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Metal-free CNTs exhibit high activity (conversion rate 99.6%, 6 h) towards the synthesis of chiral hydrobenzoin from benzaldehyde under near-UV light irradiation (320–400 nm). The CNT structure before and after reaction, the interaction between the molecule and CNTs surface, the intermediate products, the substitution effect and the influence of light on the reaction were examined using various techniques. A photo-excited conduction electron transfer (PECET) mechanism for the photocatalytic reduction using CNTs has been proposed. This finding provides a green photocatalytic route for the production of hydrobenzoin and highlights a potential photocatalytic application for CNTs.

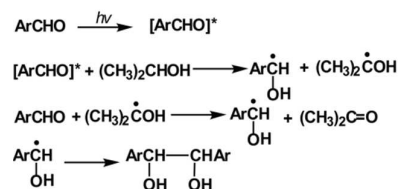
Introduction

Recently, due to their low cost, abundance and non-toxic properties, metal-free carbon nanotubes (CNTs) catalysts, have drawn extensive attention in many reactions. Examples of this are the oxidative dehydrogenation of ethylbenzene to produce styrene and the oxidative aromatization reactions.^{1–5} It is well known that CNTs have strong absorption of light up to the near IR range^{6,7} and a wealth of free electrons on the surface⁸. Combining the light absorption and the catalytic properties of CNTs may develop new photocatalysts. However, there are no reports on whether the electrons in CNTs can be activated by light for photocatalytic applications.

Hydrobenzoin (1,2-diphenyl-1,2-ethanediol) and its derivatives have been used in various areas of chiral chemistry and have a broad range of applications in synthetic chemistry^{9–11}. Various synthesis routes have been employed to prepare hydrobenzoin including Sharpless asymmetric dihydroxylation of alkenes,¹² resolution of racemic diols,¹⁰ asymmetric transfer hydrogenation of benzil/benzoin¹¹, and asymmetric pinacol coupling of benzaldehyde¹³. Among these methods, asymmetric pinacol coupling of benzaldehyde was first reported in 1973 by Mukaiyama using a stoichiometric amount of titanium reagent.¹⁴ This is recognised as the most direct, efficient and economical route for this particular reaction.^{15–19} Over the past few decades, most research on this topic has

focused on exploring chiral Ti(IV)-salen complex, Mo and V catalysts.^{20–23} In fact, the pinacol coupling reaction can also be achieved under sunlight irradiation with the addition of hydrogen-donating reagents such as alcohols (e.g. MeOH, EtOH, i-PrOH) without using toxic metal complex catalysts (Scheme 1)²⁴. Unfortunately, the reaction rate is rather low due to the low solar spectrum absorption efficiency.^{24, 25} Therefore, searching for a heterogeneous photocatalyst that effectively harvests solar energy could be a solution toward a highly effective hydrobenzoin synthesis.

Scheme 1 The reaction mechanism for the photochemical reduction of benzaldehyde under sunlight irradiation.²⁴



In this study, commercial multi-walled CNTs (Timesnano, $S_{\text{BET}} = 61 \text{ m}^2/\text{g}$, purified by soaking in HCl solution) were used for the photocatalytic synthesis of chiral hydrobenzoin from benzaldehyde. For the first time, we report that CNTs exhibit high photocatalytic activity and considerable selectivity. Moreover, the photocatalytic process on CNTs can shift the light response from middle-UV range (200–320 nm), which needed for the photochemical reaction between benzaldehyde and isopropanol, to visible range (400 nm). We also find that the CNTs surface can induce the reaction by a different pathway compared to photochemical reduction of benzaldehyde, and the activity increases with an increase in temperature. The synergistic effect of the light irradiation and CNTs plays a crucial role in the reaction. It provides a green and effective photocatalytic route for the synthesis of hydrobenzoin without a complex catalyst and avoids the

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pollution problems associated with using heavy metals.²⁶ Potential applications for this alternative synthesis are suggested for procedures linked to life science and pharmacy science.

Results and discussion

The photocatalytic performance (Fig. 1) of the pristine CNTs for synthesis of chiral hydrobenzoin from benzaldehyde was investigated under light irradiation (300 W Xe lamp, 320-700 nm, 749 mW/cm²) in Ar atmosphere (1 atm) at different temperatures. The conversion rate (hydrobenzoin selectivity) were 50.0% (79.3%), 56.8% (86.2%), 87.4% (88.0%), 99.6% (89.6%) and 97.1% (87.9) at 45, 55, 65, 75 and 85 °C, respectively. Three hydrobenzoin products, including (1*R*,2*R*)-1,2-diphenylethane-1,2-diol [or (*R,R*)-hydrobenzoin], (1*S*,2*S*)-1,2-diphenylethane-1,2-diol [or (*S,S*)-hydrobenzoin], and (1*R*,2*S*)-1,2-diphenylethane-1,2-diol [or (*R,S*)-hydrobenzoin], were obtained and the side product benzyl alcohol was also obtained. (*R,R*)-hydrobenzoin and (*S,S*)-hydrobenzoin were the main products (selectivity >87.5%), where the latter was less than the former. It can be seen that the conversion rate and the selectivity both increased with the increasing temperature. It is noted that acetone was also obtained after the reaction, which confirms that isopropanol was the hydrogen donor. In the absence of light, the reaction yielded the sole product benzyl alcohol with relatively low conversion rates: 11.2%, 15.9%, 18.2%, 24.3% and 25.1% at 45, 55, 65, 75 and 85 °C, respectively (Fig. 1). Evidently, the reaction proceeded in different pathways in the presence and absence of light. Control experiments were carried out in the absence of CNTs and it was found that no product was detected either under light irradiation or in the dark, suggesting that CNTs play a crucial role in promoting this reaction. The CNTs catalyst exhibits high activity and considerable selectivity for the production of hydrobenzoin from benzaldehyde under light irradiation (749 mW/cm²) at 75 °C and these conditions were selected as the optimised condition for the following study unless otherwise stated.

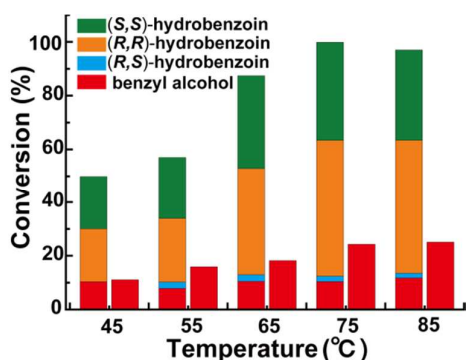


Fig. 1 Photocatalytic performance of CNTs in the synthesis of chiral hydrobenzoin from benzaldehyde at different temperatures (Left: light, Right: dark). Reaction conditions: 1 mmol benzaldehyde, 65

mg CNTs, 10 mL isopropanol, 1 mL KOH isopropanol solution (0.1 mol/L), 6 h, 1 atm Ar.

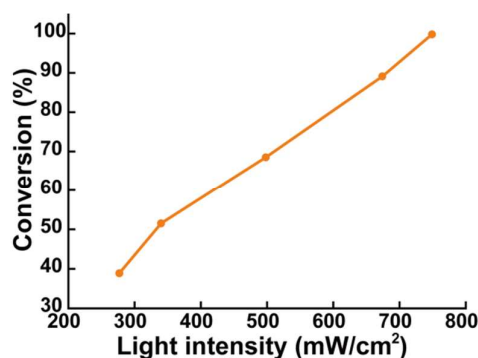


Fig. 2 Influence of light intensity on the conversion of benzaldehyde.

Table 1 Influence of irradiation wavelength on the benzaldehyde reduction products.

Entry	Light source	Catalyst	Products
1	dark	-	N.R.
2	dark	CNTs	B.A.
3	200-320 nm (Xe light) ^a	-	B.A. H.B.
4	200-320 nm (Xe light) ^a	CNTs	B.A. H.B.
5	320-400 nm (Xe light) ^b	-	N.R.
6	320-400 nm (Xe light) ^b	CNTs	B.A. H.B.
7	375 nm (LED)	CNTs	B.A. H.B.
8	400 nm (LED)	CNTs	B.A. H.B.
9	450 nm (LED)	CNTs	B.A.
10	420-700 nm (Xe light) ^c	-	N.R.
11	420-700 nm (Xe light) ^c	CNTs	B.A.

B.A. = benzyl alcohol; H.B. = hydrobenzoin; N.R. = no reaction.

^aNot controlled by applying optical filters. The real irradiance is ranged from 200-700 nm. ^bControlled by applying a band-pass filter. ^cControlled by applying a 420 nm long-pass optical filter.

The output spectra of the light sources are shown in Fig. S1.

The light intensity and wavelength can affect the photocatalytic activity. Fig. 2 shows the performance of photocatalytic synthesis of chiral hydrobenzoin under different light intensity. The conversion rate increased almost in a linear relationship from 38.9% to 99.8% when the light intensity increased from 277 to 749 mW/cm². This trend reveals that the photocatalytic reductions are driven by light, where a higher intensity can excite more electrons in CNTs and thereby enhance the interaction of CNTs with reactants.²⁷ The irradiation wavelength also affects the photocatalytic reaction activity as listed in Table 1. A series of different wavelengths (200-320, 320-400, 420-700 nm) were controlled using Xe light source equipped with band-pass or long-pass filters. In the absence of CNTs, the reduction of benzaldehyde occurred only

under middle-UV-light with wavelength shorter than 320 nm, which is deduced from the results that the reaction occurs under 200-320 nm light irradiation. It did not occur under irradiation by longer wavelengths in the ranges of 320-400 and 420-700 nm (Entry 5 and 10). This confirms the reduction of benzaldehyde under middle-UV light is a photochemical reaction as stated in the Introduction section. In the presence of CNTs, the photocatalytic reduction of benzaldehyde to benzyl alcohol can take place even in the dark (Entry 2). When the incident light contains UV wavelengths (320-400 and 200-320 nm), both benzyl alcohol and hydrobenzoin (the main product) were obtained (Entry 4 and 6). When the wavelength of the light was longer than 420 nm, no hydrobenzoin was obtained (Entry 11). The production of hydrobenzoin is more difficult than production of benzyl alcohol due to the higher energy barrier for producing hydrobenzoin than for benzyl alcohol. Controlled experiments using single colour LEDs were also performed. The conversion to hydrobenzoin occurred under 375 and 400 nm irradiation but did not occur under 450 nm irradiation when conducted at 75 °C (Entry 7, 8 and 9). The reaction did not occur under 450 nm LED light even when the reaction temperature was elevated to 200 °C. This shows that the light response shifted at least 80 nm, from below 320 nm to 400 nm for the production of hydrobenzoin when CNTs were added. This indicates that the wavelength of the light determines the reduction ability and confirms that the synergistic effect of light and CNTs is crucial for the catalytic activity.²⁸ To explain the mechanism, the interaction between the molecule and CNTs surface, the CNTs structure before and after reaction, the substitution effect, the influence of base, and the intermediate products were examined in the following study.

To better understand the interaction between benzaldehyde and CNTs, the Fourier transform infrared (FT-IR) differential spectra of the CNTs before and after vapour benzaldehyde adsorption were compared (Fig. S5). After gaseous benzaldehyde adsorption on the surface of CNTs, the free C=O vibration at 1725 cm⁻¹ and free C-H stretching vibration at 2807, 2734 and 2724 cm⁻¹ were clearly seen. This indicates that the aldehyde groups (-CHO) of benzaldehyde were not involved in aggregation state (intermolecular hydrogen bond interaction) or covalent bond to the CNTs surface.²⁹ Therefore, benzaldehyde was most likely to be adsorbed on CNTs surface via π - π interaction. Density functional theory (DFT) calculation was also employed to investigate the interaction between benzaldehyde and CNT. The optimised structure and differential charge density analysis also confirmed that benzaldehyde interact with CNT through π - π stacking due to the flexible π electron cloud of CNT (Fig. S16 and Fig. S17a).

In most cases, the catalytic active sites are attributed to the functional groups on the surface when CNTs are used as metal-free catalysts.³⁰⁻³⁴ Five types of CNTs with different amounts of functional groups were prepared in this study by reduction or oxidation treatment of the commercial CNTs. The type and amount of functional groups were identified from the XPS spectra (Fig. S10).³⁵ However, there is no obvious linear

relationship between the amount of surface groups and the activity. The Raman spectra of those CNTs were also investigated (Fig. S11) and the results showed that the performance was inversely proportional to the area ratio D band and G band of CNTs (Fig. S12). The area ratio of D/G (I_D/I_G) Raman peaks can be used to quantitatively determine the defect concentration of CNTs. Generally, the higher the I_D/I_G ratio, the more the defects are presented.^{4, 36} This indicates intrinsic nature of CNTs with less defects can be beneficial to the reaction. To make this clear, the commercial CNTs were calcined at 3000 °C under Ar atmosphere to minimise the defects and functional groups (Raman spectrum shown in Fig. S14). The conversion rate using the calcined sample reached 88.4% in 2 h, which is much higher than commercial CNTs (Fig. S13). Therefore, it is deduced that the CNTs was the photocatalyst for the following reasons: (1) CNTs absorb light in the range of 200-700 nm (Fig. S3) and conduction electrons in CNTs gain energy from the light absorption.^{37, 38} (2) The electrons excited by the light with wavelength longer than 420 nm are not able to reduce benzaldehyde, which could be due to the electrons cannot meet the energy barrier of reduction. (3) The catalytic performance was from intrinsic CNTs rather than surface groups of CNTs. The pristine CNTs exhibited good recyclability — the conversion rate slightly decreased and became stable at ~91% after five successive rounds (Fig. S6). The X-ray diffraction (XRD) patterns of the used catalyst (5 cycles) still exhibits typical (002) and (004) diffraction peaks of CNTs although in a weaker intensity compared to the pristine CNTs (Fig. S2). In addition, other form of carbon material such as expanded graphite ($S_{\text{BET}} = 46 \text{ m}^2/\text{g}$) also exhibit the similar conversion rate (97.2%) with commercial CNTs under the identical conditions. This further confirms that the intrinsic carbon surface is the active site.

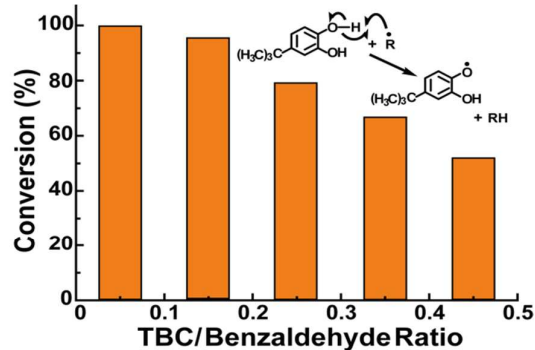


Fig. 3 Conversion of benzaldehyde under different ratio of TBC/benzaldehyde. The inset shows the reaction between TBC and carbon radical.

To investigate whether the reaction is a radical mechanism, different amounts of 4-*tert*-butylcatechol (TBC), an effective scavenger of carbon radicals, was added to the reaction system. The conversions of benzaldehyde were 99.4%, 95.2%, 79.2%, 66.8%, and 51.9%, with TBC/benzaldehyde ratios at 0.05, 0.15, 0.25, 0.35, and 0.45, respectively (Fig. 3), highlighting that benzaldehyde conversion decreased as more TBC was added. It is well known that TBC first transforms into

a stable phenoxyl radical which is attributed to the hydrogen atom transfer from the phenolic OH to a carbon radical. Then the reaction was hindered when the phenoxyl radical combined with another carbon radical.^{39, 40} The phenoxyl radical signal was identified by the electron paramagnetic resonance (EPR) spectroscopy (Fig. S4). This indicates that the synthesis of hydrobenzoin from benzaldehyde is a carbon radical mechanism. When TBC was added to the system, it consumed a stoichiometric amount of carbon radicals and thus hindered the reaction. When excess TBC was added at the beginning of the reaction, the conversion to hydrobenzoin was not observed. In the absence of TBC, the time course for the photocatalytic synthesis of chiral hydrobenzoin under light irradiation (749 mW/cm²) at 75 °C is shown in Fig. 4. The hydrobenzoin yield gradually increased as the reaction proceeded. The yield of benzyl alcohol rose to a certain level (< 10%) in the initial reaction stage, then did not appear to increase any further, which is obviously lower than for the dark reaction yield (24% at 75 °C). These time profile results indicate that the formation of hydrobenzoin under light irradiation has an induction period and that the radical reaction process is a faster process compared to formation of benzyl alcohol. Once the carbon radicals are formed, conversion to benzyl alcohol is no longer favoured.

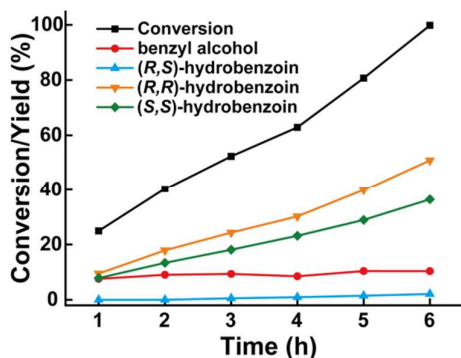


Fig. 4 Time profile for the photocatalytic reduction of benzaldehyde on CNTs at 75 °C. The conversion of benzaldehyde and the yield of different products are plotted against the reaction time.

KOH also plays an important role in the reaction. Time profile for the photocatalytic reduction of benzaldehyde in the absence of KOH is shown in Fig. 5. Only trace amount of hydrobenzoin products were observed in the absence of KOH within 6 h. Instead, benzil was the main product. This indicates that the C-C coupling of two C radicals occurs prior to the reduction process. Benzil was gradually reduced to hydrobenzoin after an extended reaction time. This also indicates that the conversion of benzaldehyde to benzil is the fast step and the conversion of benzil to hydrobenzoin is the slow step. The addition of KOH greatly increases the reaction rate from benzaldehyde to benzil, which is consistent with previous reports.^{41, 42} A different phenomenon was observed with the photoreduction of benzaldehyde under middle-UV-light (200-320 nm) in the absence of CNTs. During the

photoreduction process, benzaldehyde can be readily converted to hydrobenzoin in the absence of KOH (Fig. S8). This indicates that the reactions driven by light and light&CNTs follow different pathways, although the distribution of the products did not differ much (Fig. S7).

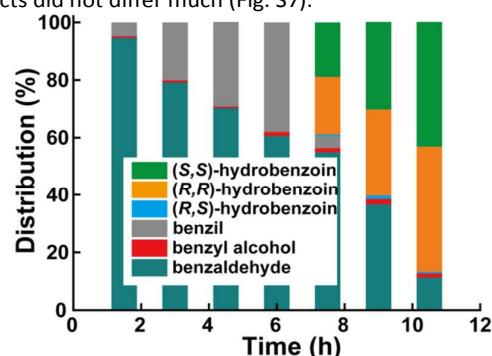


Fig. 5 Time-dependent distribution of benzaldehyde and the corresponding products during reaction in the absence of KOH. The total amount of benzaldehyde and the products is normalised to 100%.

Table 2 The conversion of benzil at different conditions.

Entry	Base	Catalyst	Wavelength (nm)	Benzil conv.(%)
1	KOH	CNTs	320-700 ^a	65.2
2	KOH	-	320-700 ^a	51.2
3	KOH	CNTs	-	-
4	KOH	-	-	-
5	-	-	320-700 ^a	55.1
6	KOH	-	420-700 ^b	-
7	KOH	CNTs	420-700 ^b	-
8	-	-	400 ^c	98.2

^aXe light without filter. ^bControlled by a 420 nm long-pass optical filter. ^cSingle colored LED. Reaction conditions: 1 mmol benzil, 65 mg catalyst, 10 mL isopropanol, 1 mL KOH isopropanol solution (0.1 mol/L), 75 °C, 6 h, 1 atm Ar.

Since benzil was observed to be an intermediate product, it was used as the reactant to study the reaction mechanism. When benzil was employed for the direct hydrogenation reaction in isopropanol solution, a rapid reaction occurred under light irradiation (320-700 nm, Xe light; or 400 nm LED) either in the absence or presence of CNTs (Table 2, Fig. S9). However, the reaction did not occur when irradiated under light with wavelength at 420-700 nm either in the presence or absence of CNTs. These results indicate that benzil can be readily transformed to hydrobenzoin by the hydrogenation reaction under near-UV light irradiation without the aid of CNTs and KOH. Benzoin could also be an intermediate product as it was observed (selectivity ~10%) during the reduction of benzil. No hydrobenzoin was observed when benzoin was used as a reactant in isopropanol solvent under light irradiation (320-700 nm Xe light; or 400 nm LED) and the main product was benzaldehyde (the cleavage product). It was reported that benzil can be reduced to benzoin in isopropanol solvent under

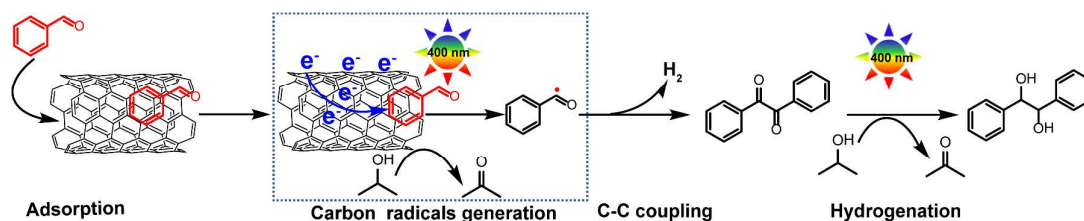


Fig. 6 Schematic diagram of the proposed reaction mechanism.

UV light irradiation but cannot be further reduced to hydrobenzoin in a one-photon absorption process.⁴³ Therefore, it is deduced that one benzil molecule should accept two photons to directly yield hydrobenzoin due to the high light intensity in this study. The apparent quantum yield (AQE) for the production of hydrobenzoin was 1.2%, which measured with irradiation light at 375 nm under the optimised reaction condition (calculation details shown in the ESI).

In an isopropanol-free condition, the benzaldehyde reduction products including benzil, benzoin and hydrobenzoin were detected, although the conversion is very poor (Table S2). This further confirms that CNTs can initiate the reaction under light but the reaction cannot proceed in the absence of an electron donor (e.g. isopropanol). The observation of hydrobenzoin in the isopropanol-free condition indicates that the hydrogen generated from the abstraction of H from benzaldehyde can be added to benzil. It is noted that the formation of carbon radicals and the subsequent C-C coupling reaction was accompanied by the abstraction of H from the -CHO group of benzaldehyde and H₂ should release from the reaction system. The H₂ amount was measured in a 10 times magnified reaction system by GC analysis and the total amount was 15.2 μmol after 6 h reaction (Fig. S15).

To understand the substituent influence on the reaction, we conducted the CNTs catalysed reduction reaction using benzaldehyde derivatives with an electron donating group (-OCH₃) or with an electron withdrawing group (-Cl) at the para or ortho position to the -CHO group. None of the compounds with a second substituent on the benzene ring was reduced to diol (Table S1). This could be due to the steric hindrance-induced weak adsorption of the benzaldehyde derivatives with more than one substitution group. When the reaction was conducted under middle-UV-light (200-320 nm, Xe light) irradiation, the above derivatives converted to the corresponding diol products (Table S1). This indicates that CNTs catalysed process is advantaged to control the selectivity: when both benzaldehyde and its derivatives are contained in the reaction solution, the catalyst surface will only permit the reaction of benzaldehyde under near-UV light irradiation (e.g. only benzaldehyde was reduced to diol when both benzaldehyde and 4-chlorobenzaldehyde were added into the reaction system, Table S1).

Based on the above analysis, a photo-excited conduction electron transfer (PECET) mechanism has been proposed

which can be broken down into the following phases (Fig. 6). Initially, benzaldehyde is absorbed on CNTs surface via π-π interaction. Consequently, the hot electrons of CNT transfer to the aromatic ring that has stronger interaction with CNT surface under near-UV light irradiation. The transferred electron should be shared by the π system that may include the carbonyl group which may moderate the excitation of benzaldehyde radical. The formed benzaldehyde radical can be stabilized by the delocalised π electrons of CNTs (Fig. S17b). The isopropanol solvent behaves as an electron donor. Furthermore, the collision of radicals results in the C-C coupling reaction and formation of benzil.^{30,44,45} Finally, benzil is reduced by hydrogen sourced from isopropanol to produce hydrobenzoin under light irradiation. CNTs act as catalyst mainly in the first two steps. Then the surface will be self-regenerated for another catalytic cycle. It is obviously that the light-driven catalytic pathway in the presence of CNTs is distinctly different from the thermal catalytic pathway and the photochemical reaction between aromatic aldehyde and isopropanol.

Conclusions

In conclusion, a new photocatalytic route for the synthesis of chiral hydrobenzoin on CNTs was found and the reaction mechanism was investigated. The photocatalytic process can be effective for light wavelengths in the range 320-400 nm. This is greatly red shifted compared to the light response in the photochemical process which only occurs when wavelengths below 320 nm are used. This study provides a green photocatalytic route for the production of hydrobenzoin and highlights a potential application for CNTs. The efforts should be focused on uncovering the underlying mechanism of CNTs photocatalysis, controlling the selectivity to benzil and to enantiomerically pure hydrobenzoin products, and applying CNTs in other reactions in future study.

Acknowledgements

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