

Porous (001)-faceted Zn-doped anatase TiO₂ nanowalls and their heterogeneous photocatalytic characterization

Siti Khatijah Md Saad¹, Akrajas Ali Umar^{1*}, Hong Quan Nguyen², Chang Fu Dee¹, Muhamad Mat Salleh¹ and Munetaka Oyama³

¹Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

²Dept. Materials Science and Engineering, National Chiao Tung University, Hsin Chu, Taiwan, ROC

³Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan

Corresponding authors: akrajas@ukm.edu.my; Tel.: +603 89118547; Fax: +603 89250439.

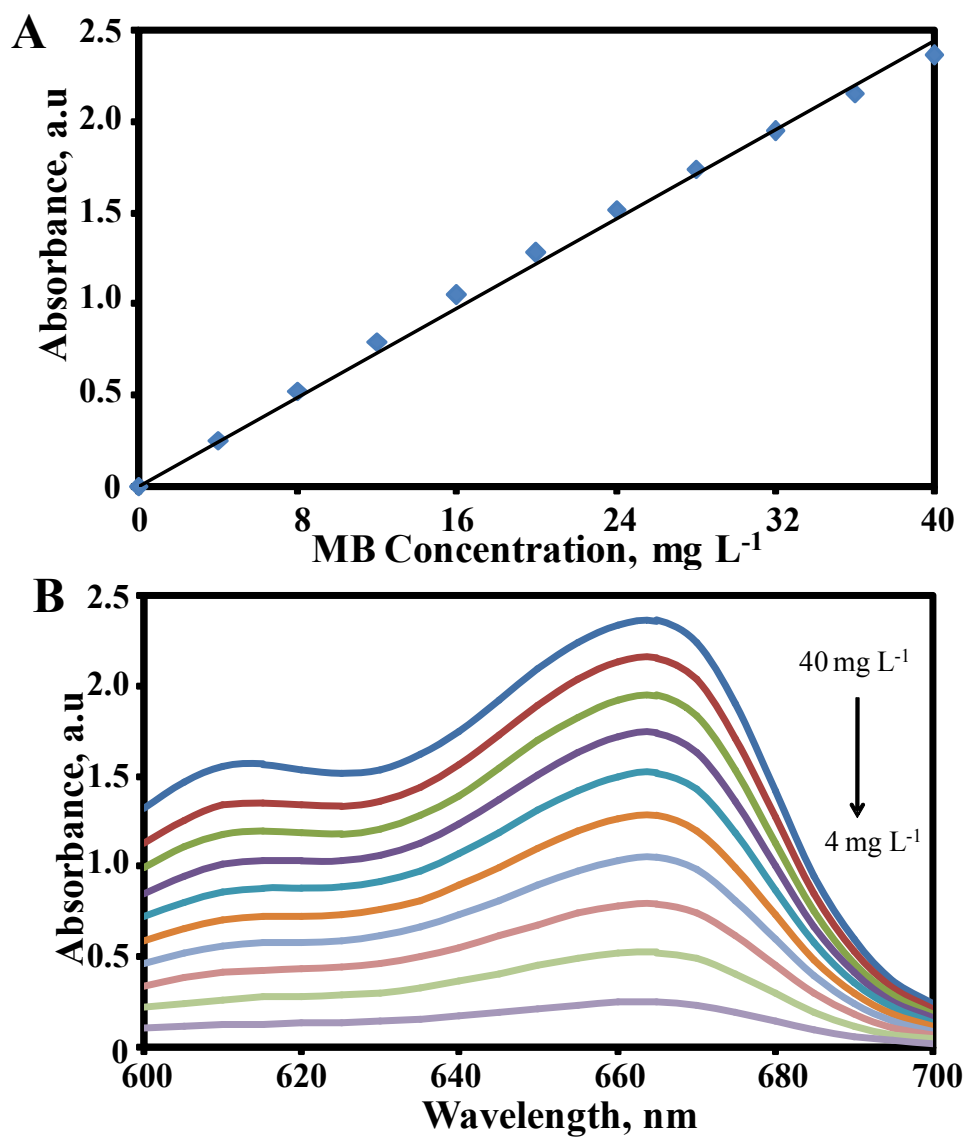


Fig. S1 (A) Calibration curve for MB concentration in mg L⁻¹ at absorption wavelength of 665 nm. (B) shows their corresponding absorption spectra.

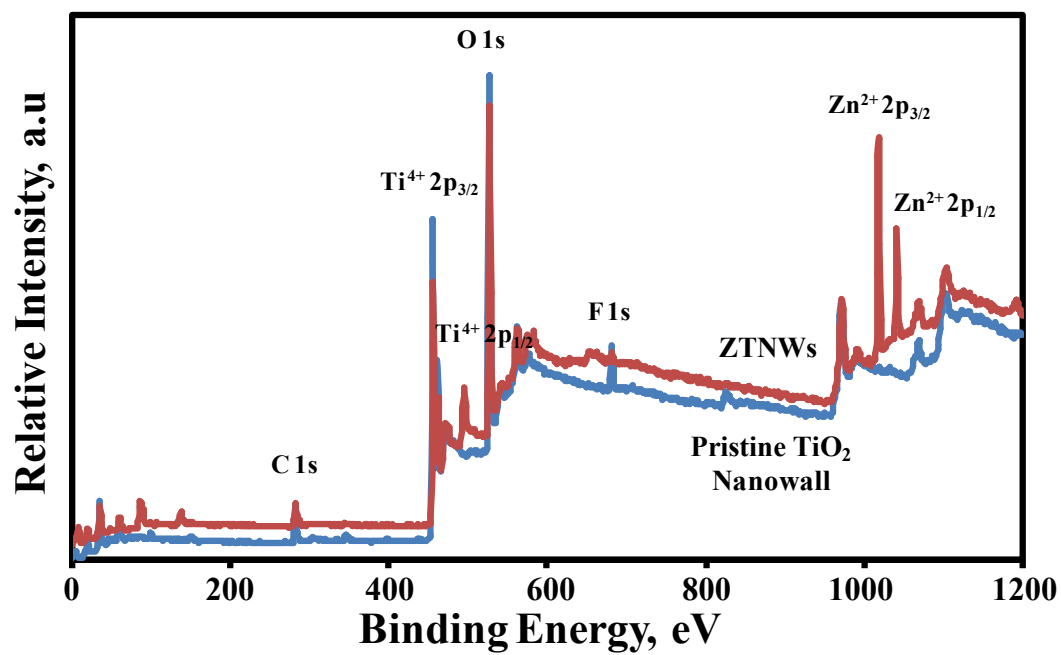


Fig. S2 Wide scan spectra of XPS for TNW and ZnTNW

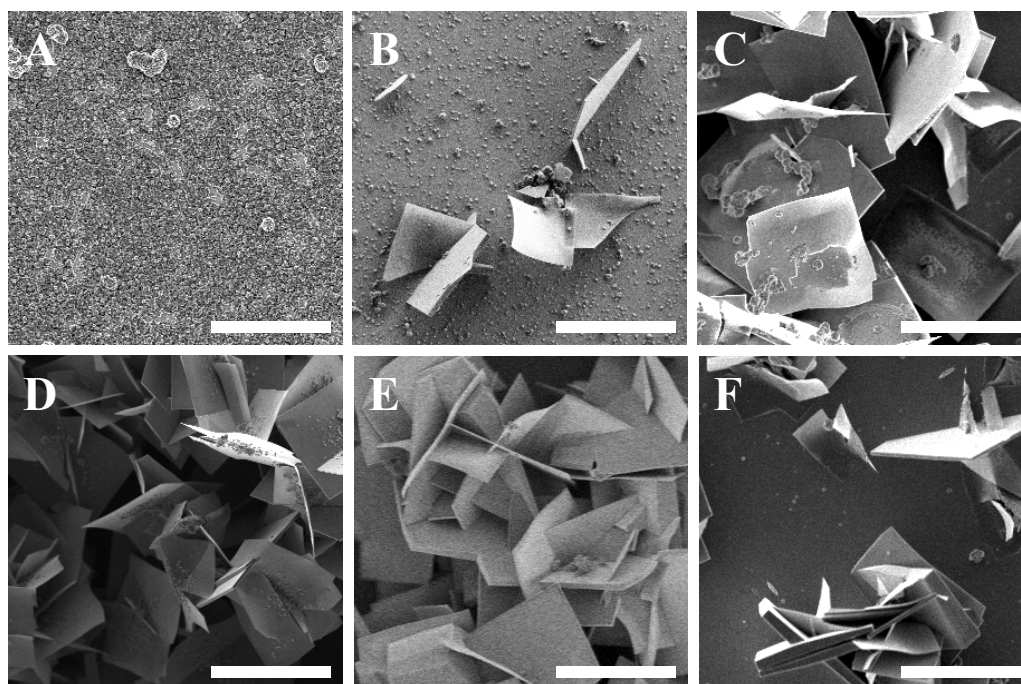


Fig. S3 FESEM micrograph of ZnTNW prepared using HMT at concentration of (A) 0.01, (B) 0.05 (C) 0.1, (D) 0.3, (E) 0.5 and (F) 0.7 M respectively. Scale bars are 10 μm .

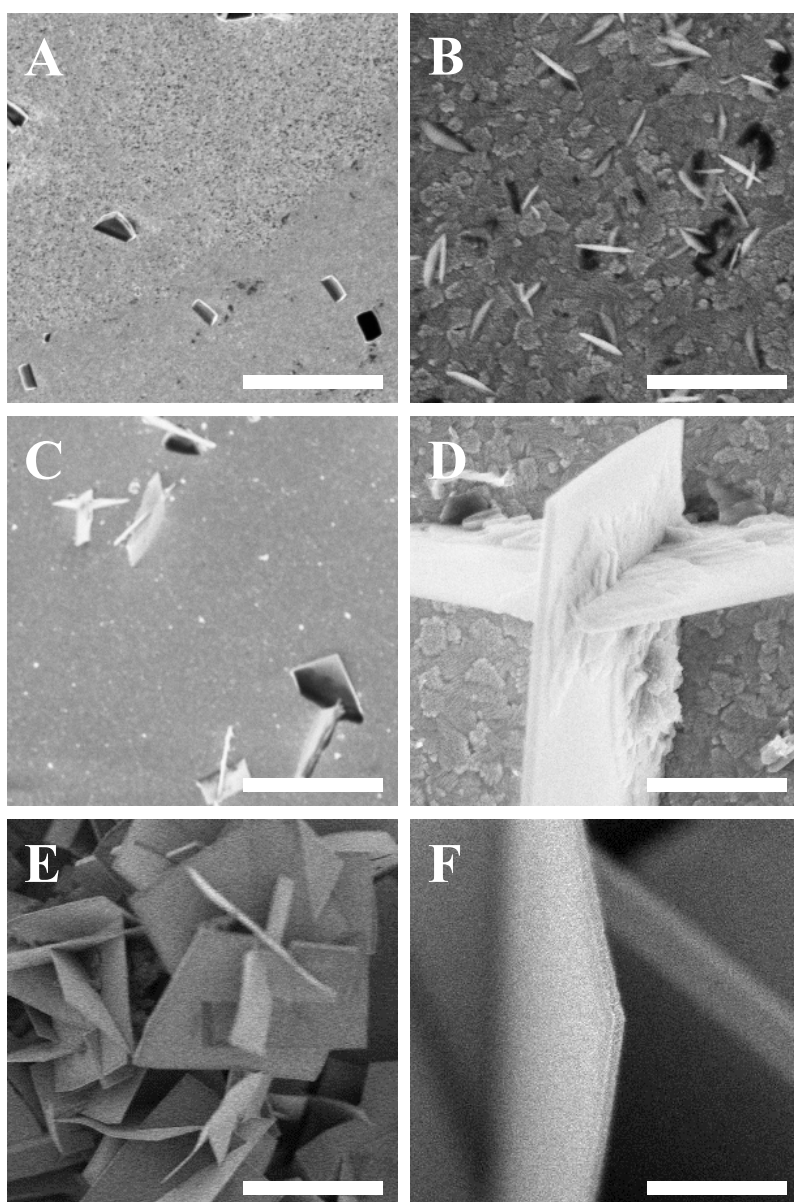


Fig. S4 FESEM micrograph for temperature treatment on ZnTNWs for different temperature of (A) 50 (B) 70 and (C) 90 °C, respectively. Scale bars are 10 μ m.

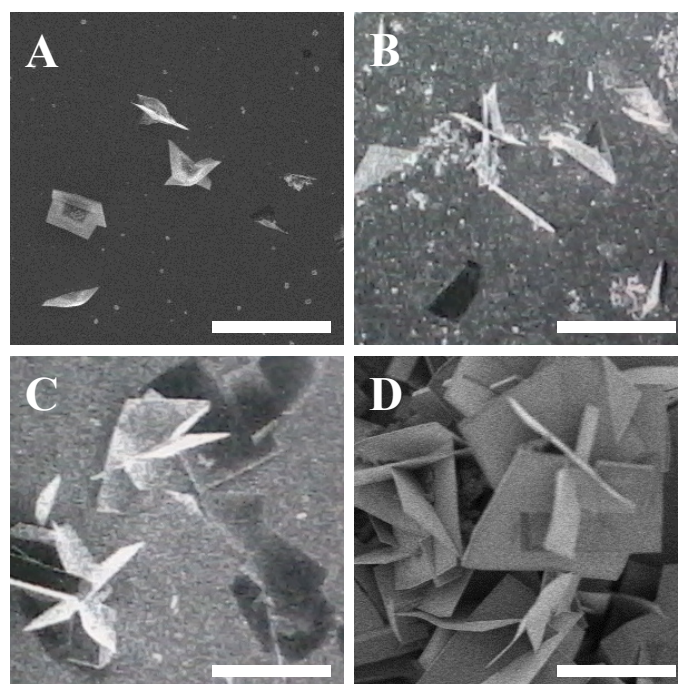


Fig. S5 FESEM micrograph of ZnTNW for different time growth at (A) 2h 30 min, (B) 3 h (C) 4h, and (D) 5h respectively. Scale bars are 10 μ m.

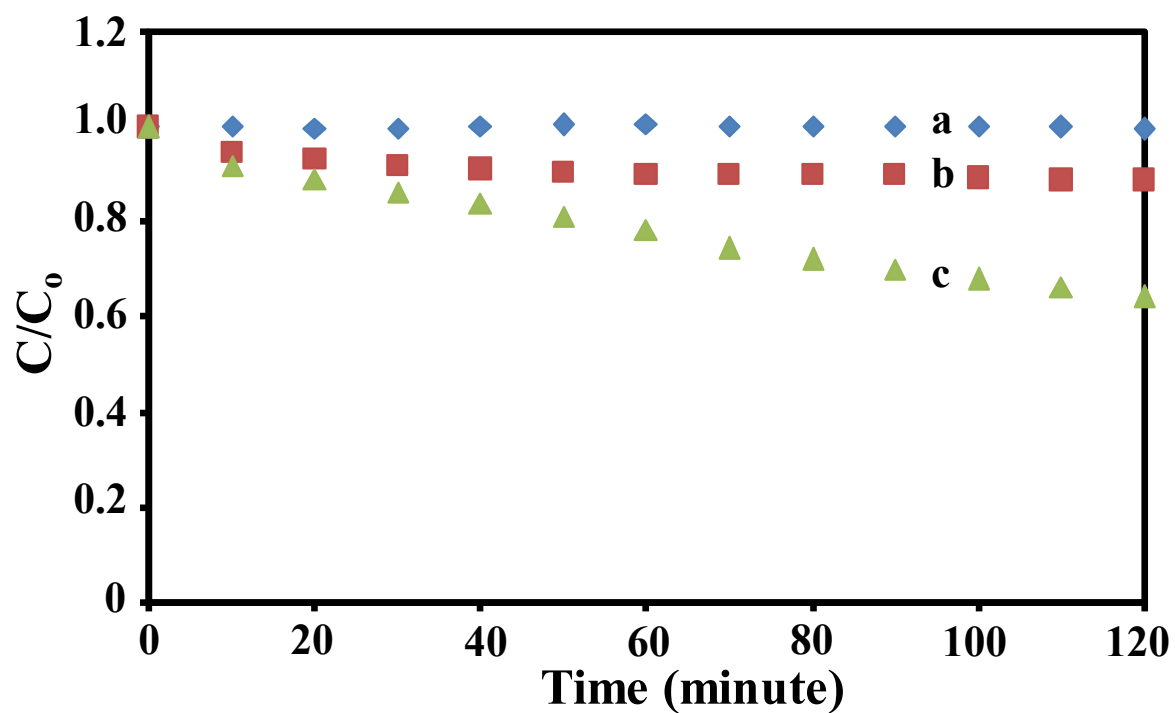


Fig. S6 Kinetic rate of MB degradation MB degradation studied for 120 minutes under different circumstances a) UV irradiated without catalyst, (b) ZTNW without UV irradiation, and (c) UV irradiated ZTNW.

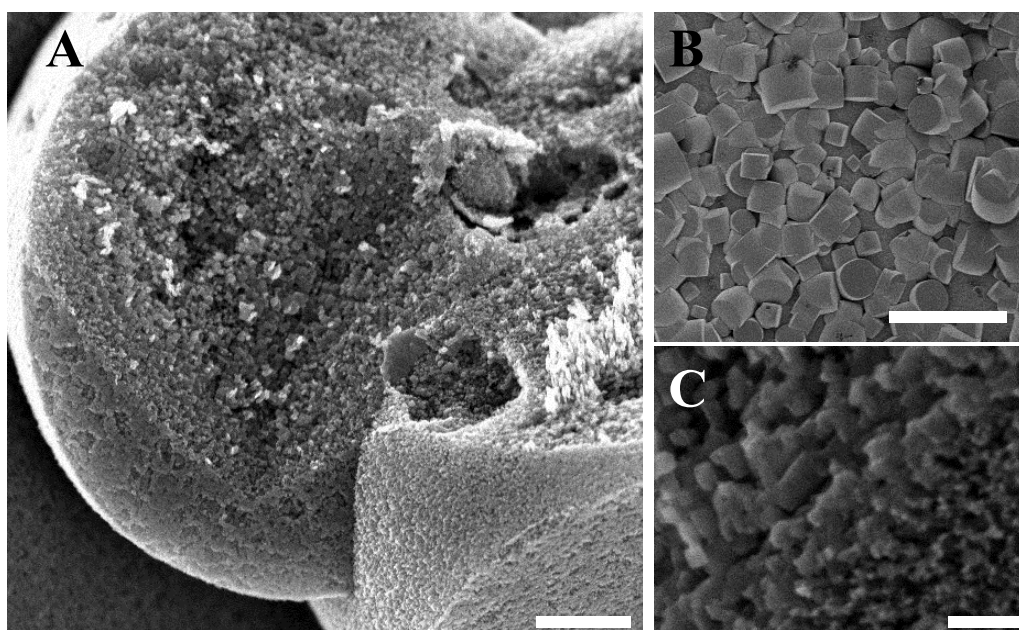


Fig. S7 (A-B) FESEM image of “bulk-volume” structure of porous TiO₂ microtablet (PTM). (C) High-resolution FESEM image showing detailed structure of nanocuboid and nanowires decorated the surface of PTM. Scale bars are 1 μm, 20 μm and 100 nm for (A), (B) and (C) respectively.

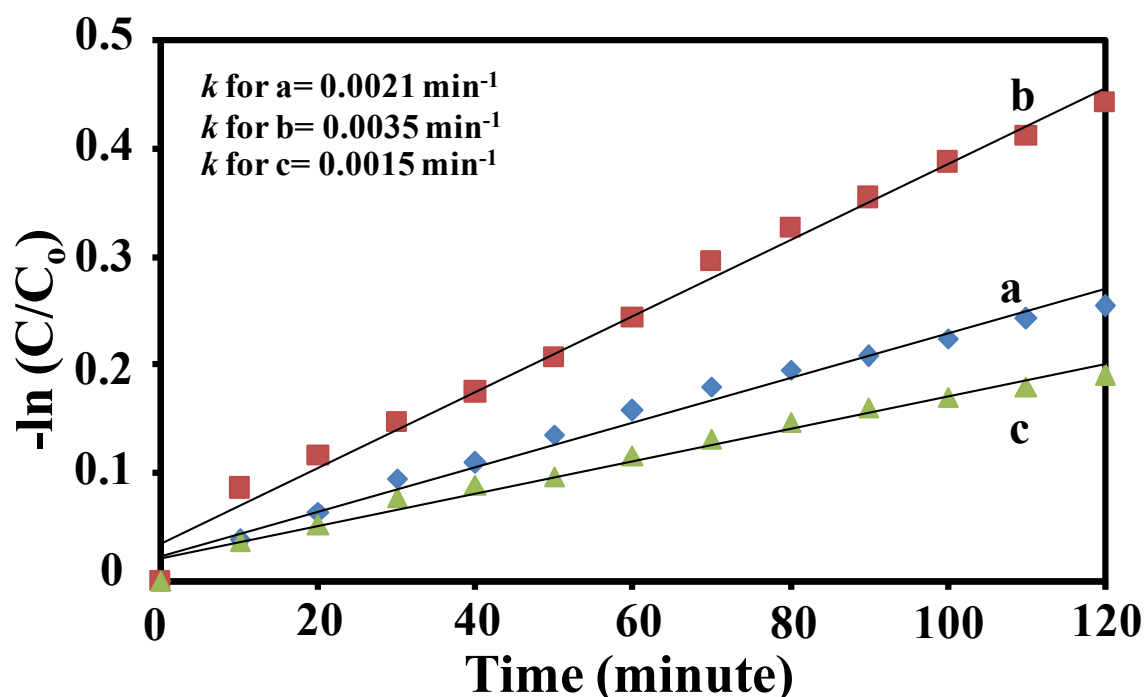


Fig. S8. Degradation kinetic of methylene blue under the ZnTNW catalyst with different Zn ions concentration, namely 4.77 (a), 7.65 (b) and 2.32 %. The samples were prepared using zinc salt concentration of 0.2, 0.5 and 1.0 mM, respectively, in the standard growth solution.

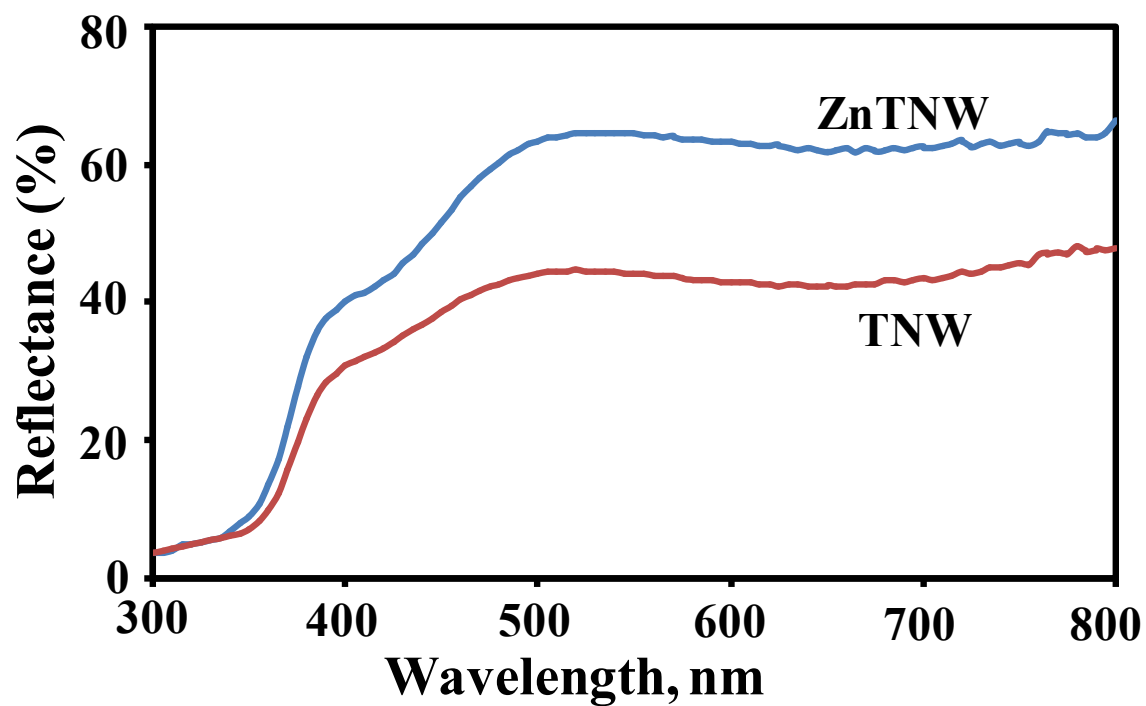


Fig. S9. Diffuse reflectance spectra of ZnTNW (a) and TNW (b).

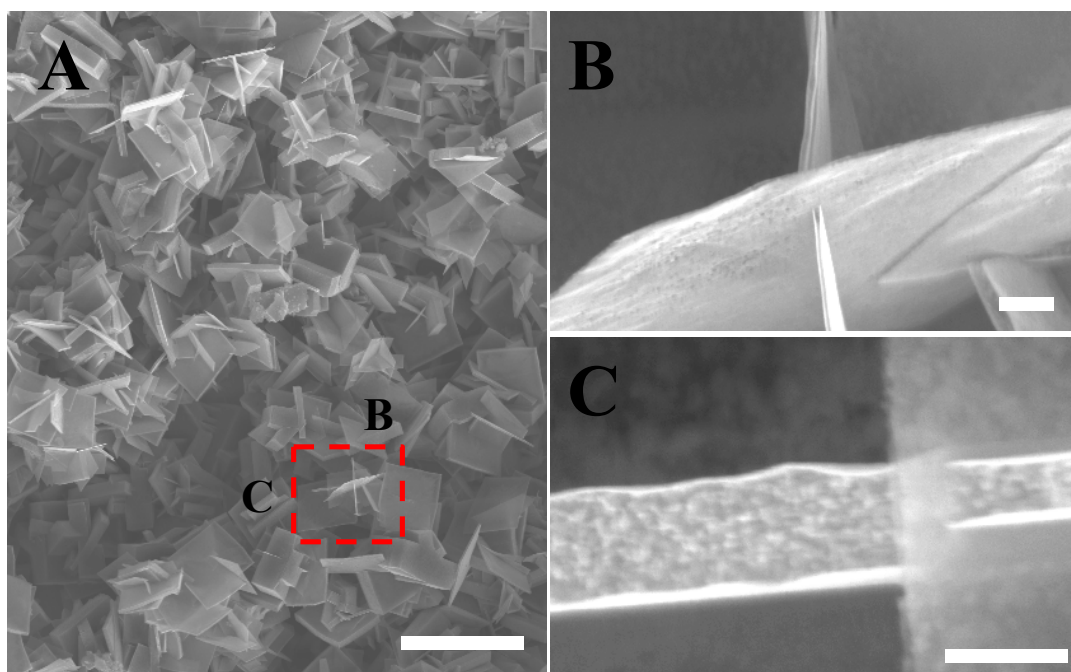


Fig. S10. FESEM image of ZnTNW after use in photocatalytic degradation of methylene blue. Scale bars are 10 μm in A and 200 nm in B and C.

Table S1. Crystallinity parameter for TNW and ZnTNW.

Sample	Crystallite Size (nm)	Peak Position, (101)	FWHM
ZnTNW	11.65	25.22	0.73
TNW	8.02	25.21	1.06

Nitrogen adsorption characterisation

We further study the total surface area of ZTNW by using Brunner-Emmet-Teller (BET) method by using Nitrogen adsorption-desorption technique at a temperature of -196°C . Since finding the surface area for the samples directly grown on the substrate seems impossible depending on the amount of the samples and the size of the substrate, we modify our prepared sixteen ITO glasses substrate with the size of 0.5×1.0 cm which was subsequently cleaned using standard cleaning method explained earlier. The weight of the blank samples was recorded after the cleaning process which will later be used in determining the exact weight of samples deposited on the ITO for nitrogen adsorption study. The cleaned ITO substrate was then used in preparing ZTNW with two substrates per bottle prepared using the same synthesis method without any modifications. The ZTNW prepared on this ITO glass was then underwent the same annealing procedure with annealing temperature of 400 oC for 30 minutes. The weight of freshly annealed samples was then directly weighed after taking out from the furnace. The total weight sample was determined by subtracting the annealed sample weight with the blank ITO weight. From this calculation, it was found that the total weight of the sample is 0.0035 g which is sufficient for nitrogen adsorption measurement. The sample prepared will not undergo degassed technique as we want the surface area measured to be in the same condition with the sample used for MB degradation study.

By using the BET method, we found out that the surface area, S_{BET} for ZTNW is 114.69 g m^{-2} . The S_{BET} obtained for this sample was relatively in comparison to powdered TiO_2 nanoparticles that are commonly used or prepared by other researcher, which was in the range of 80 - 150 g m^{-2} . However the S_{BET} for ZTNW was definitely lower when compared to our previously reported results for PTM sample that was 160.92 g m^{-2} . This was expected as compared to the PTMs samples, ZTNW is only consists of plates with smaller pores while the PTM was decorated with nanowires or nanograss-like TiO_2 structure with size of 20 nm on top of the microtablet. For degradation efficiency comparison for different shape of TiO_2 using different TiO_2 shape, we also studied the MB degradation for PTM which was prepared using our reported technique.