 nm.

Characterization of synthesized N-CDs

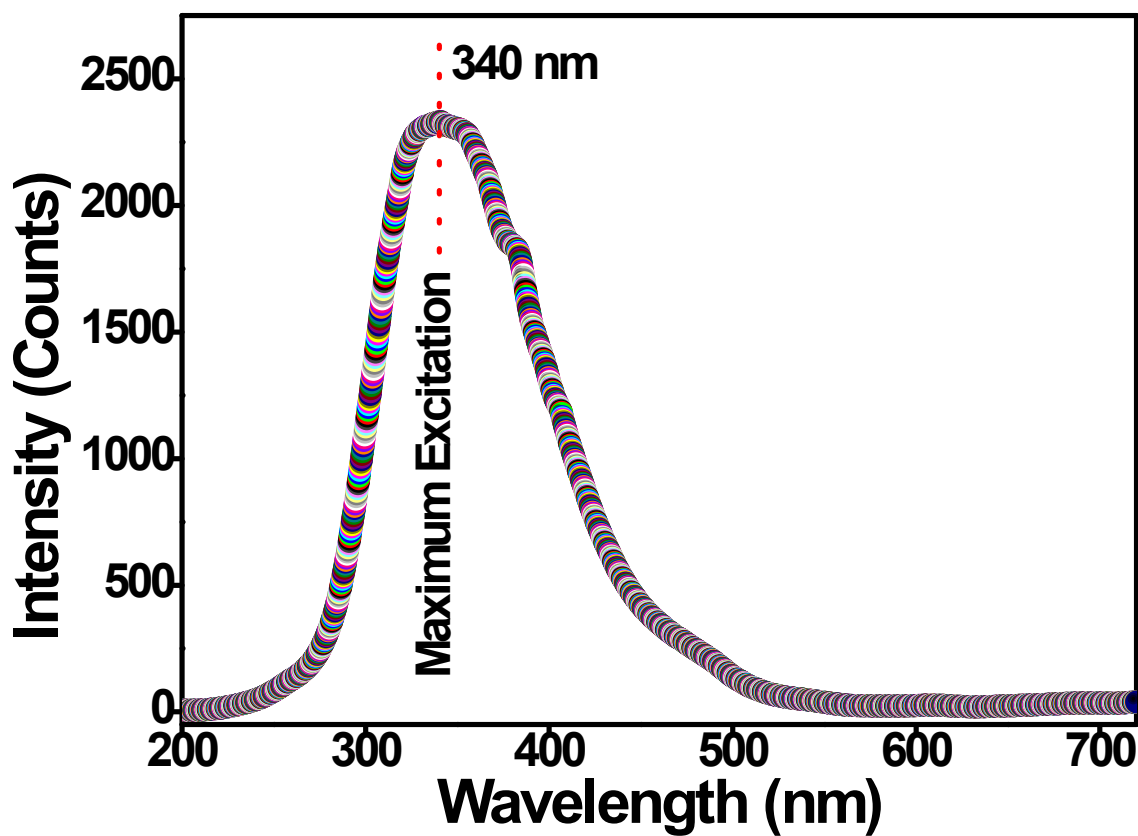


Fig. S1 Fluorescence excitation spectrum of the synthesized N-CDs.

Characterization of prepared N-CDs@ZnO composite

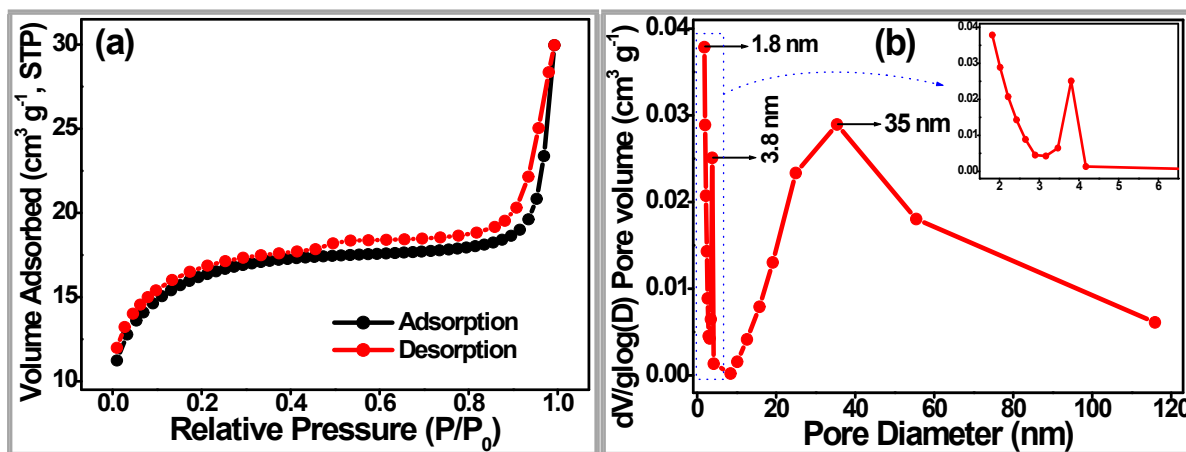


Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution graph of the prepared N-CDs@ZnO composite.

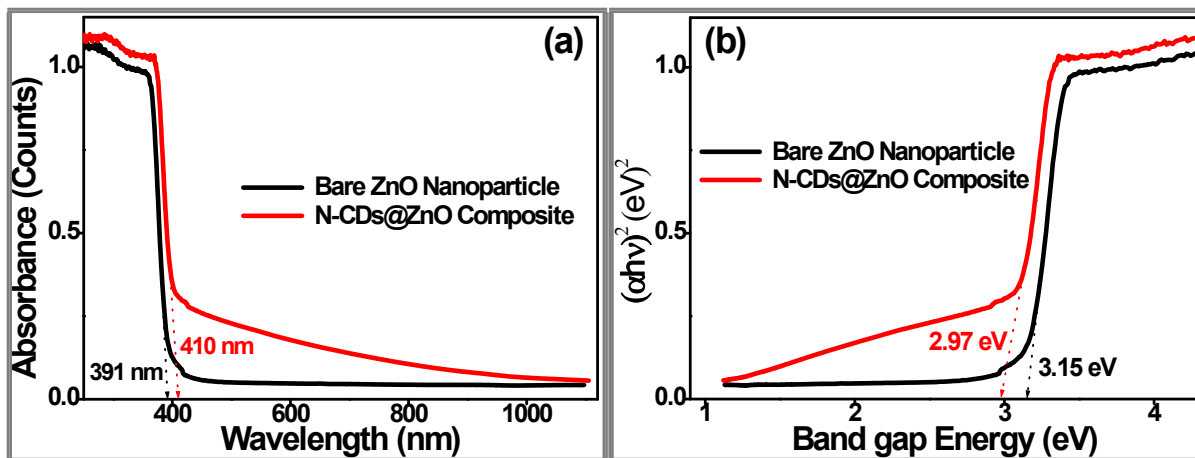


Fig. S3 (a) UV-vis diffuse reflection spectra (UV-DRS) and (b) Tauc plots of the prepared bare ZnO nanoparticles and N-CDs@ZnO composite.

Photocatalytic degradation analysis

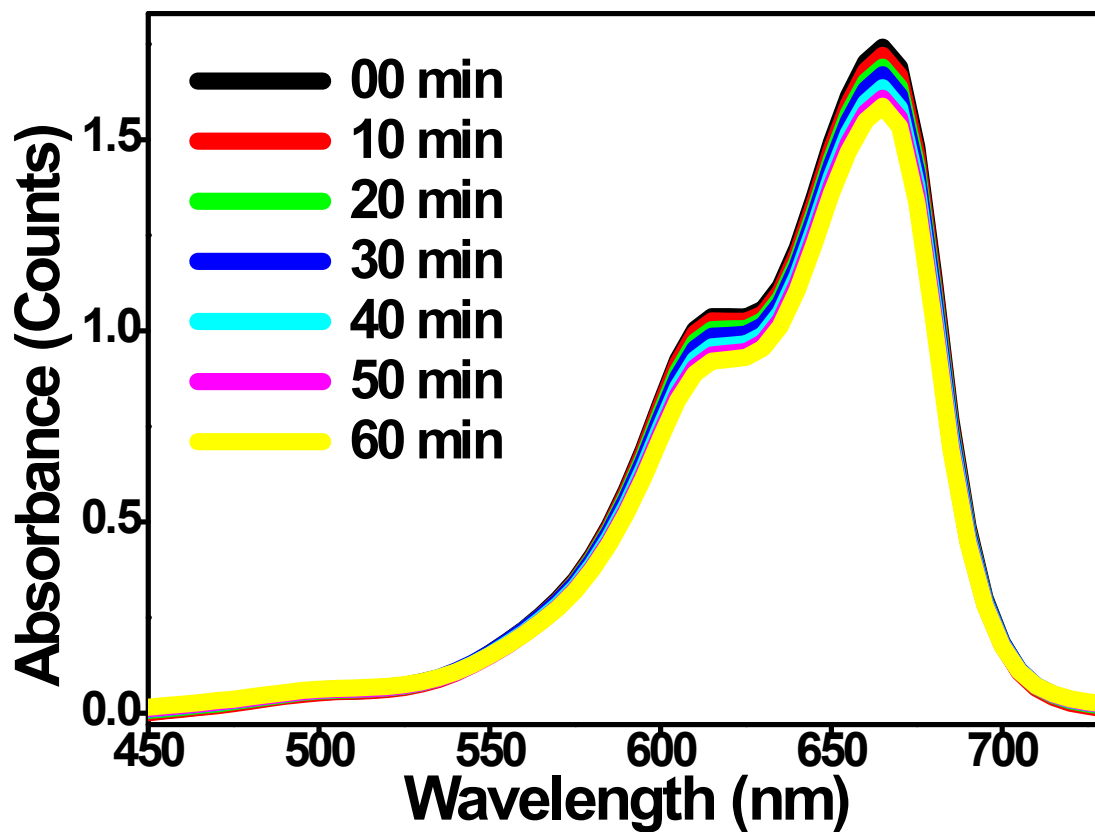


Fig. S4 UV-vis absorption spectra of aqueous methylene blue solution before and after irradiation in the absence of photocatalyst as a function of irradiation time under UV-light irradiation.

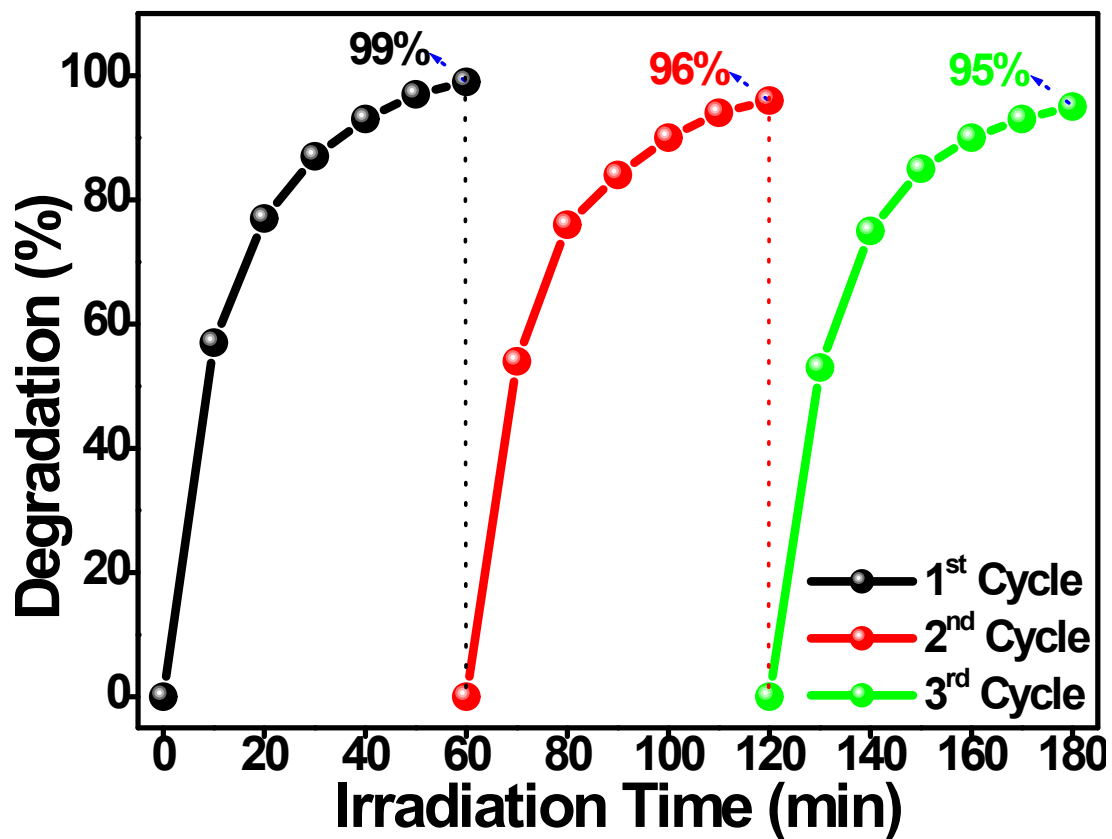


Fig. S5 Photocatalytic stability of the N-CDs@ZnO composite for the degradation of methylene blue with three cycling runs under UV-light irradiation.

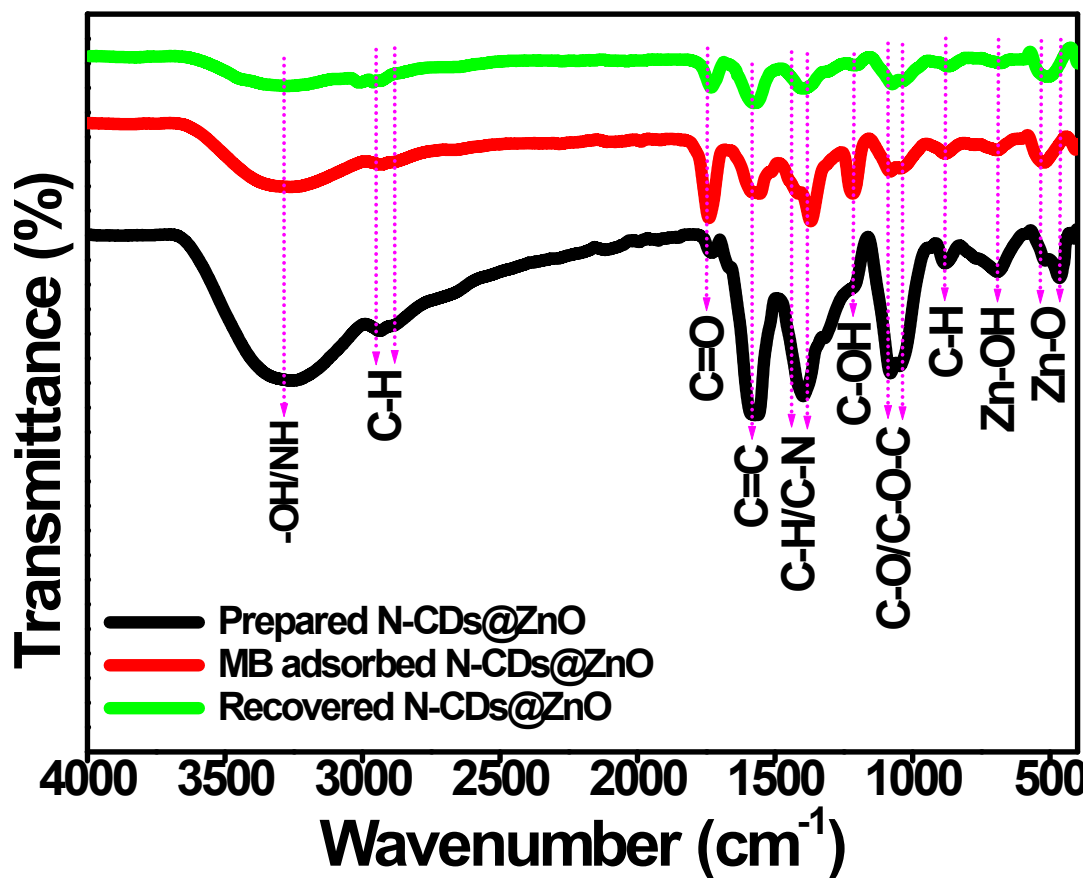


Fig. S6 ATR-FTIR spectra of prepared N-CDs@ZnO composite, MB adsorbed N-CDs@ZnO composite, and recovered (after photodegradation of MB dye) N-CDs@ZnO composite.