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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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## Novel triazole-modified chitosan @ nickel nanoparticles: efficient and recoverable catalysts for Suzuki Reaction

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We have developed an efficient strategy for the preparation of uniform sized spherical NiNPs supported on chitosan surface via a "click". This heterogeneous catalyst has demonstrated a promising catalytic activity for the Suzuki-Miyaura coupling. Furthermore, the obtained catalyst can be easily separated from the reaction mixture by centrifugation and reused several times with no significant loss of activity.

#### Introduction

Published on 08 February 2017. Downloaded by Fudan University on 08/02/2017 13:43:28.

Generally, the transition metal-catalyzed cross-coupling reactions have played a crucial role in synthetic organic chemistry.<sup>1</sup> There are different types of competitive strategies for the formation of carbon-carbon and carbon-heteroatom bonds in cross-coupling chemistry.<sup>2-6</sup> Among them, palladium is still regarded as one of the most successful method for cross-coupling reactions in both academic and industrial synthesis.<sup>7</sup> However, the use of effective palladium-free systems has recently gathered a great deal of attention, due to the robust demand of palladium and its limited resources. Therefore recent attention has been focused on employing other available and cost-effective metal catalyst.<sup>8</sup> Recently nickel-based catalytic systems has emerged as a viable alternative to Pd catalyzed cross-coupling reactions.9 A brief survey in the literature display that, most of these reactions are extensively performed under homogeneous catalytic system using various Ni sources and ligands in organic solvents.<sup>10</sup> Despite of the significant application of the homogeneous catalytic systems they suffer from serious drawbacks such as the difficulty in separation of the residual metal from the reaction mixture and the ability to recover and reuse catalyst. These problems can cause damage to the environment and cost for the industry, which strongly limit the wider applicability of these systems for various organic

syntheses. Therefore, in recent years, there has been growing interest towards heterogenization of the existing homogeneous catalytic systems using different supports. This strategy can provide novel recyclable and reusable solid catalysts that facilitate the separation of the often expensive or toxic catalyst from the reaction mixture, making the catalytic processes valuable and cost-effective for wide industrial applications.<sup>11</sup> There have been numerous reports on the immobilization of the homogeneous catalysts using various insoluble supports such as as silica, <sup>12, 13</sup> polymers, <sup>14, 15</sup> alumina,<sup>16, 17</sup> zeolites,<sup>18, 19</sup> carbon nanotube<sup>20-23</sup> and etc. Recently, natural materials, in particular Bio-based polymers are one of the applicable and interesting architecture for solid catalysts. As one kind of the widely used biopolymers, chitosan is natural, safe, inexpensive and biocompatible polysaccharide, which is derived from crustacean resources such as crabs, shrimps, prawns, lobsters and cell walls of some fungi. These polysaccharides have been widely employed for various applications in manufacturing processes,<sup>24</sup> agriculture,<sup>25</sup> food,<sup>26</sup> biomedical,<sup>27</sup> drug delivery.<sup>28</sup> Chitosan has also been extensively utilized as environmentally benign polymeric supports for catalytic applications due to its hydrophilicity, presence of hydroxyl and amino groups, unique threedimensional structure, excellent chelating property and mechanical properties.<sup>29-35</sup> Herein, as part of our ongoing investigations on the synthesis and applications of efficient catalyst in organic synthesis, 36-38 we have prepared triazolemodified chitosan @ nickel nanoparticles which were synthesized by reaction of an alkynlated imino- thiophene ligand with azide functionalized chitosan via a click chemistry, for application in transition metal catalyzed organic reactions. The obtained catalyst was found to be an efficient and recyclable nanocatalyst for the Suzuki-Miyaura cross-coupling reaction.

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<sup>+</sup>Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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#### **Result and Discussion**

#### Preparation and characterization of the catalysts

The synthetic route for the preparation of triazole-modified chitosan @ nickel nanoparticles is depicted in Scheme 1. The compound 1 was firstly prepared by a simple condensation of 4-aminophenol with thiophene-2-carbaldehyde, which is subsequently reacted with propargyl bromide to preparation of an alkynlated imino- thiophene ligand. In the following step, the azide group was introduced into the chitosan surface according to the reported procedure.<sup>39</sup> Then azidated chitosan underwent a click process with compound 2 in the presence of active copper(I) to furnish the chitosan-triazole support. Ultimately, the resulting triazoles were further treated with NiCl<sub>2</sub> in the presence of hydrazine hydrate as reducing agent to produce the desired solid catalyst.



**Scheme 1** Synthesis of triazole-modified chitosan @ nickel nanoparticles. Reaction conditions: (a) thiophene-2-carbaldehyde, MeOH, reflux, 3 h; (b) propargyl bromide,  $K_2CO_3$ , acetone, 50  $^{\circ}C$ , 24 h; (c) triflyl azide (TFA), aqueous HCl. NaHCO<sub>3</sub>, CuSO<sub>4</sub>.5H<sub>2</sub>O, MeOH, r.t., 5 d; (d) 2, Cul, DMF/THF (1:1, V/V), r.t., 72 h; (e) NiCl<sub>2</sub>/EtOH solution, 12 h, r.t., and then hydrazine hydrate, r.t., 2 h.

FT-IR Spectroscopy was used to confirm the modifications of the chitosan surface (Fig. 1). Compared to the spectrum of the unmodified chitosan, a new peak appears at 2100 cm<sup>-1</sup> in azidated chitosan, which revealed the successful immobilization of  $N_3$  moiety on the surface of chitosan. Meanwhile, according to the results of elemental analysis, the loading of the azide group on the chitosan surface was determined to be 0.3 mmol g<sup>-1</sup>.



Fig.1 FT-IR spectra of alkynlated imino- thiophene ligand (a), azidated chitosan (b), triazole- modified chitosan (c), triazole- modified chitosan-Ni (d)

As shown in Fig. 1c, the disappearance of azide peak signifying completion of the click reaction between compound 2 and all azide groups. In addition, the characteristic peaks of 1592 cm<sup>-1</sup> (C=N vibration) and 1500 cm<sup>-1</sup> (C=C vibration of the aryl ring) are observed. In Fig. 1d, the imine group shifts to reduced frequency ( $\Delta v = 37$  cm<sup>-1</sup>) when coordination with nickel occurs. The above results confirm the successful attachment of imino-thiophene ligand and subsequent coordination of nickel nanoparticles onto chitosan. This catalyst was also characterized by EDX, SEM, TEM, ICP and XRD analysis. The presence of elements of C, N, O, S and Ni in the structure of catalyst was confirmed by EDX analysis (Fig. 2). Meanwhile, the quantitative determination of the nickel content, as determined by ICP was obtained to be 1.37%.



Fig.2 EDX spectrum of catalyst

As shown in Fig. 3, X-ray diffraction spectroscopy (XRD) pattern of catalyst that matched well with that of it (Reference code: 03–1051) indicate the existence of Ni (0) species on the surface of chitosan substrate. The strongest peak at  $2\theta = 20^{\circ}$  correspond to chitosan and other peaks in the sample at  $2\theta$  of

 $44.5^{\circ}$ ,  $51.8^{\circ}$  and  $76.7^{\circ}$  attributed to the diffraction of (111), (200) and (220) crystal planes of Ni (0).<sup>40</sup>



Fig.3 XRD pattern of catalyst

The particle size, shape and morphology of the synthesized nanomaterial were investigated by Scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) imaging techniques. As displayed in Fig 4 (A and B), TEM micrographs of the fresh catalyst reveals that nickel nanoparticles have a narrow size distribution with uniform and discrete spherical in shape. On the other hand, the DLS measurement shows that these particles have average diameter of 10 nm, indicating that our methodology is efficient



**Fig.4** TEM images of nanocatalyst (a and b), SEM photographs of catalyst (c) A histogram representing the size distribution of nanoparticles (d)

for the synthesis of Ni nanoparticles on the surface of chitosan in small size which are appropriate for the catalytic applications. The information about the surface morphology of functionalized chitosan was also investigated by scanning electron microscopy (SEM). As shown in Fig. 4c, the organic components with sphere-shaped morphology and monotonic nanometer-sized particles exist on the surface of the chitosan.

#### **Catalytic activity tests**

After synthesis and characterization of the catalyst, the catalytic competence of the newly designed chitosan based nickel nanocatalyst was investigated in the Suzuki-Miyaura reaction using 4-bromoanisole and phenylboronic acid as the model substrates under various conditions such as base, solvent, temperature, reaction time and catalyst loading. The observed results are presented in table 1. The initial experiments were carried out by running the model reaction in the presence of  $K_2CO_3$  as base and 0.2 mol% of catalyst in different solvent at 90  $^{\circ}$ C. The best result is obtained when toluene is used as solvent (Table 1, Entry 4). Noting the importance of base in this transformation, in our next set of experiments, the effect of various bases on the efficiency of this procedure was studied. On the basis of this study, K<sub>2</sub>CO<sub>3</sub> gave maximum conversion percentage. The temperature effect for the cross-coupling reaction was also surveyed. It was found that the improvement in reaction results was obtained at 90 °C. As respects, in lower temperatures the desired product was obtained in lower yields. Further, the effect of catalyst loading on the conversion was also studied. It was found that the higher yield was observed when the reation was carried out with 0.2 mol% of catalyst, while less than this values of catalyst led to a decrease in the yield of the product. To explore the scope and generality of the protocol, the present study is extended to various aryl halides with phenylboronic acid under the optimized conditions. Results summarized in Table 2 show that aryl bromides and iodides coupled smoothly with phenylboronic acid carrying either electron-withdrawing or electron-releasing substituents in relatively short reaction times. Compared with the corresponding bromo analogues, the less active chlorobenzene and its derivatives gave moderate to good yields and needed a longer times. It was also found that an increasing steric hindrance of ortho- substituted aryl halides gave lesser yield than those obtained with para-substituted ones.

#### **Reusability and heterogeneity test**

The possibility of recycling of a heterogeneous catalyst is one of the most indispensable aspects to determine its sustainability and industrial applications. In order to study this property, the recyclability of this system was investigated by using bromobenzen and phenylboronic acid as model substrates. For this purpose, at the end of the reaction, the catalyst material was separated by centrifugation, washed thoroughly with water and ethanol, dried and reused for subsequent runs. The recycling experiment demonstrated that quantitative conversion to the corresponding product was observed for six runs (Fig. 5). This observation was further supported by XRD and TEM analysis of the recovered catalyst.

DOI: 10.1039/C6NJ03789E Journal Name

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A comparison of the XRD patterns of the fresh and recovered catalyst reveals that both samples exhibited similar XRD patterns even after being subjected to six runs (Fig. S1, ESI<sup>+</sup>). Also, TEM image of the recovered catalyst clearly shows that the structure of the catalyst has no noteworthy change in comparison with fresh catalyst (Fig. S2, ESIT). To probe this point that the catalyst is truly functioning in a heterogeneous manner, a standard hot filtration test was conducted by coupling bromobenzene and phenylboronic acid. During this test, the solid catalyst was removed from the reaction mixture by filtration under hot condition after 1 h and the determined conversion was 27% (analyzed by GC). The residual solution was then allowed to react further under similar experimental conditions for an additional 7 h. The obtained results clearly indicate no further increment in the conversion percentage of the reactants. Additionally, the ICP result of the resultant supernatant only showed 0.04 ppm of the Ni species is lost into solution during the course of the reaction. So, these observations approved the high catalytic activity and good stability of the catalytic system. To compare the efficiency of the present catalytic system with previously reported catalysts in the Suzuki reaction, we have tabulated the results of these catalytic systems, in Table 3. It can be clearly seen that our catalyst is much better than the literature precedents in terms of reaction condition, reaction time, yield, recovery and reusability.



Fig. 5 Reusability of the catalyst

#### **Experimental section**

All chemical reagents were purchased from Merck Chemical Company and used without further purification. <sup>1</sup>H-NMR spectra were recorded on a Bruker 400 spectrometer using deutrated DMSO-d6 and CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. X-ray diffraction (XRD) powder patterns were obtained using an X'PERT MPD, with Cu K $\alpha$  radiation (40 kV, 30 mA). Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope. FT-IR spectroscopy (JASCO FT-IR 680-Plus spectrophotometer) was employed for characterization of products. Also we used Inductive coupled plasma Perkin Elmer Optima 7300 DV. Gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm) was used for consideration of reaction conversions and yields. Scanning electron micrographs of the catalyst were taken on [FE-SEM, HITACHI (S-4160)]. The acknowledgements come at the end of an article after the conclusions and before the notes and references.

<b>Table 1</b> Effect of different parameters for the reaction of 4-bromoanisole with phenylboronic acida								
Entry	Solvent	T(°C)	Base	Yield <sup>b</sup>				
1	PEG400	90	K <sub>2</sub> CO <sub>3</sub>	32				
2	EtOH	90	K <sub>2</sub> CO <sub>3</sub>	25				
3	THF	90	K <sub>2</sub> CO <sub>3</sub>	43				
4	Toluene	90	K <sub>2</sub> CO <sub>3</sub>	94				
5	DMF	90	K <sub>2</sub> CO <sub>3</sub>	78				
6	DMSO	90	K <sub>2</sub> CO <sub>3</sub>	75				
7	Toluene	90	КОН	58				
8	Toluene	90	K <sub>3</sub> PO <sub>4</sub>	87				
9	Toluene	90	NaHCO <sub>3</sub>	76				
10	Toluene	80	K <sub>2</sub> CO <sub>3</sub>	83				
11 <sup>c</sup>	Toluene	90	K <sub>2</sub> CO <sub>3</sub>	68				

<sup>a</sup> Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), amount of catalyst (0.2 mol%), time (5 h) and solvent (5.0 ml). <sup>b</sup> GC yield. <sup>c</sup> The amount of catalyst reduced to 0.1 mol%.

#### Synthesis of imino-thiophene ligand (1)

Thiophene-2-carbaldehyde (10 mmol) and p-aminophenol (10 mmol) were added into 25 mL of methanol and solution was refluxed for 3 h. Afterward, the solvent was removed and the pure product 1 was obtained. Yellow crystals; <sup>1</sup>H NMR (400 MHz, DMSO-d6): 9.53 (s, 1H), 8.76 (s, 1H), 7.74 (d, J = 6.8 Hz 1H), 7.60 (d, J = 4 Hz, 1H), 7.17–7.21 (m, 3H), 6.79 (d, J = 11.6 Hz, 2H).

#### Synthesis of compound (2)

propargyl bromide 5.2 mmol) was added dropwise to a solution of compound 1 (5 mmol) and  $K_2CO_3$  (10 mmol) in acetone (10 mL), and the mixture was stirred at 50 °C for 24 h under a nitrogen atmosphere. The resulting solid was then filtered and washed several times with  $Et_2O$  and acetone to obtain a brown solid powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.55 (s, 1H), 7.46 (d, J = 6.8 Hz, 1H), 7.43 (d, J = 4.4 Hz, 1H), 7.2 (d, J = 8 Hz, 2H), 7.09–7.12 (m, 1H), 6.97 (d, J = 8 Hz, 2H), 4.68 (s, 2H), 3.56 (s, 1H)

#### Synthesis of azide-functionalized chitosan <sup>39</sup>

To a solution of chitosan (0.5 g) in 0.5 M aqueous HCl. NaHCO<sub>3</sub> (9.3 mmol, 20 ml), CuSO<sub>4</sub>.5H<sub>2</sub>O (0.09 mmol) and triflyl azide (TFA) solution (5.95 mmol) were added. Afterward, 15 ml of

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methanol was added and the solution was stirred at room temperature for 5 days. Finally, the solid particles were filtered and washed several time with acetone, HCl solution (5% solution in water) and then water and finally dried at room temperature.

# Preparation of imino-thiophene ligand-functionalized chitosan via click reaction

Azide functionalized chitosan (0.5 g) and compound 2 (2mmol) were mixed with CuI (0.1 mmol) in DMF/THF (1:1, V/V) solution, and the reaction mixture was then stirred at room temperature for 72 h. Finally, the reaction mixture was filtered and washed sequentially with Et<sub>2</sub>O, H<sub>2</sub>O and then acetone and dried in vacuum at 60 °C.

## Preparation of triazole-modified chitosan @ nickel nanoparticles

At first, chitosan (0.2 g) was dispersed into 100 mL ethanol and 3.4 mL of 0.1 mol  $L^{-1}$  NiCl<sub>2</sub>/ethanol solution dropped into the above solution and stirred for 12 h at room temperature. Then, 2 mL of hydrazine was dropwise added to the above mixture with vigorous stirring at a temperature of 60 °C. After 2 h, the catalyst was separated by filtration, washed several times with ethanol and deionized water, and finally vacuum dried at room temperature.<sup>41</sup>

#### Conclusions

In summary, we have reported the preparation of new functionalized chitosan with an alkynlated imino- thiophene ligand via a "click" route. The newly designed material has been applied as an economical and effective support for heterogeneous nickel nanoparticle which was efficiently used as catalysts for Suzuki cross-coupling reactions. Furthermore, this catalytic system shows negligible leaching and maintains

high catalytic activity over six successive cycles. Additionally,
high catalytic activity, broad substrate scope, reusability and
the use of an inexpensive chitosan and nickel make it a
desirable protocol from environmental and industrial view
point.

		<b>Table 2</b> Suzuki cross-coupling reaction of various aryl           halides with phenylboronic acid <sup>a</sup>							
Entry	$R_1C_6H_4X$	х	Time (h)	Yield (%) <sup>b</sup>					
1	Н	Ι	2.5	98					
2	Н	Cl	7	84					
3	Н	Br	4	96					
4	4-CH <sub>3</sub>	Cl	9	76					
5	4-CH <sub>3</sub>	Ι	3.5	98					
6	4-CH <sub>3</sub>	Br	6.5	91					
7	4-CH <sub>3</sub> O	Br	5	92					
8	4-CH <sub>3</sub> O	Ι	4	98					
9	4-CH <sub>3</sub> O	Cl	9	79					
10	2-COCH <sub>3</sub>	Br	8	54					
11	4-COCH <sub>3</sub>	Br	3.5	95					
12	4-NO <sub>2</sub>	I	1	98					
13	4-NO <sub>2</sub>	Cl	7	87					
14	4-NO <sub>2</sub>	Br	3	97					

 $^{\rm a}$  Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol), solvent (4 ml), catalyst (0.2 mol%), 90  $^{\rm o}$ C,  $^{\rm b}$  Isolated yield

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 Table 3 Comparison of catalytic activity of the Ni (0)/Chitosan catalyst with literature precedents using Ni based homogeneous and heterogeneous catalysts for Suzuki-Miyaura cross coupling reaction

Entry	Catalyst	$R_1C_6H_4X$	х	conditions	Yield (%)
1	Ni (0)/Chitosan	4-CH <sub>3</sub>	Br	$K_2CO_3$ , Toluene, 90 °C, 6.5 h	91 (This work)
2	Ni (0)/Chitosan	4-COCH <sub>3</sub>	Br	$K_2CO_3$ , Toluene, 90 °C, 3.5 h	95 (This work)
3	octahedral nickel(II) benzoylhydrazone complex	н	Br	Toluene, K <sub>2</sub> CO <sub>3</sub> , Reflux, 8 h	83 <sup>42</sup>
4	Ni(II) mounted on graphite (Ni/Cg)	4-CH <sub>3</sub>	Br	K₃PO₄, PPh₃, LiBr, dioxane, 180-200 °C, 9h	87 <sup>43</sup>
5	Magnetic Fe–Ni Alloy	4-CH <sub>3</sub> O	I	NaOH, PCy <sub>3</sub> , dioxane, 120 °C, 12h	95 <sup>44</sup>
6	HPMC stabilized Ni Nanoparticles	4-COCH <sub>3</sub>	Br	Ethylene Glycol, Cs <sub>2</sub> CO <sub>3</sub> , 100 <sup>°</sup> C, 20 h	99 <sup>45</sup>
7	Ni-TC@ASMNP	4-NO <sub>2</sub>	I	$K_3PO_4$ , PPh <sub>3</sub> , dioxane,100 °C, 10 h	98 <sup>46</sup>

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#### Acknowledgements

We gratefully acknowledge the funding support received for this project from the Isfahan University of Technology (IUT), IR of Iran, and Isfahan Science and Technology Town (ISTT), IR of Iran. Further financial support from the Center of Excellence in Sensor and Green Chemistry Research (IUT) is gratefully acknowledged.

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