

Supplementary Information

Oxygen adsorption induced surface segregation of titanium oxide by activation in carbon nanofibers for maximizing photocatalytic performance

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Experimental Section

For the manufacture of the TiO₂/CNF composites, 8 wt% polyacrylonitrile (PAN, Sigma Aldrich) solutions in dimethylformamide (DMF, Sigma Aldrich) were made. Four grams of PAN was added to a 200-mL media bottle and dissolved in 46 g of DMF. Separately, 4 g of a titanium precursor (titanium isopropoxide, Sigma Aldrich) was mixed with a few drops of acetic acid, and the mixture was slowly added to the PAN solution. The resulting solution was stirred until it was completely dissolved.

The PAN nanofiber web was obtained by electrospinning at 25 °C. The apparatus setup was composed of a spinneret, a syringe pump, and a collector. The syringe pump was used to eject the doped solution at a constant rate of 40 µL/min through a spinneret, which was connected to a power supply. When a voltage of 19 kV was applied, nanofibers were electrospun to the collector. The tip-to-collector distance (TCD) was fixed at 15 cm. For stabilization, electrospun fiber webs were heat-treated in air at 250 °C for 50 min in a convection oven. Subsequently the resulting webs were carbonized at 1600 °C. Finally, the webs were activated in an oxygen atmosphere with various holding times (0, 10, 30, and 60 min) at 500 °C.

The morphology of the nanofibers was observed using a field emission scanning electron microscope (FE-SEM, NOVA Nano SEM 450) and a transmission electron microscope (TEM, Tecnai G2 F20, FEI). X-ray diffraction was carried out using a D/MAX2500V PC X-ray diffractometer (Rigaku, Japan) with monochromatized Cu K α as a source between 2 θ of 10 and 80° at a scan rate of 3°/min. X-ray photoelectron spectra were obtained (Thermo Scientific, K-alpha) using monochromated Al K α (1486.6 eV) X-rays at a pressure less than 3 $\times 10^{-7}$ Torr. The specific surface areas of the carbon materials were investigated using Brunauer-Emmett-Teller (BET)

analysis with nitrogen adsorption and a Multiport chemisorption/physisorption/micropore (3Flex) at 77 K after degassing the samples at 300°C for 2 h. The pore size distribution was measured from the desorption portion of the nitrogen isotherms using the Barret-Joyner-Halenda (BJH) method, which covers pore diameters in the range of 1.7 to 300 nm. Photo degradation activity was measured by the decomposition of methylene blue (MB) test. In 100 mL of 15-ppm MB, 0.1 g of ATCNF60, ACNF, and commercial TiO₂ powder (P25, Degussa) were dispersed to form three solutions. Each solution was stirred for 2 hr in a dark room. When equilibrium was reached, a fluorescent lamp was used to irradiate each solution with UV light. The MB concentration was measured every 2 min using a UV-Visible spectrometer (V670, JASCO Inc.). For the cycle test, samples were washed with DI water and dried to remove residues after each cycle.

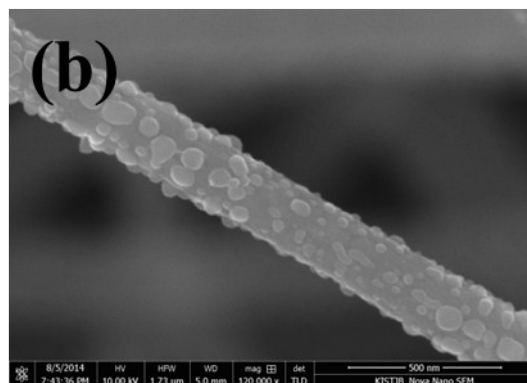
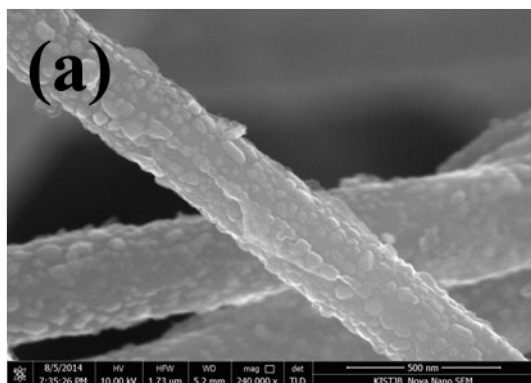
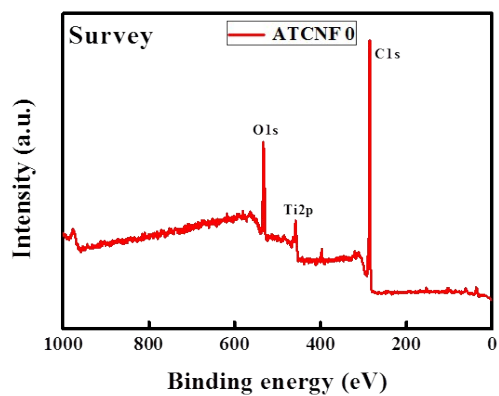
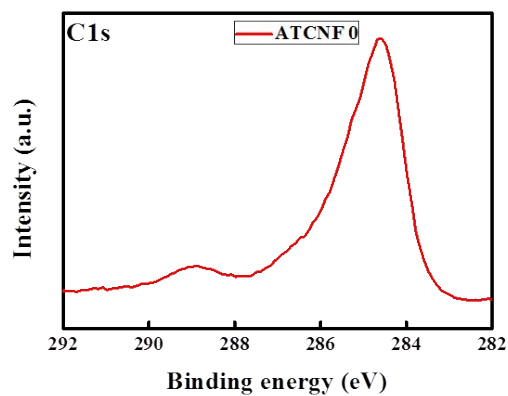


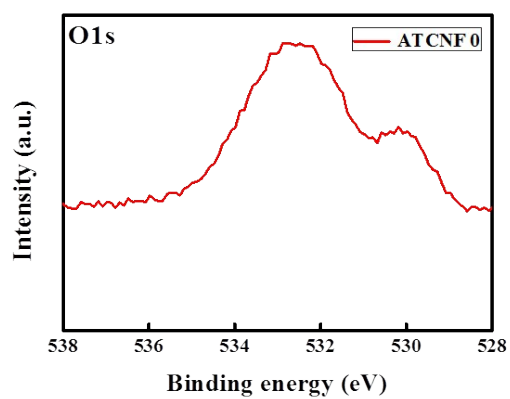
Figure S1 – SEM images of (a) ATCNF10 and (b) ATCNF30



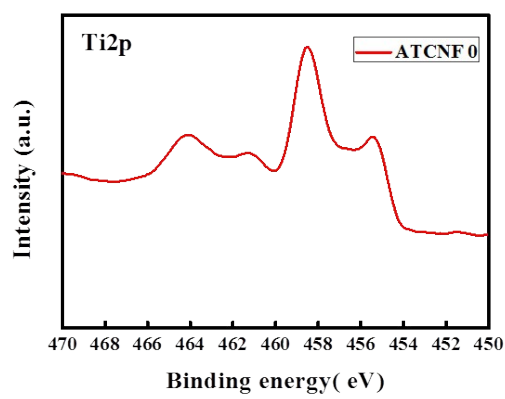
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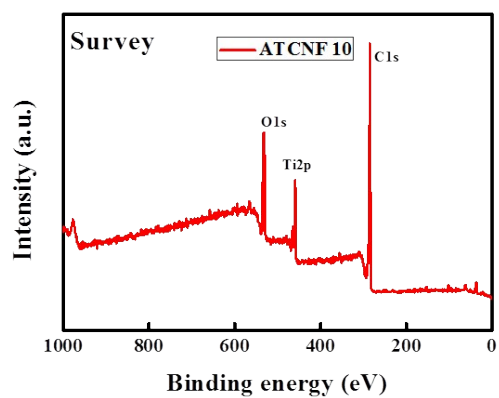
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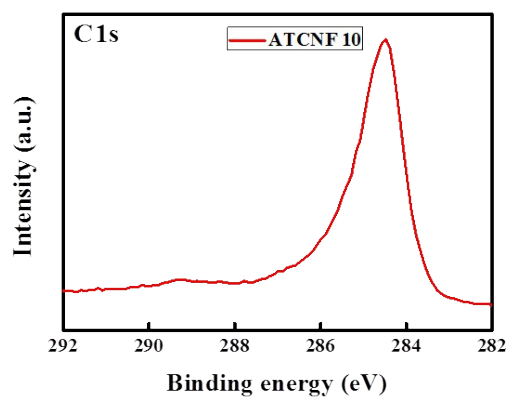
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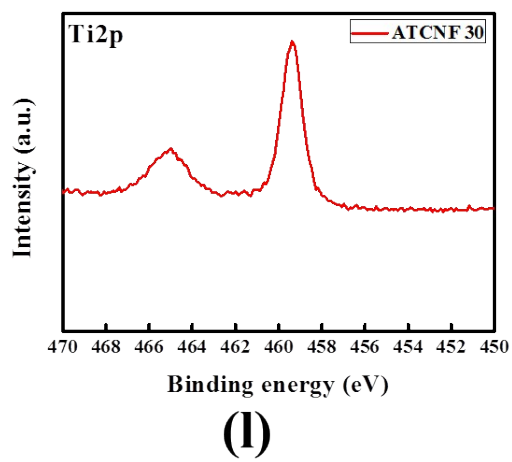
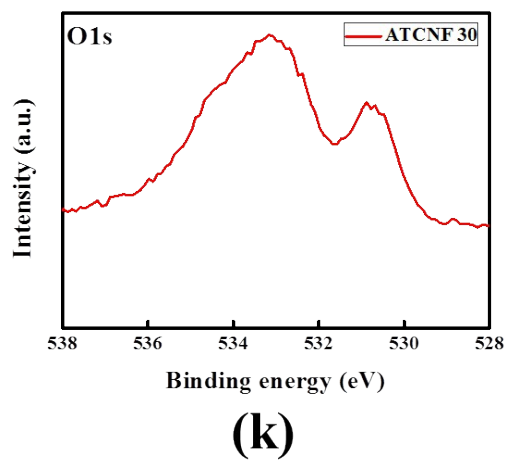
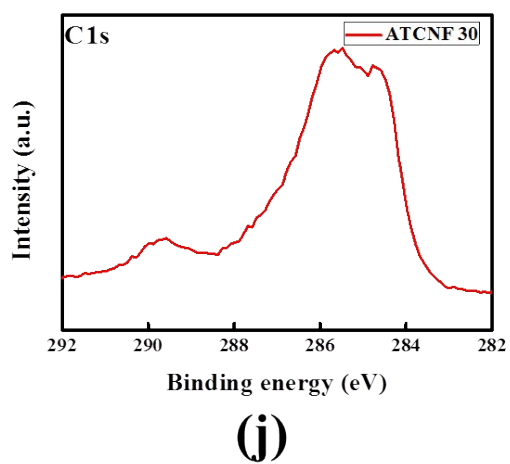
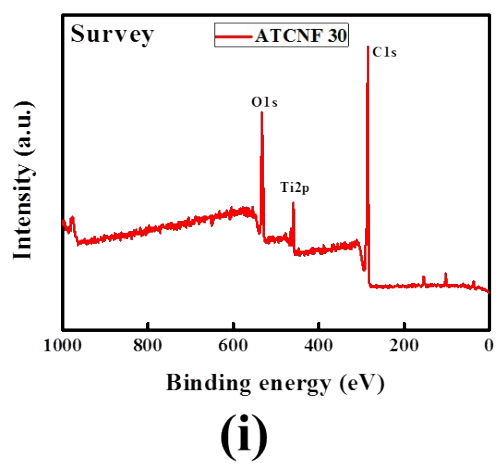
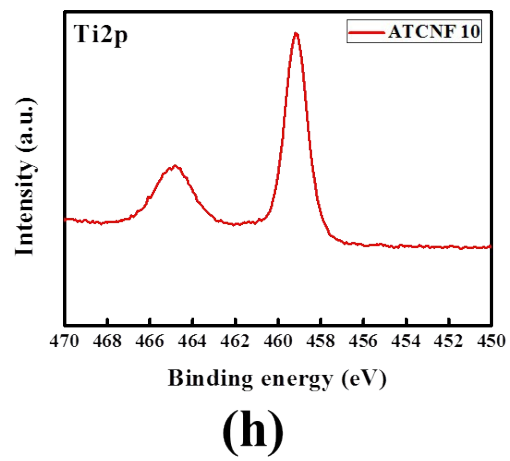
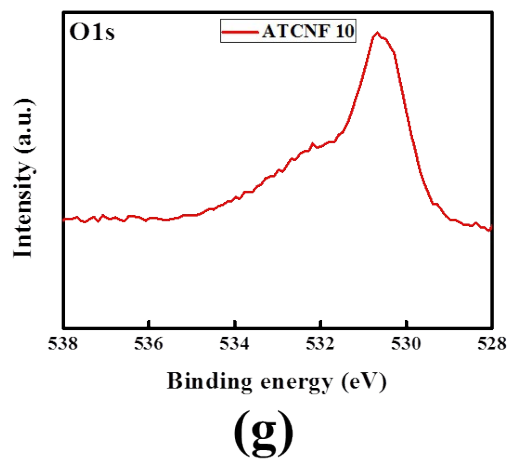
(d)



(e)



(f)



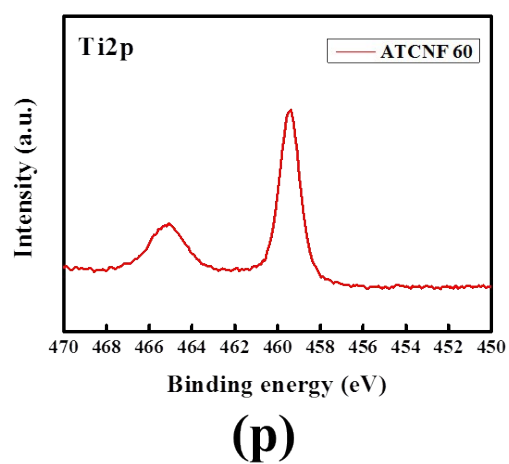
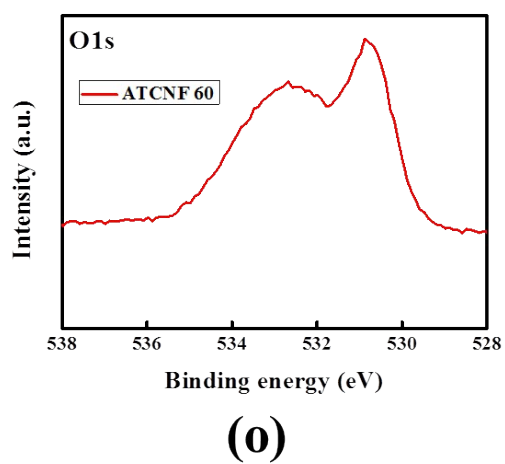
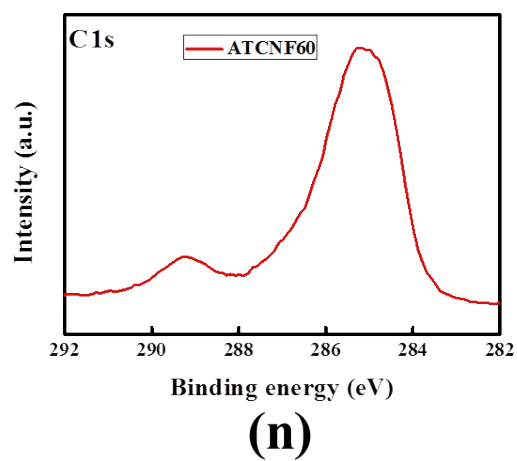
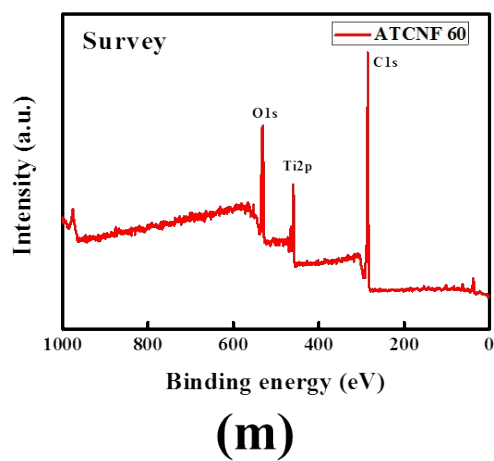


Figure S2 – XPS spectra for survey, C1s, O1s, and Ti2p of ATCNF0 (a, b, c, d), ATCNF10 (e, f, g, h), ATCNF30 (i, j, k, l), and ATCNF60 (m, n, o, p)

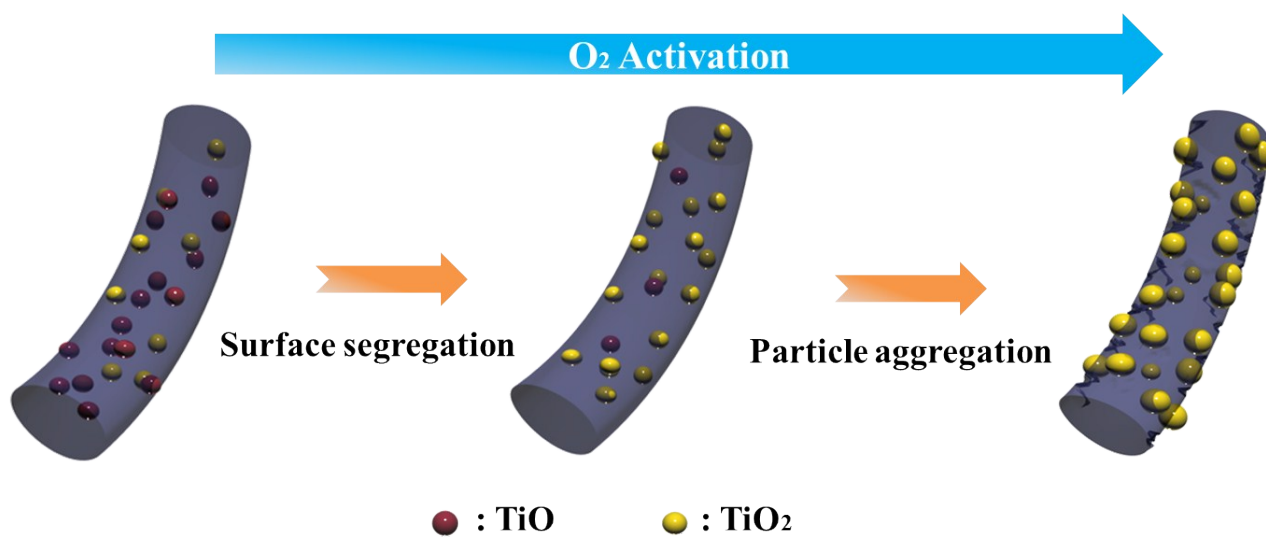
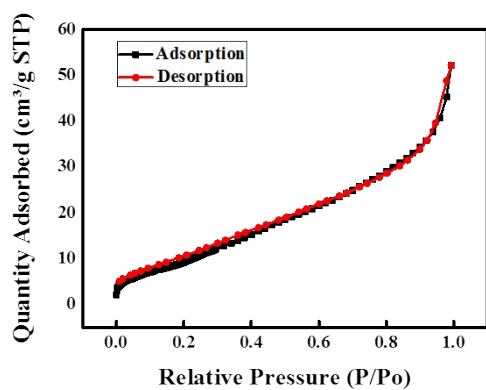
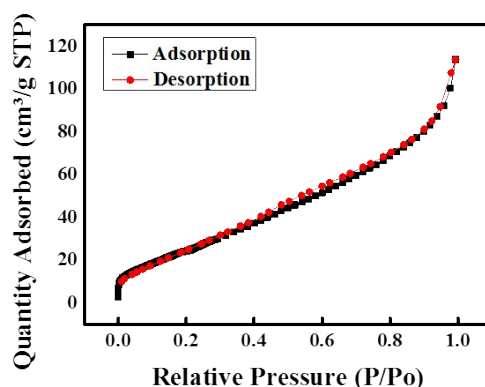


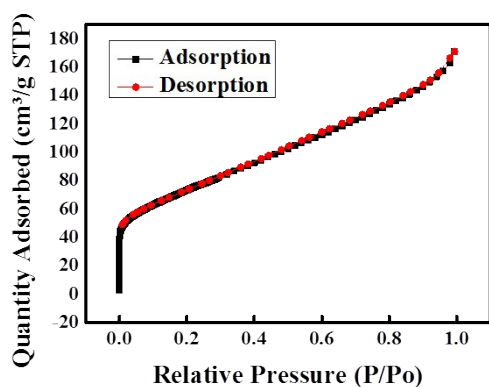
Figure S3 – Scheme of TiO₂ nanoparticle aggregation on the surface of CNFs.



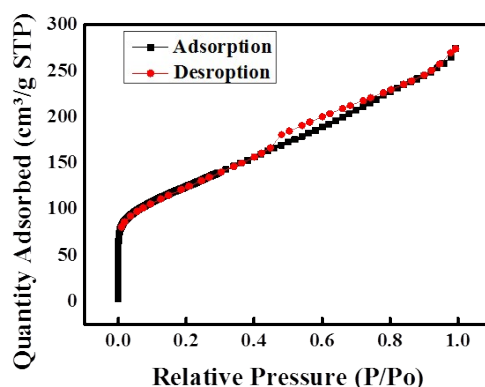
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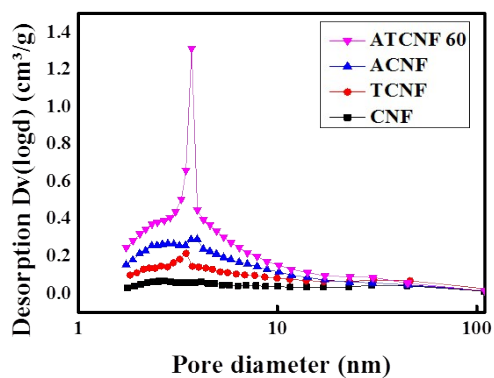
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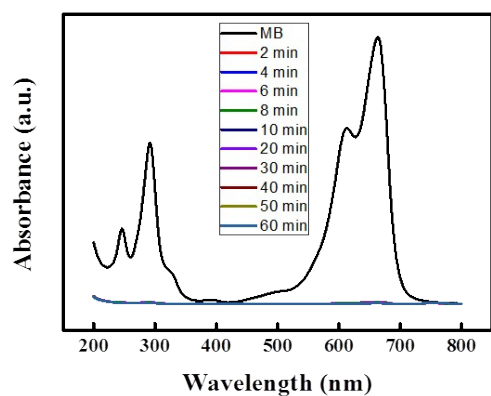


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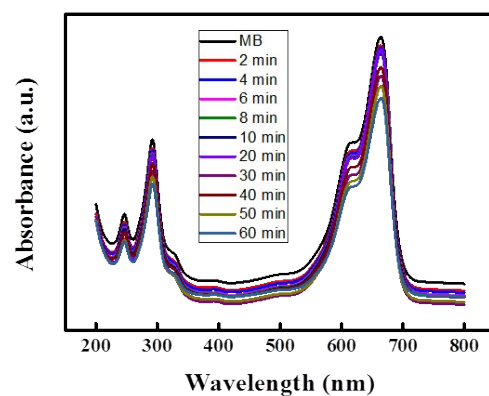


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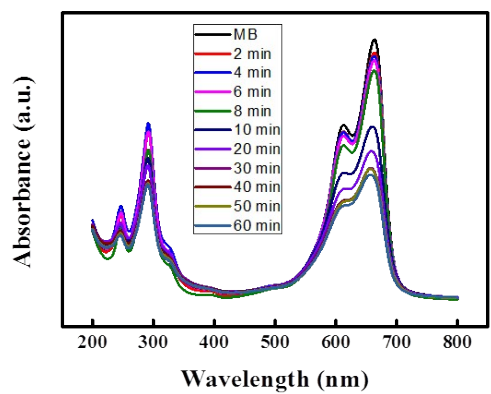
Figure S4 – Isotherm of low temperature nitrogen adsorption/desorption of (a) CNF, (b) TCNF, (c) ACNF, (d) ATCNF60, and (e) their pore diameter distributions.



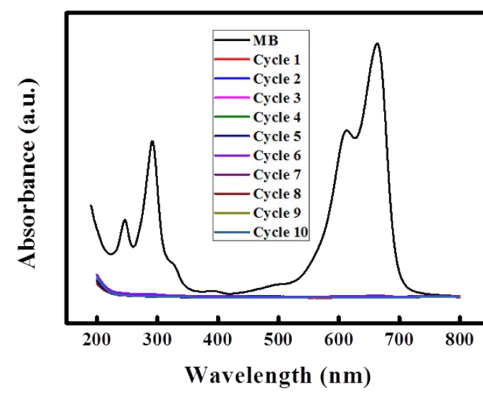
(a)



(b)



(c)



(d)

Figure S5 – UV-Vis analyses of MB degradation with (a) ATCNF60, (b) ACNF, (c) TiO₂, and (d) ATCNF60 for cyclic test