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A promising catalyst for exclusive para hydroxylation of substituted aromatic hydrocarbons under UV light

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Herein, we describe a waterborne polymer/carbon dot nanocomposite system as an efficient, resourceful and sustainable photocatalyst for para-selective hydroxylation of substituted aromatic compounds using H₂O₂ under UV light. The polymer matrix and carbon dot generate a synergistic catalytic system. A unique structural attribute of the functionalities in this catalytic system attracts the aromatic substrates into the close proximity and activates them. Additionally, the flexible molecular box like structure of the hyperbracnhed polymer provides the ability for favorable three point interaction with several substrates having various sizes by means of their multiple force networks and the increased accessibility of the active sites. The catalyst can be stored on bench top for months and reusable without considerable loss in its activity. The reaction was exclusively selective toward para hydroxylation irrespective of the nature of the substituents (electron donating or electron withdrawing) in the aromatic hydrocarbons. Hence, it is one of the most promising catalysts for selective hydroxylation of substituted aromatic hydrocarbons.

The regioselective hydroxylation of aromatic hydrocarbons is one of the most demanding reactions in organic synthesis¹ as it gives rise to hydroxyl-arene motif which is a core unit of many modern polymers, agrochemicals and pharmaceuticals.² The introduction of the hydroxyl moiety directly and selectively into aromatic ring is a challenging task in the domain of organic synthesis. Processes in the prior art used metal based catalysts for the hydroxylation of aromatic rings but the reactions afforded low yields and poor selectivity.^{3,4} Of late, several iron based heterogeneous catalysts⁵⁻⁸ have also been developed for hydroxylation of aromatic hydrocarbons to overcome the shortcomings of homogeneous catalysis including catalysts decomposition, tedious recovery and nonreusability. However, an excess amount of the substrate has always been utilized to prevent dihydroxylation and reactions are performed at ambient temperature with low turnover number. More recently, hydroxylation reactions of aromatic hydrocarbons are catalysed by nonheme iron in the presence of peroxide with low regio-selectivity.9-13 Similarly, the hydroxylation of aromatic compounds catalysed efficiently by zeolites^{14,15} have also been reported recently but never reached exclusive p-selectivity. We have also reported the enhanced p-selective nitration of aromatic compounds at para position using the pores of zeolite beta with low Si/Al ratio.¹⁶ The catalysis by zeolite has certain drawbacks like irreversible adsorption or steric blockage of the products leads to its deactivation, the unfeasibility of using their micro porosity for the synthesis of bulky molecules. Due to greater polarity of functional compounds in the micro porous structure of zeolites, it is more difficult to exploit their shape selectivity. On the other hand, exclusive selective p-hydroxylation is also possible through enzymatic catalysis involving three-point binding of the substrate but this reaction was confined to a few examples.¹⁷ However, catalysis by enzyme offers a number of disadvantages. It remains insufficiently stable for commercial applications; recovery of the enzyme from the reaction mixture for subsequent reutilization is always troublesome, difficulty in isolating the product from the reaction mixture which is generally present in low concentrations. Hence, there is an unmet need to provide commercially scalable process for the selective parahydroxylation in aromatic hydrocarbon that can be carried out at ambient conditions with recoverable and reusable low-cost metal free catalyst. In order to meet this goal under the norms of green chemistry¹⁸ and to mimic enzymes, we demonstrate here a facile yet unexplored protocol presenting carbon dot encapsulated in waterborne dendritic polyurethane as a

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Electronic Supplementary Information (ESI) available: General Experimental Methods, Preparation of CD by hydrothermal method, Preparation of carbon dot impregnated waterborne hyperbranched polyurethane, Calculation for solid contents in CD, General synthetic Procedures for hydroxylation of aromatic hydrocarbons, Recycling potential of the catalyst, UV-visible spectra and TEM images of CD@WPU, FTIR spectra and other characteristics of WPU, CD and CD@WPU, ¹H NMR and ¹³C NMR spectra of compounds, Reference. See DOI: 10.1039/x0xx00000x

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Figure 1. CD@WPU catalysed hydroxylation under UV light. This route entails the hydroxylation of aromatic hydrocarbon at para position with 100% selectivity. The effect of electron withdrawing as well as electron donating groups on aromatic ring is found to be negligible in providing 100% selectivity at para position which ultimately leads to process intensification.

promising photocatalyst for the selective hydroxylation of the aromatic compounds at para position (Figure 1). The catalytic activity of the dendritic polymers¹⁹ has been extensively studied due to their interesting cage like structure, heterogeneous nature and straightforward isolation from the reaction mixture. In this context, the photocatalysis by nanostructured materials remained in practice in the recent time^{20,21} due to the unlimited and united benefits of the homogeneous as well as heterogeneous catalytic systems and thereby making a bridge between them.²² With this view, nano dimension carbon has broadly been utilized in the past few years as a smart material with the capability to harvest photon in the UV/visible spectral region²³ and also for the development of advanced catalysts.²⁴ In the family of nano dimension carbon, carbon dot (CD) has been researched as a photocatalyst in the reduction of carbon dioxide to an organic acid,²⁵ oxidation of benzyl alcohol to benzaldehyde,^{26,27} cyclohexane to cyclohexanone²⁸ and contributed significantly as nanocatalyst underneath the umbrella of 'NOSE (Nanoparticles-catalysed Organic Synthesis Enhancement)' approach.^{29,30} The practical difficulty associated with CD in effective photocatalysis is the solubility in aqueous phase or in alcohol which gives rise to its tedious isolation from the reaction medium. In this connection, application of a polymeric matrix as a smart support paves the best way to promote the photo catalytic activity of CD on account of solid state quenching and prohibiting permitting straightforward catalyst isolation. The polymer matrix as a support also affords mechanical strength to $\ensuremath{\text{CD}^{31}}$ which is suitable for catalytic stability. In this context, the polymeric nanocomposites bestowed a novel model in material discovery due to their enormous feasibility in various applications.³² The properties physico-chemical of these polymeric nanocomposites show a considerable distinction from their bulk counterparts which can be subjected to architect such materials with tuneable features.³³

We first optimized the reaction condition by considering the hydroxylation reaction of benzoic acid (3) with H_2O_2 as a model reaction (Figure 2) under UV light at room temperature using waterborne hyperbranched polyurethane/CD nanocomposite (CD@WPU) prepared earlier³⁴. In this case 2 wt% CD on WPU was considered. The results are summarized in Table 1. The neat reaction of 3 with H_2O_2 (30% v/v) heated at 50 °C did not



Figure 2. Model reaction. It involves the optimization of the reaction condition by considering the hydroxylation of benzoic acid. Various parameters have been tested to check the selectivity of the catalyst in the presence of visible, dark and UV light. The optimization of the hydroxylation reaction was also observed at room temperature, 50 °C and 70 °C respectively.

form 4 (Table 1, entries 1 & 2). This felt the necessity of a catalyst and thus, CD@WPU was introduced to test the reaction under investigation. With the addition of 5 wt% of finely cut thin film of CD@WPU under day light at room temperature, 50 °C and 70 °C provided trace to 23% yield of 4 (Table 1, entries 3-5). Photo responsive CD falls in UV region and hence, the said reaction was conducted under UV light. In 15 min and 45 min, CD@WPU gave 76% and 90% yields respectively (Table 1, entries 6 & 7) and maximum yield was recorded in 1 h (Table1, entry 8). In the current process, when the model reaction was carried out in dark, it gave no indication of product formation (Table 1,

Table 1. Optimization of the reaction condition

Entry Conditions ^a Yie	ld (%) ^b
1 No catalyst, RT, ground, 1 h	С
2 No catalyst, 50 °C, 12 h	С
3 ^d *CD@WPU, RT, ground, visible light, 1 h T	race
4 ^d *CD@WPU, 50 °C, visible light, 9 h	17
5 ^d *CD@WPU, visible light, 70 °C, 9 h	23
6 ^d *CD@WPU, UV light, 15 min.	76
7 ^d *CD@WPU, UV light, 45 min.	90
8 ^d *CD@WPU, UV light, 1 h	98
9 ^d *CD@WPU, dark, 3 days	с
10 *CD (5 mL), UV light, 2 h	57 ^h
11 ^d WPU, 50 °C, 3 h	13
12 ^e *CD@WPU, UV light, 1 h	94
13 ^f *CD@WPU, UV light, 1 h	88
14 ^g *CD@WPU, UV light, 1 h	82
15 ^d ⁱ CD@WPU, UV light, 1 h	54
16 ^d ^j CD@WPU, UV light, 1 h	65
17 ^d ^k CD@WPU, UV light, 1 h	80
18 ^d ^I CD@WPU, UV light, 1 h	90
19 ^{d,m} *CD@WPU, UV light, 1 h	10
20 ^{d,n} *CD@WPU, UV light, 1 h	32
21 ^{d,o} *CD@WPU, UV light, 1 h	98
22 ^d *CD mixed with WPU, UV light, 2 h	74 ^h
23 ^d WPU, UV light, 3 h	с
24 No catalyst, UV light, 5 h	с

^a Reaction condition: Benzoic acid 3 (1 equivalent, 122 mg), H_2O_2 (3 equivalent, 30%, 102 mg, 0.09 mL) are homogeneously ground for the proper mixing in day light. ^b Isolated yield.* 2 wt% CD in WPU. ^c No reaction. ^d 5 wt% (11 mg) catalyst. ^e 10 wt% (22 mg) catalyst. ^f 15 wt% (34 mg) catalyst. ^g 20 wt% (45 mg) catalyst. ^h Mixture of ortho and *para* hydroxy benzoic acid. ⁱ 0.5 wt% CD in WPU. ^j 1 wt% CD in WPU. ^k 1.5 wt% CD in WPU. ⁱ 2.5 wt% CD in WPU. ^m 1 equivalent H_2O_2 . ⁿ 2 equivalent H_2O_2 .

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entry 9) even after continuing the reaction for 3 days. Again, when the reaction was conducted only in the presence of CD (Table 1, entry 10) under UV light furnished a mixture of ortho and para products whereas WPU alone at 50 °C could produce selectively 4 in lower yield (Table 1, entry 11). Hence, CD as well as WPU alone was not very effective and selective for hydroxylation of 3 and found to be highly active as well as selective in collaboration i.e., the synergistic effect of WPU on CD. Thus, the complex architecture and interior as well as exterior functionality of WPU led to the increased selectivity.³⁵ Catalyst loading was also optimized and results were tabulated in Table 1 (Entries 11-14). It was observed that 5 wt% catalyst loading with respect to the substrate (Table 1, entry 8) was sufficient for photo hydroxylation of benzoic acid. On increasing the catalyst loading from 10 wt% to 20 wt%, the yield of **4** started to decrease by keeping the reaction time constant which might be attributed to the strong adsorption of reactants on the catalyst surface which did not react further to form the product (Table 1, entries 12-14). The strong adsorption of reactants on the catalyst surface due to increase in loading was confirmed by the UV-visible analysis of the reaction mixture where the concentration of the reactants started to decrease than whatever it was. The model reaction was also tested by considering various loading (0.5 wt%, 1 wt%, 1.5 wt% and 2.5 wt%) of CD in WPU (the entire CD@WPU loading was 5 wt%) for a duration of 1 h. It was observed that the hydroxylated product 4 formed in low yield at 0.5 wt%, 1 wt%, and 1.5 wt% loading (Table 1, entries 15-17) and due to aggregation of CD on WPU at higher loading (Table 1, entry 18). The hydroxylation reaction was less effective on using 1 and 2 equivalents of H₂O₂ with respect to 3 (Table 1, entries 19, 20) but when 4 equivalent of H_2O_2 was used it gave same yield (Table 1, entry 21) akin to 3 equivalent. No further oxidation of 4 was seen when the reaction was continued for more than 1 h. Thus, it was established that 1 and 2 equivalents of H₂O₂ could not generate enough hydroxyl free radicals needed for the reaction whereas 3 and 4 equivalents did, but then low amount was preferred in order to follow green chemistry approach. Besides CD encapsulated in CD, when CD mechanical mixed with WPU used as a catalyst (Table 1, entry 22), it gave a mixture of ortho and para products (57%) wherein the ratio of ortho one (53%) was higher. It might be due to the presence of WPU which could work well when CD would have been encapsulated in its matrix instead of using a mixture of the two. When **3** was treated with H_2O_2 under UV light in presence of WPU, no hydroxylation was observed (Table 1, entry 23). Blank experiment using UV light also could not lead the reaction toward product formation (Table 1, entry 24).

In general, the hydroxylation was found to be clean and only para selective (100%) using 5 wt% CD@WPU in UV light and no side product formation took place. The homogeneous distribution of CD over the entire polymer matrix helps light harvesting capacity of CD@WPU nanomaterial and polymer in the same media. Here, CD is the photoactive component which can absorb UV light, while WPU provides the requisite mechanical support and its unique structural attribute brings about exclusive para selectivity in hydroxylation reaction. Furthermore, WPU brings an extra profit by producing ionic centers along the polymer chains which perform like ionomers with potent electron transfer ability. Thus, WPU has been found to be a very effective support for photocatalytic activity of CD compared to the conventional polymers.^{36,37} Additionally, both CD and CD@WPU possess suitable band gap of 3.4 eV and 3.2 eV respectively³⁷ and applicable for the light harvesting capacity in the UV region. Hence, the current reaction underwent in the presence of UV light and remained inactive in dark.

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Encouraged with these results, we next moved to the exploration of the scope of CD@WPU catalysed selective hydroxylation of substituted aromatic hydrocarbons by treating with H_2O_2 under UV light under the optimized reaction conditions. As demonstrated in Table 2, CD@WPU has been established as a robust and sustainable photo catalyst for the hydroxylation of substituted aromatic hydrocarbons furnishing the selective hydroxylated products in good to high yields (Table 2, Entries 1-9). It was noteworthy to mention that under the present reaction condition, the catalyst was found to be less effective in the hydroxylation of benzene into phenol (7%

Table 2. CD@WPU catalyzed selective hydroxylation of aromatic hydrocarbons^a.

Entry	Product	Time	Yield	Melting
		(min.)	(%) ^b	point (°C) /
				(Lit. m.p.) ^{Ref.}
1	COOH	60	98	212.7-214.5
				(213-215) ³⁹
	HO			
2	COOH	60	92	223.8-226.4
				(225-227) ⁴⁰
3		90	88	11/1 3-115 8
5		50	00	(114-116) ⁴¹
				(114 110)
	HO		76	
4	CHO	70	76	114./-115.6
				(115-116)
	HO			
5	OH	100	60	171.6-173.4
	ĺ Ì			(173) ⁴³
	HO			
6	NH2	60	90	189.1-190.8
				(187-191) ⁴⁴
	HO			
7		130	58	111.2-112.7
				(110-112) ⁴⁵
	HO			
8	CI	150	80	43.8-45.2
				(44-45) ⁴⁶
	HO			
9	CH ₃	180	70	31.6-33.4
				(32-33) ⁴⁷
	HO			

 a Reaction condition: Substrate (1 mmol), H_2O_2 (3 mmol), CD@WPU (5 wt%), UV light. b Isolated yield. The products were characterized by 1H and ^{13}C NMR and also by comparing the melting points from the literature.

yield, 9 h) and naphthalene into naphthol (2% yield, 15 h). This was because of the lack in substituents (electron withdrawing

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or donating) in the aromatic ring. Also, hydroxylation of cinnamic acid and styrene did not take place under the current reaction condition which might be due to the π - π interaction with CD of the catalyst. In general, the yield of the product was found to be good to high when the benzene ring was substituted with electron withdrawing group (EWG) and electron donating group (EDG) which activated the ring toward hydroxylation. In order to drive the catalyst selectivity for ortho position, the reaction was carried out by considering para phenylene diamine (para position was blocked) under the optimized condition. In this case, instead of hydroxylation product, it gave azobenzene-4,4'-diamine³⁸ as a coupling product (50% yield, 16 h). Thus, CD@WPU has been found to be highly active, stable and 100% selective towards para hydroxylation of aromatic hydrocarbons which has been lacked in the previously reported catalysts.⁹⁻¹⁷

The hydroxylation reaction of aromatic hydrocarbons (mentioned in Table 3) was repeated using only CD as a catalyst to check the amount of ortho, meta and para hydroxylated product formation. It was found that carbon dot could only produce a mixture of ortho and para products (Table 3, entries 1-9). However, only nitrobenzene furnished

meta hydroxylated product along with ortho and para isomers (Table 3, entry 3). It can be seen from this table that the hydroxylation reaction was uncontrolled leading to the production of mixture of ortho, meta and para isomer. In this case, no selectivity at para position was seen. This may be due to non-selective nature of CD.

Table 3. CD catalysed hydroxylation of aromatic hydrocarbons

Entry	Time	Ortho	Meta	Para	Net yield
	(min)	(%)	(%)	(%)	(%) ^b
1	60	33	-	24	57
2	60	8	-	7	15
3	90	7	15	4	26
4	70	6	-	11	17
5	100	10	-	4	14
6	60	4	-	7	11
7	130	2	-	4	6
8	150	11	-	13	24
9	180	5	-	3	8

^aReaction condition: Substrate (1 mmol), H_2O_2 (3 mmol), CD (5 wt%), UV light. ^b Isolated yield. The products were characterized by ¹H and ¹³C NMR and also by comparing the melting points from the literature.

Under the norms of green chemistry, recycling is a key concern in catalysis. Hence, the recycling potency of CD@WPU catalyst has also been tested using the model reaction (Figure 2) under the optimized condition. The data obtained as presented in Table 4 demonstrate that CD@WPU has been recycled from fresh up to the 4th run without loss in its action. However, slightly longer reaction time was required afterwards to achieve the desired yield of **4** because the finely sliced thin film of CD@WPU slightly stuck amongst each other after 4th run. Also, the activity of the catalyst decreased in the fifth cycling. The UV-Visible analysis confirmed apparently no change in intensity up to 4th cycle, however, slight decrease in

intensity was observed 5th cycle onwards (Figure S1, ESI). This indicated some extent of dissolution (though not substantial) of CD after 5th cycle. Further, comparison of TEM images of fresh catalyst and spent catalyst after 4th cycle (Figure S2, ESI), revealed some extent of clustering of the nanomaterial in the later. Thus, we believe that dissolution as well as movement of CD within the polymer matrix to cause aggregation deactivated the efficiency of the catalyst. In order to avoid the use of excess amount of catalysts and to clarify the recyclability of CD@WPU, the reaction condition with a low yield as mentioned in entry 15 of Table 1 was carried out and the outcome for this event was also akin to Table 4 (Table S1, ESI).

Table 4. Recyclability of CD@WPU^a.

Entry	Run	Time (min)	Yield (%) ^b
1	Fresh	60	98
2	1 st	60	98
3	2 nd	60	98
4	3 rd	60	98
5	4 th	60	98
6	5 th	80	98
7	6 th	100	98

 $^{a}Reaction$ condition: 3 (5 mmol, 610 mg), $H_{2}O_{2}$ (15 mmol, 510 mg), CD@WPU (5 wt%, 56 mg), UV light. b Isolated yield.

The mechanism of the reaction is not very clear. However, on the basis of above results, a very probable free radical mechanistic pathway (Figure 3) has been proposed. At the very outset, under UV light irradiation, CD in CD@WPU acts as the electron reservoirs to entrap photo-induced electrons from the conduction band which assists the efficient partition of electrons (e) and holes (h) enhancing the photo catalytic activity.⁴⁸ The proposed plausible mechanism may proceed in different paths for aromatic ring substituted with electron donating (EDG) and electron withdrawing groups (EWG). In case of EDG, the ortho and para positions (I) of the aromatic ring are rich in partial negative charges i.e. electron density.⁴⁹ The electron deficient h⁺ may interact at these positions and expels one electron out of it. But three point interaction of the molecular box like structure of dendritic polymer⁵⁰ with the EDG containing aromatic ring, blocks the ortho position and keeps the para position (II) available for the incoming hydroxyl radical (OH·) to form para-hydroxylated product (III) thereon. On the other hand, electron snatching nature of EWG generates partial positive charges at ortho and para positions (IV) of the aromatic ring.⁴⁹ But the three point interaction of the dendritic polymer with the aromatic ring leaves only para position (V) unmasked. Hence, the e from electron-hole pair gets driven toward only available para position wherein the radical attacks thereof to produce expectedly ОH hydroxylated product (VI). In the entire scene, OH· radical is generated from H₂O₂ under UV light.⁵¹

Actually, WPU having surface functional groups -NH-C(=O)-O-, -O-C=O, -OH, $-NH_2$ facilitates a strong interaction with CD to provide a unique box like structure which in turn acting as the binding sites for the reactants. Similarly, graphitic CD with passivated surface states (which include -C=O, -OH, -O-C-O-) is

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Figure 3. (a) Insight into the plausible reaction mechanism for the selective hydroxylation of aromatic hydrocarbons at para-position catalyzed by CD@WPU. (I) = reactant, (II) = reaction intermediate and (III) = hydroxylated product in case of aromatic hydrocarbons substituted with electron donating group (EDG). (IV) = reactant, (V) = reaction intermediate and (VI) = hydroxylated product in case of electron withdrawing group (EWG). Free radical mechanistic pathway. (b) three point interaction of the substrate by polymer. Molecular recognition was possible only by three point binding as in enzymes.

capable of absorbing UV-visible light and thus functions as a photo catalytic module in the hydroxylation reaction (Figure S3, ESI). Therefore, this unprecedented work demonstrated unambiguously that our system, hyperbranched polyurethanes encapsulated carbon dot displays 100% molecular recognition possibly only by three point binding as in enzymes for the first time in the annals of chemistry for all varied and diversified substrates as described in this manuscript. Traditionally, the regioselective electrophilic substitution depends on ortho/para or meta positions for the electronic donating and electronic withdrawing groups already present on aromatic rings, respectively. None of these variations are observed with respect to selectivity and yields in the current hydroxylation reaction, but always provide p-hydroxylated products exclusively, possible only through free radical mechanism by induction of molecular recognition in the cavities of polymer matrix.

Conclusions

In summary, we devised a fruitful protocol for the one pot hydroxylation of substituted aromatic hydrocarbons under UV light catalyzed by novel, environmentally benign, metal free and biodegradable waterborne hyperbranched polyurethane/carbon dot nanocomposite based catalyst system (CD@WPU) catalyst system. The reactions were found to be clean and no side product formation was observed. The reaction was completely selective toward para hydroxylation irrespective of the nature of the electron donating as well as electron withdrawing groups in the aromatic hydrocarbons. The selectivity as well as light harvesting tendency of CD@WPU catalyst was imparted when CD was immobilized on the polymer matrix (WPU) in the aqueous media rendering extra stability to it and making the material resourceful in photo catalysis. The protocol bequeaths various advantages such as high yields of the hydroxylated products, safe to handle, experimental ease, using commercially available greener H_2O_2 , no byproduct formation, unfussy recoverability and reusability of the metal free catalyst making it sustainable, beneficial and benevolent alternate over the existing tactics. Therefore, as disclosed herein, we are expectant that the UV light active heterogeneous catalysts would find tremendous applications for new chemical transformations.

Notes and references

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