

## Utilising anatase nano-seeds coupled with a visible-light antennae system (Cu-Pd-N) for effective photo-organic transformations.

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### Table of Contents

S1. Gas chromatography-mass spectrometry (GC-MS) .....	3
S2. Inductively coupled plasma – mass spectrometry (ICP-MS) .....	3
S3. Electron microscopy .....	3
S4. Raman spectroscopy .....	7
S5. UV/Vis spectroscopy .....	7
S6. Powder diffuse reflectance UV/Vis spectroscopy .....	7
S7. Powder X-ray diffraction.....	7
S8. Photoluminescence spectroscopy .....	7
S9. X-ray photoelectron spectroscopy .....	8
S10. Purpose Built LED Solar Simulator for Photocatalytic Reactions .....	8
.....	9
S11. Experimental Procedure for Photocatalytic Reactions using Cu/Pd-N-TiO <sub>2</sub> . .....	10
S11.1. Typical experimental procedure for the oxidation of benzylic alcohols using Cu/Pd-N-TiO <sub>2</sub> . .....	10
S11.2. Typical experimental procedure for the photodegradation of dyestuffs (methylene blue and eosin Y). .....	10
S12. Alcohol quantification using gas chromatography-mass spectrometry .....	11
S12.1. 4-Octylphenol calibration curve .....	11
S12.2. Quantitative formulations to detect the remaining alcohol after the reaction process. ....	12

S13. TiO <sub>2</sub> derivatives .....	19
S13.1. Nitrogen functionalised titanium dioxide .....	19
S13.2. Cu/Pd-N-TiO <sub>2</sub> .....	19
S13.3. Methylene blue and eosin Y preparation .....	19
S14. Chromatograms.....	20

## S1. Gas chromatography-mass spectrometry (GC-MS)

All the reactions studied using GC-MS were conducted on a Shimadzu QP2010SE.

The GC columns used in the study were:

- 1) InertCap 5MS/Sil
- 2) Zebron ZB-5ms+

Both columns had the same specifications: 0.25 mm I.D.  $\times$  30 m,  $df = 0.25 \mu\text{m}$ .

The GC program on the Shimadzu QP2010SE gas chromatograph-mass spectrometer was set accordingly:

- Column temperature: 40 °C (1-minute hold) - 12 °C/minute - 200 °C
- Carrier gas: He at 1.32 mL/min
- Detection: MS
- Sample volume: 3  $\mu\text{L}$

Internal standard volume: 3  $\mu\text{L}$

## S2. Inductively coupled plasma – mass spectrometry (ICP-MS)

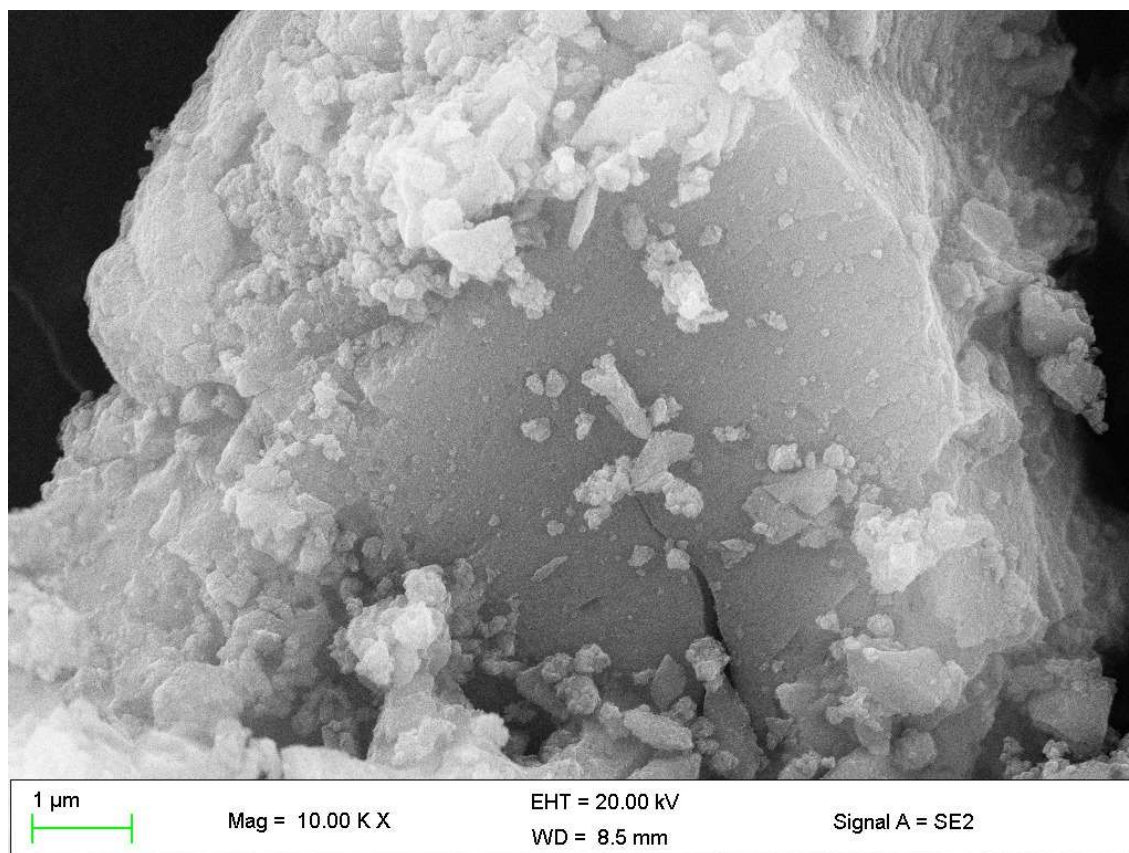
The samples were prepared by aqua-regia digestions and the resultant digests were analysed for metals. Results were calculated back with mass and volume used in the digestions.

## S3. Electron microscopy

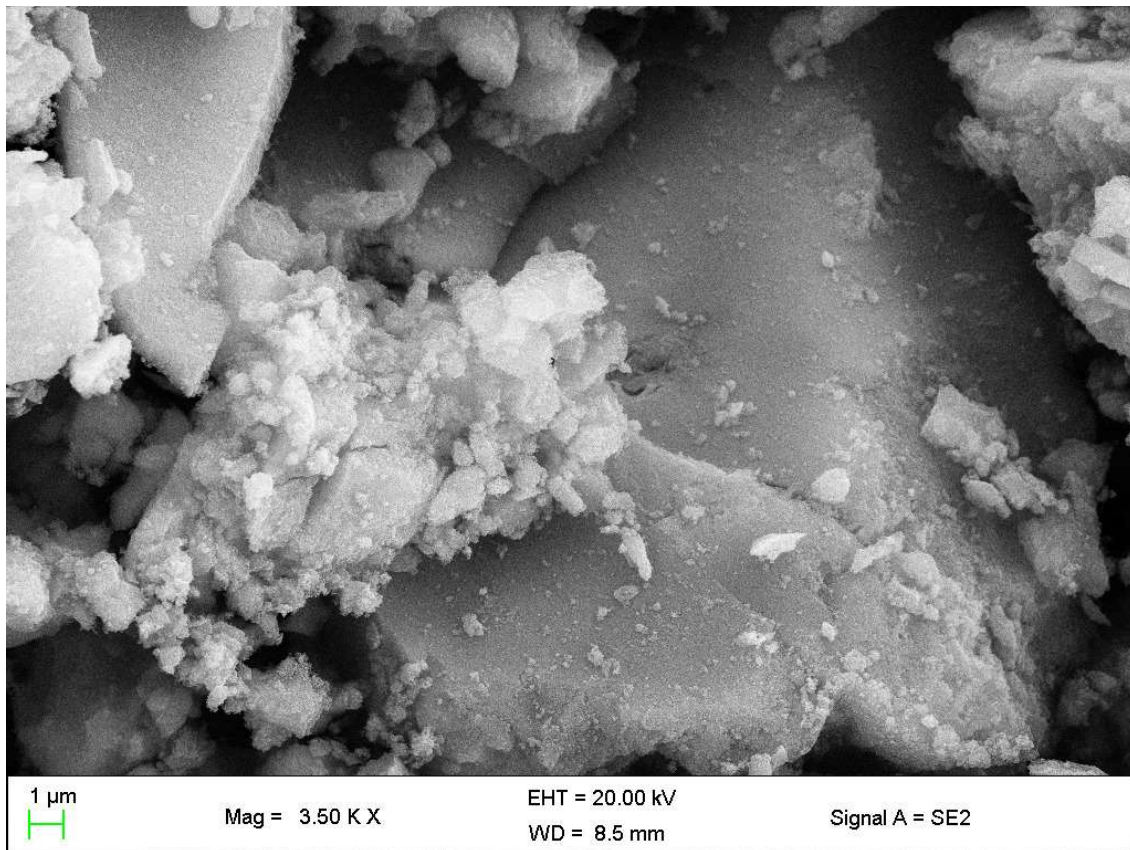
All scanning electron micrographs were collected using a Zeiss Ultra Plus FEGSEM (field emission gun scanning electron microscope). The data was processed using Zeiss SmartSEM UIF V05.04.02.00 and AzTec for EDX analyses. Samples were mounted on carbon adhesion tape that was bound to metal stub holders. Both high and variable pressure vacuum analyses were utilised to obtain the respective magnifications. At high pressure, the samples were gold coated to avoid charging. All transmission electron micrographs were collected on a JEOL 2100 high resolution transmission electron microscope for HRTEM, EDX and STEM analyses. The images were taken using Gatan Digital Micrograph V2.10.1282.0 software. The

energy-dispersive X-ray spectroscopic studies were performed on an Oxford X-Max 80mm<sup>2</sup> SDD (Silicon drift detector) analyser using Oxford Instruments Inca V4.15 software.

### S3.1. Scanning electron micrographs of uncalcined Cu/Pd-N-TiO<sub>2</sub> and calcined N-TiO<sub>2</sub>.



**Figure S1:** Scanning electron micrograph of uncalcined Cu/Pd-N-TiO<sub>2</sub>.



**Figure S2:** Scanning electron micrograph of calcinated N-TiO<sub>2</sub>.

### 3.2. Elemental mapping of calcinated Cu/Pd-N-TiO<sub>2</sub>

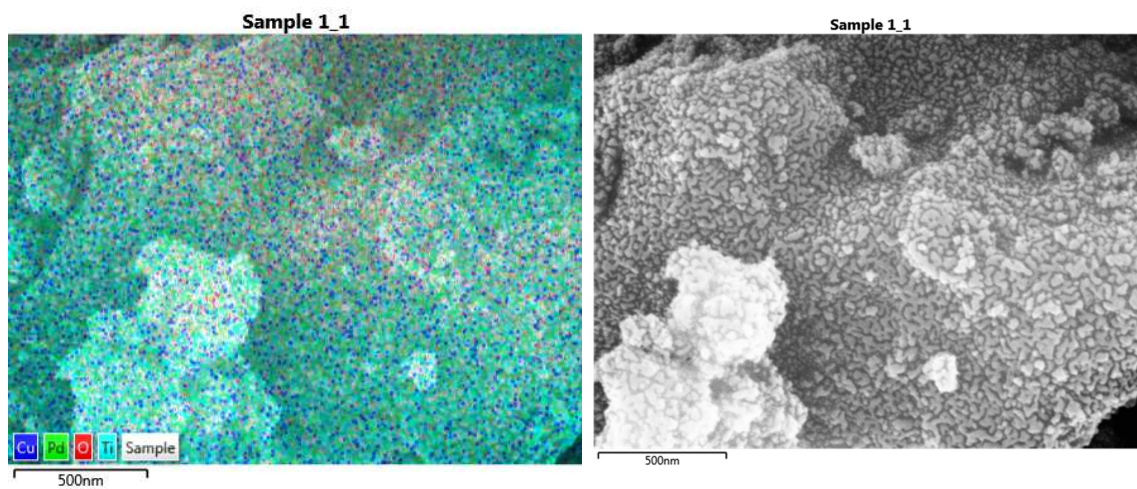
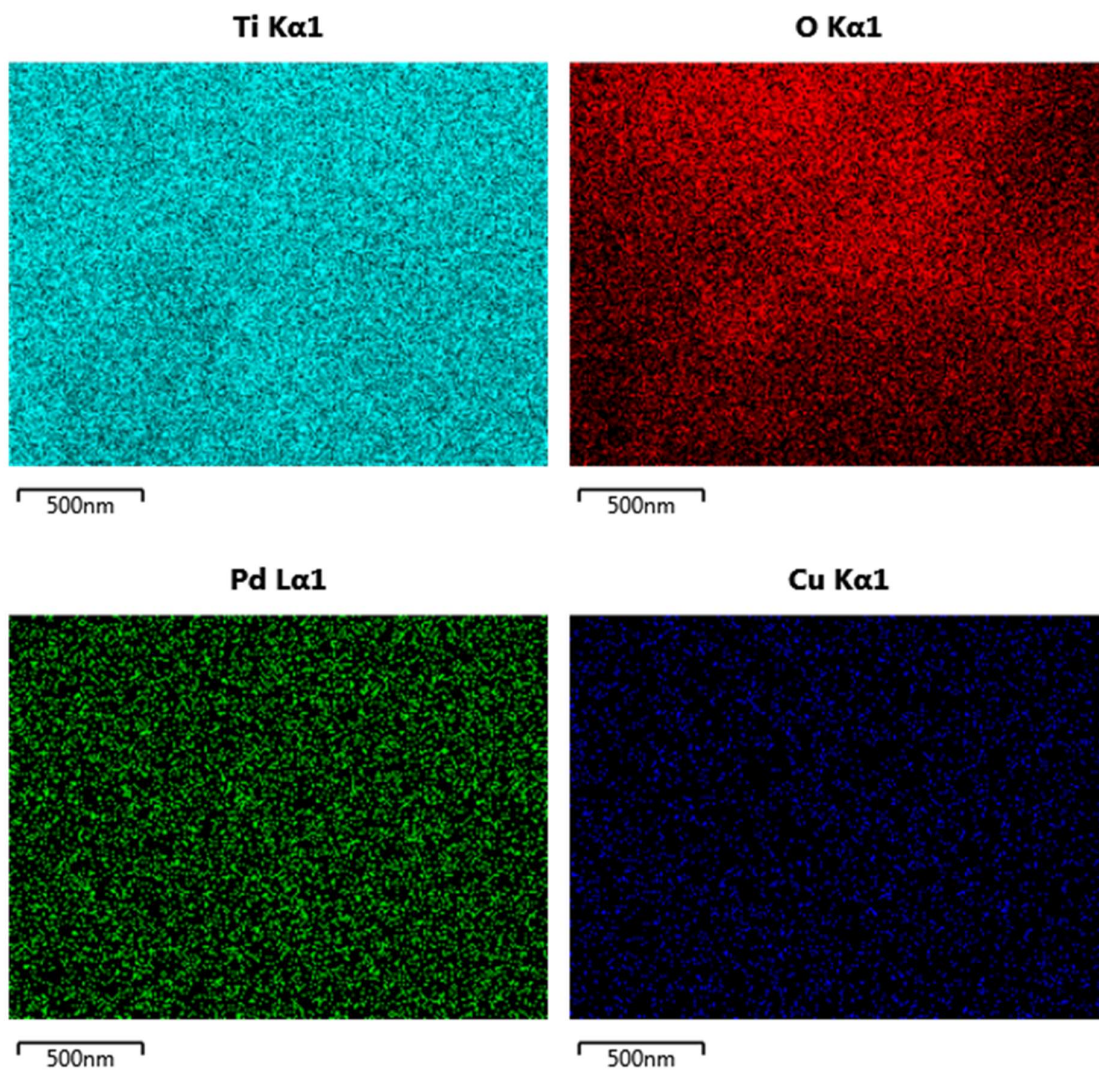


Figure continued overleaf.



**Figure S3:** Calcinated Cu/Pd-N-TiO<sub>2</sub> depicting element mapping of Ti, O, Pd and Cu species.

## S4. Raman spectroscopy

The instrument used in this study has been listed below:

- 1) Renishaw® inVia Raman microscope. The software used was Renishaw's WiRE (Windows-based Raman Environment).

## S5. UV/Vis spectroscopy

The optical absorbance measurements of methylene blue and eosin Y were studied in solution on a PG Instruments Limited T80 UV/VIS spectrophotometer. Data was processed with UVWin5 analytical software (V5.1.1.1).

## S6. Powder diffuse reflectance UV/Vis spectroscopy

Powdered semiconductor samples were studied on a Shimadzu UV-2600 UV/Vis spectrophotometer that was equipped with a Shimadzu ISR-2600/ISR-2600Plus integrating sphere attachment.

## S7. Powder X-ray diffraction

The samples were prepared for X-ray diffraction analysis using the back-loading preparation method.

A PANalytical Empyrean Diffractometer equipped with a X'Celerator detector and Co-K $\alpha$  radiation was used for all the analyses. The generator was set at 40 kV (voltage) and 40 mA (current). Phase identifications and Rietveld analyses were performed using the HighScore Plus software, version 3.0d.

## S8. Photoluminescence spectroscopy

Emission spectra were collected from 360-900 nm. A continuous He-Cd laser produced a 325 nm excitation wavelength and was used in all experiments. A restriction to the laser pulse (120 Hz) was applied. The signals from a Horiba iHR320 monochromator were collected from a photomultiplier tube that was coupled to a lock-in amplifier. The samples were mounted as thin powder films.

## S9. X-ray photoelectron spectroscopy

System: PHI 5000 scanning ESCA microprobe.

Mounting method: The samples were mounted as thin powder films.

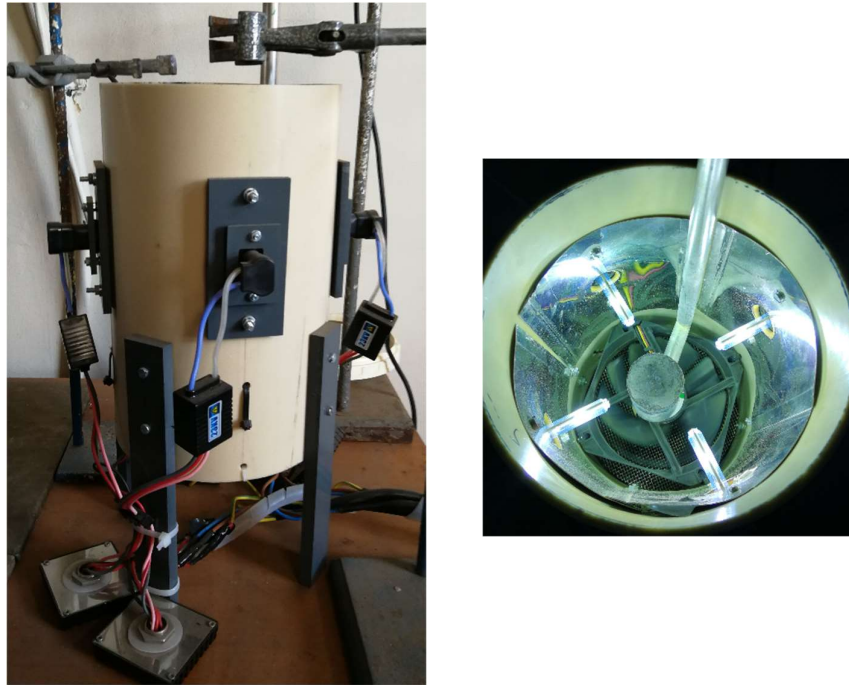
A 100  $\mu\text{m}$  diameter monochromatic Al  $K_{\alpha}$  X-ray beam ( $h\nu = 1486.6$  eV) was generated by a 25 W, 15 KV electron beam and was used to analyse the different binding energy peaks. Carbon was used as the binding energy reference and the corresponding data was shifted towards 284.5 eV ( $C1s$ ). The fitting software used was OriginPro 9.1. A Gaussian function was used to perform the XPS curve fitting with either a manual (for high background noise samples) or Shirley-type background subtraction.

Surface sputtering was performed using an  $\text{Ar}^+$  ion gun (2 KV, 2  $\mu\text{A}$ ), and a low-energy neutraliser electron gun. This process minimised surface charging and removed surface contamination on the powdered samples during storage.

## S10. Purpose Built LED Solar Simulator for Photocatalytic Reactions

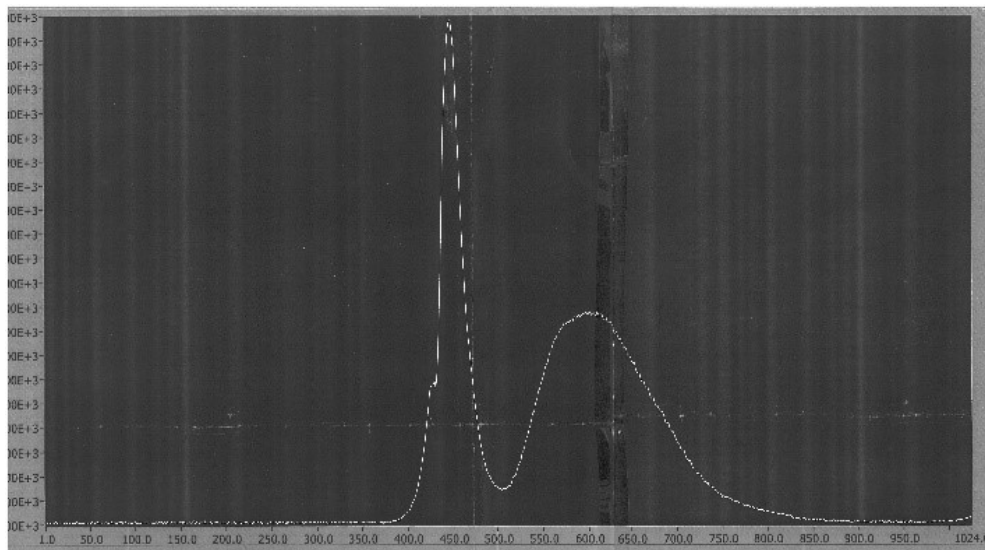
An in-house LED solar simulator was built for the application of photocatalysing the oxidation of alcohols to aldehydes and photodegrading methylene blue and eosin Y (**Figure S4**).





**Figure S4:** Constructed purpose-built LED solar simulator.

The emission spectrum of the LED solar simulator was accurately detected using a Newport Oriol Instruments minispectrometer (model-number: 78356), which was calibrated against visible laser lines and is depicted in **Figure S5** below.



**Figure S5:** The purpose-built LED solar simulator and emission spectrum collected from a

Newport Oriel Instruments minispectrometer (model-number: 78356), which was calibrated against visible laser lines. The result of the analysis confirmed that the LED solar simulator did not emit UV light, thus confirming the activation of Cu/Pd-N-TiO<sub>2</sub> using visible light only. In addition, all of the alcohol oxidation reactions were performed in borosilicate test tubes, which prevents UV transmission.

- The LED brand used was: HID Xenon Super Vision HID Head Lamp.
- The solar light intensity was: 6000 K
- Luminous flux: 3-point position average around the inside of the reactor at 10 cm distances from the lamps =  $1387 \times 10^2$  Lux

## S11. Experimental Procedure for Photocatalytic Reactions using Cu/Pd-N-TiO<sub>2</sub>.

### S11.1. Typical experimental procedure for the oxidation of benzylic alcohols using Cu/Pd-N-TiO<sub>2</sub>.

In a borosilicate test tube (7.5 mL), 2.5 mL toluene (dry-molecular sieves) was added, followed by 20 mg Cu/Pd-N-TiO<sub>2</sub>. 0.1 mmol of the benzylic alcohol was carefully dispensed into the solvent. Next, the test tube was bubbled with medical-grade gaseous oxygen for a period of 1.5 minutes; after which, the test tube was sealed with a rubber septum, parafilm and teflon tape. The headspace of the tube was filled with gaseous oxygen for 30 seconds. The contents of the test tube were irradiated using a purpose-built LED solar simulator for five hours with continuous stirring. After the irradiation period, the reaction contents were filtered through cotton wool and a *ca.* 80 ppm solution was quantitatively analysed using gas chromatography-mass spectrometry on a Shimadzu QP2010SE equipped with a Zebron ZB-5MSplus column.

### S11.2. Typical experimental procedure for the photodegradation of dyestuffs (methylene blue and eosin Y).

Methylene blue and eosin Y were prepared at 80 ppm stock solutions (20 mg in 250 ml volumetric flasks and topped up to mark with de-ionised water). For each photo-degradation reaction, 5 mL of 80 ppm stock solution were dissolved in 15 mL de-ionised water to prepare 20 mL of 20 ppm organic dyestuff solution for analysis. Prior to photocatalysis degradation,

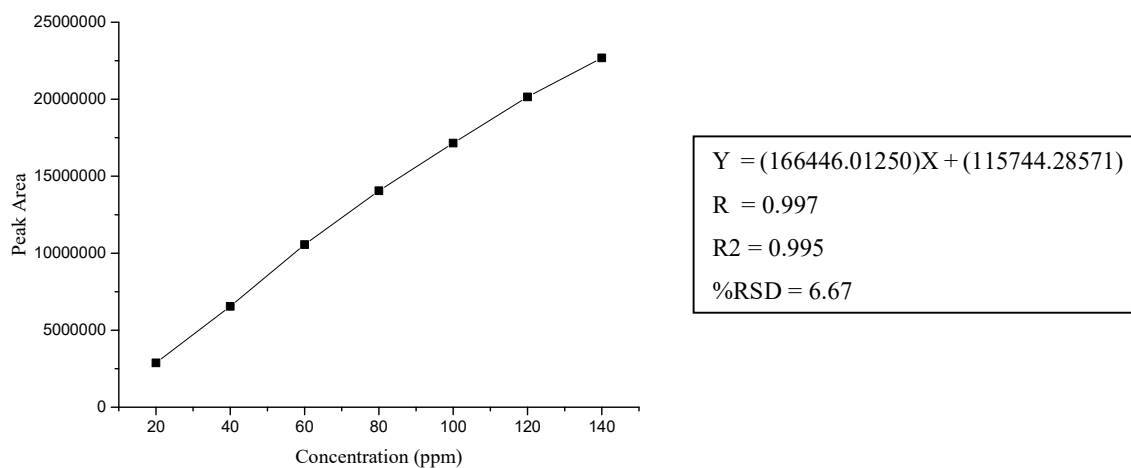
the 20-ppm solution with thirty milligrams of Cu/Cu-N-TiO<sub>2</sub> were left for 30 minutes in the dark to achieve a substrate-photocatalyst adsorption-desorption equilibrium. Sampling aliquots were collected at 15-minute intervals for the first hour, then every hour until the seventh hour (the sampling times [from time = 0 minutes] were: 15, 30, 45 minutes, 1, 2, 3, 4, 5, 7 hours respectively). The absorbance of each aliquot was spectrophotometrically analysed on a PG Instruments Limited T80 UV/VIS spectrophotometer. Data was processed with UVWin5 analytical software (V5.1.1.1).

## S12. Alcohol quantification using gas chromatography-mass spectrometry

### S12.1. 4-Octylphenol calibration curve

The accurate quantification of oxidised products from the use of Cu/Pd-N-TiO<sub>2</sub> required an internal standard during the chromatographic process. For this purpose, 4-octylphenol was introduced into the study (Tables 2, 3 and 8). An internal standard using gas chromatography was chosen as the appropriate quantitative method as many starting material/product(s) made it impractical to perform a full external calibration curve for each reaction. In addition, the low reaction scale (0.1–0.2 mmol) made it experimentally impossible to purify the product in sufficient quantity.

A calibration curve (20–140 ppm) was constructed using 4-octylphenol (**Figure S6**).



**Figure S6:** 20–140 ppm calibration curve of 4-octylphenol that was used to quantitate the conversion of alcohols to aldehydes.

During the work up stage after each reaction, a product concentration of approximately 80 ppm was prepared. The concentration (*ca.* 80 ppm) was chosen to fall within the internal standard's calibration set (20–140 ppm), which would further improve the accuracy of the respective (alcohol and internal standard) response factors.

S12.2. Quantitative formulations to detect the remaining alcohol after the reaction process.

The conversion of alcohols into aldehydes was quantitatively measured using gas chromatography-mass spectrometry (GC-MS) on a Shimdazu QP2010SE equipped with a Zebron ZB-5MSplus column. Gas chromatography was the chosen quantitative technique to determine the oxidised product due to the low reaction scale (0.1–0.2 mmol).

Therefore, an internal standard (4-octylphenol) was calibrated against each alcohol tested after which, relative response factors were calculated and used as references to determine the amount of unreacted alcohol that remained after each photocatalytic reaction, and hence the alcohol conversion. The internal standard was also calibrated against the corresponding aldehyde for the accurate quantification of the aldehyde's yield and selectivity.

The response factor of the selected alcohol was based upon the relationship between peak area and the concentration of the alcohol. The same equation applied to the corresponding aldehyde, as noted in **Equation S1**.

$$RF = \frac{PA_A}{[A]} \quad \text{Equation S1}$$

Where: \* RF = Response factor

\*  $PA_A$  = Peak area of the alcohol or aldehyde

\*  $[A]$  = Alcohol or aldehyde concentration

Furthermore, in order to establish the association between the alcohol (and aldehyde) with the internal standard, which would later serve to quantify the remaining alcohol in the reaction test

(or the amount of aldehyde formed), a response factor of the alcohol (and the corresponding aldehyde) relative to the internal standard needed consideration (**Equation S2**).

From the expression,

$$\text{RRF} = \frac{\text{RF}_A}{\text{RF}_{\text{IS}}} \quad \text{Equation S2}$$

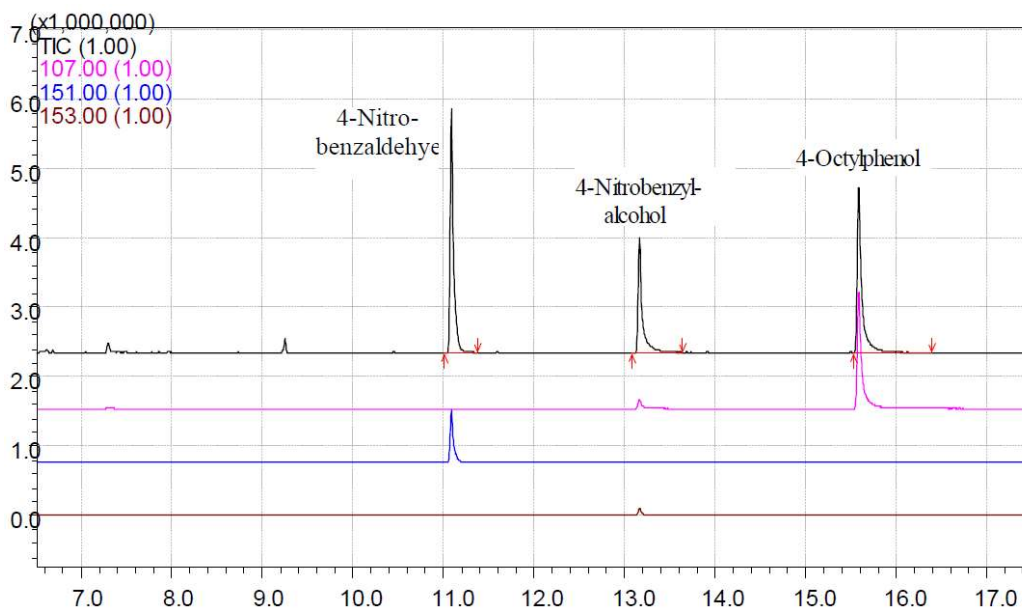
Where:

\* RRF = Relative response factor

\*  $\text{RF}_A$  = Response factor of the alcohol or aldehyde

\*  $\text{RF}_{\text{IS}}$  = Response factor of the internal standard or aldehyde

Consider for example **Figure S7**:



**Figure S7:** Chromatogram of 4-nitrobenzyl alcohol oxidation to 4-nitrobenzaldehyde with the respective internal standard (4-octylphenol).

**Consider for example Figure S7:** The chromatogram representing the oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde and the presence of the internal standard (4-octylphenol) to quantitate the reaction progress.

Note: A Slight incompatibility existed between the polarity of starting alcohols and/or solvent with the column stationary phase, which was observed from the minor peak tailing in selected chromatograms.

The peak areas of 4-nitrobenzyl alcohol, 4-nitrobenzaldehyde and 4-octylphenol were integrated to obtain their respective values (4-nitrobenzyl alcohol [5272312], 4-nitrobenzaldehyde [8754300] and 4-octylphenol [5361877]) in **Figure S7**.

From independent response factor chromatograms, the response factors for 4-nitrobenzyl alcohol (131809.09) and 4-nitrobenzaldehyde (139243.91) were calculated. From these response factors, the relative response factors to the internal standard were subsequently determined (4-nitrobenzyl alcohol [0.78] and 4-nitrobenzaldehyde [0.82]). The relative response factor values of the alcohols and aldehydes used in the photo-oxidation studies have been tabulated below (**Table 1**).

**Table 1:** Relative response factors for the alcohols and aldehydes used in the photo-oxidation studies

Alcohols	Relative Response Factors (RRF)	
	Alcohol (OH) RRF (OH)	Aldehyde (CHO) RRF(CHO) <sup>b</sup>
3,4-Dimethoxybenzyl alcohol	1,11	1,03
4-Methoxybenzyl alcohol	1,12	1,08
4-Nitrobenzyl alcohol	0,78	0,82
2-Naphthalene methanol	1,62	1,46
Cinnamyl alcohol	1,23	1,28
3-Clorobenzyl alcohol	0,99	Not available
Benzyl alcohol	1,14	1,01
Cyclohexanol	0,77	0,58
4-Methylbenzyl alcohol <sup>b</sup>	0,88	Not available

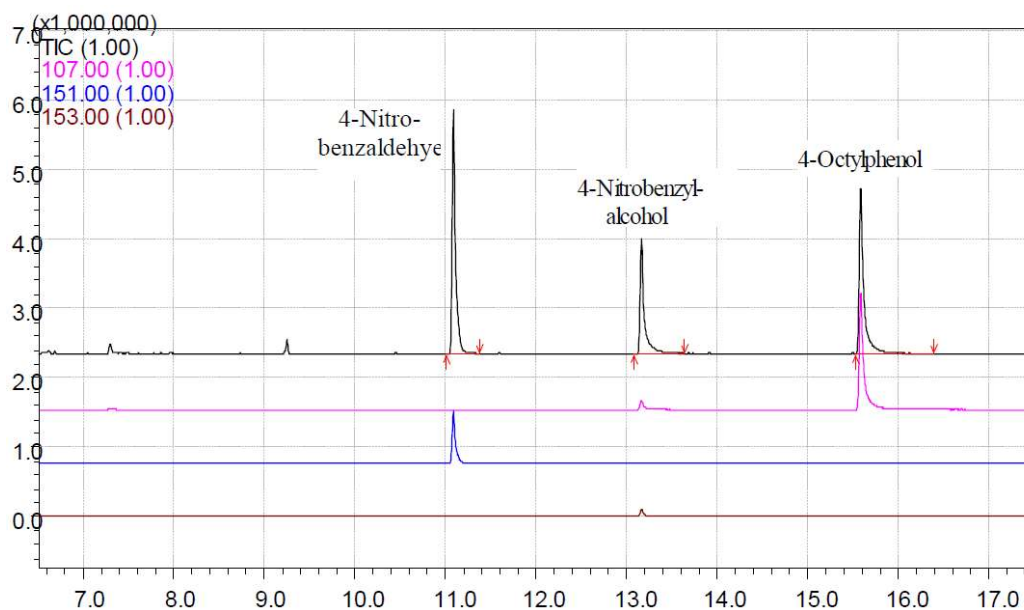
<sup>b</sup>Not available, the corresponding aldehyde was not available to determine the relative response factor.

Once the quantitative parameters were collected (relative response factors for both 4-nitrobenzyl alcohol and 4-nitrobenzaldehyde), the sample (**Figure S7**) could be quantitatively analysed.

The concentration of the remaining 4-nitrobenzyl alcohol after the reaction was calculated from knowing the response factor of 4-nitrobenzyl alcohol and 4-octyl phenol after combining **Equation S1** and **Equation S2**:

$$[A] = PA_A \times \frac{[IS]}{PA_{IS}} \times \frac{1}{RRF_A} \quad \text{Equation S1}$$

For example: The oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde (Figure S8).



**Figure S8:** The chromatogram representing the oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde using Cu/Pd-N-TiO<sub>2</sub>.

Calculations:

$$\begin{aligned}
 [\text{OH}] &= PA_{\text{OH}} \times \frac{[\text{IS}]}{PA_{\text{IS}}} \times \frac{1}{RRF_{\text{OH}}} \\
 &= PA_{\text{OH}} \times \frac{[\text{IS}]}{PA_{\text{IS}}} \times \frac{1}{\frac{RF_{\text{OH}}}{RF_{\text{IS}}}} \\
 &= 5272312 \times \frac{31.52}{5361877} \times \frac{1}{\frac{131809.09}{170019.28}} \\
 &= 39.98 \text{ ppm} \pm 6.67 \%
 \end{aligned}$$

The concentration (39.98 ppm) of 4-nitrobenzyl alcohol noted above was the remaining alcohol in the reaction solution after the five-hour reaction period. The same calculation (**Equation S4**)



was used to determine the corresponding 4-nitrobenzaldehyde concentration after the five-hour reaction period (62.86 ppm).

Note: Prior to analysing the reaction contents (**Equation S8**), the crude mixture was too concentrated for a direct injection into the GC-MS. An approximate analyte concentration of 80 ppm was prepared as it was within the calibration curve's concentration range (20–140 ppm). The sample dilution (to achieve an *ca.* 80 ppm analyte solution) was prepared accordingly:

Sample dilution factor:

Assuming 0 % conversion of 0.1 mmol 4-nitrobenzyl alcohol in 2.5 mL toluene (reaction solvent), the alcohol concentration would be calculated as follows:

$$0.1 \text{ mmol of 4-methylbenzyl alcohol} = 15.31 \text{ mg}$$

$$15.31 \text{ mg in 2.50 mL} = 6124.00 \text{ ppm}$$

To achieve an alcohol concentration of *ca.* 80 ppm, a 59.38 $\times$  dilution was introduced (25.26  $\mu$ L of the reaction analyte in 1474.47  $\mu$ L of solvent). The total volume prepared for GC-MS analysis = 1.5 mL.

At 0 % conversion, the concentration of 4-nitrobenzyl alcohol was:

$$= 6124.00/59.38$$

$$= 103.13 \text{ ppm}$$

The conversion of 4-nitrobenzyl alcohol was then determined as follows:

$$C = \frac{[OH]^0 - [OH]^t}{[OH]^0} \times 100 \quad \text{where } [OH]^0 = \text{alcohol concentration at the start of the reaction, i.e. 0\% conversion and } [OH]^t = \text{alcohol concentration remaining at the end of the reaction period 't'.$$

$$C = \frac{103.13 - .98}{103.13} \times 100$$

$$= 61 \%$$

The yield of 4-nitrobenzylaldehyde was then determined as follows:

$$Y = \frac{[CHO]^t}{[OH]^0} \times 100 \quad \text{where } [CHO]^t = \text{aldehyde concentration at the end of the reaction period 't' and } [OH]^0 = \text{the alcohol concentration at the start of the reaction period.}$$

$$Y = \frac{62.86}{103.13} \times 100$$

$$= 61 \%$$

The selectivity for 4-nitrobenzaldehyde was then determined as follows:

$$S = \frac{[CHO]^t}{[OH]^0 - [OH]^t} \times 100 \quad \text{where } [CHO]^t = \text{aldehyde concentration at the end of the reaction period 't', } [OH]^0 = \text{alcohol concentration at the start of the reaction, i.e. 0\% conversion and } [OH]^t = \text{alcohol concentration remaining at the end of the reaction period 't'.$$

$$S = \frac{62.86}{103.13 - .98} \times 100$$

$$= \geq 99 \%$$

## S13. TiO<sub>2</sub> derivatives

### S13.1. Nitrogen functionalised titanium dioxide

Nitrogen functionalised titanium dioxide (N-TiO<sub>2</sub>) was prepared according to a literature method reported by Wang *et al.*<sup>[1]</sup> In a typical synthetic procedure, TTIP (10.55 mmol, 3.12 mL) was added drop-wise into de-ionised water (15 mL) followed by the addition of nitric acid (25 %, 4 mL). The mixture was continuously stirred until the titanium hydroxide (Ti[OH]<sub>4</sub>) precursor had dissolved from acid assistance (30 minutes). Nitrogen was introduced after aqueous ammonia (25 %) was added to obtain a solution of pH *ca.* 9. Once the nitrogen source was added, the heterogeneous aqueous mixture was filtered, and the white precipitate was washed several times with de-ionised water. The nitrogen functionalised titanium dioxide was oven dried at 45 °C and calcinated at 350 °C for 2 hours, which afforded a yellow powder that was finely ground for further use.

### S13.2. Cu/Pd-N-TiO<sub>2</sub>

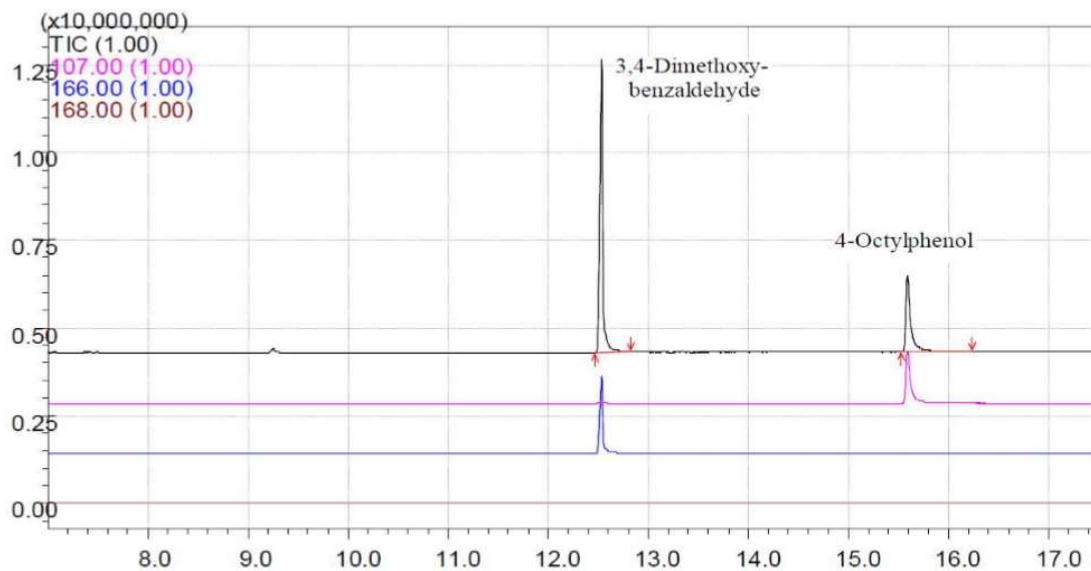
In a typical synthetic procedure, TTIP (10.55 mmol, 3.12 mL) was added drop-wise into de-ionised water (15 mL) followed by the addition of nitric acid (25 %, 4 mL). The mixture was stirred until the titanium hydroxide (Ti[OH]<sub>4</sub>) precursor had dissolved from acid assistance (30 minutes). Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (62.09 μmol, 15 mg in 2 mL absolute ethanol) and Pd(OAc)<sub>2</sub>·4H<sub>2</sub>O (30 mg in 2 mL absolute ethanol and 1 mL methanol) were prepared, added dropwise to the acidified aqueous titanium solution and proceeded with ten minutes stirring at room temperature. Aqueous ammonia (25 %) was subsequently added to lower the pH to *ca.* 9, which introduced the nitrogen component to the system. The solution colour turned light blue with a light blue precipitate forming upon addition of aqueous ammonia. After the neutralisation stage, the solution was filtered and the light blue Cu/Pd-N-TiO<sub>2</sub> precipitate was oven dried at 45 °C and calcinated at 350 °C for 2 hours. The resultant material, which was light brown in colour was ground to a fine powder for instrumental characterisations.

### S13.3. Methylene blue and eosin Y preparation

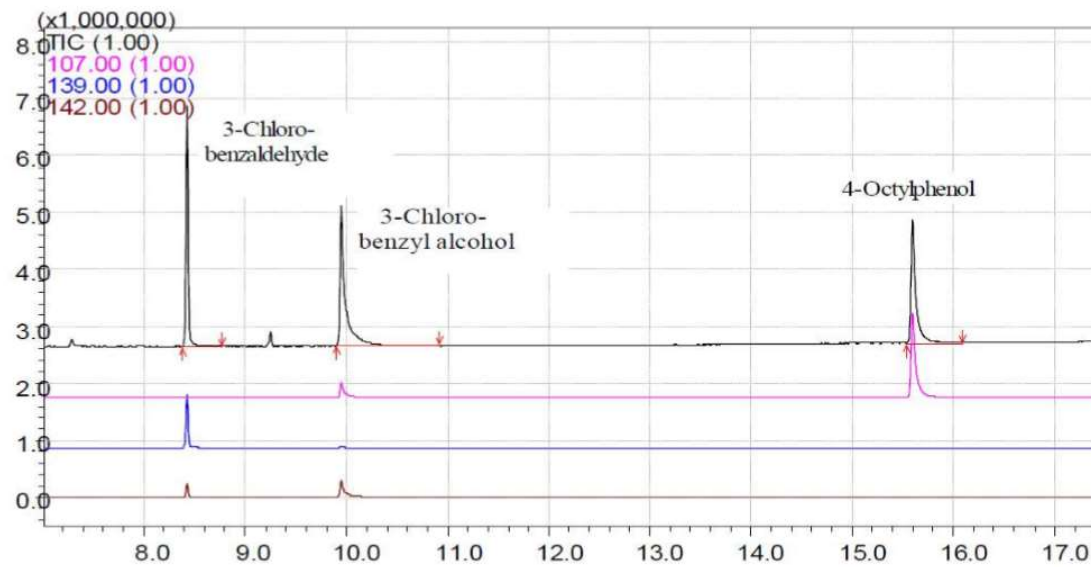
Methylene blue and eosin Y were prepared at 80 ppm stock solutions (20 mg in 250 mL volumetric flasks and topped up to mark with de-ionised water). For each photo-degradation reaction, 5 mL of 80 ppm stock solution were dissolved in 15 mL de-ionised water to prepare 20 mL of 20 ppm organic dyestuff solution for analysis.

## S14. Chromatograms

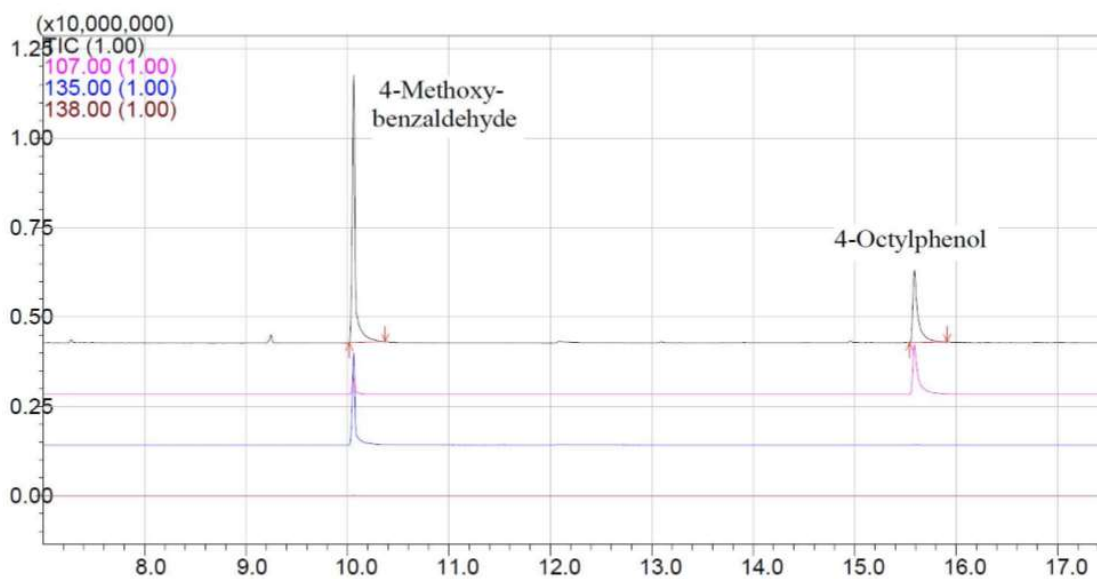
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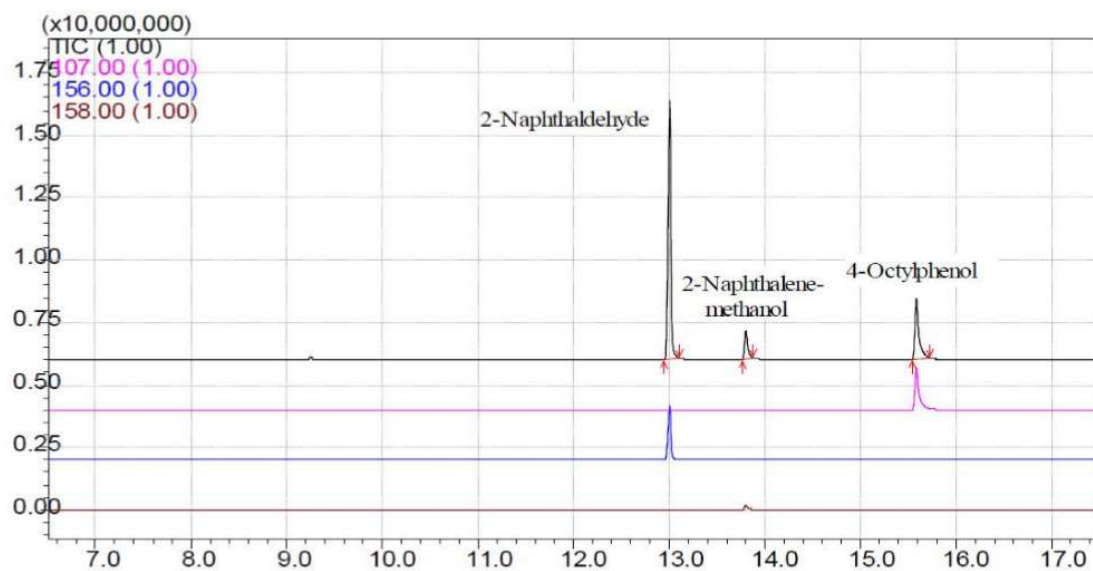
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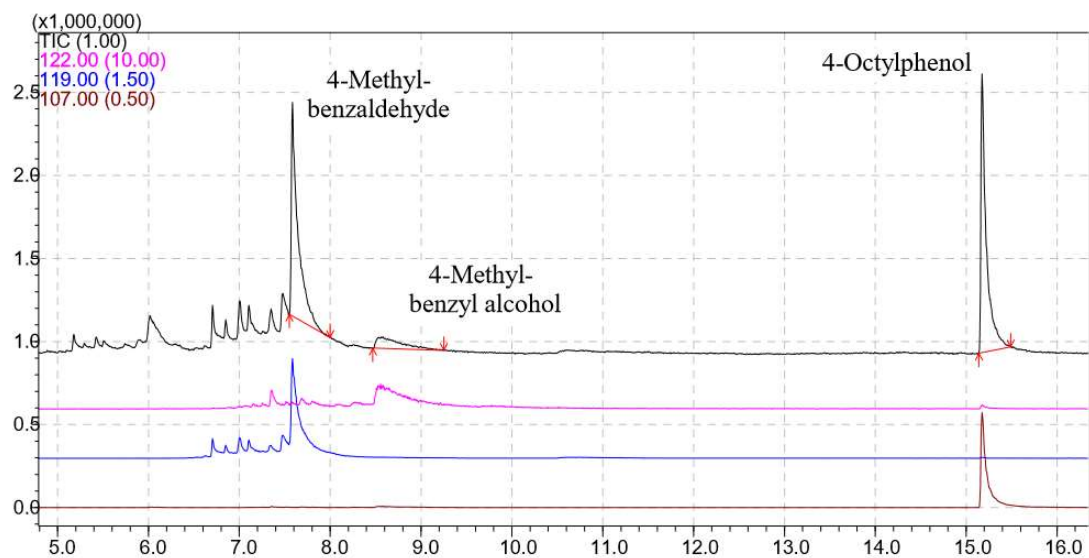
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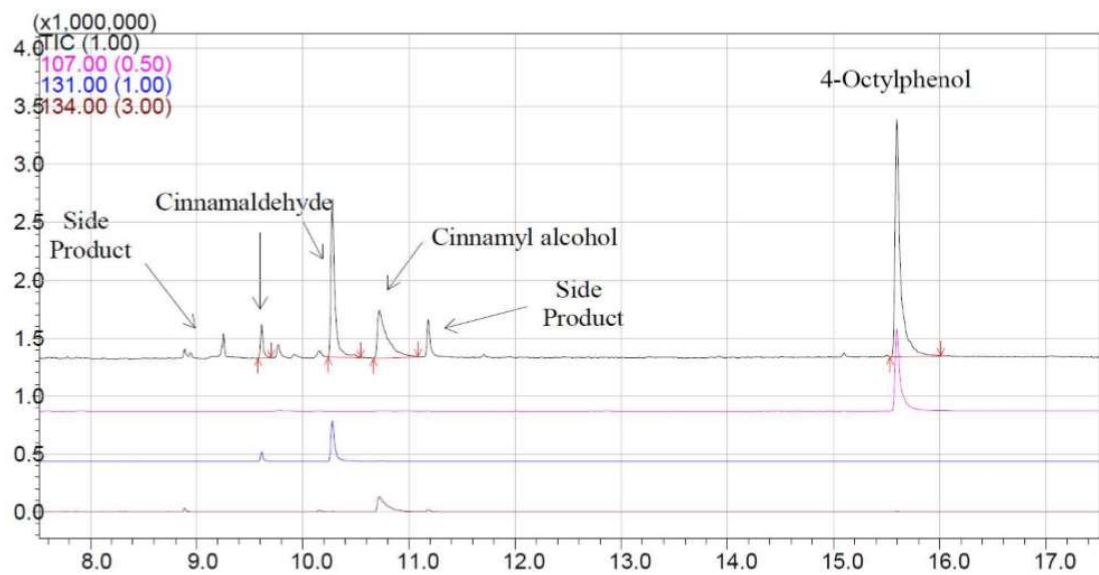
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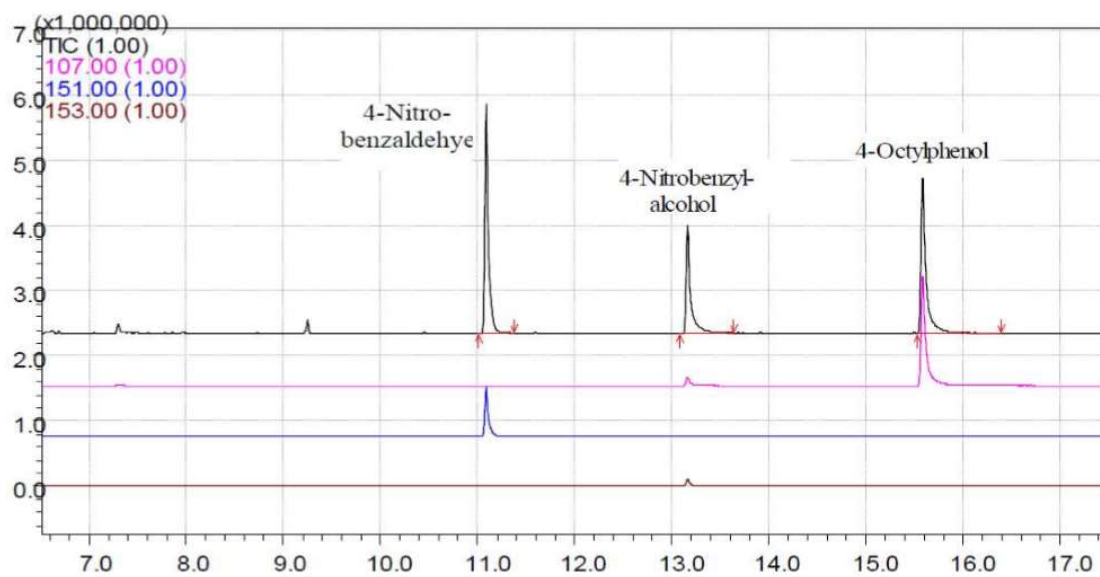
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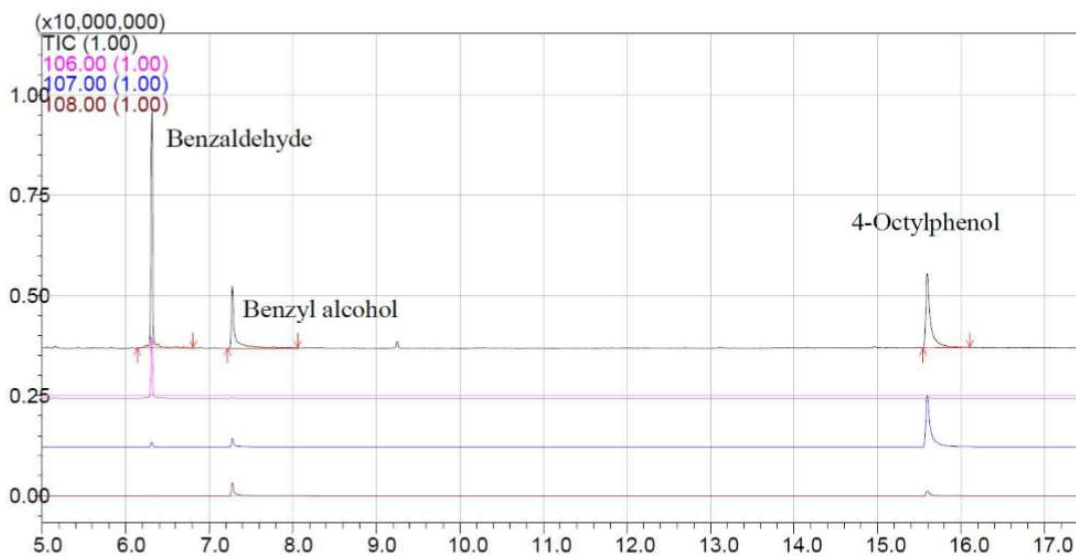
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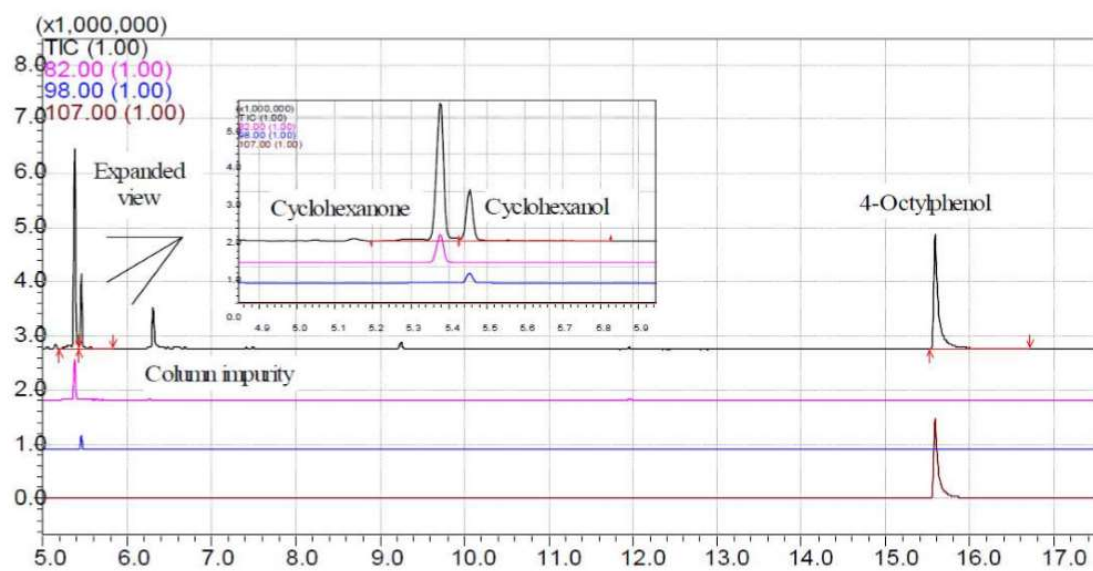
Entry 7



Entry 8



## Entry 9



## References

- [1] J. Wang, W. Zhu, Y. Zhang, S. Liu, *The Journal of Physical Chemistry C* **2007**, *111*, 1010-1014.