Supporting Information

Nanocrystalline Cellulose Derived Doped Carbonaceous Material for Rapid Mineralization of Nitrophenols under Visible Light

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Characterizations

N-TiO_2/C was characterized by different analytical techniques. The surface morphology of N-TiO_2/C was studied using SEM and TEM techniques. SEM was performed using a JEOL SEM (JSM 7000F) instrument equipped with an EDAX Pegasus EDS system. SEM images were taken at different magnifications. Surface area and porosity measurements of the adsorbent were performed using Micromeritics ASAP 2020 Brunauer Emmett Teller (BET) instrument. A JEOL 2100F TEM was used to get clear images of TiO_2 and graphitic carbon and measured the average distance of crystal lattice of TiO_2. Thermal gravimetric analysis (TGA) was performed with a Shimadzu DTG-50 thermal analyzer, where sample was heated from 25 to 850 ℃ at a heating rate of 5 ℃ min^{-1}. XPS study of the sample was performed using a Thermo K-Alpha XPS system. The data obtained from XPS study were analyzed using Thermo Scientific Avantage XPS software package. The binding energies were calibrated with respect to C 1s peak at 284.00 eV from the carbon composition of the sample. XRD analysis was performed using a Brüker D8 Discover instrument to analyze the TiO_2 nanoparticles. FT/IR analysis was done using a Nicolet 6700 Thermo Scientific FT/IR spectrometer equipped with a DLaTGS detector and a XT-KBr beam splitter. KBr pellets were made for the FT/IR analysis and the spectrums were recorded in the range of 400-4000 cm^{-1}. UV/Vis studies were performed using Varian Cary 5000 UV-Vis-NIR spectrometer. The absorbance of the sample solutions was measured at their corresponding absorption maxima (λ_{max}). A Shimadzu (USA), GCMS-QP2010 Ultra, gas chromatograph (Narrow-bore capillary column; length, 30 m; inner diameter, 0.25 mm; temperature range, 320/350 ℃) integrated directly to the mass spectrometer was used to detect intermediate products formed during degradation. The concentrations of ions (NH_4^+ and NO_3^-) and quantity of TOC remained after degradation were measured using IC and TOC analyzer, respectively (American Interplex Corp., AR, USA).

Photocatalytic study

Catalytic efficacy of N-TiO_2/C was tested by performing the photodegradation of NPs both under UV light and visible light separately. UV light with a wavelength of 254 nm was used (model UVG-11, Upland, CA, USA). A LED lamp (ABI True 24 W Tuna Blue LED Bulb) having the wavelength of 400 to 750 nm was used for the photodegradation study. In this study, 4-NP, 2-NP, 3-NP, and 2,4-DNP were used for degradation. In a batch experiment, 20 mg of N-TiO_2/C was added to 50 mL of 10 mg L^{-1} NP solution of desired pH. Initially, the mixture was sonicated under dark for 5 min. Then the mixture was kept in dark without sonicating for 1 h to establish adsorption/desorption equilibrium. At that point, the mixture was irradiated with light for the degradation study with constant sonication for a stipulated time. The temperature of the reaction was kept at constant room temperature using a water bath. During the photocatalysis, 5 mL aliquot of the sample was taken out in every 1 h. The mixture was centrifuged to separate the heterogeneous catalyst from the solution. After 2 min of centrifugation at 1000 rpm, the upper clear solution was analyzed using a Varian Cary 5000 UV-Vis-NIR spectrometer at their corresponding absorption maxima (λ_{max}) and the degradation efficiency was calculated using Eq. (S1).

$$Degradation\ efficiency = \frac{(C_o - C_t)}{C_o} \times 100 \qquad \text{(S1)}$$

Where, C_o = initial concentration of NP solution and C_t = concentration of NP solution at time t.

Kinetics study

Details of the kinetics studies have been given in the main text. In short, the kinetics of 4-NP degradation was studied using first-order kinetics model, Langmuir adsorption isotherm model, and Langmuir-Hinshelwood (L-H) adsorption kinetics model. Different initial concentrations (10, 15, 20, and 50 mg L^{-1}) of the 4-NP solution at pH 3 were taken for the kinetics analysis. 20 mg of N-TiO_2/C was added to the solution for each experiment, which was sonicated for 5 min under dark and kept unperturbed for 1 h under dark to establish adsorption-desorption equilibrium. The temperature was maintained at 25 °C. After 1 h adsorption of 4-NP on N-TiO_2/C, the concentrations of 4-NP in the solution were determined by UV/Vis analysis and that concentrations were used as initial concentrations for L-H adsorption kinetics study. Once the adsorption-desorption equilibrium was established, the suspensions were irradiated with visible light for 150 min separately to study the degradation kinetics.

Analyses

GC/MS study

NP solution undergoes degradation after illumination of light in the presence of the catalyst. The decrease in the concentration of NP in the solution was observed from the characteristic absorption peak of the UV/Vis spectrum at the corresponding λ_{max} value. The intermediate products formed during photocatalytic degradation of NP were analyzed using GC/MS technique. The procedure for the GC/MS analysis was performed according to the literature procedure with slight modifications.[1,2] In this study, the reaction was prematurely stopped right after 30 min of visible light irradiation. The mixture was then filtered and acidified to pH 1.5 by adding 0.1 N HCl solution drop-wise. Organic intermediates were extracted from 20 mL of the solution using 3 × 10 mL of ethyl acetate. The combined ethyl acetate solution was dried over anhydrous sodium sulfate (Na_2SO_4). The solution was then filtered and taken in a round bottom flask and then further concentrated under vacuum. The residue obtained in the round bottom flask was treated with 200 µL of bis(trimethylsilyl)trifluroacetamide (BTSTFA) at room temperature to functionalize the hydroxyl groups or the carboxylic acid groups present in the degraded products. Additional 500 µL of ethyl acetate was added to the mixture and the mixture finally analyzed using a GC/MS.

TOC and IC analysis

After degradation of 4-NP, small acidic and alcoholic intermediates along with the mineralized products formed were analyzed using TOC and IC analysis. In this study, 50 mL of 10 mg L^{-1} 4-NP solution at pH 3 was taken in a beaker and 20 mg of N-TiO_2/C was added to it. The mixture was sonicated with the continuous shining of visible light. The sample was collected by filtration after 7 h of reaction for TOC and IC analysis.

FT/IR study

The degradation of 4-NP was also studied by FT/IR analysis. To analyze the degradation of 4-NP (10 mg L^{-1}) into its intermediate products, 20 mg of N-TiO_2/C was added to 50 mL of the 4-NP solution at pH 3. After a stipulated time of visible light irradiation, 50 mL of the suspension was taken out, centrifuged, filtered, and concentrated at 50 °C for overnight. The solid products obtained at different time intervals were further dried in a vacuum oven and stored in dark before analysis. FT/IR samples were prepared by mixing the degraded products with anhydrous KBr and a pellet was prepared by using a pellet press. Finally, FT/IR spectrums were recorded for different samples.

Effect of dissolved oxygen and radical quenchers on photodegradation

The degradation of NPs was initiated either by reactive oxygen species such as $^{\bullet}OH$ or $O_2^{\bullet-}$ or both radicals generated on the surface of the catalyst. To study the effect of these radicals for the degradation, 50 mL of 10 mg L^{-1} 4-NP solution at pH 3 was sonicated with 20 mg of N-TiO_2/C under visible light. Dissolved oxygen may play role in generating these radicals in different concentrations. Therefore, the experiment was also performed by purging the 4-NP solution containing N-TiO_2/C with O_2 gas 1 h prior to light irradiation and continuously throughout the reaction. A control reaction was performed by purging the solution with N_2 gas under similar condition. Additionally, the effect of the radical quenchers for the degradation of the 4-NP solution was studied. For this batch of the experiments, isopropanol, which is a $^{\bullet}OH$ radical quencher, and ascorbic acid, which is $O_2^{\bullet-}$ radical quencher were used. The quenchers used in the experiment were 10 times more concentrated than 4-NP at pH 3 in the reaction mixture. In this experiment, 50 mL of 10 mg L^{-1} concentrated 4-NP solution was taken in a beaker. 20 mg of N-TiO_2/C was added to it. In the above mixture, 6.4 µL isopropanol (d=0.785 g mL^{-1}) or 5 mg of ascorbic acid was added, so as to make their concentration of 100 mg L^{-1} in the mixture. Then, the mixture was sonicated for 5 min in dark and kept in dark without disturbing for 1 h. After 1 h, visible light was irradiated to study the effect of the radical quencher on 4-NP degradation.

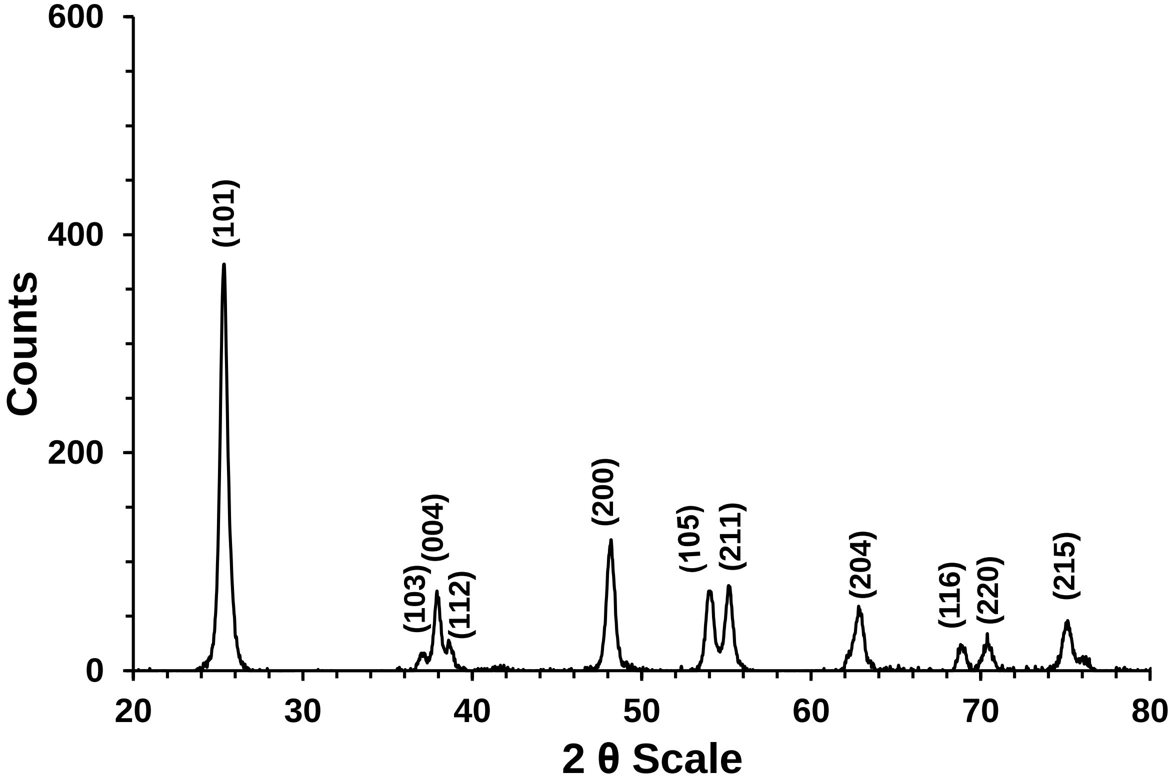


Figure S1: XRD pattern of N-TiO_2/C catalyst indicating with lattice planes.

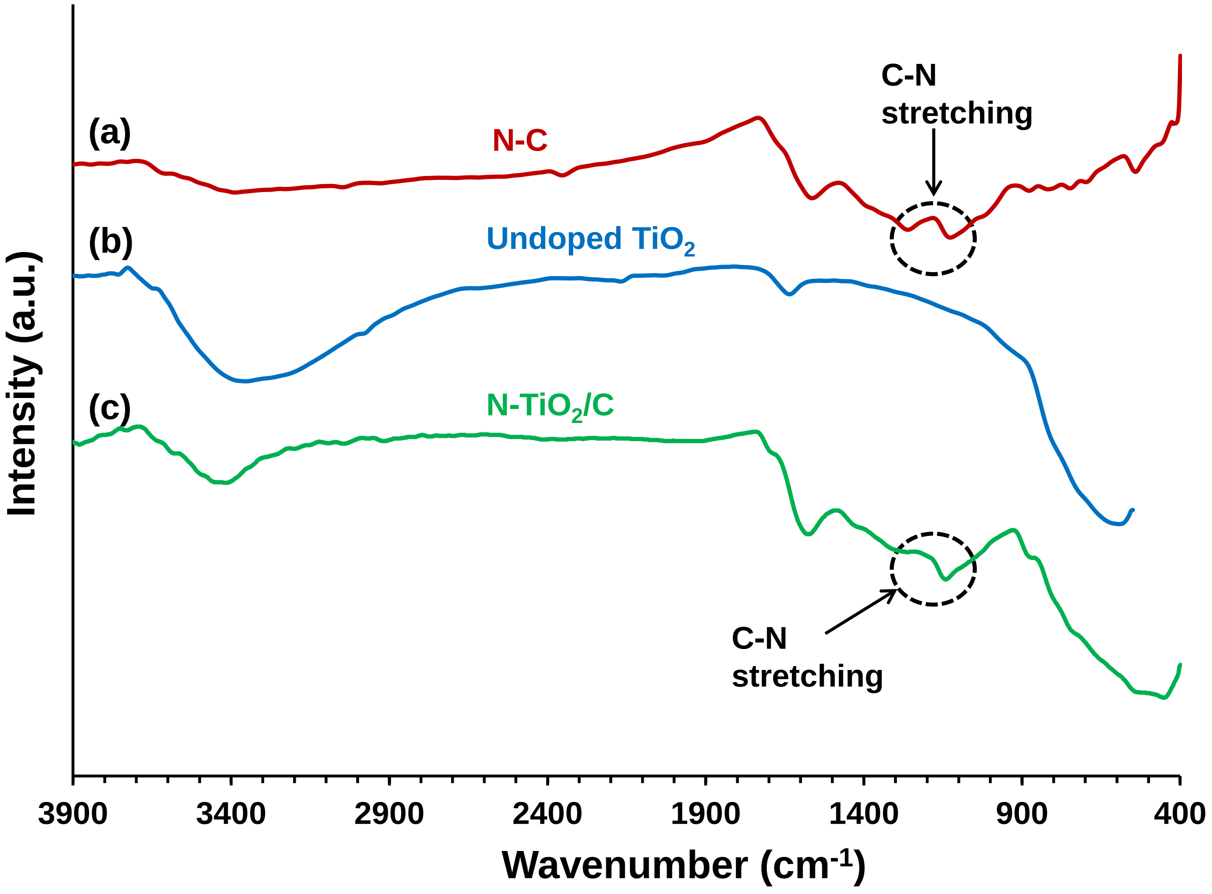
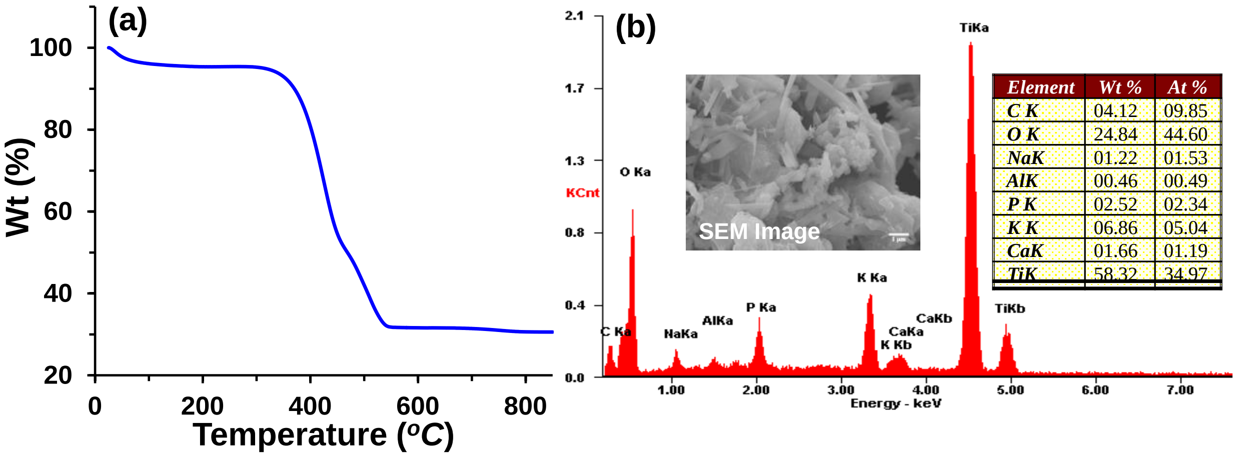


Figure S2. FT/IR spectra of a) N-C, b) TiO_2, and c) N-TiO_2/C materials using KBr pellet.



Element	*Wt %*	*At %*
C K	04.12	09.85
O K	24.84	44.60
NaK	01.22	01.53
AlK	00.46	00.49
P K	02.52	02.34
K K	06.86	05.04
CaK	01.66	01.19
TiK	58.32	34.97

Figure S3. (a) TGA curve of N-TiO_2/C materials and (b) EDAX spectra of residual material after TGA. Inset shows the SEM image and a table of elemental content of the residual material.

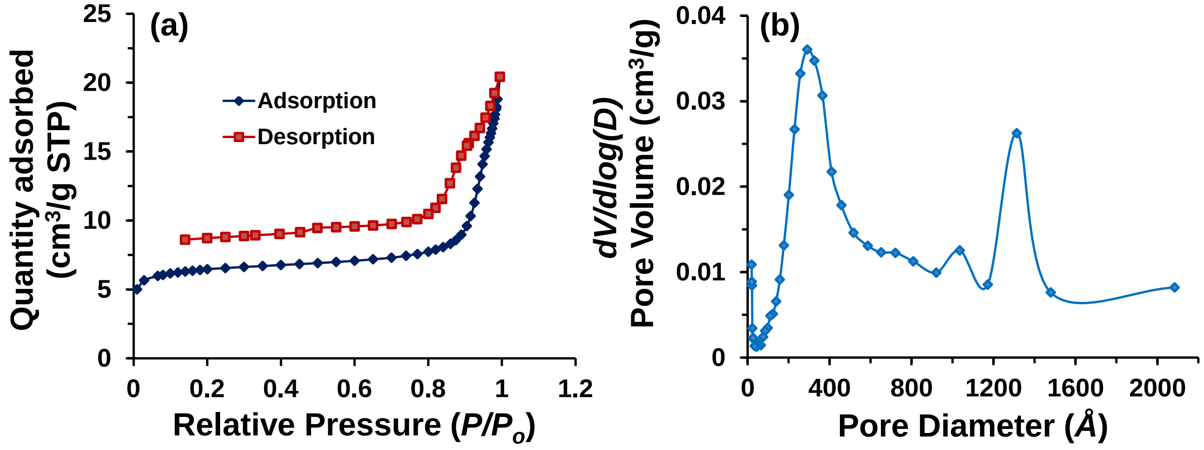


Figure S4. BET analysis of N-TiO_2/C material showing a) linear isotherm plot and b) BJH pore size distribution plot.

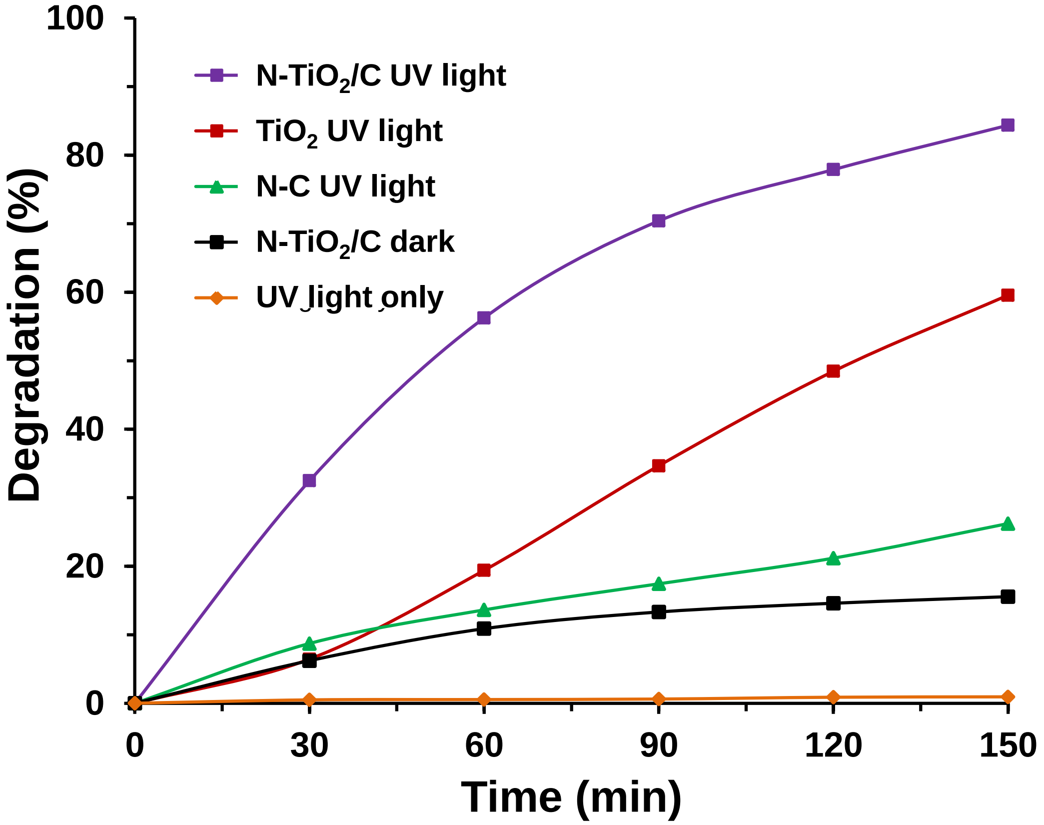


Figure S5. Comparative study of the catalytic activity of different materials. Experimental conditions: 10 mg L^{-1} 4-NP solution at pH 3, 20 mg of catalyst, and UV light ($\lambda = 254$ nm) at room temperature.

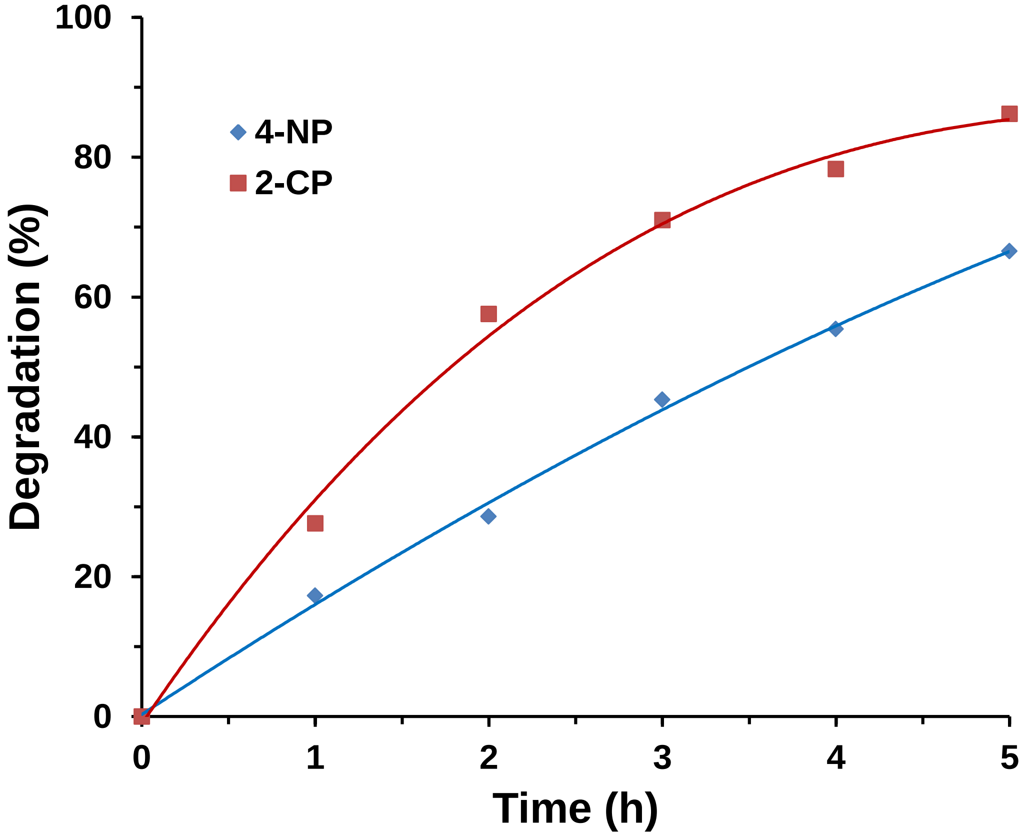


Figure S6. Comparison of the degradation of 4-NP and 2-CP after 5 h. Experimental conditions: 10 mg L^{-1} solution at pH 3, 20 mg of N-TiO_2/C at room temperature under visible light.

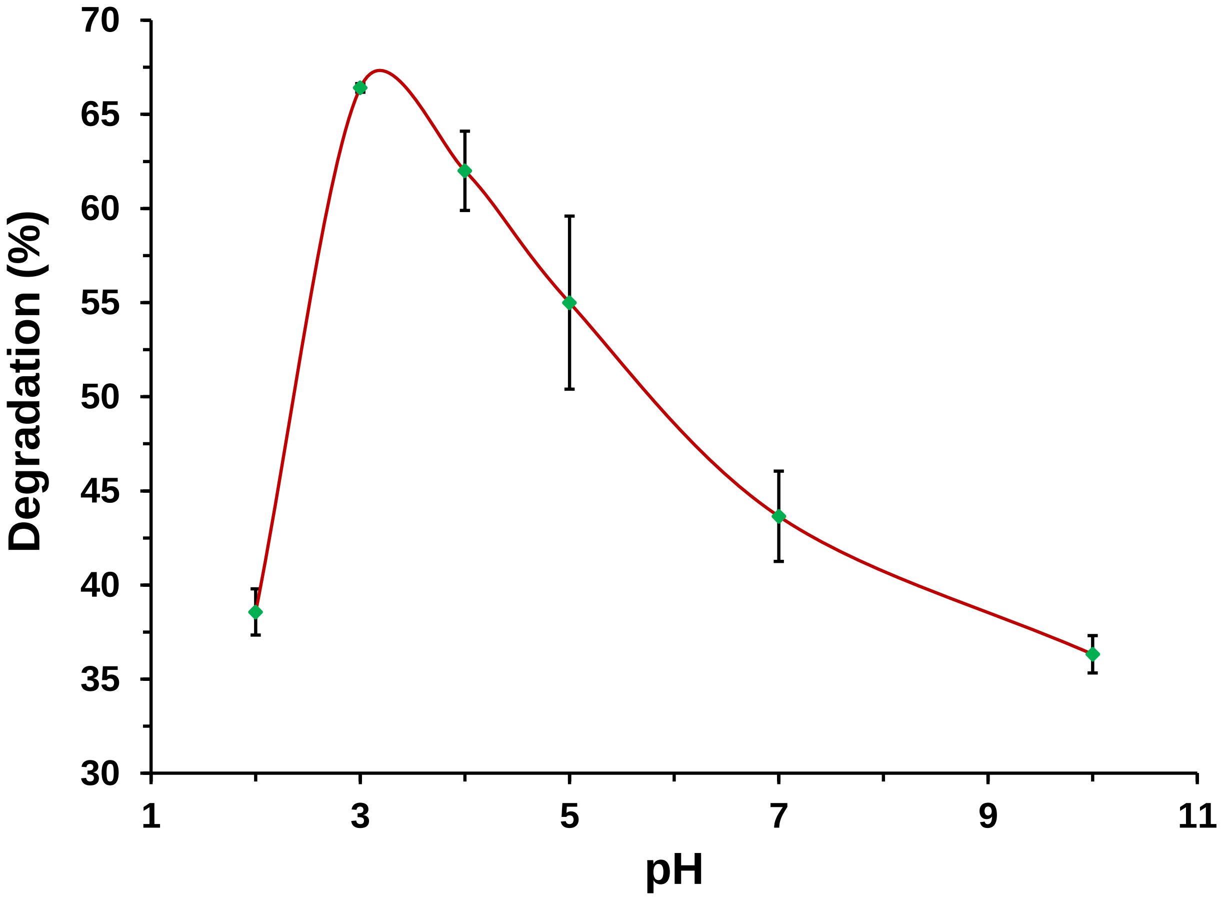


Figure S7. Effect of pH on degradation of 4-NP after 4 h of reaction. Experimental conditions: 10 mg L^{-1} NPs solution at desired pH, 20 mg of N-TiO_2/C at room temperature under visible light.

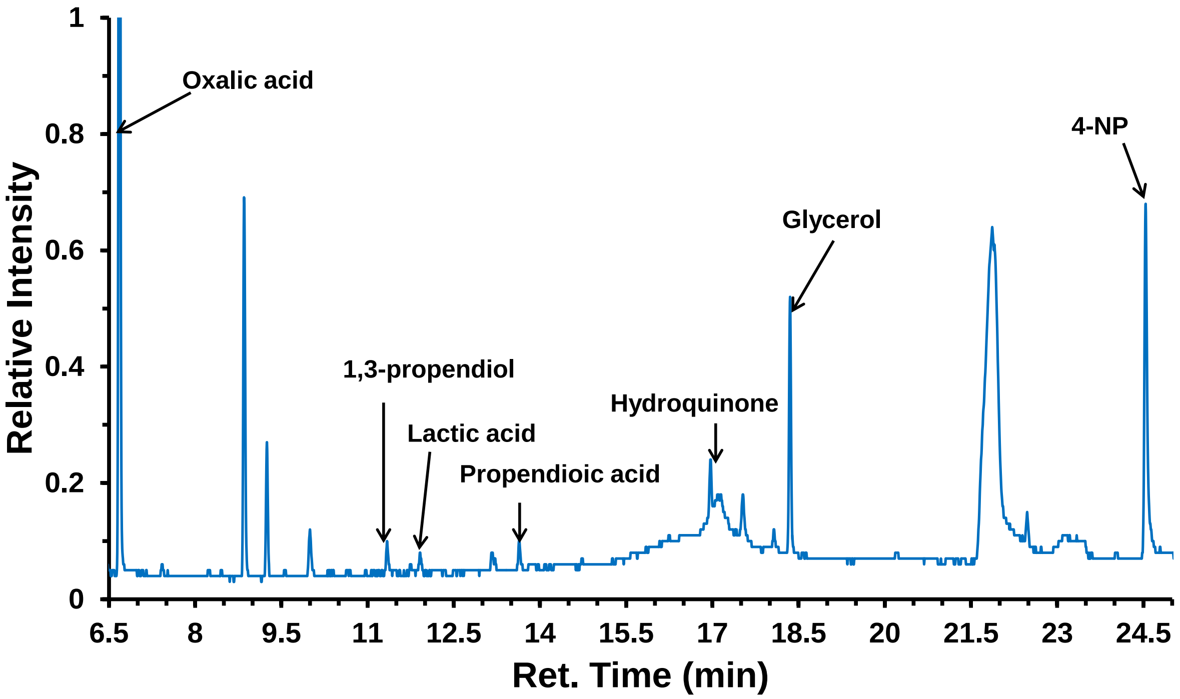


Figure S8. GC chromatogram of 4-NP degraded products after 30 min of photocatalytic degradation.

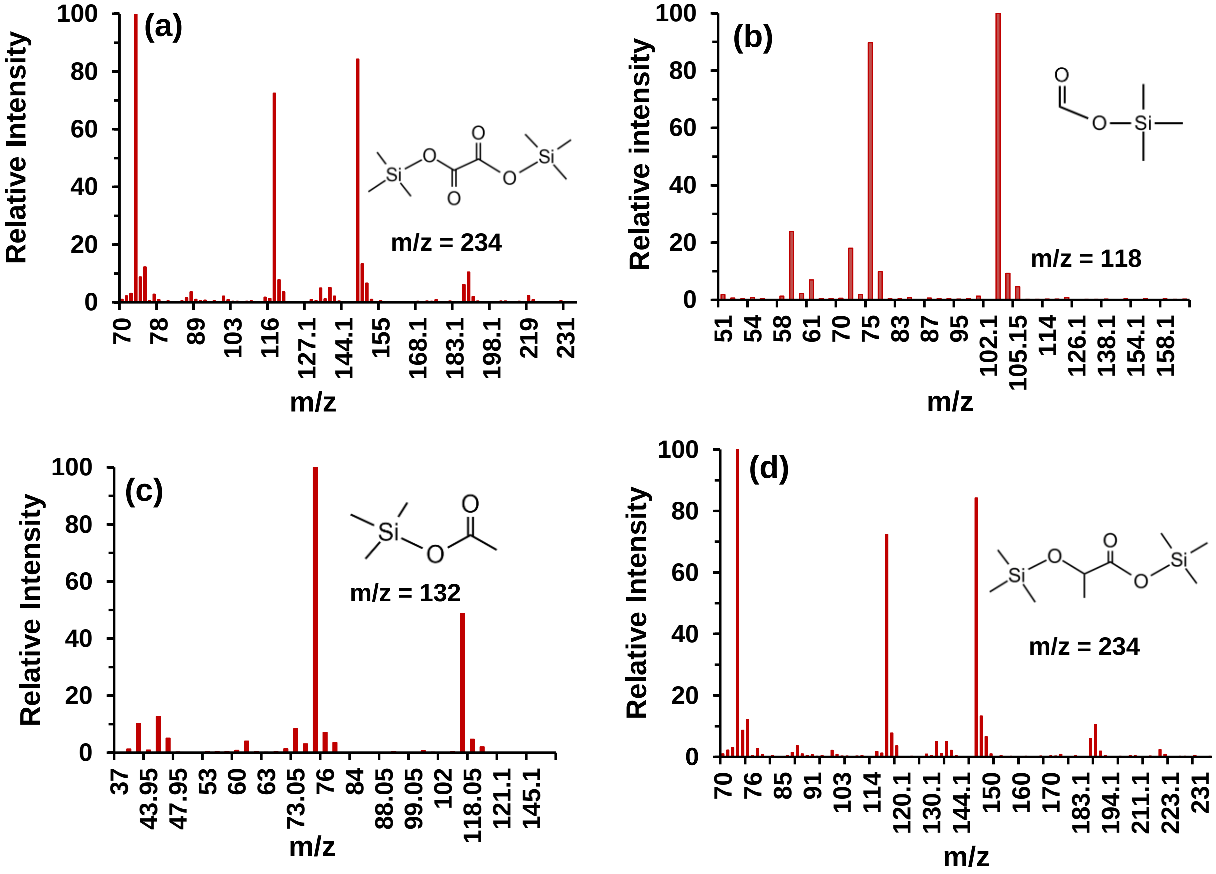


Figure S9. Mass spectra of TMS derivatives of different acidic intermediate products a) oxalic acid, b) formic acid, c) acetic acid, and d) lactic acid formed by visible light induced 4-NP degradation.

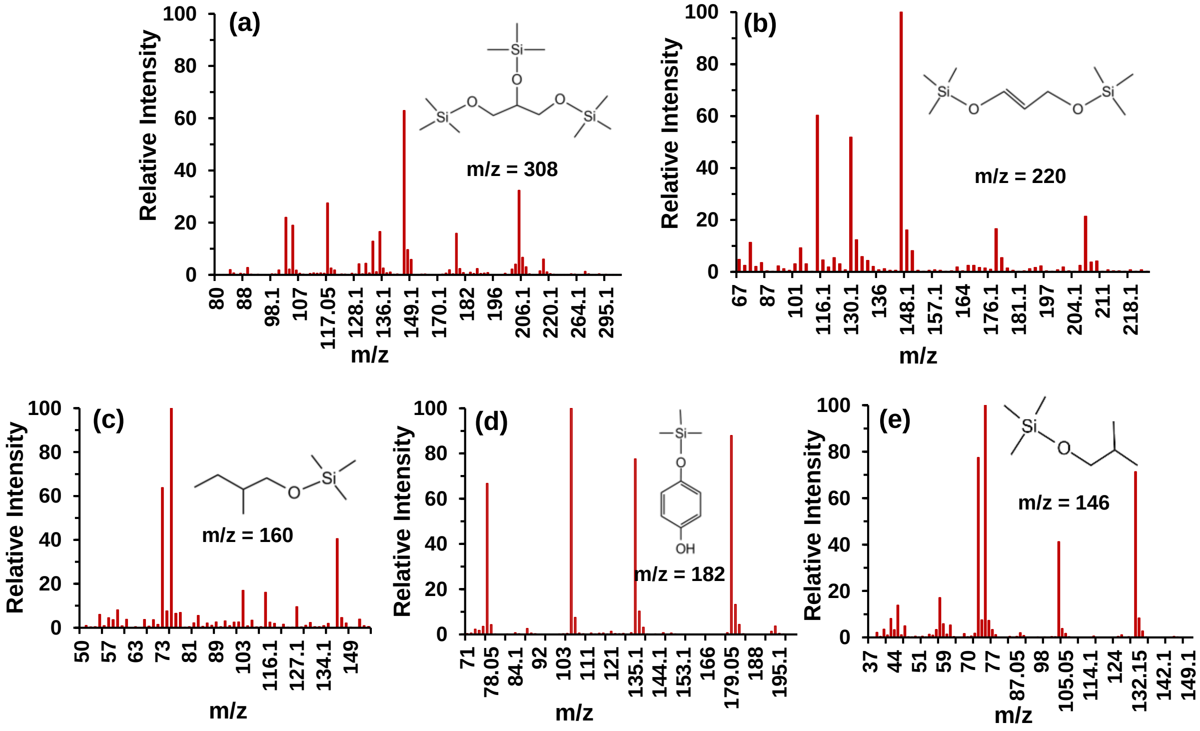


Figure S10. Mass spectra of TMS derivatives of different alcoholic intermediate products a) glycerol, b) 1,3-propendiol, c) 2-methyl-1-butanol, d) hydroquinone, and e) isobutanol formed by visible light induced 4-NP degradation.

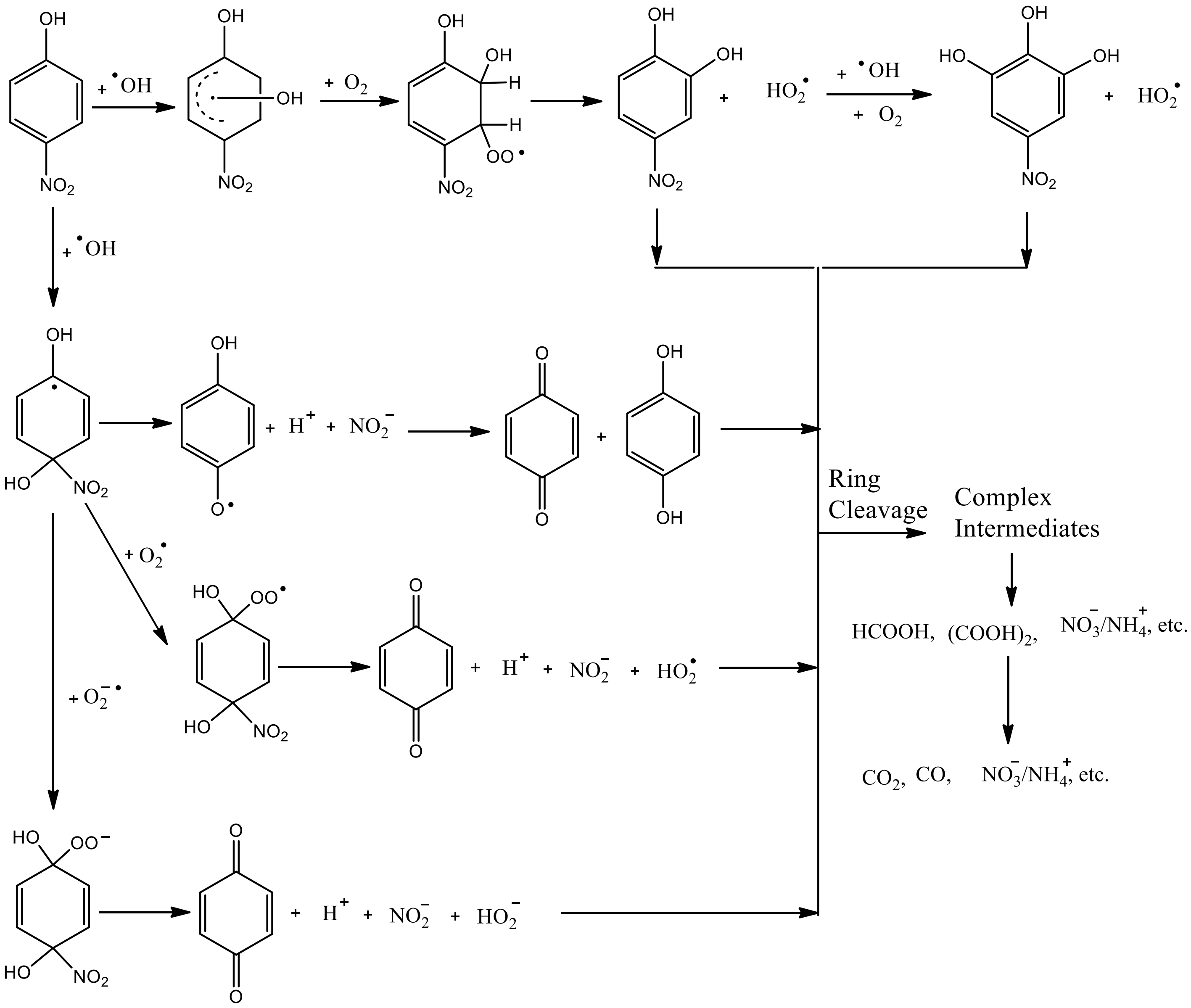


Figure S11. The possible mechanism of 4-NP degradation by •OH or $O_2•^-$ radical attack on the benzene ring.

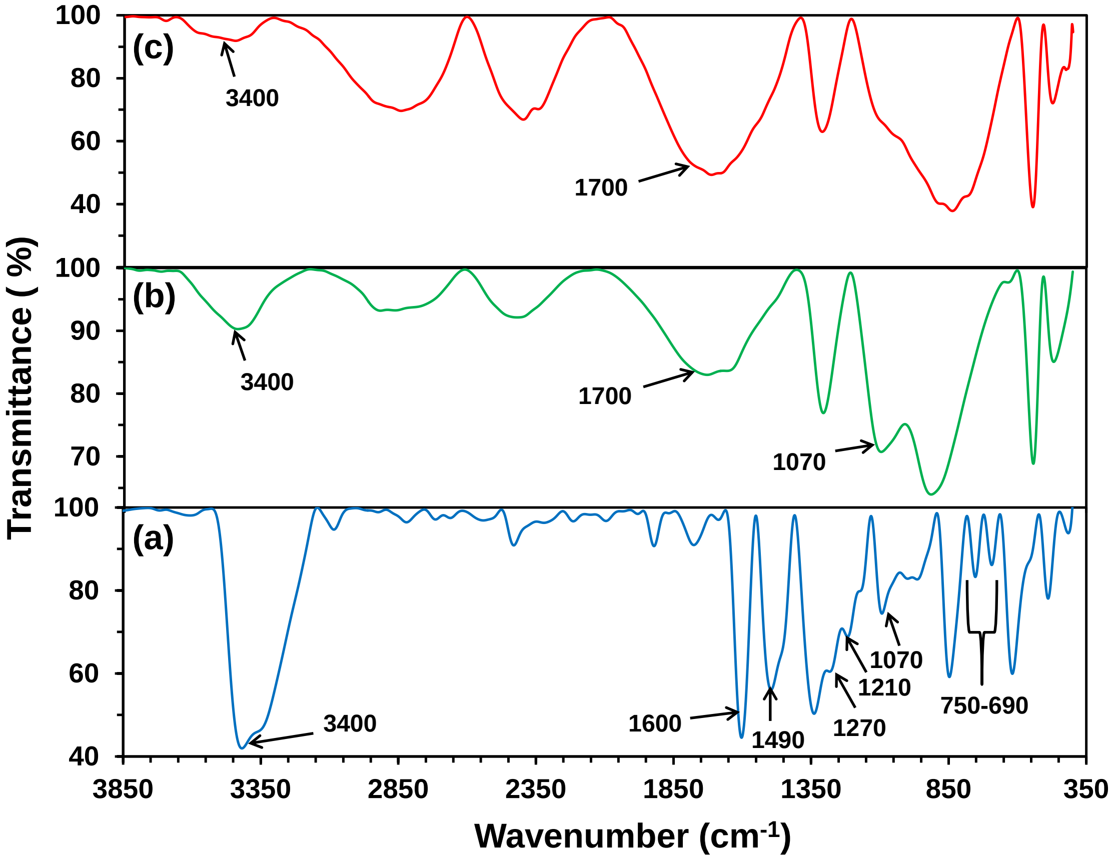


Figure S12. FT-IR spectra of a) solid 4-NP before degradation, and samples obtained after b) 4 h, and c) 7 h degradation of the 4-NP solution under visible light. Experimental conditions: 10 mg L^{-1} 4-NP solution at pH 3, 20 mg of N-TiO$_2$/C at room temperature.

Table S1. Elemental analysis of N-TiO_2/C from XPS.

Name of element	**Peak binding energy (eV)**	**Atomic%**
C	284.31	82.2
O	531.77	11.5
N	399.35	3.6
Ti	458.41	1.1

Table S2. Pseudo first order apparent rate constant values (**K_{app}**) and initial rates of the reaction (**r_o**) for the degradation of 4-NP at different initial concentrations under visible light.

C_o (mg L^{-1})	**$K_{app} \times 100$ (min^{-1})**	**r_o (mg L^{-1} min^{-1})**
7.90	0.31	2.449
14.4	0.18	2.592
18.6	0.14	2.604
49.6	0.05	2.480

References

(1) Leung, K. T.; Campbell, S.; Gan, Y.; White, D. C.; Lee, H.; Trevors, J. T. The Role of the Sphingomonas Species UG30 Pentachlorophenol-4-Monooxygenase in P-Nitrophenol Degradation. *FEMS Microbiol. Lett.* **1999**, *173* (1), 247–253.

(2) Lai, T.-L.; Yong, K.-F.; Yu, J.-W.; Chen, J.-H.; Shu, Y.-Y.; Wang, C.-B. High Efficiency Degradation of 4-Nitrophenol by Microwave-Enhanced Catalytic Method. *J. Hazard. Mater.* **2011**, *185* (1), 366–372.