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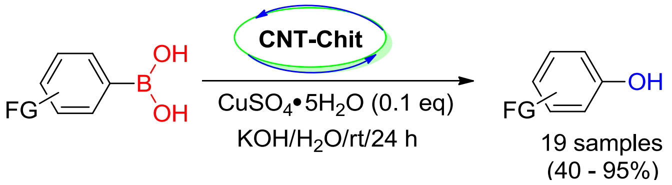
Recyclable CNT-Chitosan Nanohybrid Film Utilized in Copper-Catalyzed Aerobic *Ipso*-Hydroxylation of Arylboronic Acids in Aqueous Media

Han-Sem Kim,[a] Sung-Ryu Joo,[b] Ueon Sang Shin,[a,c]* Seung-Hoi Kim[b]*



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Recyclable CNT-Chitosan nanohybrid film utilized in copper-catalyzed aerobic *ipso*-hydroxylation of arylboronic acids in aqueous media

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ABSTRACT

A convenient heterogeneous catalytic system consisting of recyclable and reusable carbon nanotube-chitosan nanohybrid film and copper salt was developed for the aerobic *ipso*-hydroxylation of arylboronic acids. A variety of arylboronic acids bearing electron-withdrawing or electron-donating groups were smoothly transformed at room temperature in water to afford the corresponding phenols in high yields.

Chitosan is a partially deacetylated chitin which is commonly found in shells of marine crustaceans, and exists as powders, films or fibers with low porosity. Owing to its excellent biodegradability, biocompatibility, suitability for cell ingrowth, and adsorptivity for metal ions, it has been widely applied in a variety of chemistry-related areas.[1]

Despite these outstanding features of chitosan, issues related to its solubility in different media significantly limit its direct applications in organic chemistry. Since pristine chitosan is practically insoluble in organic solvents and only soluble in aqueous acids, efforts to improve its solubility in organic media or increase its surface area in organic media are required to expand its utility in organic synthesis.

To address this issue, numerous studies have focused on improving the physical properties of chitosan including its surface area, especially by the incorporation of super-strong and light-weight carbon nanotubes. There are several approaches for the preparation of CNT/chitosan nanocomposites using the physical and/or chemical bonding ability between the CNT surface and chitosan. As-prepared carbon nanotubes/chitosan (referred to as **CNT-Chit** hereafter) composite has been reported to show significantly improved physical and chemical properties.[2] With the modified properties, **CNT-Chit** nanocomposite has been frequently employed in a wide range of applications such as in biosensors, biofuel cells, drug delivery systems, scaffold fabrication, wastewater treatment, and catalyst carriers.[3]

Recently, we have successfully developed an advanced method for preparing CNT-chitosan films that are insoluble in water and possess a high chitosan surface area using a high-pressure homogenizer. It provides nanofibers with CNT-core and chitosan-shell structure and a novel CNT-Chit film formed through their close-packing. This material has the high strength and conductivity suitable for flexible electric circuits.[4] According to the scanning electron microscopic (SEM) images of the prepared-**CNT-Chit** films, the individual CNTs of the CNT-chitosan nanocomposite are fully wrapped by the hydrophilic chitosan molecules, which form a network of intermolecular hydrogen bonds. From an organic synthesis point of view, it is highly interesting that the chitosan polymer surface consisting of OH and NH_2 functionalities can act as a metal chelating ligand. Inspired by this aspect and postulating recyclability, we decided to apply the prepared-**CNT-Chit** film in the copper-catalyzed hydroxylation of arylboronic acids to obtain phenol derivatives.

Phenol and its derivatives have been frequently found in a wide range of chemical materials such as polymers, pharmaceuticals, and naturally occurring materials.[5] More importantly, it is often used as a key building block for the construction of complicated compounds. It is well-recognized that phenols are classically prepared by either nucleophilic aromatic substitution of aryl halides or the hydrolysis of arene diazonium salts, under limitations such as harsh reaction conditions, low functional group compatibility and limited accessibility of the starting compounds.[6]

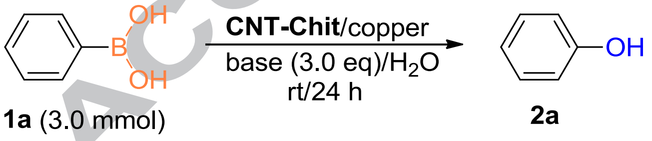
Together with these approaches, the oxidative *ipso*-hydroxylation of arylboronic acids to produce phenol derivatives has attracted considerable attention owing to unique properties such as ease of handling, ready availability, low toxicity, and high stability.[7] In most cases, strong oxidizing agents, mostly hydrogen peroxide[8] as well as other oxidants such as oxone,[9] *N*-oxide[10] and MCPBA[11] are required in stoichiometric amounts for the efficient conversion. Despite various protocols, it is highly desirable to develop mild and environmentally friendly oxidation processes in industries. In view of these aspects, catalytic oxidative hydroxylation using a greener oxidant along with a recyclable ligand in water is highly demanded. Accordingly, oxidations with molecular oxygen catalyzed by Pd(II) salts,[12] copper-promoted electrochemical hydroxylation,[13] electrochemically generated superoxide anions,[14] and photocatalytic aerobic oxidative hydroxylation mediated by visible light[15] have been developed.

Furthermore, several groups have recently reported improved copper-catalyst systems that do not require strong oxidants for the efficient hydroxylation of arylboronic acids. These approaches rely on copper-nanoparticles,[16] copper-complexes,[17] and combination of copper and a support.[18]

In our continuing research efforts to develop a suitable metal-catalyst system, we have developed an excellent heterogeneous catalyst for aerobic *ipso*-hydroxylation of arylboronic acids.[19] It consists of a combination of copper salt with recyclable and reusable **CNT-Chit** support in water, and more significantly, no strong oxidants such as peroxides and any extra additives are required. This protocol provides high stability in air and the catalytic system is effective because it can be recycled without losing its catalytic activity.

Table 1

Optimization of the hydroxylation of phenylboronic acid (**1a**)



entry	CNT-Chit (mg)[a]	catalyst (equiv)	base	yield(%)[b]
1	10.0	-	KOH	NR
2	10.0	$CuSO_4$•$5H_2O$ (0.1)	KOH	98
3	10.0	Cu_2O (0.1)	KOH	87
4	10.0	$CuCl_2$•$2H_2O$ (0.1)	KOH	83
5	10.0	CuBr (0.1)	KOH	91
6[c]	10.0	CuI (0.1)	KOH	92
7	10.0	$CuSO_4$•$5H_2O$ (0.05)	KOH	55
8	5.0	$CuSO_4$•$5H_2O$ (0.1)	KOH	52
9	0.0	$CuSO_4$•$5H_2O$ (0.1)	KOH	NR
10	10.0	$CuSO_4$•$5H_2O$ (0.1)	NaOH	56
11	10.0	$CuSO_4$•$5H_2O$ (0.1)	K_2CO_3	30
12	10.0	$CuSO_4$•$5H_2O$ (0.1)	Cs_2CO_3	32
13	10.0	$CuSO_4$•$5H_2O$ (0.1)	Na_2CO_3	28

[a] all reactions were carried out in air otherwise mentioned

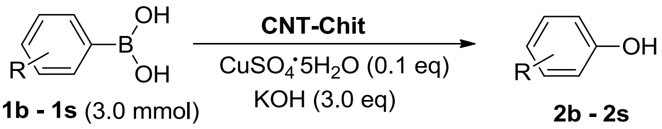
[b] isolated yield

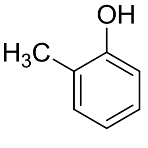
[c] stirred for 48h

An initial attempt was made with phenylboronic acid (**1a**) to screen suitable copper salts with no additional oxidizing agent under the following conditions: 10 mg of CNT-Chit nanocomposite, 3.0 equivalents of KOH, and water as solvent. Under these conditions, the role of copper salt was first verified by carring out the reaction in the absence of the copper catalyst, resulting in no expected product at all (entry 1, Table 1). To our delight, use of catalytic amounts of $CuSO_4 \cdot 5H_2O$ led to a significantly improved result in 24 h at room temperature (entry 2, Table 1). Impressed by this result, several other easily accessible copper salts such as copper (II) oxide, and copper halides were also examined under the same conditions. Gratifyingly, phenylboronic acid was completely converted in 24 h at room temperature, except when CuI was used. As shown in Table 1, most of the copper catalysts afforded generally satisfactory yields (83 to 92%). Using reduced amounts of $CuSO_4 \cdot 5H_2O$ or **CNT-Chit** significantly affected the reaction efficiency (entries 7 and 8, respectively). In addition, as expected, no conversion was observed in the absence of **CNT-Chit** (entry 9). When the base was replaced with NaOH, K_2CO_3, or Cs_2CO_3, no advantage over KOH was observed. Considering the operability and practicability, we chose $CuSO_4 \cdot 5H_2O$ as the catalyst and KOH as the base for the desired conversion.

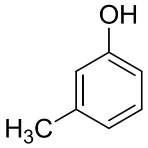
Table 2

Scope of arylboronic acids

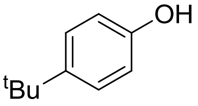




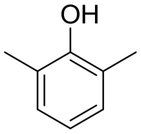
2b (95%)[a]



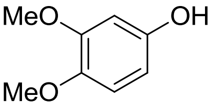
2c (92%)



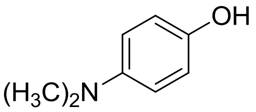
2d (90%)



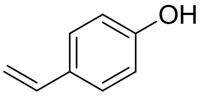
2e (85%)



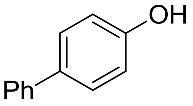
2f (93%)



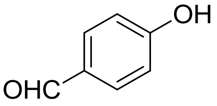
2g (89%)



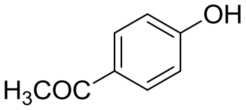
2h (91%)



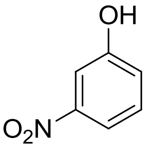
2i (95%)



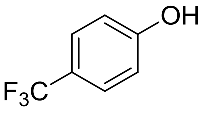
2j (90%)



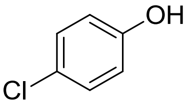
2k (89%)



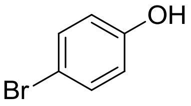
2l (88%)



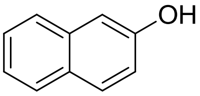
2m (90%)



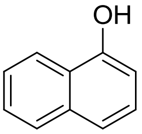
2n (89%)



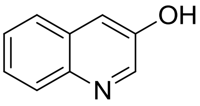
2o (90%)



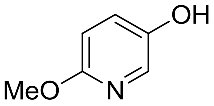
2p (94%)



2q (93%)



2r (91%)



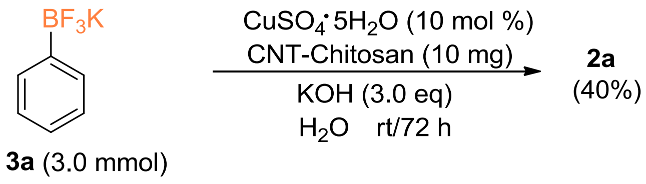
2s (90%)

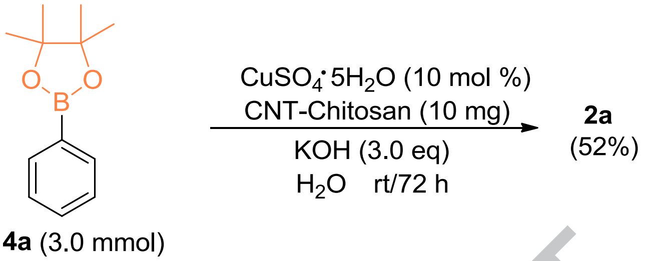
[a] number in parenthesis is isolated yield

Having identified the optimal conditions, we next explored the efficiency of **CNT-Chit** platform in copper-catalyzed aerobic oxidation of various arylboronic acids to phenols (Table 2). Regardless of the electronic properties of the arylboronic acids, the transformation was successful, resulting in the corresponding phenols in high yields. The sterically hindered arylboronic acid (**2e**) was well adapted, and the steric hindrance did not signicantly affect transformation. Various functional groups such as alkoxy (**2f**), amino (**2g**), vinyl (2h), phenyl (**2i**), carbonyls (**2j** and **2k**), nitro (2l), trifluoro (**2m**), halogens (**2n** and **2o**), and naphthalene ring (**2q**) were compatible with the reaction. Notably, heteroaryl boronic acids are also amenable to this protocol. A couple of heteroaryl boronic acids were examined under the same conditions, leading to the desired products, hydroxyl heterocyclic aromatics (**2r** and **2s**) in satisfactory yields.

Scheme 1

Hydroxylation of phenylboronic acid surrogates

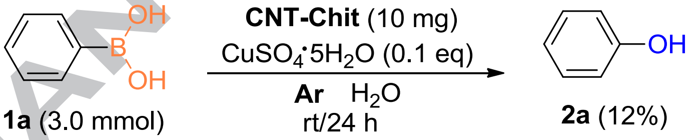




It is of interest that our new platform worked for phenylboronic acid surrogates as well in a similar fashion. Transformation of both potassium phenyltrifluoroborate (**3a**) and phenyl boronic acid pinacol ester (**4a**) to phenol required an extended reaction time under the same conditions used before, and the reaction proceeded at a slightly reduced rate, affording phenol (**2a)** in lower yields (Scheme 1).

Scheme 2

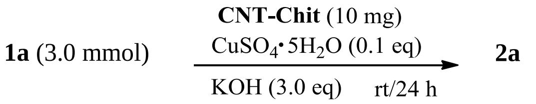
Control reaction



To gain insights into the possible mechanism, a control experiment was executed (Scheme 2). When the model reaction was carried out under positive argon pressure, conversion of **1a** to **2a** was not complete in 24 h at room temperature, leading to severely reduced isolated yield, which is consistent with the result of previous study.[18a] This observation clearly indicate that our reaction also proceeds in a similar fashion as illustrated in previous report.[17b]

Table 3

Reusability test



run	1st	2nd	3rd	4th	5th
yield (%)	98	98	95	95	95

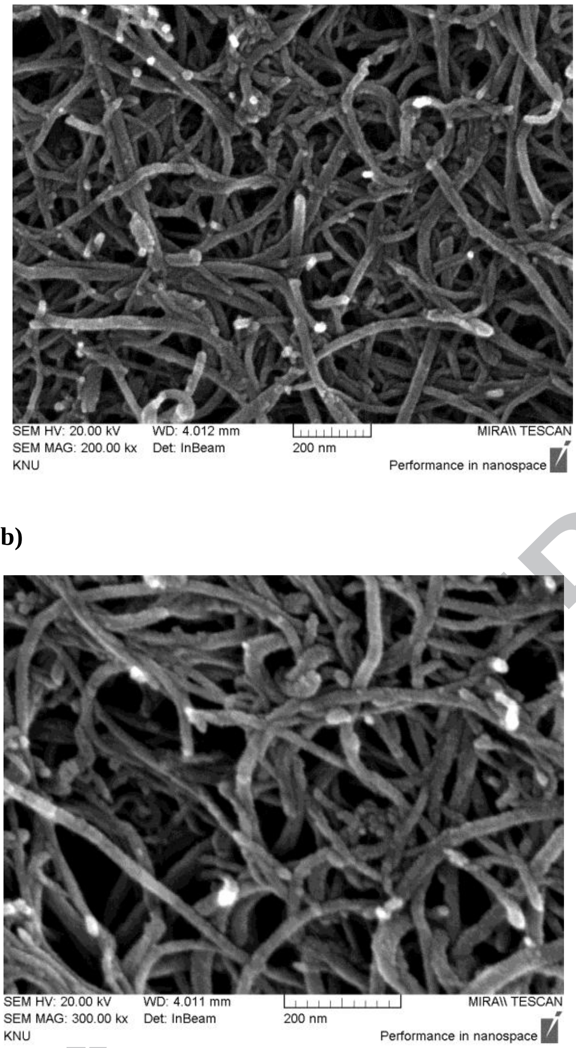
The recyclability of the **CNT-Chit** film was also investigated. The platform, which is insoluble in water, could be simply recovered by filtration after the completion of the reaction. Then, the collected platform could be washed with water followed by diethyl ether and allowed to dry in air, and reused directly in the subsequent reactions without any further purification. The recovered platform was reused up to 5-times without losing its activity in terms of the isolated product yield (Table 3).

As described previously, the surface of the **CNT-Chit** films, in which each CNT fiber is coated with Chit molecules to form CNT/Chit core/shell nanohybrid structure and closely packed by self-assembly, is composed of numerous chitosan molecules bearing both -OH and -NH_2 functional groups. Presumably, these functionalities could be acting as chelating ligands for the copper catalyst. Consequently, the deformation of the surface area could be crucial for the present catalytic system Therefore, the change in the morphology of **CNT-Chit,** especially after catalytic cycles should be investigated. To this end, we further analyzed and compared the surface of the **CNT-Chit** films before and after use by SEM. As shown in Figure 1 below, no obvious change can be detected even after five consecutive uses.

Figure 1

SEM images of **CNT-Chit** before (a) and after (b) the reaction

(a)



Another potential aspect of our reaction system is a sorption of copper-metal in chitosan. According to the previous reports,[20] both chitosan and chitosan derivatives can bind with copper (II) ion to form a complex in an aqueous solution. To address this issue, we also carried out a supplementary experiment to figure out the possibility of copper complexation in our reaction system. The hydroxylation of **1a** was carried out using the **CNT-Chit** film recovered from the initial hydroxylation of **1a** without any further treatment. No additional copper catalyst was used in this supplementary experiment, providing **2a** in a severely lowered isolated yield (31%). Despite the paucity of comprehensive investigation on copper absorption, it could be inferred that Cu-complexation was partially occurred and the resulting complex catalyzed the transformation in our reaction system.[21]

In conclusion, we have developed a convenient and efficient method for the synthesis of substituted phenols via a copper-mediated *ipso*-hydroxylation of arylboronic acids. The use of recyclable **CNT-Chit** film and water as the solvent render the protocol economical and environmentally friendly. Regardless of whether the boronic acid substrates bear electron-withdrawing or electron-donating groups, the transformation occurred smoothly to afford the corresponding phenols in high yields. This result could be attributed to the chelating effect of nitrogen and/or oxygen atoms in chitosan. Remarkably, the targeted products can be easily obtained by a simple workup operation after the completion of the reaction. High product yield and recyclability of the **CNT-Chit** film should be emphasized.

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19. General procedure for reduction of aryl/heteroaryl boronic acids to phenols: a flask was charged with 3,4-dimethoxyphenylboronic acid (1.0 mmol), CuSO$_4$•H$_2$O (0.02 g, 0.1 mmol), CNT-Chit film (10.0 mg), KOH (0.17 g, 3.0 mmol), and H$_2$O (5.00 mL). Then, the flask was stirred at room temperature in open air for 24 hours. At the end of the reaction, the reaction mixture was filtered and washed with water. Then, the filtrate was acidified with dilute aqueous HCl and extracted with diethyl ether (3 × 10 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. Purification by flash column chromatography on silica gel (70% hexanes/ 30% ethyl acetate) afforded 0.1433 g of 3,4-dimethoxyphenol (**2f**) in 93% isolated yield as an off-white solid (m.p. = 79-82 ^{o}C); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.70 (d, 1H, *J*=8.8 Hz), 6.46 (d, 1H, *J*=2.4 Hz), 6.34 (dd, 1H, *J*=8.8, 2.4 Hz), 5.84 (br s, 1H), 3.79 (s, 3H), 3.76 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ = 150.3, 149.8, 142.9, 112.5, 105.9, 100.6, 56.6, 55.7 ppm. HRMS (EI$^+$): *m/z* calcd. for $C_8H_{10}O_3$: 155.0703, found: 155.0707.

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21. Further studies on the preparation of metal-(functionalized)chitosan complexes and their catalytic applications in organic synthesis are currently undertaken in our laboratory and the results will be reported in due course.

Highlights:

- ✧ Convenient heterogeneous catalytic system
- ✧ Greener conditions; recyclable and reusable catalyst in water
- ✧ Facile carbon nanotube(CNT)-chitosan nanohybrid film
- ✧ Versatile copper-catalyzed aerobic *ipso*-hydroxylation
- ✧ Satisfactory isolated yield of the corresponding product phenols