Tuning Selectivity Among Acetalisation, Pinacol Coupling and Hydrogenation Reactions of Benzaldehyde by Catalytic and Photochemical Pathways at Room Temperature

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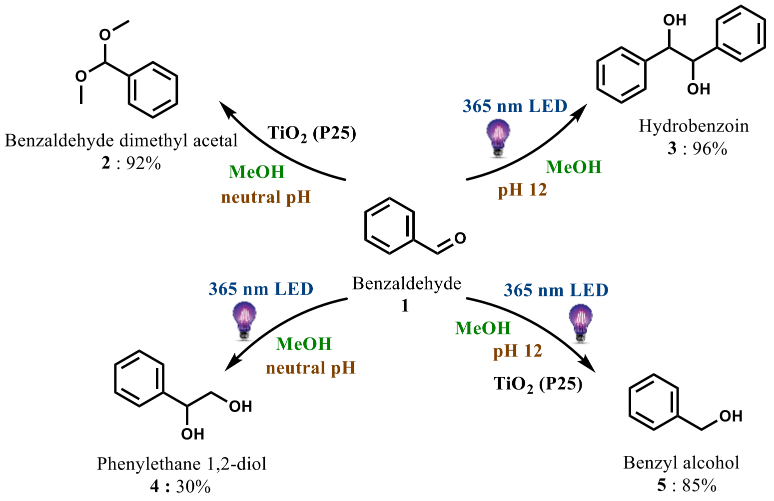
Abstract

Benzaldehyde is one of the industrially most useful feedstocks and its transformation to high-value chemicals is very attractive. Different transformations of benzaldehyde, such as acetalisation, pinacol coupling and hydrogenation, have been achieved herein by adjusting pH, light source and selection of a catalyst. Consequently, the corresponding products have been obtained with excellent yields (e.g. 92% yield for acetalisation, 96% yield for pinacol coupling and 85% yield for hydrogenation). The mechanisms behind each transformation were studied and it revealed that pinacol coupling reaction was achieved through a photochemical process under 365 nm irradiation at pH 12, where the introduction of the TiO_2 (P25) catalyst would completely shift the selectivity towards benzyl alcohol through a photocatalytic pathway and to benzaldehyde dimethyl acetal via low-temperature thermal catalysis.

Benzaldehyde, as the simplest aromatic aldehyde, can be derived from renewable biomass (e.g. cheery, peach seeds). It is also one of the most abundant building blocks in chemical industry[1]. Since its first isolation in 1803, many types of valuable chemicals have been produced using benzaldehyde as the raw material, including various aldehydes, alcohols, diols, acetals, rendering wide applications in pharmaceutical, fragrance and flavour industries[2].

Despite the relatively mature transformation technologies that have been widely used so far, most processes still suffer from harsh reaction conditions (e.g. high temperature, high pressure), complex multi reaction steps and complicated post-treatments. Acetals are common intermediates in organic synthesis, while the conventional method for acetalisation of aldehyde often requires a homogeneous system with strong Brønsted mineral acids[3,4,5]. As a result, facing a series of concerns, e.g. complex product separation, catalyst recycle and the induced system corrosion[6,7] leading to high capital and operation costs. The construction of C-C bonds via pinacol coupling is of paramount significance in organic chemistry, and photochemistry could offer a mild and efficient pathway driven by solar energy[8]. However, it is challenging due to the very negative reduction potential of direct aldehyde conversion required[9]. This reaction could happen with precious metals and/or homogenous metallic complexes catalyst[10], while it normally suffers from limited stability and low solubility. Moreover, some toxic reagents are inevitably involved in these methods, raising economic and environmental concerns. Diols, such as 1-phenylethane-1,2-diol, are widely recognised as readily accessible building blocks in organic chemistry[11], while often require multi-step synthetic protocols, resulting in low carbon atom utilisation efficiency[12]. Hydrogenation of aldehyde by the thermal catalysis has been well investigated [13,14], always involving the pure hydrogen gas, which is highly combustible[15]. Besides, they are mainly carried out in homogeneous systems in most cases[2], leading to time-consuming recycling and separation processes.

Herein, a green and reliable approach has been developed to transfer benzaldehyde into four valuable chemical products with both high yield and high selectivity. Through manipulation of general experimental parameters, including adjusting pH, presence/absence of light irradiation, the use of a photocatalyst TiO_2 (P25), smart pathways to specific value-added products have been established (Scheme 1). Moreover, the mechanisms have been investigated, and isotopic labelling experiment was conducted to identify an efficient pinacol coupling pathway. This work provided a simple but effective method to synthesise different compounds with high selectivity from benzaldehyde, which gives new insight for further development of photocatalysis and photochemistry.



Scheme 1 Four different pathways for benzaldehyde transformations and corresponding product yield (%)

Results and discussion

Table 1 Experimental conditions for the transformations of benzaldehyde **1**^{a}.

Entry	Catalyst (mg)	Atmosphere	pH^b	Light source	Con. (%)^c	S_2. (%)^c	S_3. (%)^c (*meso* : *dl*)	S_4. (%)^c	S_5. (%)^c
1	-	Argon	Neutral	-	-	-	-	-	-
2	P25	Argon	Neutral	-	92%	> 99%	-	-	-
3	P25	Air	Neutral	-	91%	> 99%	-	-	-
4	P25	Argon	12	-	-	-	-	-	-
5	-	Argon	Neutral	365 nm LED	76%	12%	48% (53% : 47%)	40%	-

6	-	Argon	Neutral	> 420 nm (Xe)	-	-	-	-	-
7	-	Argon	Neutral	Xe full arc	73%	72%	16% (57% : 43%)	12%	-
8	-	Argon	Neutral	450 nm LED	-	-	-	-	-
9	-	Argon	12	365 nm LED	96%	-	> 99% (59% : 41%)	-	-
10	P25	Argon	12	365 nm LED	98%	-	6% (47% : 53%)	-	94%
11	PC50	Argon	12	365 nm LED	97%	-	14% (51% : 49%)	-	86%
12	Al_2O_3	Argon	12	365 nm LED	91%	-	> 99% (55% : 45%)	-	-
13[d]	-	Argon	12	365 nm LED	-	-	-	-	-

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[a]Substrate **1** (1 mmol), catalyst (30 mg), solvent (15 ml methanol), 25 °C, 2h. [b]pH 12: 0.01 M KOH in methanol. [c]Determined by GC-MS. [d]Substrate changed to benzil (1 mmol), S_2 is the selectivity to benzaldehyde dimethyl acetal, S_3 is the selectivity to hydrobenzoin, S_4 is the selectivity to phenylethane 1.2-diol, S_5 is the selectivity to benzyl alcohol as illustrated in Scheme 1.

We found that it is very interesting to tune conversion, in particular selectivity in four different reaction processes, by only change one or two experimental parameters. As illustrated in Scheme 1, four reaction pathways have been achieved with four different products, including benzaldehyde dimethyl acetal, hydrobenzoin, phenylethane 1.2-diol and benzyl alcohol.

Acetalization of benzaldehyde. In the presence of P25 TiO_2 (about 20 nm particle size and 50 m^2/g surface area), the formation of benzaldehyde dimethyl acetal (product 2) could be realised within 2 h at room temperature, with a surprising selectivity (nearly 100%) and yield (92%) (Table 1, entry 2). It was clear that the gas atmosphere did not affect the acetalisation of benzaldehyde as a similar yield could be achieved when the experiment was exposed to air (Table 1, entry 3). In contrast, no conversion of the reactant was observed in the absence of P25 (Table 1, entry 1), indicating the important role of the catalyst P25. Actually, the acetal formation mechanism was widely investigated in organic chemistry[3], the conversion process with the assistance of P25 was proposed. (Figure S1, supporting information). When the benzaldehyde was adsorbed on the surface of P25, it could be activated by the Brønsted acid sites (H^+) on the surface of P25 to form a protonated intermediate[16]. Afterwards, this intermediate reacted with methanol to generate a hemiacetal, accompanying by deprotonation. Subsequently, the hydroxyl group of the hemiacetal underwent protonation, following by a dehydration process, resulting into the formation of a highly reactive oxonium ion. The next step was the addition of another methanol to the unstable oxonium ion, and after removing a proton again, the final product acetal generated. Therefore, the formation of acetal was a typical two-steps process, in which the formation of hemiacetal was a reversible reaction. However, the corresponding hemiacetal was not detected by the GC-MS either in the published or our study, suggesting that the subsequent generation of the acetal product was faster than the formation of the hemiacetal[3]. The lack of observation of hemiacetal was also previously reported in other reaction systems[3,17]. According to the proposed mechanism, pH was important to provide accessible H^+ for the protonation of hemiacetal. The pH of the solution was adjusted to 12 by the addition of alkaline in order to support the hypothesis. Notably, no conversion of benzaldehyde could be observed as expected (Table 1, entry 4), consistent with previous reports[3] and the proposed mechanism.

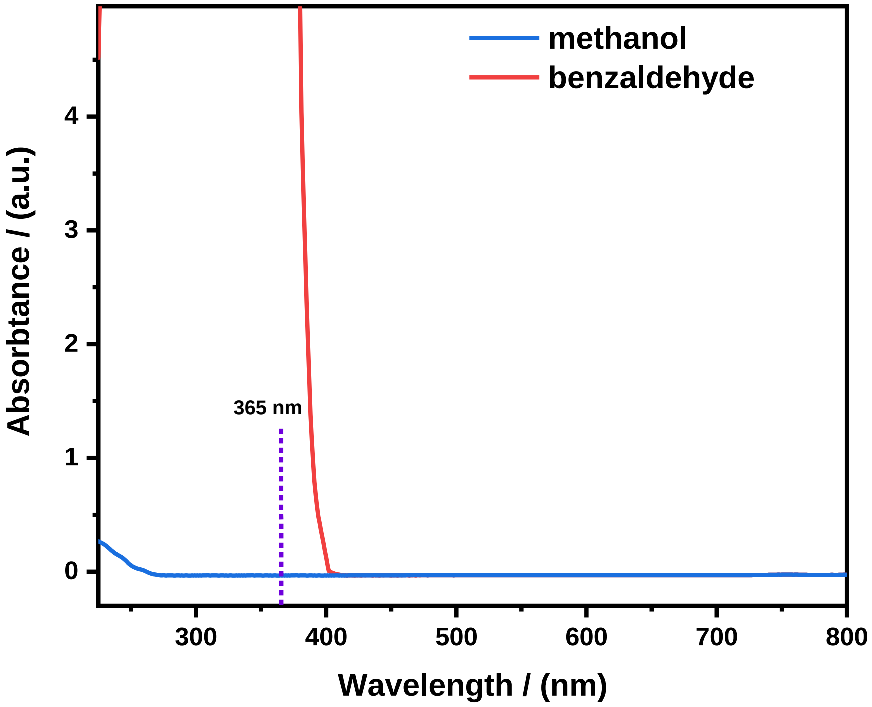


Figure 1 The UV-Vis spectrum of methanol and benzaldehyde.

Photochemical pinacol coupling of benzaldehyde. As mentioned above, pinacol coupling is important in the synthesis of pharmacologically important agents. Interestingly, in the absence of a photocatalyst, 76% of benzaldehyde could be converted into products **2**, **3** and **4** (selectivities: 12%, 48% and 40%, respectively) under irradiation of 365 nm LED (Table 1, entry 5). The pH influence was also investigated and from the results (Table S1, supporting information), acid condition could not prevent the formation of acetalisation[18], leading to a very low selectivity to the pinacol coupling . KOH was then introduced to adjust the pH to 12 (Table 1, entry 9). Surprisingly, when the pH increased to 12, the acetalisation process was successfully prevented[19], and the formation of product **4** also disappeared. The formation of **4** was supposed to be a simple addition process between benzaldehyde and methanol, and highly likely under alkaline condition the cleavage occurred[20,21]. As such the reaction exhibited a notable high selectivity (>99%) towards **3** (*meso*:*dl*=59:41) with an almost complete conversion of benzaldehyde. This is superior to all the previous results, including both thermo-catalysis and photocatalysis, as all of them required either complex and precious catalysts or complex reaction conditions[9,22,23,24,25,26,27,28,29]. The mechanism of pinacol coupling was then investigated.

UV-vis absorption spectrum was acquired in order to identify the photosensitive species in this system. As shown in Figure 1, benzaldehyde could absorb light with a wavelength less than 400 nm. Thus, the 365 nm LED was able to excite the benzaldehyde molecule to drive the photochemical process, consistent with previous reports[30,31]. To further confirm this process, a series of control experiments were then conducted under irradiation with different wavelengths (Table 1, entries 5-8). It should be noted that the Xenon light source equipped with a 420 nm long-pass filter (>420 nm) and 450 nm LED could not drive the photochemical processes. In addition, conversion of benzaldehyde was observed when the Xenon lamp with full-arc wavelength was used. All the above results suggested that this photochemical process can be manipulated by UV photons.

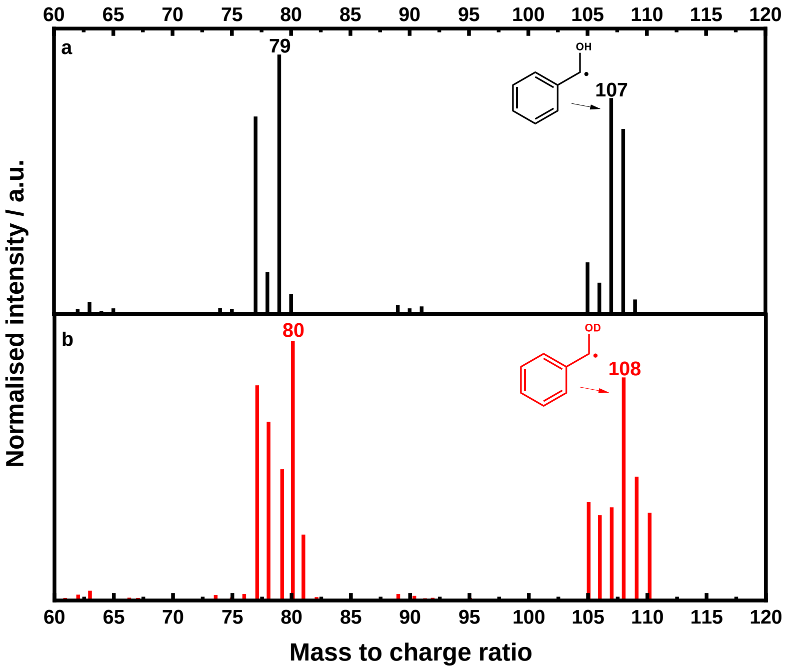
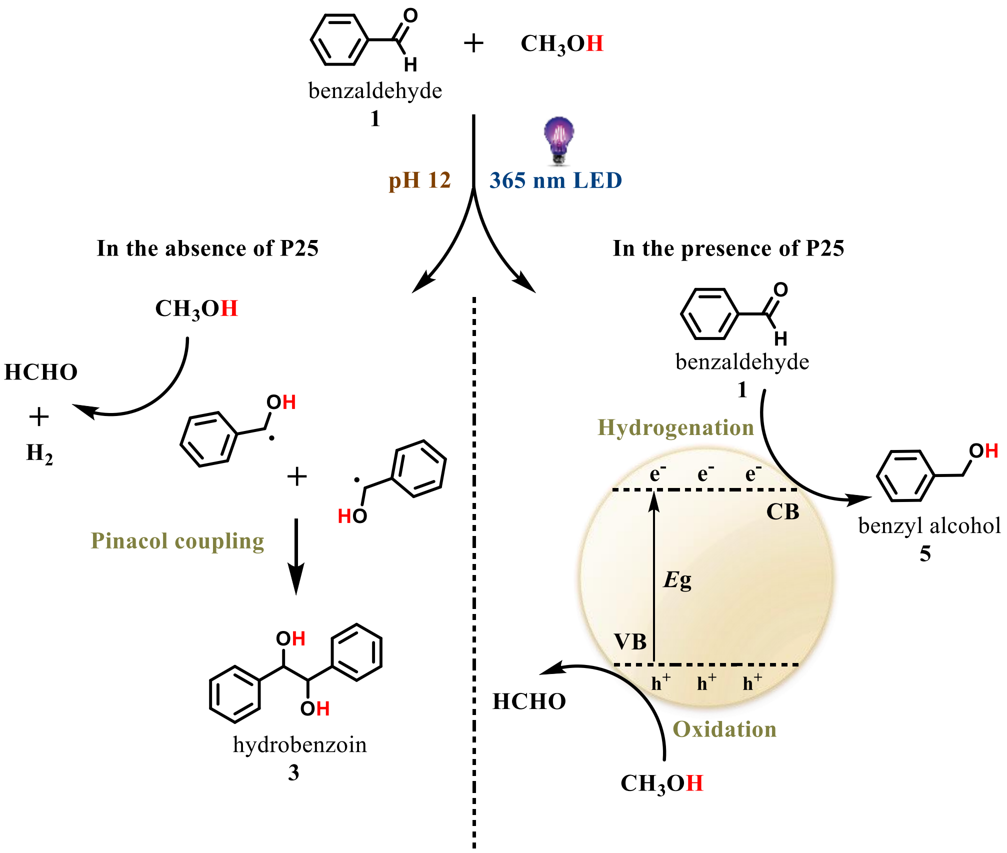


Figure 2 Isotopic labelling of pinacol coupling reaction of benzaldehyde. a: Substrate **1** (1 mmol), methanol solvent (15 ml), 365 nm LED, pH 12, 25 °C, 2h. b: Substrate **1** (1 mmol), CD_3OD solvent (15 ml), 365 nm LED, pH 12, 25 °C, 2h.

It was reported that pinacol coupling of benzaldehyde in alcohol under near-UV light irradiation consisted of two steps[32], the first step was the formation of benzil, and the second step was the hydrogenation of benzil to form hydrobenzoin (this step does not require the participation of a catalyst)[33]. However, benzil was not detected in our GC-MS analysis. To further prove this, benzil was then used as the reactant in methanol solvent, and no conversion was observed with 365 nm LED irradiation in the absence of a catalyst (Table 1, entry 13). The isotopic labelling experiment was further carried out in CD_3OD to investigate the mechanism. Figure 2 shows that only two deuterons were detected and they were each linked with the oxygen atom in hydrobenzoin. This result eliminated the possibility of benzil as an intermediate in the reaction process. This is because if the formation of product **3** was from the reduction of benzil, then when the C=O was reduced, both the protons added onto benzil should be deuterons, and the molecular mass would increase by 4 in total. However, the isotopic labelling result indicated there were only two deuterons on product **3** (two hydroxyl groups), which suggested that the H at -HC=O in benzaldehyde was preserved and the reduction process happened after benzaldehyde became carbon radicals upon absorbing UV photons. Based on the above analysis, a photochemical mechanism has been proposed and shown in Scheme 2 (left panel). Initially, benzaldehyde was excited by 365 nm photons and became reduced carbon radicals. Meanwhile, solvent methanol was oxidised into formaldehyde and released H_2 (detected by GC). Consequently, the collision of those reduced carbon radicals resulted in the C-C coupling reaction and the formation of hydrobenzoin.

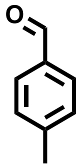
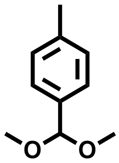
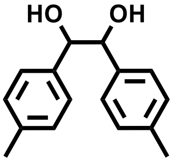
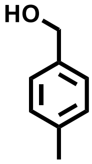
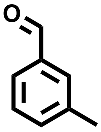
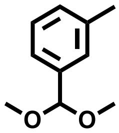
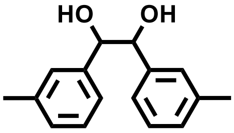
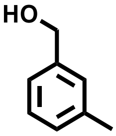
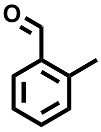
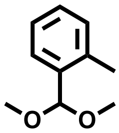
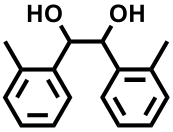
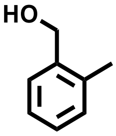
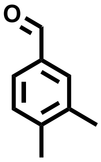
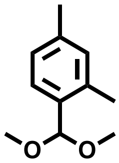
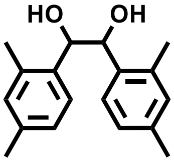
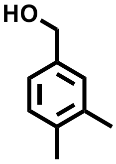
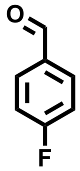
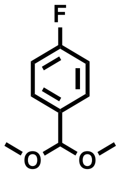
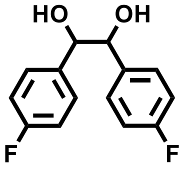
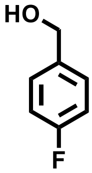
Photocatalytic hydrogenation of benzaldehyde. A notable shift in selectivity occurred when P25 was introduced into the system as a photocatalyst (Table 1, entry 10). Under alkaline condition, the selectivity towards product **3** dramatically decreased to 6%, while a 94% selectivity towards benzyl alcohol appeared after the introduction of the photocatalyst P25. Anatase TiO_2 (PC50) with a similar surface area to P25 was also tested. The result was shown in Table 1, entry 11. it was found that conversion of benzaldehyde remained similar (97%), but the selectivity to benzyl alcohol was reduced to 86%, which was likely due to the efficient charge separation in P25 compared to the pure single-phase PC50. The pH influence was also investigated (Table S1, supporting information), and the result indicated that acid condition could not inhibit the formation of acetalisation[18], leading to a lower selectivity (32%) towards the hydrogenation product. It was supposed that P25 provided reaction sites for benzaldehyde to be adsorbed on so the carbon radicals would have less possibility to collide with each other. To better understand the interaction between P25 and benzaldehyde, Al_2O_3 was chosen to replace P25 (Table 1, entry 12). Al_2O_3 is not a photocatalyst and after Al_2O_3 was added, only pinacol coupling reaction occurred in the system and the formation of product **5** was not observed. This result suggested that the hydrogenation of benzaldehyde was not a simple surface adsorption process. It was a photocatalytic process that happened on the surface of P25. The proposed mechanism was shown in Scheme 2 (right panel)[34]. P25 was excited after absorbing UV light as indicated by its UV-vis absorption spectrum (Figure S3, supporting information), then electron-hole pairs ($e^- + h^+$) were generated[35]. These charges next migrated to corresponding reaction sites. The adsorbed benzaldehyde on the P25 surface could be reduced by the photoelectrons at the reduction site. We further proved the similar mechanism of hydrogenation of benzaldehyde by the isotopic labelling results (Figure S4, supporting information). The methanol solvent behaved as a hole scavenger, was then oxidised by photo-holes. Based on the results, this photocatalytic hydrogenation process was more favourable for carbon radicals compared to collide with each other in the presence of photocatalyst P25, resulting in extremely high selectivity to product 5 other than product 3.



Scheme 2 Purposed mechanisms for photochemical pinacol coupling of benzaldehyde (left panel) and photocatalytic hydrogenation of benzaldehyde (right panel).

The scope of aldehydes was extended to further prove the above results, which were shown in Table 2. Several aldehydes have been investigated. It was clear that electron-donating group (-CH_3) at either para, meta, or ortho position would not affect the proposed selectivities tuning. For substrate **6-8**, 99% yield of desired acetal products and alcohols were obtained (**6a-8a**, **6c-8c**) and all the yields of pinacol coupling products were over 90% (**6b-8b**). For substrate **9**, high yields for all three pathways were observed too (97% yield for **9a**, 93% yield for **9b** and 96% yield for **9c**). However, when the electron-withdrawing group (-F) was added to para position (**10**), the selectivity towards pinacol coupling dropped to 57% (**10b**). In contrast, the selectivities towards acetalization or hydrogenation pathways remained similar, 96% for **10a** and 97% for **10c,** respectively. Cyano group (-CN) was also tested. However, the substrate did not absorb photons at 365 nm, thus could not undertake these transformations (UV-vis spectrum results of those substrates were shown in Figure S5, supporting information). All these are consistent with the proposed reaction pathways.

Table 2 Scope of different aldehydes.

Substrate	Acetalisation[a] (yield / %)	Pinacol coupling[b] (yield / %) (*meso*:*dl*)	Hydrogenation[c] (yield / %)
 **6**	 **6a,** > 99%	 **6b,** 98% (54:46)	 **6c,** > 99%
 **7**	 **7a,** > 99%	 **7b,** 94% (58:42)	 **7c,** > 99%
 **8**	 **8a,** > 99%	 **8b,** 95% (62:38)	 **8c,** > 99%
 **9**	 **9a,** 97%	 **9b,** 93% (49:51)	 **9c,** 96%
 **10**	 **10a,** 96%	 **10b,** 57% (52:48)	 **10c,** 97%

All yields were determined by GC-MS. [a]Acetalisation: Substrate (0.5 mmol), P25 (30 mg), solvent (15 ml methanol), 25 °C, 2h. [b]Pinacol coupling: Substrate (0.5 mmol), 15 ml solvent (pH 12: 0.01 M KOH in methanol), 365 nm LED, 25 °C, 2h. [c]Hydrogenation: Substrate (0.5 mmol), P25 (30 mg), 15 ml solvent (pH 12: 0.01 M KOH in methanol), 365 nm LED, 25 °C, 2h.

In conclusion, a green and versatile method to achieve acetalisation, pinacol coupling and hydrogenation of benzaldehyde was found and excellent results were obtained. Through a photochemical pathway, pinacol coupling of benzaldehyde was achieved in the absence of P25 at pH 12 with 96% conversion and 100% selectivity. The mechanism of this reaction was studied by isotopic labelling experiment and the result indicated that the reaction process was different from the previous report as this was a one-step process without benzil being the intermediate. Compared to other reported systems, this was so far the most economically friendly and efficient method to achieve such high yield product because it did not require any catalyst and complicated experimental conditions. 85% yield for hydrogenation was achieved in the presence of P25 photocatalyst and under 365 nm irradiation. The catalyst could completely shift the selectivity towards pinacol coupling (100%) to benzyl alcohol (94%) because benzaldehyde radicals prefer to adsorb on the surface of P25 and be reduced by photoelectrons instead of colliding and combining each other. Acetalisation was also achieved using P25 catalyst with a yield of 92% via a low temperature thermal catalytic pathway. These results provided an effective method to synthesise different compounds with high selectivity from benzaldehyde, providing new insight for further development of photocatalysis and photochemistry.

Acknowledgements

Authors thanks the Leverhulme Trust (RPG-2017-122), Royal Society-Newton Advanced Fellowship grants (NA170422) and Royal Society Leverhulme Trust Senior Research Fellowship (SRF\R1\21000153).

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