'Green' chitosan bound silver nanoparticles for selective C–C bond formation via in situ iodination of phenols

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ABSTRACT

Herein we report on the use of chitosan–Ag NP composite as an efficient catalyst in selective C–C coupling of phenolic compounds in the presence of molecular iodine. This is the first report on the C–C coupling with Ag NPs as the catalyst. The reactions were carried out with phenol and a few of its derivatives as well as naphthols. The results indicate that the reaction proceeded via the formation of *p*-iodophenol followed by *o–p* coupling leading to the products. The reactions were complete in 3 h with high yields. When the *para*-position of phenol was blocked by a substituent then iodination at the *ortho*-position could only be observed and the formation of coupled products did not occur. In the case of naphthols *o–o* coupling could only be observed. Based on the results a mechanism is proposed for the coupling reaction occurring at the surface of Ag NP.

1. Introduction

Chemical reactions involving C–C bond formation continue to evoke research passions in the development of synthetic methods involving systems as diverse as aliphatic and aromatic compounds to complex polymers. These developments are being driven by the demands in pharmaceutical, agrochemical, polymer and even electronic industries where C–C bond formation is an important step in the designer intermediate generation, towards building complex architectures of a variety of organic molecules. As an example one can consider the case of coupling of phenols which is essential in the generation of a number of pharmacologically useful compounds such as terpenes, lignanes, tannins, flavanoids and alkaloids [1–3]. Further, selective C–C coupling of phenol derivatives have been used in the generation of metal complexes used as chiral metal catalysts and helical polymers [4–7]. Typically, coupling reactions of phenols are performed using oxidizing agents such as FeCl$_3$, ferricyanides and oxides of Pb(II), Ti(III) and V(V) [8–12]. However, their use results in poor selectivity in the product formation and generation of mixtures of quinones, dimers, trimers and polymers. In addition, some of these reagents are environmentally hazardous for large-scale usage. Further, in many instances the selectivity in

coupling is either not achieved or can be achieved through blocking appropriate positions in the aromatic ring, which require additional reagents, catalysts and not to mention the increase in the number of reaction steps and consequent yields. A new method that would involve minimum and greener reagents, reduced number of steps and that provides greater selectivity would arguably be a welcome addition to the repertoire.

Recently, a broad range of C–C coupling reactions, such as Suzuki, Heck, Sonogashira and Hiyama reactions, have been performed efficiently with the use of metal nanoparticles (NPs) as catalyst under homogeneous or heterogeneous condition. For example, Crooks and co-workers [13–15] reported that dendrimer encapsulated Pd NPs could be used as efficient catalyst for Suzuki coupling reactions in homogeneous conditions. In addition, chitosan supported Pd NPs were used for C–C coupling under heterogeneous catalysis [16–18]. Separately, Au NPs and Ag NPs have been used as catalysts for oxidation and reduction of a few selected molecules [19–22]. Interestingly, although there have been reports of coupling reactions involving Ag NPs and Au NPs in a medium [23–24], microheterogeneous coupling with high selectivity using an isolated polymer–Ag NP composite has not been reported. We have recently reported the development of a "green" chitosan–Ag NP (Chit–Ag NP) composite using chitosan as both reducing as well as stabilizing agent in the presence of NaOH. The resultant composite consisted of 21.6 mg of Ag per gram of chitosan. The average size of the Ag NPs present in the composite was 4.0 ± 1.2 nm and they exhibited high catalytic efficiency for the reduction of 4-nitrophenol to 4-aminophenol, and also have high antimicrobial activities [25–26]. Also, the composite

is soluble in water at acidic pH, while it precipitates out when the pH is turned alkaline.

In the present article, we report the use of the Ag NPs present in the composite as an efficient catalyst, in selective C–C coupling of phenolic compounds, in the presence of molecular iodine. This is possibly the first known report on C–C coupling with Ag NPs as the catalyst. Typical reactions were carried out with phenol and a few of its derivatives as well as naphthols. The results indicate that the reaction proceeded via the formation of *p*-iodophenol followed by *o–p* coupling leading to the product. Interestingly, when the *para*-position of phenol was blocked by a substituent then only iodination at the *ortho*-position could be observed, without the formation of coupled products. On the other hand, in the case of naphthols *o–o* coupling could only be observed. Based on the observed results, a mechanism is proposed for the coupling reaction occurring at the surface of Ag NPs.

2. Experimental

2.1. Materials

Phenol and its derivatives and iodine were purchased from Sigma–Aldrich Chemical Corporation. Absolute ethanol, ethyl acetate (EtOAc), hexane and dichloromethane were purchased from Merck.

2.2. Synthesis of chitosan–Ag nanoparticles (Chit–Ag NPs)

Chit–Ag NP composite was prepared by a procedure recently developed in the laboratory [25]. The details of the method are given in the reference. 0.2 g of Chit–Ag NP composite powder was dissolved in 100 mL of 0.1% (v/v) acetic acid in water. The resulting Chit–Ag NP composite was used as a stock solution for catalysis.

### 2.3. General procedure for the synthesis of the compounds

Substrates (1.0 mol dm^{-3}) were added to a solution of catalyst dissolved in a mixture of water (0.4 mL) and absolute ethanol (0.6 mL). The mixture was stirred for 1 min, followed by the addition of molecular iodine (0.6 mol dm^{-3}). The stirring was continued at room temperature until the completion of the reaction as indicated by thin layer chromatography (TLC). The reaction mixture was then poured into 10 mL of water and then extracted with dichloromethane (3× 15 mL). The extracted organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure to furnish crude product. The crude product was further purified by column chromatography (hexane: EtOAc (9:1)) to provide pure product.

2.4. Analytical measurements

NMR spectra (400 MHz for ^{1}H and 100 MHz for ^{13}C) were recorded using a DRX-400 Varian spectrometer with CDCl$_3$ as the solvent and Me$_4$Si as internal standard. Column chromatography was performed on silica gel (60–120 mesh) using ethyl acetate (Merck) and hexane (Merck) as eluent. The mass spectra were recorded using a Waters instrument (ACQUITY^{TM} UPLC) in ESI mode.

3. Results and discussion

It was observed that when phenol was treated with molecular iodine in the presence of the catalyst 6-iodo-2,4′-bis-1,1′-phenol was formed (Scheme 1). The product was obtained in high yield
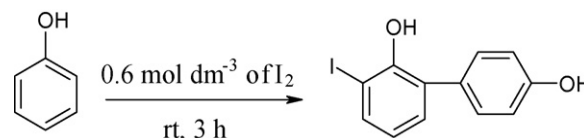
Scheme 1. Chit–Ag NP catalyzed *o–p* phenolic coupling reaction.

when 1.0 M of the substrate was stirred with 0.8 g/L of Chit–Ag NP composite solution at room temperature and in the presence of 0.6 M molecular iodine. Also, the reaction was complete in 3 h. The concentration of Ag was 0.16 mM. The number of Ag NPs in solution was calculated to be 4.8×10^{16} NPs/L [25]. The above concentration of the composite was found to be the best (with 100% yield of the product), as at lower concentrations complete conversion was not achieved and the intermediate compound (*p*-iodophenol) was present in the reaction mixture. For example, at 0.4 g/L and 0.6 mg/L of the composite the yields of the coupling product were 55 and 62%, respectively, while *p*-iodophenol was formed in large excess. Plot of the product yield versus surface area of Ag NP catalyst (Fig. 1) indicated rapid increase in product yield with the surface area. As is clear from the figure, at lower values of surface area, the intermediate compound was produced in high yield, whereas yield was 100% at a minimum surface area of 2.5 m^2/L. On the other hand, when the available surface area of the NPs was low the product did not form at high yield even after prolonged stirring (12 h). Thus it can be concluded that the total available surface area of the nanocatalyst is crucial for the formation of coupled products in the present system. Further, it may be mentioned here that when the reaction was carried out in presence of bulk Ag no coupling could be observed. Also, the intermediate (*p*-iodophenol) was not formed. It is known that enormous increase in surface area and surface free energy in the NP in comparison to the bulk metal makes the metal NPs efficient catalysts [27–29]. The present results demonstrate that Ag NPs, similar to other traditional metal NPs (Pt, Pd, Rh and Ru), could be used as efficient catalyst for C–C coupling reactions [30–33].

Further, it was found that optimum concentration of molecular iodine necessary to form the coupling product with high yield (>95%) was 0.6 M, under the above reaction condition. At lower concentrations either no product was formed or product was formed with low yield, while excess starting material (phenol) was present in the reaction mixture. A plot of the product yield with the amount of iodine – shown in Fig. 2 – indicates that the yield increased rapidly with the concentration of iodine, the highest being at 0.6 M.
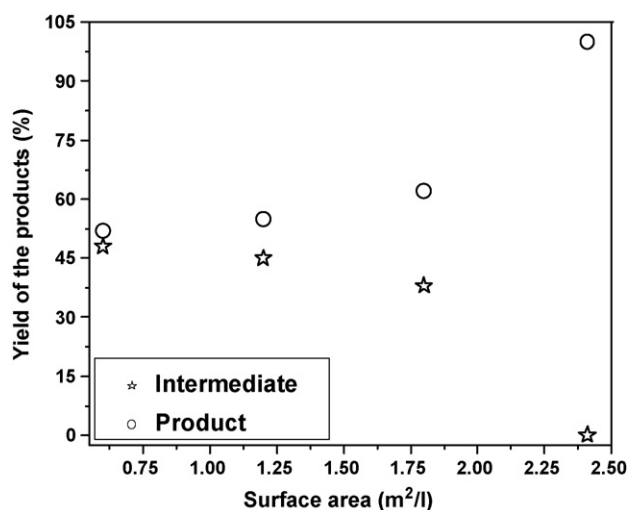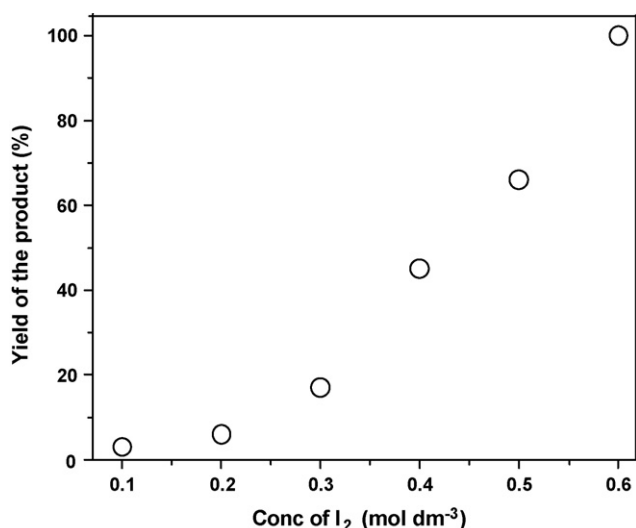

Fig. 1. The plot of the surface area per unit volume of the total Ag NPs in the composite versus the yield of the product. The concentration of I$_2$ was 0.6 M.

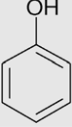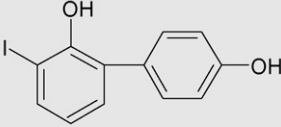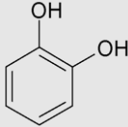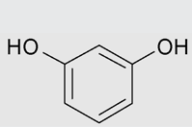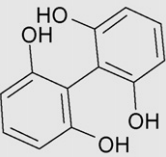**Fig. 2.** The plot of the selective coupling product of phenol with concentration of molecular iodine. The amount of the composite was 0.8 g/L.

The requirement of excess iodine in the reaction could be due to the formation of its well-known complex with chitosan [34–36] (in the composite). At lower concentrations of iodine, chitosan–iodine complex might have been formed exclusively and preferentially, rendering the availability of iodine low for reaction to occur at the surface of the Ag NP catalyst, while at higher concentrations excess
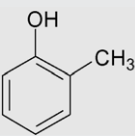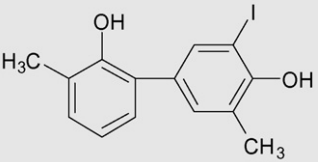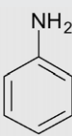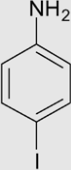
iodine may be available for the formation of coupling product. It was also observed that use of iodine beyond 0.6 M led to a slurry mixture and the product could not be easily isolated and hence not pursued further in this regard. It is important to mention here that when the amount of the composite used was higher (>0.8 g/L) – keeping the concentration of iodine constant – the yield of the coupling product decreased. The amount of the unreacted starting materials was also high (in comparison to the product)—that increased with the increasing amount of the composite (in the presence of a constant amount of iodine). Interestingly, it was observed that at the completion of the reaction (3 h), complete conversion took place and the intermediate p-iodophenol was also consumed completely in the process (when optimum concentrations of iodine and composite were used). Thus careful choice of concentrations of iodine as well as the catalyst is important in obtaining products with high yield.

In order to have a better understanding of the mechanism of the coupling reaction and the scope of the reaction with substituted phenols, further reactions were carried out with ortho- and para-substituted phenols. The results are shown in Tables 1 and 2, respectively. The ortho-substituted phenols yielded coupling product exclusively – except for catechol – (Table 1), while para-substituted ones resulted in iodinated phenols instead of coupling products (Table 2) under the same reaction condition. Moreover, the yields of the iodinated product of para-substituted phenols were ≥ 98%. Although, the two ortho-positions are available for reactions in para-substituted phenols, the iodination took place only in one ortho-position (Scheme 2). Therefore, the above results clearly indicate that para-position of phenols should be free and

Table 1
Chit–Ag NP catalyzed selective o–p phenolic coupling reaction via iodination.

Entry	Substrate (a)	t [h]	Product (b)	Yield (%) (a, b)
1	OH (phenol)	3	iodo-hydroxy-biphenyl-OH	75
2	OH, OH (catechol)	3	–	–
3	HO, OH (resorcinol)	3	HO, OH / OH, OH binaphthol-type	70
4	OH, CH₃ (o-cresol)	3	H₃C, OH / I, OH, CH₃	78
5	NH₂ (aniline)	0.5	NH₂, I (4-iodoaniline)	98

(a) Yields refer to isolated yields. (b) Compounds were analyzed by ^{1}H NMR, ^{13}C NMR and TOF mass spectroscopy.

Table 2
Chit–Ag NP catalyzed coupling of *p*-substituted phenols.

Entry	Substrate, R (a)	t (h)	Yield (%) (b)
1	−CH$_3$	2	85
2	−NH$_2$	3	–
3	−NO$_2$	3	–

(a) Yields refer to isolated yields. (b) Compounds were analyzed by ^{1}H NMR, ^{13}C NMR and TOF mass spectroscopy.
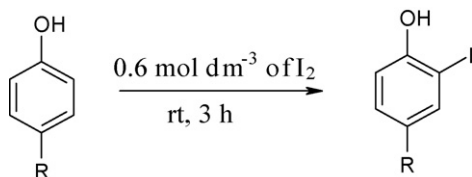
Scheme 2. Chit–Ag NP catalyzed C–C bond formation of *para*-substituted phenols.

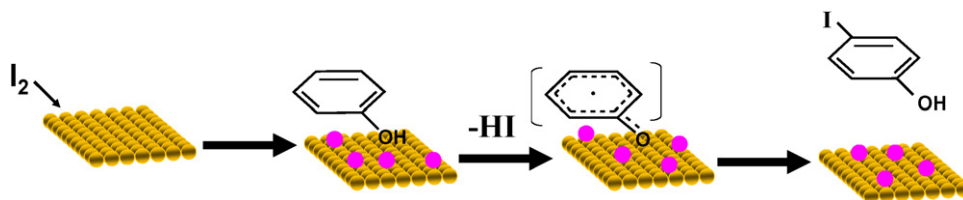available for the coupling reaction to take place. Interestingly, *ortho*- or *para*-amino or nitro-substituted phenols did not provide any iodinated phenol or coupling product. Further, 1,2-dihydroxy benzene (catechol) resulted in neither iodination nor coupling product formation even when the reaction was carried out for a relatively longer period. Additionally, in the case of naphthols, the coupling products were devoid of iodinated compounds (Table 3). The product formation was through 2-2′ coupling for α-naphthol, while 3-3′ coupling occurred in β-naphthol. Recently, Temma et al. reported the oxidative cross coupling of the naphthol derivatives using a chiral catalyst [37–39]. Their observation was that coupling of β-naphthol or β-naphthol derivatives mainly took place at the carbon nearest to the hydroxyl group. Similarly, Gao et al. [40] concluded that the hydroxyl group at *ortho*-position remains attached to the copper metal centre in the complex, leading to selective coupling in metal catalyzed reactions.

The above results demonstrated that under the present reaction conditions, C–C coupling of phenols took place between *ortho*- and *para*-positions of the two moieties. This was evident from the

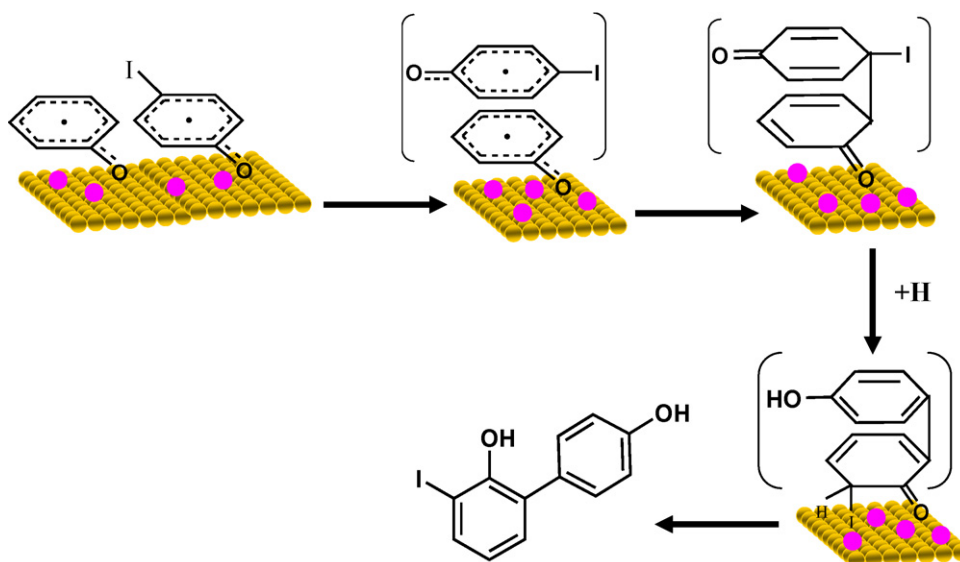absence of coupling of the reagents in which the *para*-positions were blocked (Table 2). On the other hand, when one of the *ortho*-positions was blocked by substitution, the coupling took place with the other free *ortho*-position (except for the −OH substitution). The absence of intermediate or product formation from catechol could be due to strong intramolecular hydrogen bonding between the neighboring OH groups, preventing adsorption on the surface of the NP catalyst. It can therefore be concluded that one of the *ortho*-positions and the *para*-position of the phenols must be free in order for the selective coupling to take place. This was further confirmed by detection of *p*-iodophenol as the intermediate. Therefore, the above observations suggest that selective coupling of the phenols, under the present reaction conditions, took place via formation of *p*-iodophenol as the intermediate. At lower concentrations of the catalyst, the formation of coupled product was low, which gradually increased with increasing catalyst concentration and consequently the yield of the *p*-iodophenol decreased. On the other hand, at higher concentrations of the catalyst, *p*-iodophenol, albeit formed quickly, was converted into the coupled product. It is well known that molecular iodine adsorbs onto the surface of bulk Ag under ultra-high vacuum (UHV) condition and splits into iodine atoms [41–43]. The iodine atoms generated on the surface can further react with organic moieties for iodination. Similarly, in the present experimental conditions, molecular iodine when added to Chit–Ag NPs dissociates into iodine atoms, and the resulting iodine atoms remain adsorbed onto the surface of the NPs; which in turn would react with phenol adsorbed on the surface. The iodine atoms present on the surface may first abstract hydrogen from phenol leading to adsorption of phenoxyl radical on the surface. This is followed by iodination at the *para*-position and subsequent desorption from the surface leading to the formation of *p*-iodophenol. The plausible process for *p*-iodophenol formation is schematically shown in Scheme 3. The proposed mechanism is consistent with the report that the OH group of phenol can be weakly chemisorbed onto Ag metal surface, with the ring plane nearly parallel to the surface [44–45]. Further, it is worth pointing out here that when NaI was added to the reaction mixture instead of molecular iodine, with the same amount of catalysis (0.8 g/L), there was neither formation

Table 3
Chit–Ag NP catalyzed coupling of naphthols.

Entry	Substrate (a)	t (h)	Product (b)	Yield (%) (a, b)
1		3		83
2		3		85

(a) Yields refer to isolated yields. (b) Compounds were analyzed by ^{1}H NMR, ^{13}C NMR and TOF mass spectroscopy.

Scheme 3. A plausible mechanistic pathway for the formation of *p*-iodophenols by Chit–Ag NP catalysts. Iodine on the surface is indicated by purple spheres. (For interpretation of the references to color in this scheme legend, the reader is referred to the web version of the article.)

Scheme 4. A plausible mechanistic pathway for the formation of selective coupling of phenol by Chit–Ag NP catalyst.

of any iodinated product nor coupling reaction took place. This is because addition of I⁻ onto Ag NPs surface might result in the formation of silver–iodide complex at the surface of the NPs and the resulting complex may be converted into molecular silver iodide, which is known to be catalytically inactive for selective coupling of phenols [46–47]. Thus iodine atoms derived from molecular iodine at the surface of Ag NPs are possibly responsible for the formation of intermediate as well as coupling products.

Further, based on the results with different substituted phenols, a plausible mechanism for the formation of C–C coupled product is shown in Scheme 4. Here again, the iodine atoms present on the surface facilitate the adsorption of phenoxyl radical as well as *p*-iodophenoxyl radical on the surface. The two phenoxyl radicals subsequently form a stable species having sandwich-type geometry on the surface (Scheme 4). This geometry results in *ortho–para*-coupling between the two with elimination of HI. This is followed by iodination at the *ortho*-position that is nearest to the surface and the results are *ortho*-iodinated C–C coupled products. It has been demonstrated in other coupling reactions and from the minimum energy calculation that the sandwich-type geometry [48–49] between the two phenoxyl radical species as shown in Scheme 3 is the most stable form. Perkins and co-workers have shown that this sandwich-type geometry, with the staggered configuration, could lead to either the *o–o* coupling or *o–p* coupling of phenols [50]. Their observation was that at room temperature *o–p* coupling led to the major product formation, whereas at higher temperatures the *o–o* coupling was the route to the major product formation. This is consistent with our observations of selective *o–p* coupling via intermediate *p*-iodophenol formation at room temperature and the surface of the Ag NP played the key role in the selectivity of phenolic coupling. This conclusion is further substantiated by the works of Bent and coworkers [51,52], where it was suggested that adsorbed iodobenzene molecules tilt away from surface plane and in this configuration the transient phenyl radical formed upon C–I bond dissociation has sufficient life time – possibly physisorbed in a second layer – to find and couple with another flat lying phenyl group bound directly to the Cu (1 1 1) surface. C–C coupling of phenols could be further facilitated by the excess co-adsorbed iodine atoms on the Ag NP surface, because the co-adsorbed iodine atoms on the surface can reduce the reaction barrier of phenolic coupling [53,54]. This is supported by the observation that the yield of *o–p* coupling product increased with increased amounts of adsorbed iodine. Further, in the reactions involving naphthols, iodine atoms

present on the surface may facilitate the formation of napthoxyl radical, which subsequently leads to coupling with the neighboring moiety, without the formation of a sandwich complex.

4. Conclusion

In this article we have reported the use of a novel and green method in the formation of selective coupling of phenols and its derivatives using a Chit–Ag NP composite as the catalyst. Iodine atoms present on the surface of Ag NP catalyst played a major role in the formation of selective coupling via *p*-iodophenol intermediate. Also, the formation of stable sandwich-type geometry between phenoxyl radical and *p*-iodophenoxyl radical provides the key step in *o–p* coupling with high yield. The present approach is expected to open new vistas in synthetic organic chemistry; especially Ag NP catalyzed C–C coupling reactions beyond the chosen present examples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.02.006.

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