



Queensland University of Technology
Brisbane Australia

This is the author's version of a work that was submitted/accepted for publication in the following source:

Wang, Yunwei, Ren, Pengju, Gu, Xianmo, Wen, Xiaodong, Wang, Yingyong, Guo, Xiangyun, [Waclawik, Eric R.](#), [Zhu, Huaiyong](#), & [Zheng, Zhanfeng](#)
(2016)

Probing the mechanism of benzaldehyde reduction to chiral hydrobenzoin on the CNT surface under near-UV light irradiation.
Green Chemistry, 18(6), pp. 1482-1487.

This file was downloaded from: <https://eprints.qut.edu.au/93783/>

© Copyright 2016 Royal Society of Chemistry

Notice: *Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source:*

<https://doi.org/10.1039/c5gc02168e>

Electronic Supplementary Information (ESI)

Probing the mechanism of benzaldehyde reduction to chiral hydrobenzoin on CNTs surface under light irradiation

Yunwei Wang, Pengju Ren, Xianmo Gu, Xiaodong Wen, Yingyong Wang, Xiangyun Guo, Eric R. Waclawik, Huaiyong Zhu and Zhanfeng Zheng*

Table of Contents

Section 1 Experimental section	3
Materials, Characterisation, Catalytic performance evaluation, AQE calculation	
Fig. S1 The output spectra of LED and Xe light sources.	
Section 2 Catalyst structure.....	5
Fig. S2 XRD spectra of the purified CNTs and the CNTs after 5 cycles.	
Fig. S3 UV-Vis spectrum of purified CNTs.	
Fig. S4 EPR spectra of the supernatant in the presence of 0.035 mmol 4- <i>tert</i> -butylcatechol (TBC) after 1 h reaction.	
Fig. S5 FT-IR spectra of (a) purified CNTs, (b) differential spectra of CNTs after benzaldehyde vapour adsorption, and (c) liquid benzaldehyde.	
Section 3 Photocatalytic performances.....	7
Fig. S6 Recyclability of CNTs in benzaldehyde reduction reaction for five cycles.	
Fig. S7 The photocatalytic selectivity under 375 nm LED light in the presence of CNTs and under 200-320 nm Xe light.	
Fig. S8 The product in the absence of KOH and CNTs under UV light irradiation (200-320 nm Xe light).	
Fig. S9 The distribution of photocatalytic products from benzil at different reaction conditions in line with those in Table 2.	
Fig. S10 X-ray photoelectron (XPS) spectra of different CNTs.	
Fig. S11 Raman spectra of CNTs after different treatment.	
Fig. S12 The yield of (<i>R,R</i>)-hydrobenzoin and the area ratio of D/G XPS peaks of CNTs are plotted against the conversion of benzaldehyde.	
Fig. S13 Time profile for the photocatalytic reduction of benzaldehyde on CNTs -	

3000 at the optimised condition.

Fig. S14 Raman spectrum of CNTs-3000.

Fig. S15 Time-dependent H₂ evolution during photocatalytic conversion of benzaldehyde.

Table S1 The conversion of substituted benzaldehyde under near-UV light irradiation (320-700 nm Xe light) in the presence of CNTs and under middle-UV light irradiation (200-320 nm Xe light).

Table S2 The distribution of photocatalytic products from benzaldehyde under 320-700 nm irradiation in the absence of isopropanol.

Section 4 Mass spectra of the products15

Mass spectra of the catalytic products and intermediate products.

Section 5 Theoretical section.....18

Fig. S16 Optimised structure of benzaldehyde adsorbed on CNT.

Fig. S17 (a) Differential charge density for benzaldehyde adsorbed on CNT, where the yellow and blue regions represent the increased and decreased electron density, respectively. (b) Spin density distribution for benzaldehyde radical adsorbed on CNT, where the red and blue regions represent orbital phase φ^+ and φ^- .

Section 1 Experimental section

Materials. Multi-walled CNTs were purchased from Timesnano (Product Code: TNGM5) and all the other chemicals were from Sinopharm Chemical Reagent Co. Ltd. The obtained CNTs were purified via soaking in concentrated hydrochloric acid, then washed with distilled water and dried in air.

In the oxidation process, purified CNTs (0.3 g) were treated in concentrated nitric acid (25 mL) under refluxing for 10-20 h; the corresponding products were named as X-CNTs (X means the oxidation time). In the reduction process, the above oxidised CNTs (0.1 g) were refluxed in the mixture of hydrazine hydrate (2 mL) and distilled water (50 mL) for 12 h; the corresponding products were labelled as Xr-CNTs (X means the oxidation time).

The CNTs sample, which was calcined at 3000 °C in Ar atmosphere, was designated as CNTs-3000.

Characterisation. The catalysts were analyzed by transmission electron microscopy (TEM, JEOL 2010), X-ray photo-electron spectroscopy (XPS, Kratos XSAM800, Al K α = 1486.6 eV), X-Ray diffraction spectroscopy (XRD, Bruker D8 Advance, Cu K α , 40 kV), UV-vis spectroscopy (Hitachi UV-3900), FT-IR spectroscopy (Nicolet Magna-IR 550-II) and Raman spectroscopy (Horiba LabRAM HR800). EPR measurements at the X-band were performed on a Bruker EMX EPR spectrometer equipped with a TM-110 (ER 4103 TM) cylindrical cavity. The samples were irradiated and measured at 293 K.

Catalytic performance evaluation. The photocatalytic performance of CNTs for synthesis of chiral hydrobenzoin was investigated. Typically, the reactant mixture was consisted of 10 mL isopropyl alcohol, 1 mL KOH isopropyl alcohol solution (0.1 mol/L), 1 mmol benzaldehyde and 65 mg CNTs. The mixture was maintained at 75 °C for 6 h under light irradiation (300 W Xe lamp, 749 mW/cm²) in Ar atmosphere (1 atm). Two 300 W high-pressure xenon lamps, including PLS-SXE300UV (Beijing Trusttech Co. Ltd, 200-700 nm, used when wavelength below 320 nm was required) and CEL-HXF300 (Beijing Aulight Co. Ltd., 320-700 nm), and three singled colour LEDs (375 nm, 400 nm and 450 nm, Fancy. Tech. Co. Ltd) were used as light source. The light source was mounted on the top of the reactor. The intensity of irradiation light was controlled by adjusting the distance between the light source and the reaction liquid. The light intensity was measured at the cross-section of the light and the upper liquid surface using an optical power meter (Model 1918-R, Newport). The photocatalytic products were analyzed by a Bruker SCION SQ GC-MS spectrometer.

Apparent quantum yield (AQE) calculation

Reaction conditions: benzaldehyde (10 mmol), isopropyl alcohol (100 mL), KOH isopropyl alcohol solution (0.1 mol/L, 10 mL), CNTs (650 mg), 6 h, 75 °C, Ar atmosphere (1 atm), UV-LED light (375 nm), irradiation area and intensity (19.7 cm², 40 mW/cm²) at the reaction liquid surface.

The number of photons involving in the reaction can be calculated from the amount of generated hydrobenzoin molecules. Four photons were absorbed to obtain one hydrobenzoin molecule. The amount of hydrobenzoin [1 mmol benzaldehyde × 38% (conversion) × 87% (selectivity)] after 6 h was used for the calculation.

The number of incident photons can be calculated from the equation: $N = \frac{E\lambda}{hc}$, where E, λ , h and c are the total photon energy (40 mW/cm² × 19.7 cm² × 10⁻³ × 6 × 3600 s), the light wavelength (375 × 10⁻⁹ m), Plank's constant (6.63 × 10⁻³⁴ J·s) and the speed of light in vacuum (3 × 10⁸ m/s), respectively.

$$\begin{aligned} \text{AQE} &= \frac{\text{number of reacted electrons (photon excited)}}{\text{number of incident photons}} \times 100\% \\ &= \frac{\text{number of hydrobenzoin molecules evolved} \times 4}{\text{number of incident photons}} \times 100\% \\ &= \frac{6.02 \times 10^{20} \times 0.38 \times 0.87 \times 2 \times 6.63 \times 10^{-34} \times 3 \times 10^8}{40 \times 19.7 \times 10^{-3} \times 6 \times 3600 \times 375 \times 10^{-9}} \times 100\% \\ &= 1.2\% \end{aligned}$$

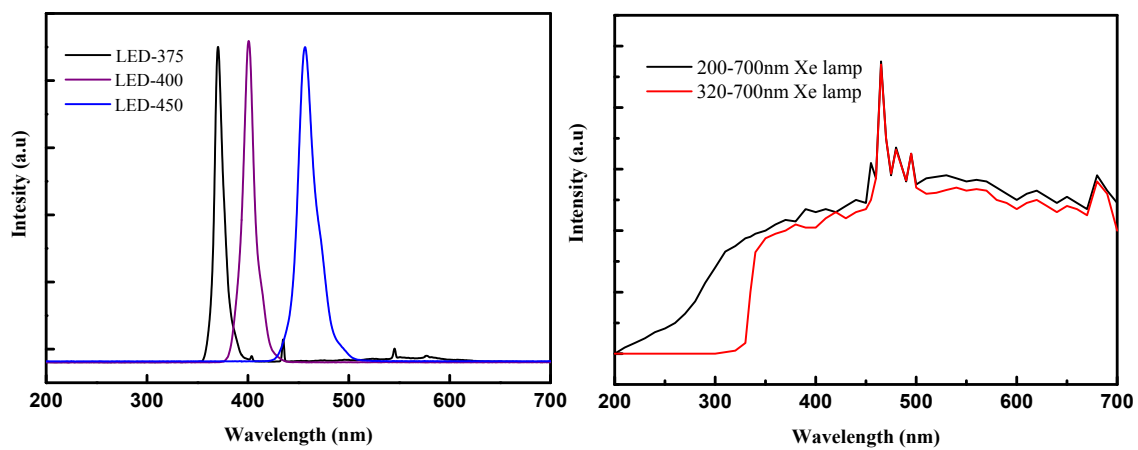


Fig. S1 The output spectra of LED and Xe light sources.

Section 2 Catalyst structure

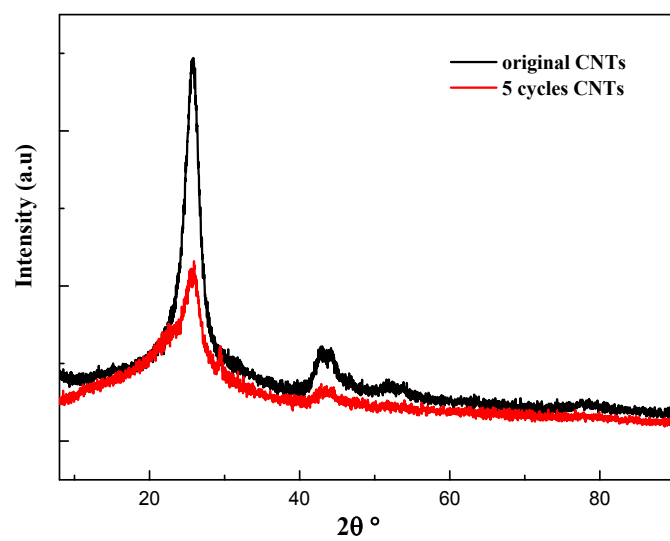


Fig. S2 X-ray diffraction (XRD) patterns of the purified CNTs and the CNTs used after 5 cycles.

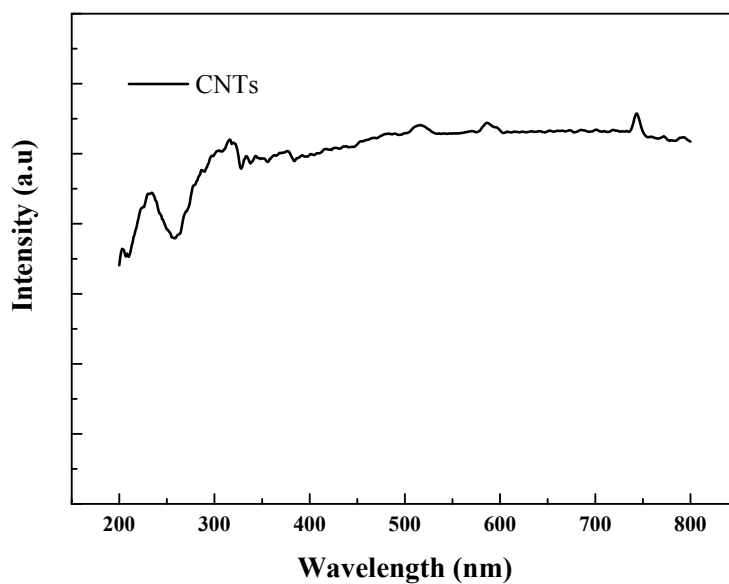


Fig. S3 UV-Vis spectrum of CNTs.

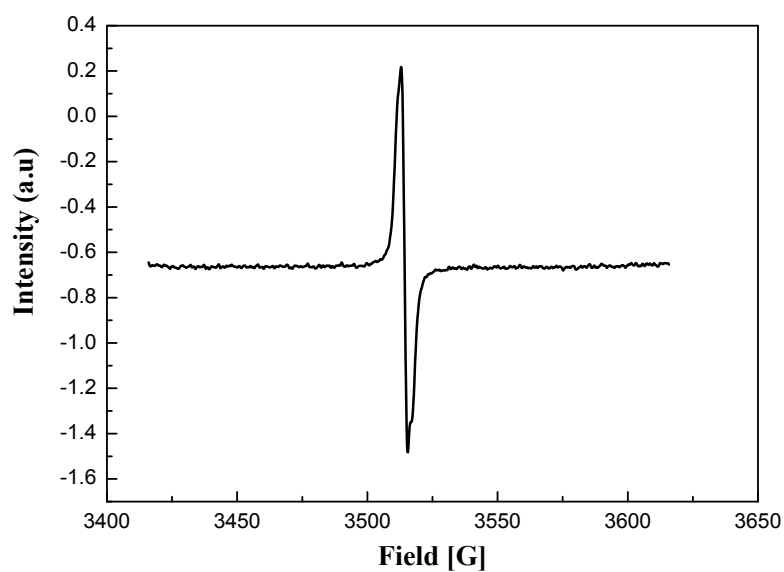


Fig. S4 Electron paramagnetic resonance (EPR) spectrum of the supernatant in the presence of 0.035 mmol 4-*tert*-butylcatechol (TBC) after 1 h photocatalytic reaction.

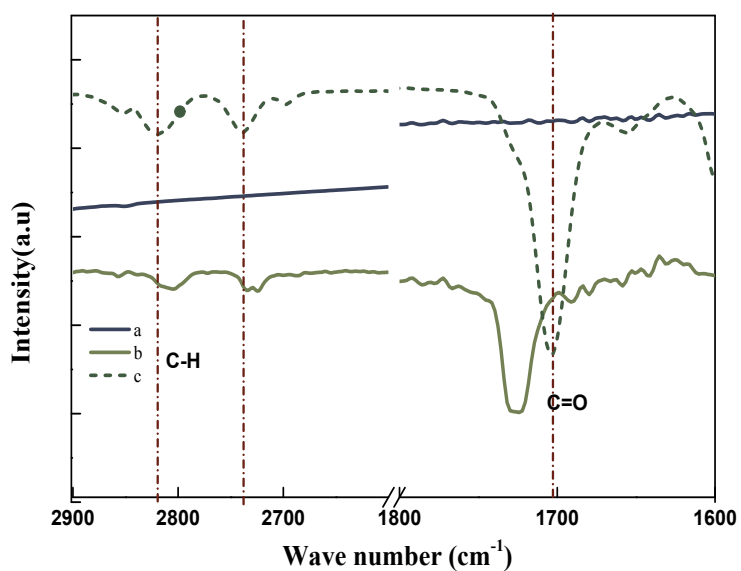


Fig. S5 FT-IR spectra of (a) purified CNTs, (b) differential spectra of CNTs after benzaldehyde vapour adsorption, and (c) liquid benzaldehyde.

Section 3 Photocatalytic performance

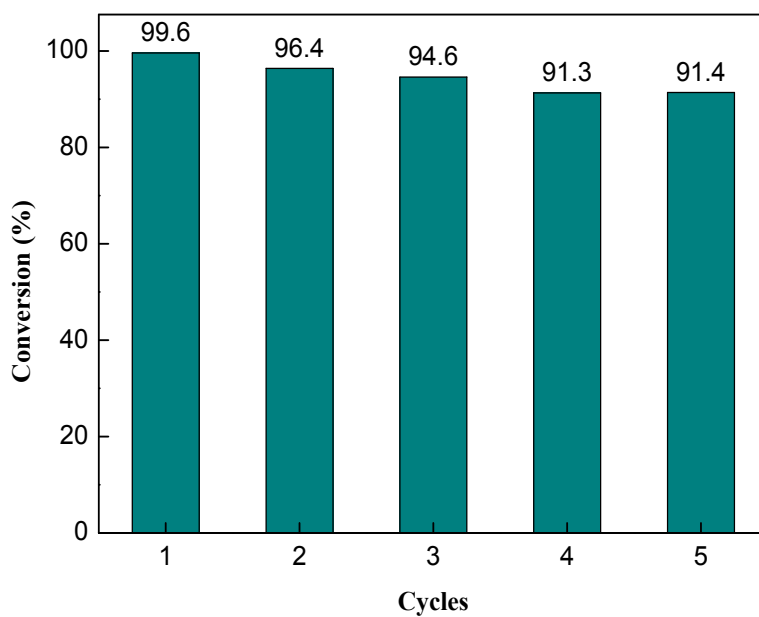


Fig. S6 Recyclability of CNTs in benzaldehyde reduction reaction for five cycles.

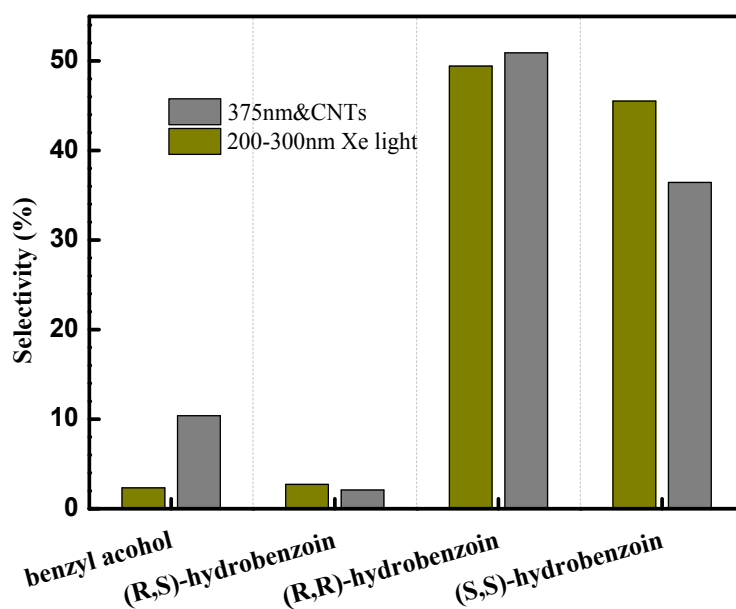


Fig. S7 The photocatalytic selectivity under 375 nm LED light in the presence of CNTs and under 200-320 nm Xe light.

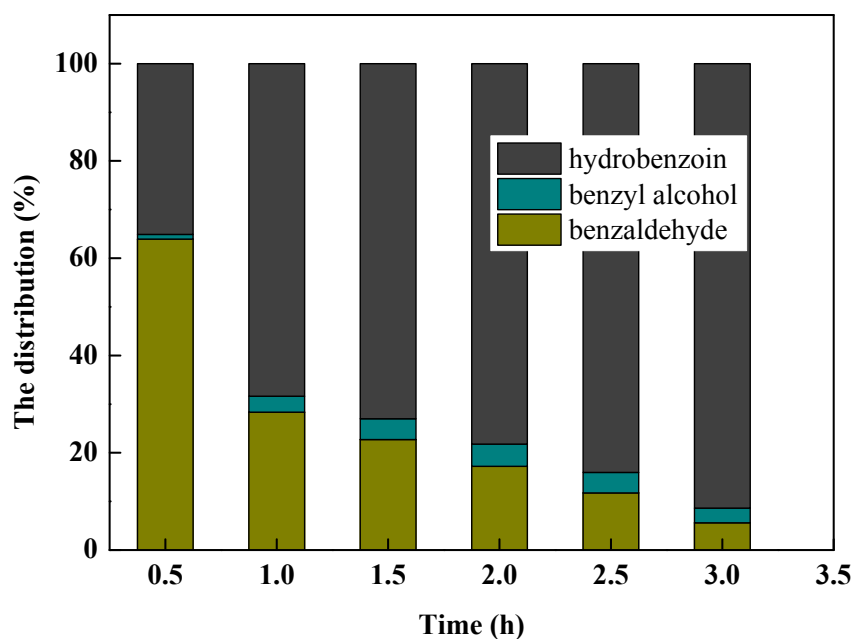


Fig. S8 The product in the absence of KOH and CNTs under UV light irradiation (200-320 nm Xe light).

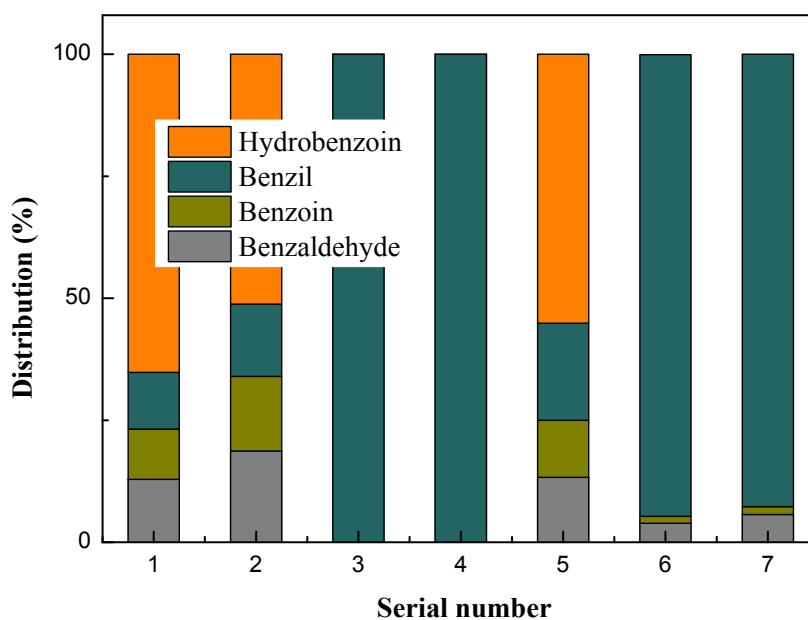


Fig. S9 The distribution of photocatalytic product from benzil at different reaction conditions in line with those in Table 2.

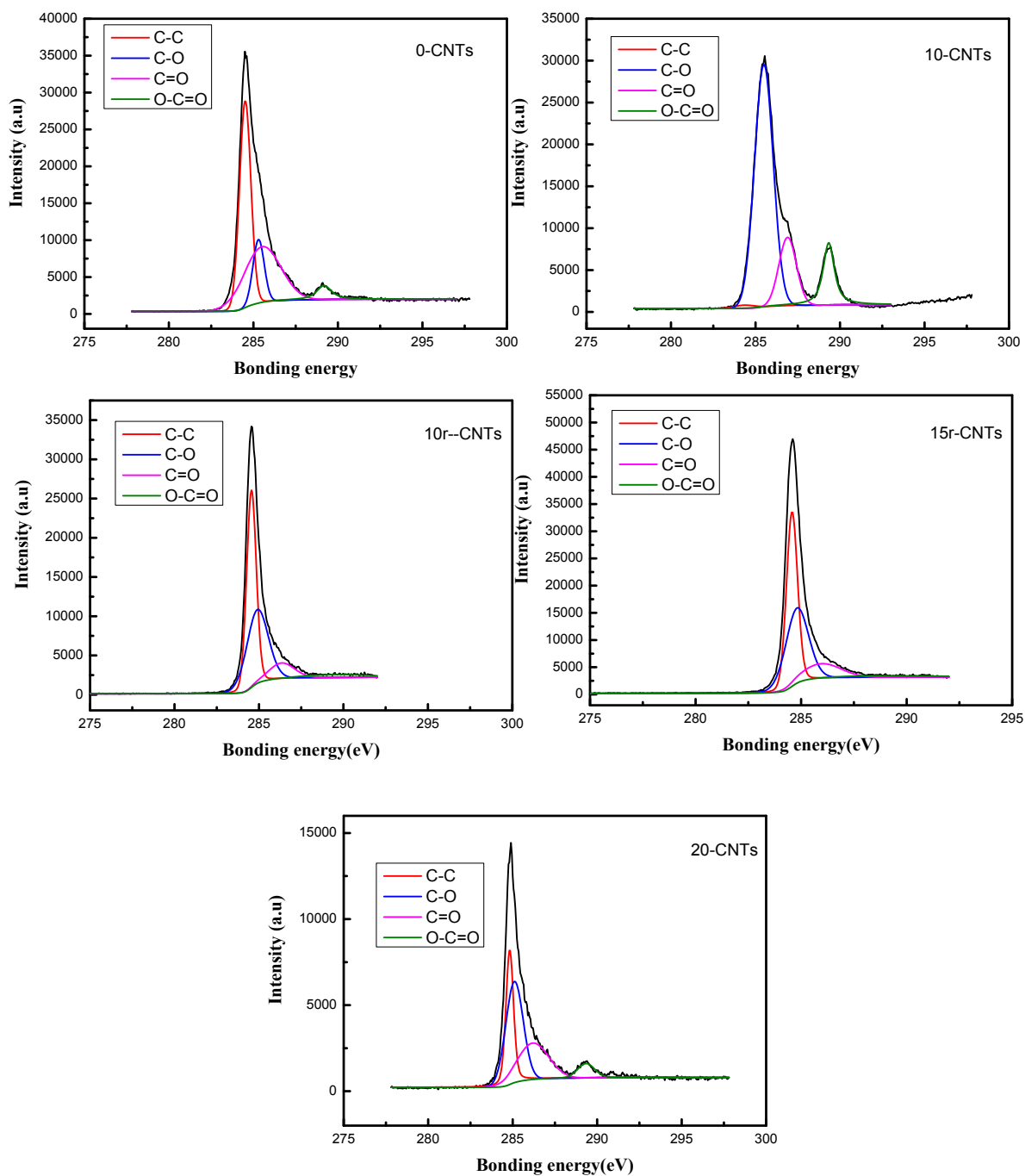


Fig. S10 XPS spectra of different CNTs.

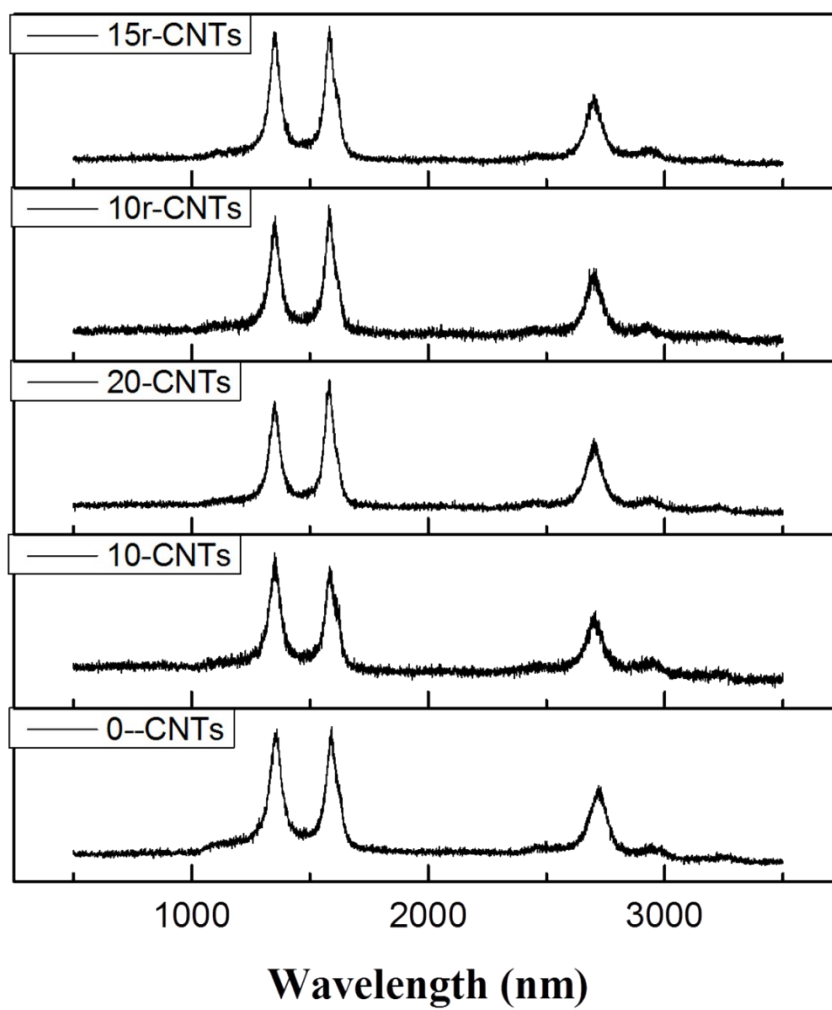


Fig. S11 Raman spectra of CNTs after different treatment.

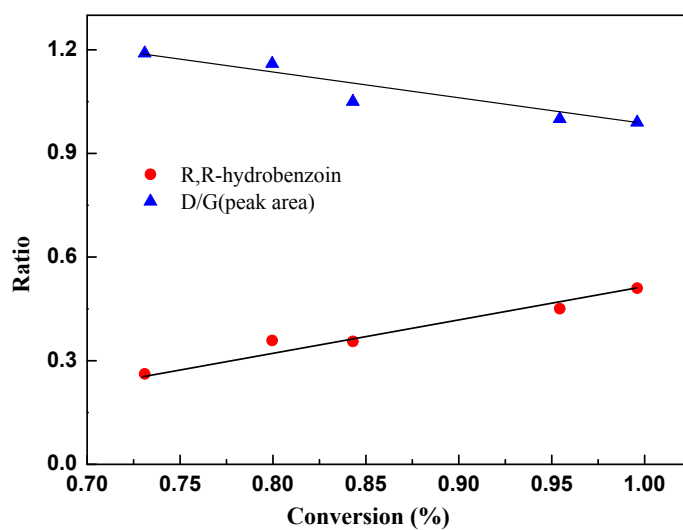


Fig. S12 The yield of (*R,R*)-hydrobenzoin and the area ratio of D/G XPS peaks of CNTs are plotted against the conversion of benzaldehyde.

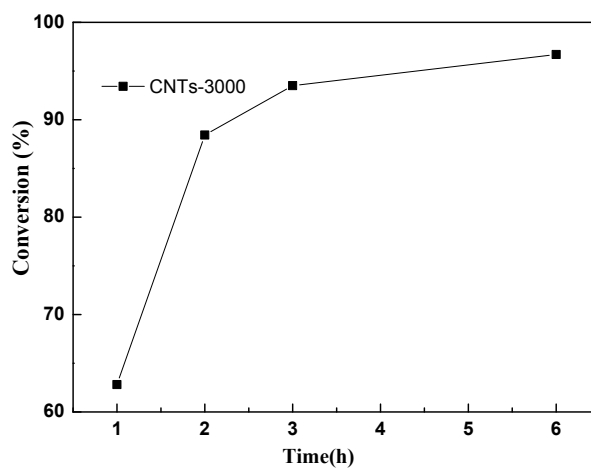


Fig. S13 Time profile for the photocatalytic reduction of benzaldehyde on CNTs - 3000 at the optimised condition.

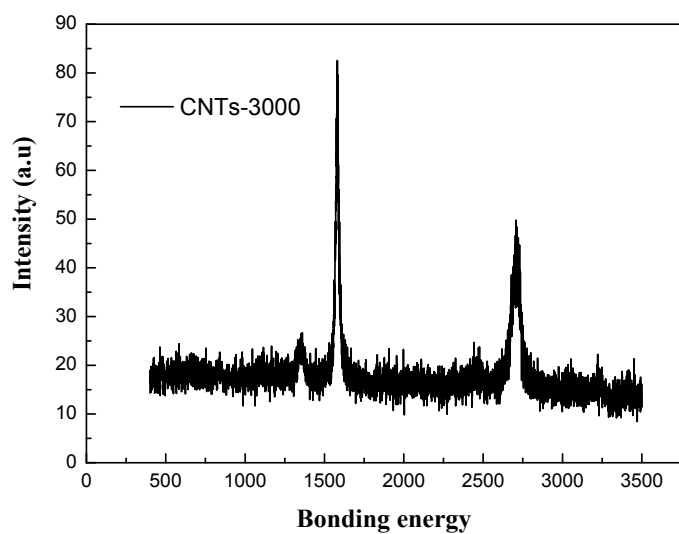


Fig. S14 Raman spectrum of CNTs-3000.

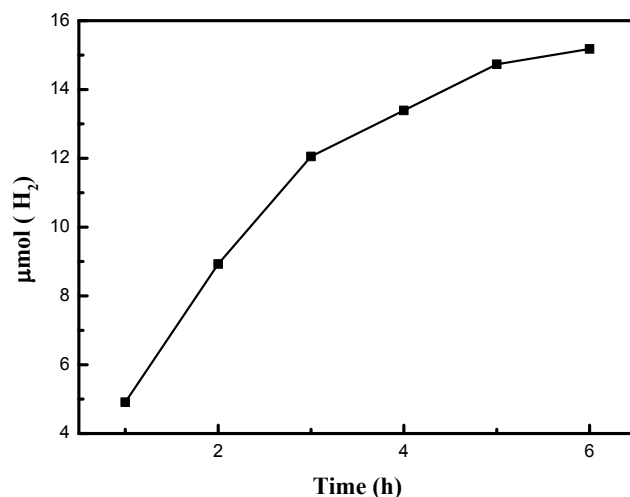

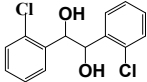
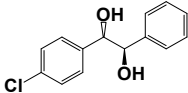
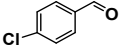

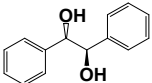
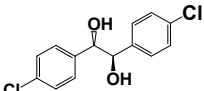
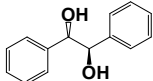
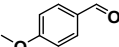
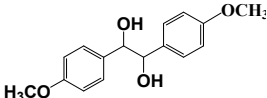
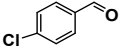
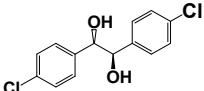


Fig. S15 Time-dependent H_2 evolution during the photocatalytic conversion of benzaldehyde. Reaction conditions: 10 mmol benzaldehyde, 100 mL isopropyl alcohol, 10 mL KOH isopropyl alcohol solution (0.1 mol/L), 650 mg CNTs, 1 atm N_2 , 75 °C, 6 h. The H_2 production reactions were performed in a flowing system (N_2 gas flow rate at 0.78 L/h) in a quartz reactor (400 mL) under a 300W Xe Lamp. The reaction system was pre-degassed by N_2 purging for 30 min. During the reaction, 1 mL of gas was sampled from the flowing system and analyzed by gas chromatography (GC-7920, Beijing Aulight Co., Ltd., MS-5Å column, TCD, Ar carrier).

Table S1 The conversion of substituted benzaldehyde under near-UV light irradiation (320-700 nm Xe light) in the presence of CNTs and under middle-UV light irradiation (200-320 nm Xe light).

Entry	Substrate	Yield (%) ^a	Yield (%) ^b
1		0	21.6 
			40.86 
2	 	94.71 	18.90 
			40.24 
3		0	43.1 
4		0	34.7 

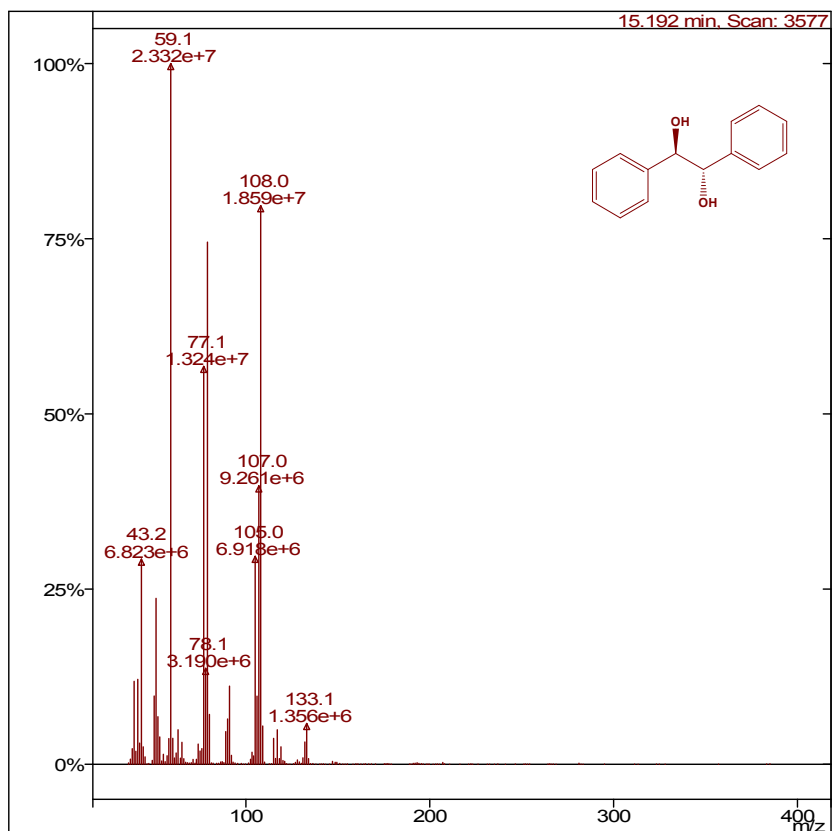
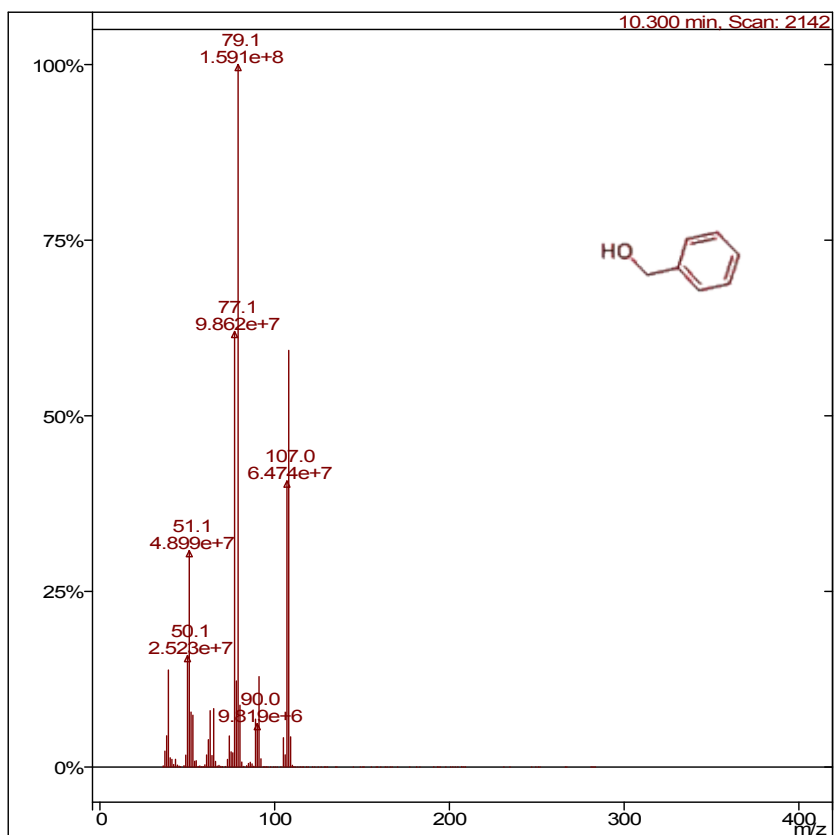
^a320-700 nm Xe light, 749 mW/cm², 65 mg CNTs. ^b200-320nm Xe light, 749 mW/cm²; The reactant mixture consists of 10 mL isopropyl alcohol, 1 mL (1 mmol/L KOH isopropyl alcohol solution), 1 mmol substrates, 6 h, 75°C.

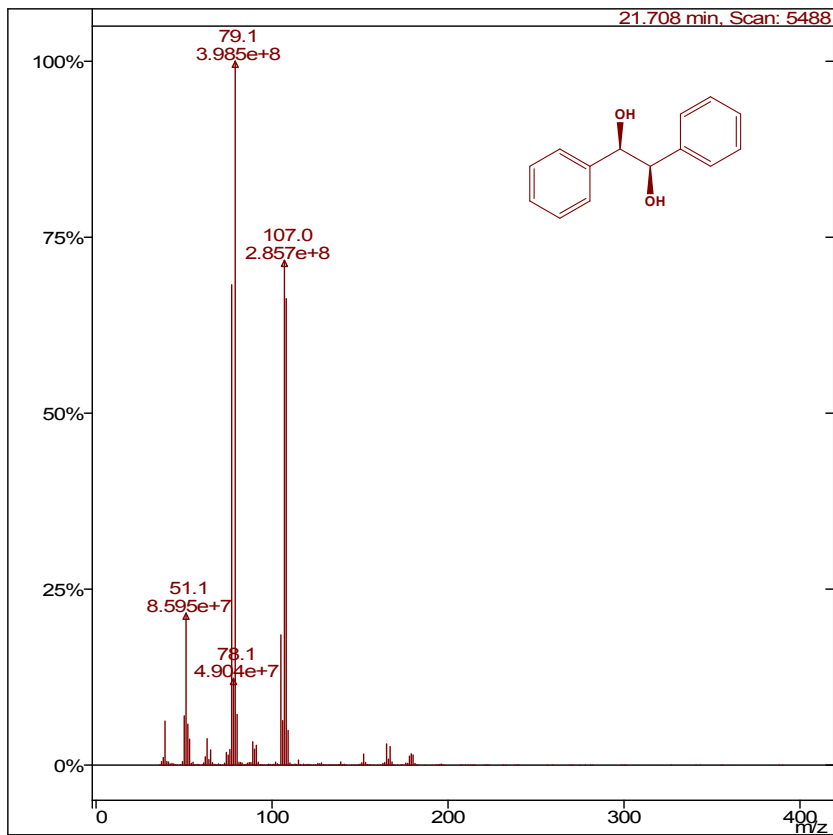
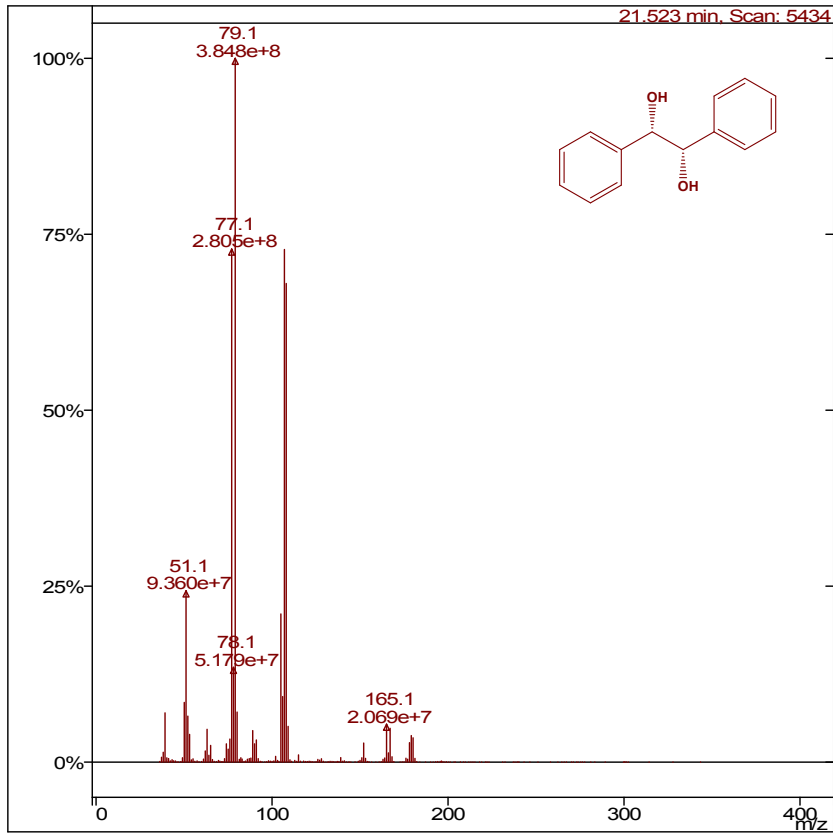
Table S2 The distribution of photocatalytic products from benzaldehyde under 320-700 nm irradiation in the absence of isopropanol.

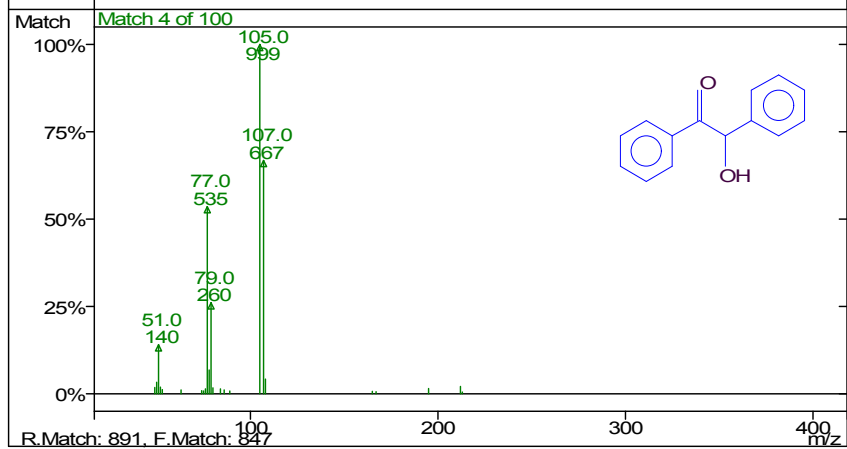
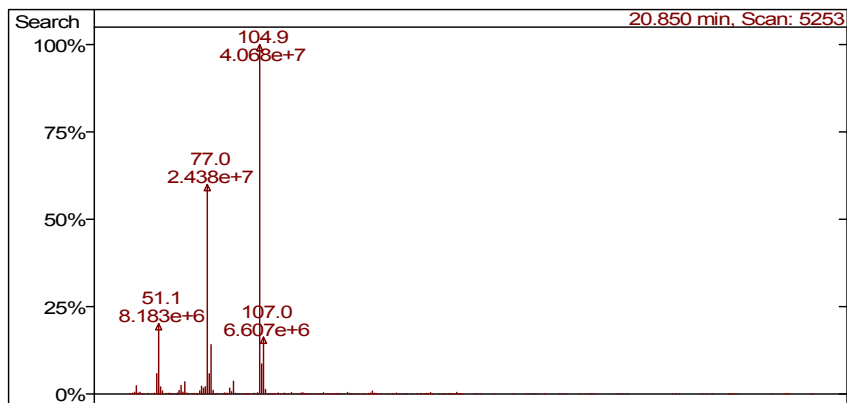
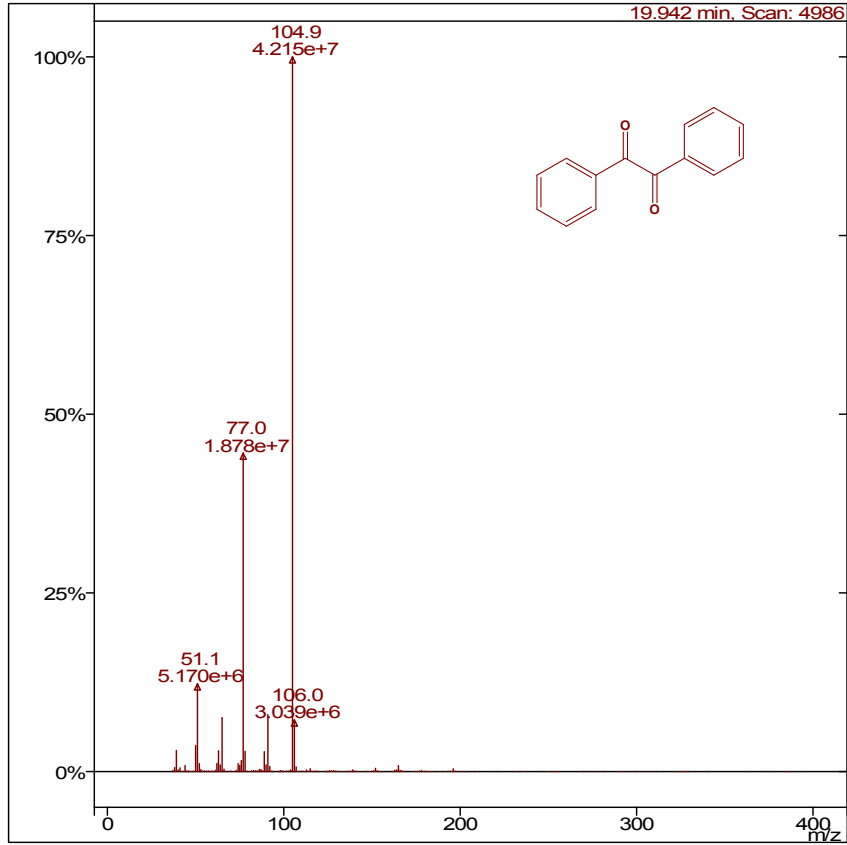
component	benzaldehyde	benzyl alcohol	benzil	benzoin	hydrobenzoin	unknown compound
Content (peak area %)	94.19	0.48	0.52	1.11	1.21	2.47

Reaction conditions: 320-700 nm Xe light, 749 mW/cm², 65 mg CNTs, 5 mg KOH, 10 mmol benzaldehyde, 6 h, 75 °C.

Section 4 The mass spectra of the product and intermediate products







Section 5 Theoretical section

DFT calculation Method. The Vienna Ab-initio Simulation Package (VASP)^[1-4] was used for all calculations with Perdew-Burke-Ernzerhof (PBE) functional^[5,6] for the exchange-correlation term and the projector augmented wave method^[7,8]. In order to take the dispersion interaction into account, the dispersion correction developed by Grimme et al. (DFT-D)^[9] was employed. The cutoff energies for optimisation and single-point calculations were set to 400 eV and 500 eV, respectively. All structures were fully relaxed to the ground state and spin-polarisation was considered for the calculations of benzaldehyde radicals. The convergences of energy and force were set to 1×10^{-4} eV and 0.05 eV/Å, respectively. We took CNT-(12, 0) as a model for carbon nanotubes and the optimised structure of benzaldehyde adsorbed on CNT was shown in Fig. S16. The binding energy of reactants and CNTs were defined as: $\Delta E = E_{\text{total}} - E_{\text{CNTs}} - E_{\text{reactant}}$.

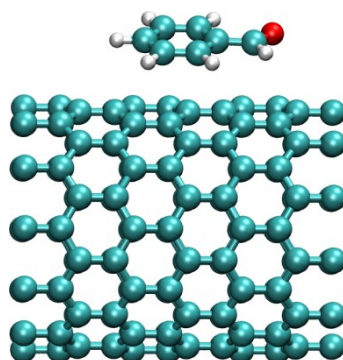


Fig. S16 Optimised structure of benzaldehyde adsorbed on CNT, where the binding energy is 38 kJ/mol. This configuration indicates that benzaldehyde interacts with CNT through π - π stacking.

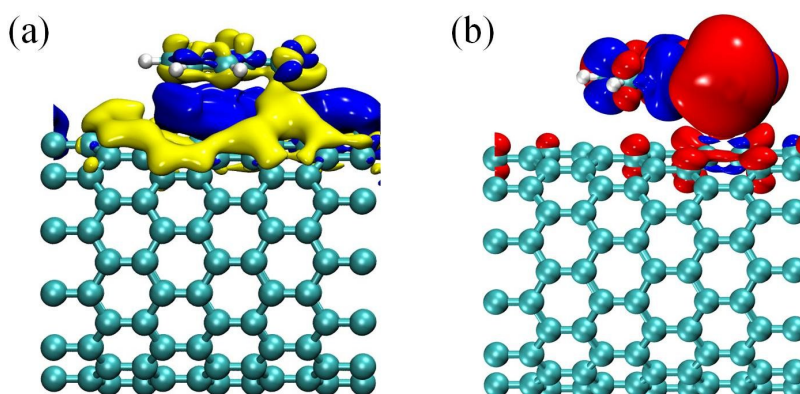


Fig. S17 (a) Differential charge density for benzaldehyde adsorbed on CNT, where the yellow and blue regions represent the increased and decreased electron density,

respectively. The noticeable electron redistribution demonstrate the π - π stacking interaction between CNTs and benzaldehyde and the flexibility of π electron cloud of CNTs. (b) Spin density distribution for benzaldehyde radical adsorbed on CNT, where the red and blue regions represent orbital phase φ^+ and φ^- . The spin electron of benzaldehyde radical delocalised to the CNTs backbone due to the relatively strong interaction with CNTs, which can stabilised the formed radical.

References

- [1] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
- [2] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
- [3] G. Kresse, J. Furthmuller, *Comp. Mater. Sci.* **1996**, *6*, 15.
- [4] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169.
- [5] P. E. Blochl, *Phys. Rev. B* **1994**, *50*, 17953.
- [6] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [7] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [8] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.
- [9] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463.