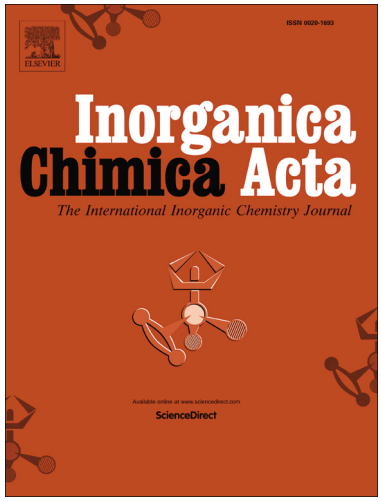

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Starch Functionalized Creatine for Stabilization of Gold Nanoparticles: Efficient Heterogeneous Catalyst for the Reduction of Nitroarenes

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Abstract: Selective reduction of nitroaromatic pollutants into amines with recoverable and reusable heterogeneous catalysts is highly desirable. Herein, we prepared and characterized an efficient novel catalyst comprising 4 nm size Au nanoparticles supported on creatine modified starch. Using this catalyst, efficient reduction of nitroarenes into amines at room temperature in aqueous media was achieved. The presence of creatine in the structure of the catalyst plays important role in amount of Au loading, efficiency of the catalyst, recycling times, and leaching of Au compared to starch supported Au without creatine.

Keywords: *Starch, Creatine, Gold, Nitro, Reduction, Heterogeneous*

1. Introduction

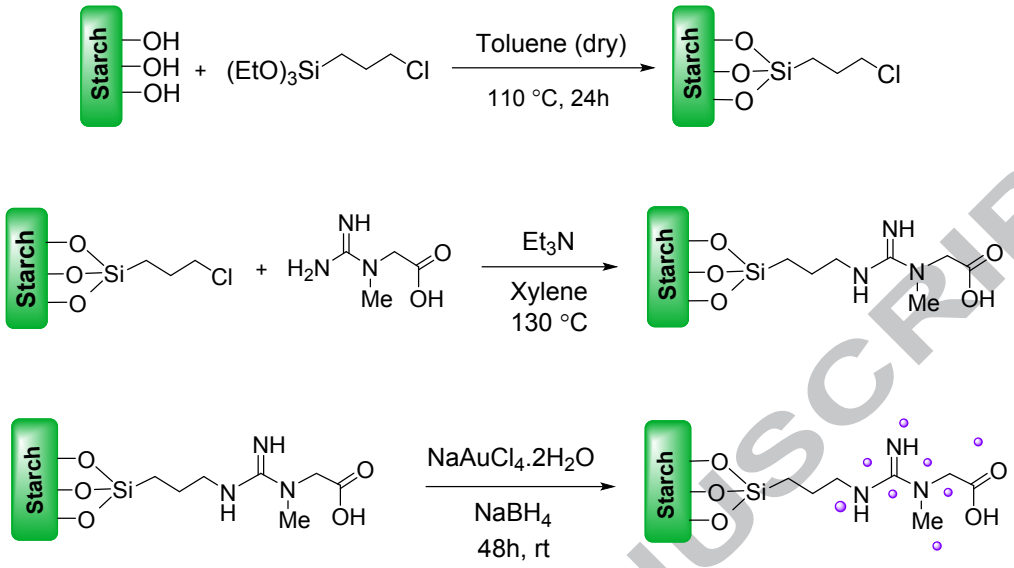
Nowadays green chemistry encourages researchers to develop new chemical process that eliminate or reduce the production of substances which are harmful for human and environment. Along this line, eliminating or reducing of the organic pollutants and development of new sustainable catalysts are two important aims of green chemistry objectives [1,2]. Nitroaromatic compounds which are potent toxic, carcinogenic and hazardous to human health are among the largest and most important groups of industrial wastes. In contrast, amines are versatile precursors in the preparation of various compounds including pharmaceuticals, dyes and agrochemicals [3,4]. Reduction of nitro compounds is one of the most reliable methods for the preparation of amines. Traditional methods such as Béchamp reduction in which aromatic nitro compounds were reduced to the corresponding aromatic amines by iron and ferrous salts catalysts in aqueous acid, is time consuming method and produce large amount of waste and is not appropriate for acid sensitive functional groups [5]. To address this issue, in recent years, catalytic hydrogenation using different transition metals and reducing sources have been developed for the reduction of nitroarenes [3,4]. For a long time, gold has been considered as an inactive metal. However, after its well-recognized catalytic activity, gold-catalyzed organic transformations have attracted a great interest in organic synthesis [6-11]. Along this line, various gold catalysts in the presence of different reducing agents have been developed successfully for the selective reduction of nitro groups under homogeneous or heterogeneous conditions[12-35]. In recent years, using various compounds as support for stabilization of transition metal and formation of heterogeneous catalysts, which generate new materials of low human toxicity and environmental impact, attract great attentions [36,37]. For instance, naturally occurring polysaccharides can be considered as excellent solid for stabilization of transition

metals[38-40]. Among different polysaccharides, starch is a polymeric carbohydrate involving glucose units connected by glycosidic bonds, which is regenerated from carbon dioxide and water by photosynthesis in plants. Different properties of starch, such as complete biodegradability, high water-swelling ratio, low cost and renewability make it a promising support for catalyst design [41-45]. On the other hand, creatine is a nitrogenous organic acid and naturally occurring substance produced in the pancreas, and liver in vertebrate animals. The main role of creatine in body is to facilitate recycling of adenosine triphosphate (ATP) via reaction of creatine with phosphate group of ATP and producing phosphocreatine in muscle and brain tissue [46].

The main goal of this work is to combine onto a solid phase (starch) a linker bonded to the natural compound (creatine) and deposit gold nanoparticles. The characterization of this gold aggregate and its efficiency as catalyst in the reduction of nitroarenes will be also assessed.

2. Results and discussion

For the preparation of the desired catalyst, commercially available corn starch was reacted with (3-chloropropyl)triethoxysilane in dry toluene giving the resulting starch containing the chloro atom at the end of the linker (starch@Cl). Then, creatine was reacted with starch@Cl in xylene using Et_3N as a base. Finally, the creatine-functionalized starch (starch@crt) was treated with $NaAuCl_4.2H_2O$ and reduced with $NaBH_4$ affording creatine-modified starch supporting Au NPs (Scheme 1). The obtained new gold composite is referred to as starch-crt@Au throughout the text. Using atomic absorption spectroscopy (AAS), the content of gold in starch-crt@Au was found to be 0.0198 mmol/g. This result indicated that 73.3% of Au species was successfully loaded on starch@crt.



Scheme 1. Synthesis of starch-crt@Au

Structure of creatine, starch@Cl and starch@crt were studied by Fourier-transform infrared spectroscopy (FT-IR). As can be seen in Figure 1, FT-IR of starch@crt showed sharp absorption peak at 1696 cm^{-1} related to C-O stretching vibrations of carboxylic acid in creatine. Also, prominent absorption peak related to C-N stretching vibrations of guanidine at 1615 cm^{-1} and peak related to NH stretching vibrations centered at 3338 cm^{-1} were observed in starch@crt confirming successful grafting of creatine on starch (Figure 1)[47].

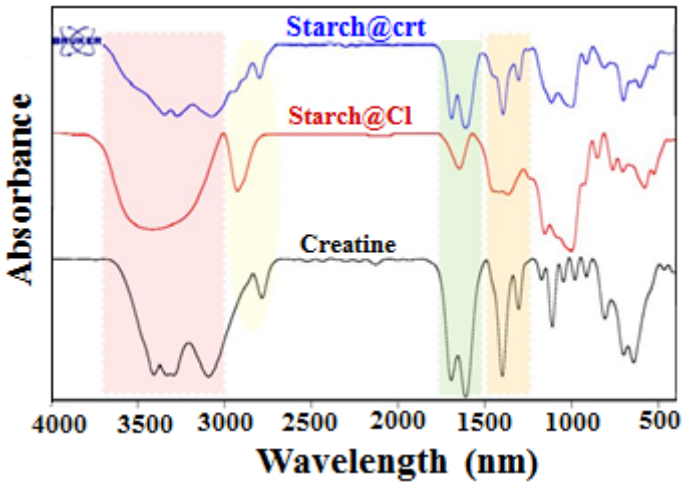


Figure 1. FT-IR spectra of creatine, starch@Cl and starch@crt

The scanning electron microscopy (SEM) images of starch-crt@Au in different magnification showed amorphous starch sheets and also the presence of Au nanoparticles (bright dots) (Figure 2).

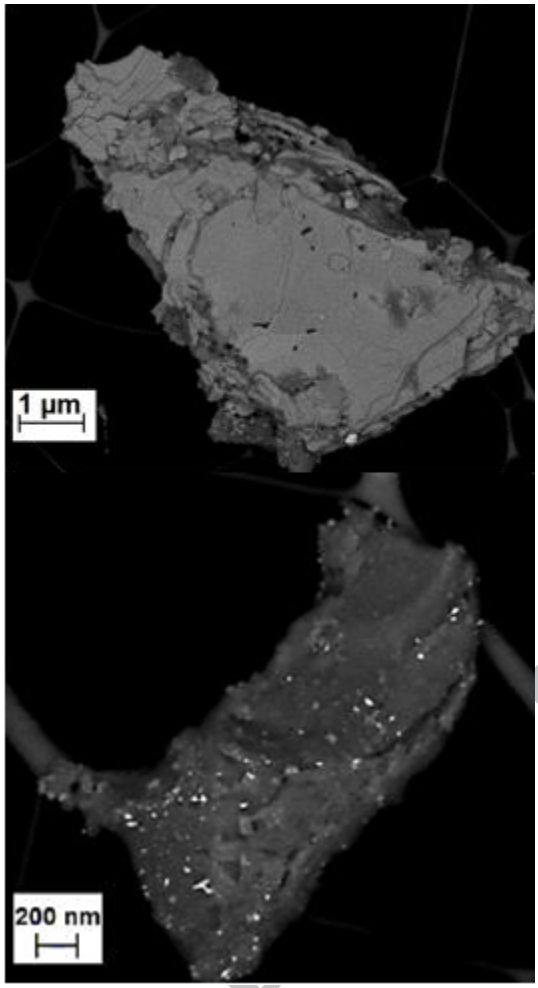


Figure 2. SEM images of starch-crt@Au

Energy dispersive spectroscopy (EDS) confirmed the existence of different elements such as Au, O, N, Si, and C into the structure of starch-crt@Au (Figure 3).

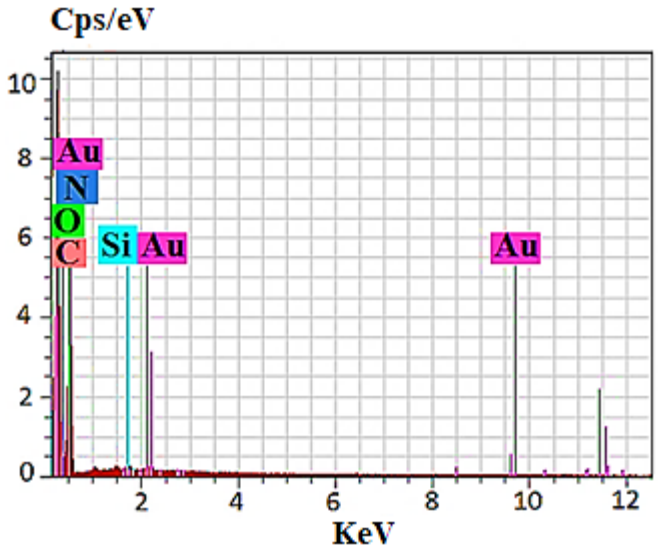


Figure 3. EDS spectra of starch-crt@Au

Furthermore, SEM-Map images of elements (Figure 4) and overlay mapping image (Figure 5) showed uniform dispersion of Au, C, N, and Si in starch-crt@Au structure.

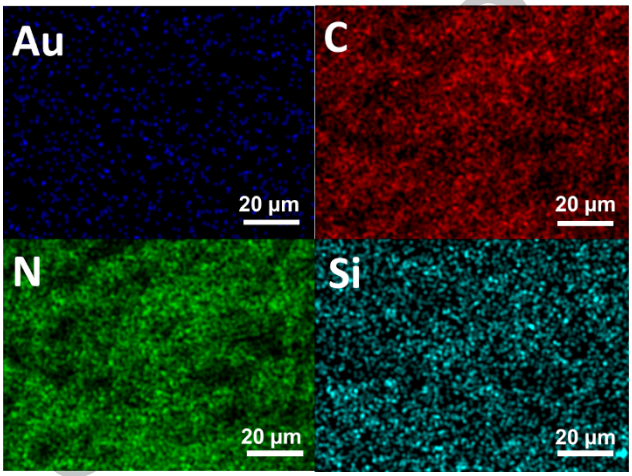


Figure 4. EDS mapping images of starch-crt@Au

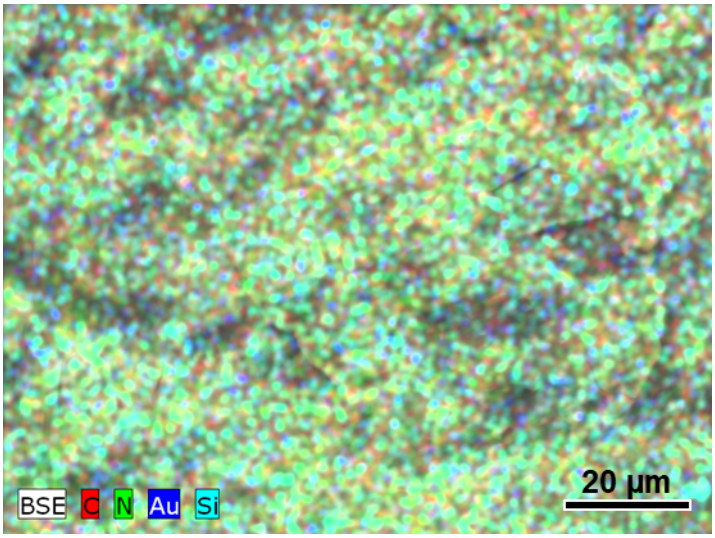


Figure 5. Overlay mapping image of starch-crt@Au

X-ray photoelectron spectroscopy (XPS) of starch-crt@Au in Au, N, C and Si regions were studied (Figure 6). The XPS spectrum in the Au 4f region showed an intense doublet at 83.6 and 87.4 eV confirming complete reduction of Au(III) to Au(0) (Figure 6a) [48]. Also, XPS analysis for the N 1s region confirmed the presence of nitrogen in the structure by appearing a peak centered at 400 eV (Figure 6b) [49, 50]. In addition, peaks located at 284.6, 286.5 and 288.2 eV were related to C 1s orbital in C–C/C–H, C–O and O–C–O forms, respectively (Figure 6c) [51,52]. Finally, Si 2p region XPS spectrum showed two binding energies at 101.9 eV and 102.8 eV, which are related to Si-O bonds (Figure 6d) [53,54].

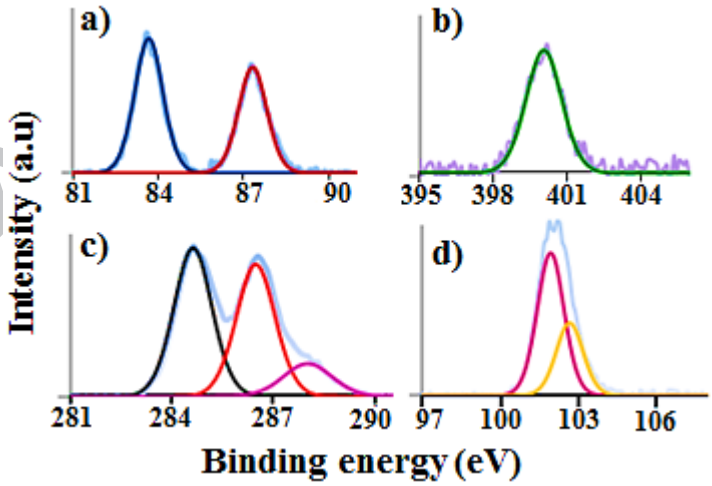


Figure 6. XPS spectra of starch-crt@Au in a) Au b) N c) C d) Si

Transmission electron microscopy (TEM) images of starch-crt@Au at different magnification levels showed presence of small size Au nanoparticles (Figure 7). The average size of Au nanoparticles using the following equation: $\overline{D} = \sum d_i n_i / \sum n_i$, was found to be 4.3 nm, where, n_i was the number of particles whose diameter was d_i (Figure 8).

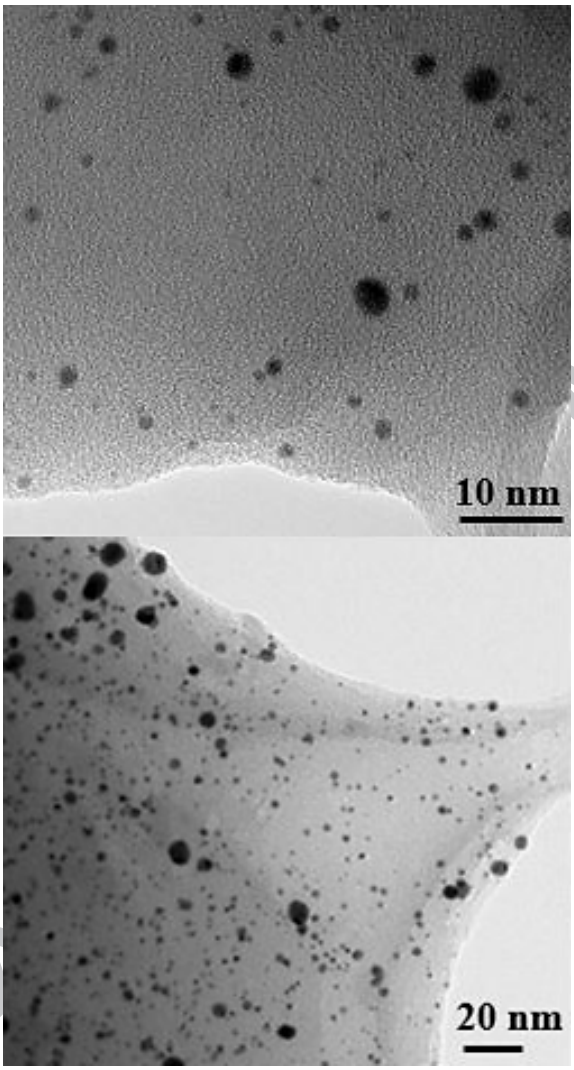


Figure 7. TEM images of starch-crt@Au

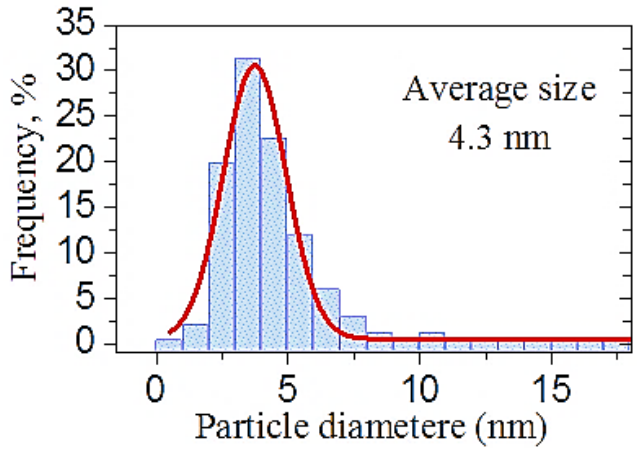


Figure 8. Distribution diagram of Au nanoparticles in starch-crt@Au

X-ray diffraction (XRD) analysis of the starch-crt@Au showed Bragg's reflections at 2θ=17°, 23° corresponding to the (200) and (211) planes of starch [55,56] and Bragg's reflections for Au(0) at 2θ=38°, 44.2°, 65° and 78° (Figure 9)[48,57].

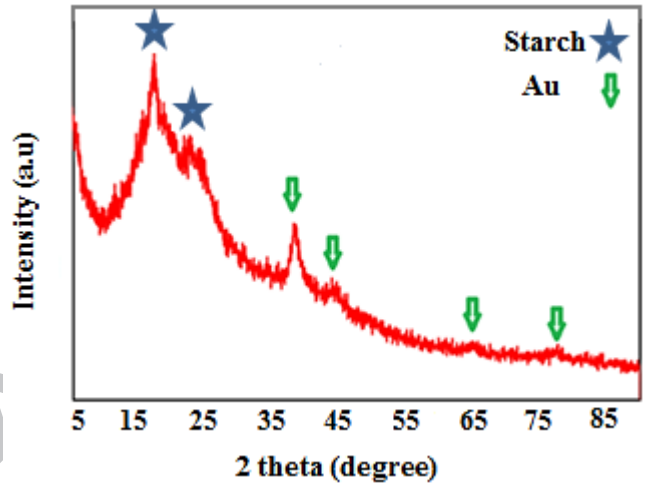
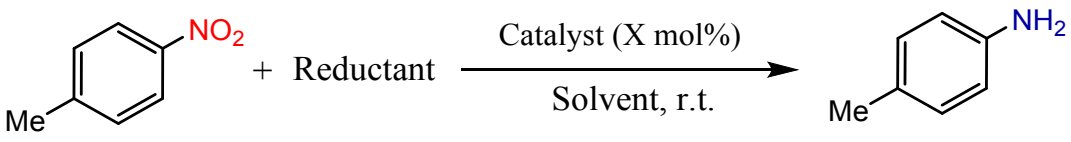


Figure 9. X-Ray diffraction analysis of starch-crt@Au

Next, the catalytic activity of starch-crt@Au was assessed in the reduction of nitroarenes to the corresponding amines. The reduction of 4-nitrotoluene was selected as benchmark reaction and the effect of different factors such as catalyst mol%, type of reductant, solvent and reaction time were studied. Initially reaction was performed using 0.01 mol% of catalyst in the presence of $NaBH_4$ (5 equiv) in water during 4 h. In this reaction, the formation of 4-aminotoluene took place in poor yield (Table 1, entry 1). With increasing the catalyst loading to 0.03-0.1 mol%, yields were improved (Table 1, entries 2-5) and 89% was obtained using 0.1 mol% catalyst (Table 1, entry 5). Then, we tried the efficiency of other reducing agents in water using 0.1 mol% of the catalyst. However, the formation of amines took place in lower yields than the reactions employing $NaBH_4$ (Table 1, entries 6-9). Other organic solvents tested, such as THF, DMF, 1,4-dioxane and EtOH gave also poor yields (Table 1, entries 10-13). While, using EtOH:H_2O (1:1) mixture as reaction medium, gave quantitative yield of the desired product in 4 h (entry 14). Shorter reaction times and lower amounts of $NaBH_4$ produced a decrement of yields (Table 1, entries 15-18). Therefore, we selected, aqueous ethanol as solvent, 0.1 mol% catalyst, $NaBH_4$ as reducing agent at room temperature as the most efficient reaction conditions (Table 1, entry 14). It should be noted that the study of reaction in the absence of this catalyst and using $NaBH_4$ (5 equiv) gave only 3% conversion (GC) to the product (Table 1, entry 19).

Table 1. Optimization of the reaction conditions for the reduction of 4-nitrotoluene



Entry	Cat (mol%)	Solvent	t(h)	reductant	Yield(%)
1	0.01	H_2O	4	$NaBH_4$	13
2	0.03	H_2O	4	$NaBH_4$	44
3	0.05	H_2O	4	$NaBH_4$	52
4	0.07	H_2O	4	$NaBH_4$	65
5	0.10	H_2O	4	$NaBH_4$	89
6	0.10	H_2O	4	Glycerol	0
7	0.10	H_2O	4	NH_2NH_2	4
8	0.10	H_2O	4	HCO_2H	0
9	0.10	H_2O	4	NH_4HCO_2	0
10	0.10	THF	4	$NaBH_4$	1
11	0.10	1,4-Dioxane	4	$NaBH_4$	0
12	0.10	EtOH	4	$NaBH_4$	1
13	0.10	DMF	4	$NaBH_4$	1
14	0.10	H_2O:EtOH	4	$NaBH_4$	100
15	0.10	H_2O:EtOH	3	$NaBH_4$	75
16	0.10	H_2O:EtOH	2	$NaBH_4$	32
17	0.10	H_2O:EtOH	4	$NaBH_4$	46[c]
18	0.10	H_2O:EtOH	4	$NaBH_4$	78[d]
19	-	H_2O:EtOH	4	$NaBH_4$	3[e]

[a] Reaction conditions: 4-nitrotoluene (0.5 mmol), reductant agent (5 equiv), solvent (2 mL).

[b] Yield determined by GC.

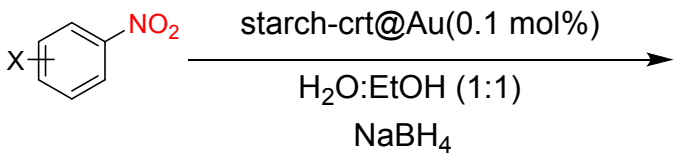
[c] Reaction run in the presence of 3 equivalents of $NaBH_4$.

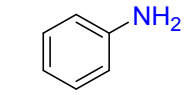
[d] Reaction run in the presence of 4 equivalents of $NaBH_4$.

[e] Reaction run in the absence of the catalyst.

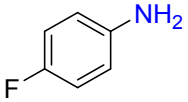
Having optimized reaction conditions, the reduction of a variety of nitroaromatic compounds were assessed. Results indicated that reduction of nitroarenes having electron withdrawing groups such as -Cl, -Br, -F, -COR proceeded very efficiently and desired amines were obtained in excellent yields. Reduction of nitroarenes possessing electron donating groups such as -Me, -OMe, -OH, $-CH_2OH$, $-NH_2$ as well as 1-nitronaphthalene and 4-nitrobiphenyl were performed and the expected products were obtained in high to excellent yields (Table 2, entries 1-20). Generally, results showed that electron rich nitroarenes reacted much more slowly than the substrates with electron deficient ones. Furthermore, reduction of 2-nitropyridine proceed well affording 2-aminopyridine in 90% yield (Table 2, entry 21). While in the case of nitroarenes having ketone or amido functional groups, selective reduction of nitro group were achieved under optimized reaction condition (Table 2, entries 22-24). In the cases of high molecular weight nitro compounds, 2wt % of TPGS-750-M as surfactant was added to the reaction mixture affording 85-89% isolated yields (Table 1, entries 25-26). In order to show how important was the effect of the creatine in the stabilization of Au-NPs, we prepared starch supported Au-NPs in the absence of ligand and studied its catalytic activity. Results indicated that, in the absence of creatine, 42% of Au was loaded on starch and also reduction of nitroarenes using starch@Au gave lower yields than starch-crt@Au (Table 2, entries 6, 8, 10 and 16).

Table 2. Reduction of structurally different nitroarenes in the presence of starch-crt@Au[a,b]

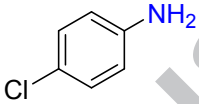




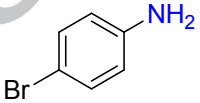
1. 4h <99%[c]



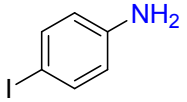
2. 2h 100%[c]



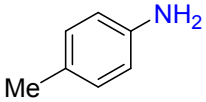
3. 4h 92%



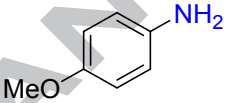
4. 4h 90%



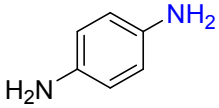
5. 6h 91%



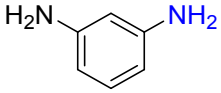
6. 4h 100%[c] (91%)[c,e]



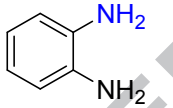
7. 7h 90%



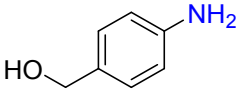
8. 4h 90% (40%)[e]



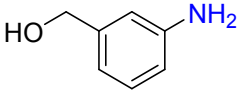
9. 2h 95%



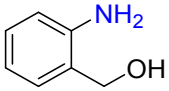
10. 4h 80% (32%)[e]



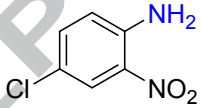
11. 4h 94%



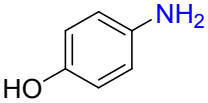
12. 4h 89%



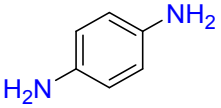
13. 6h 87%



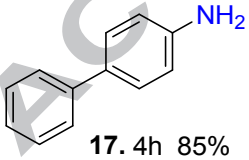
14. 4h 90%



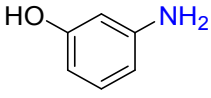
15. 4h 90%



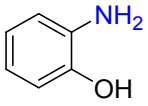
16. 4h 87%[d] (61%)[e]



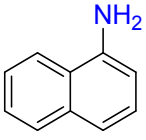
17. 4h 85%



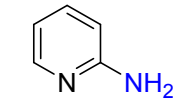
18. 3h 90%



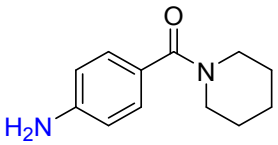
19. 7h 86%



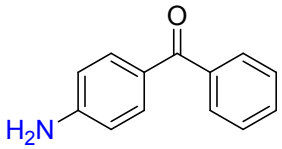
20. 4h 85%



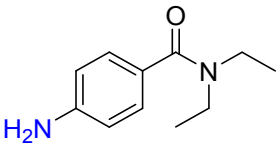
21. 7h 90%



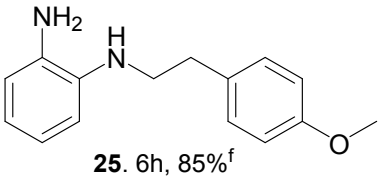
22. 4h 93%



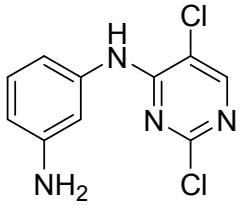
23. 4h 98%



24. 4h 87%



25. 6h, 85%[f]



26. 6h, 89%[f]

[a] Nitroarene (0.5 mmol), starch-crt@Au (0.1 mol%), $NaBH_4$ (5 equiv), H_2O:EtOH (1:1, 2 mL), at room temperature.

[b] Isolated products.

[c] GC yield.

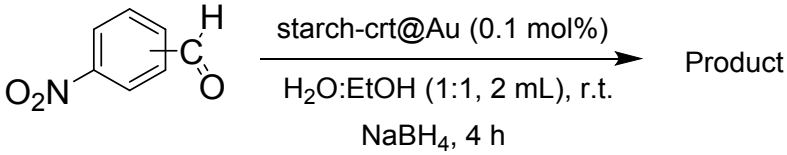
[d] Using 10 equivalent of $NaBH_4$.

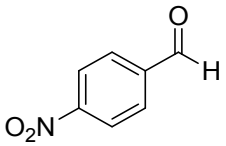
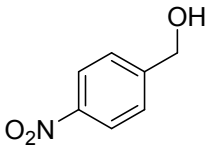
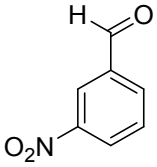
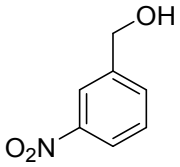
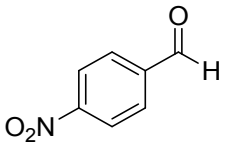
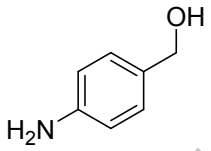
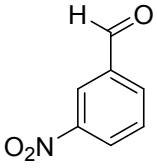
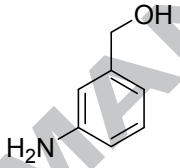
[e] Nitroarene (0.5 mmol), starch@Au (0.1 mol%), $NaBH_4$ (5 mmol), H_2O:EtOH (1:1, 2 mL), at room temperature.

[f] Reaction performed using 2wt % of TPGS-750-M as a surfactant

It should be noted that in the case of nitroarenes having a formyl group such as *m* and *p*-nitrobenzaldehydes carbonyl group was reduced to alcohol selectively whilst the nitro group remained intact under optimized reaction conditions. However, using 10 equivalents of $NaBH_4$ both aldehyde and nitro functional groups were conveniently reduced (Table 3).

Table 3. Reduction of *m* and *p*-benzaldehydes using starch-crt@Au



Substrate	Product	Yield(%)[a]
		90[b]
		70[b]
		91[c]
		89[c]

[a] GC yield.

[b] Using 5 equivalents of $NaBH_4$

[c] Using 10 equivalents of $NaBH_4$

The rates of the reduction for the three isomers of nitroaniline were also studied under optimized reaction conditions and the following rate order was: 3-nitroaniline > 4-nitroaniline > 2-nitroaniline (Figure 10). This result may be explained by the conjugation effect caused by electron donating groups. Both *para*- and *ortho*-isomer can delocalize electrons onto the nitro group and the reduction reaction rate can diminish. The *ortho*-isomer exhibited the lowest reactivity because of its steric effect.

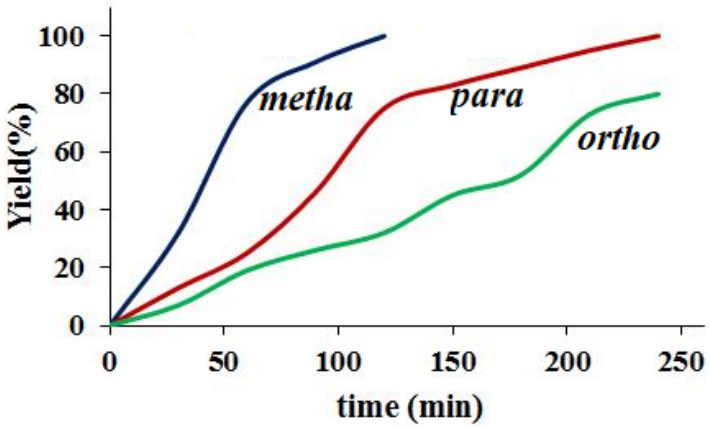
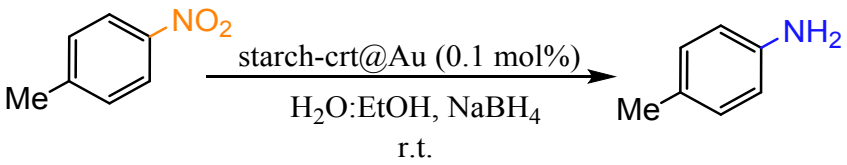


Figure 10. Reduction rates for nitroaniline isomers.

The recovery and reusing of heterogeneous catalysts are highly important since the environmental and economical points of view. Here, the recycling of starch-crt@Au in the reduction of 4-nitrotoluene under optimized reaction conditions is evaluated. Result showed that catalyst was recycled for 12 consecutive runs with negligible loss of activity (Figure 11). However, from run 13 to 16, the yield of desired product decreased to 87%. For highlighting essential rule of creatine ligand on stabilization of Au NPs and reactivity of the catalyst, we also studied recycling of starch@Au on the same reaction. The results of this study revealed that the yield of the reaction decreased to 40% in the 6th catalytic cycle (Figure 12). Furthermore, leaching of Au from starch-crt@Au and starch@Au in run 6 was investigated by AAS. Results indicated that 20% and 97% leaching occurred from starch-crt@Au and starch@Au, respectively. These facts confirmed the crucial role of creatine in the stabilization of Au nanoparticles.



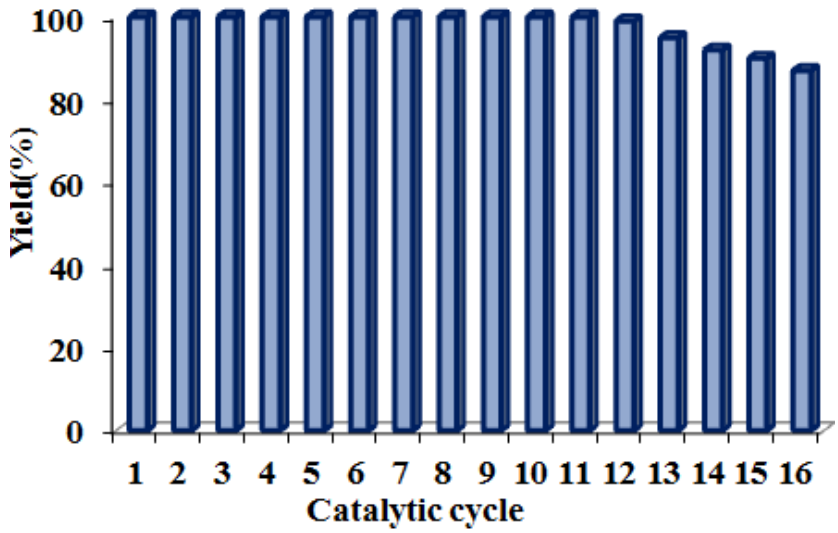


Figure 11. Recycling study of the catalyst starch-crt@Au during the reduction of 4-nitrotoluene.

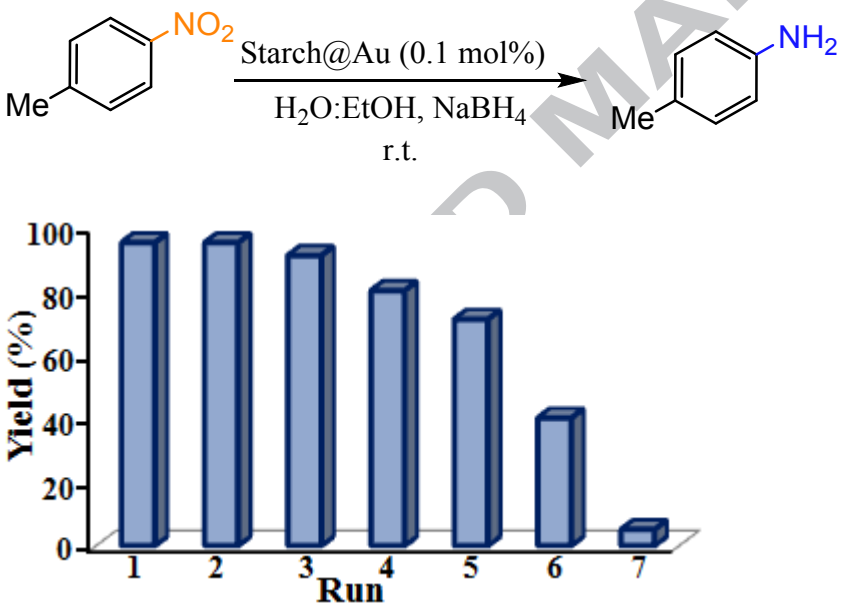


Figure 12. Recycling study of the starch@Au during the reduction of 4-nitrotoluene.

XPS spectra of the reused catalyst (starch-crt@Au) after 6th runs showed the preservation of Au(0) oxidation state and also the presence of N, C and Si species similar to fresh catalyst (Figure 13). Also, TEM images of reused catalyst after 6th runs showed the presence of almost uniform Au-NPs with average particle-size of 3.8 nm (Figure 14 and 15).

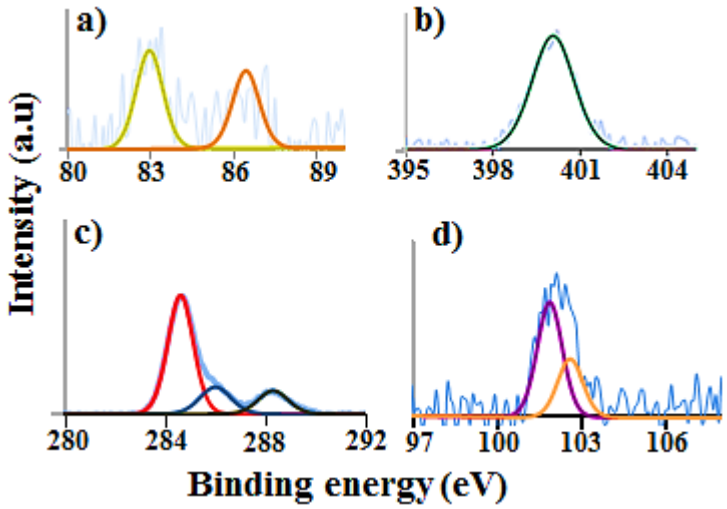


Figure 13. XPS spectra of reused catalyst starch-crt@Au a)Au b) N c) C d) Si.

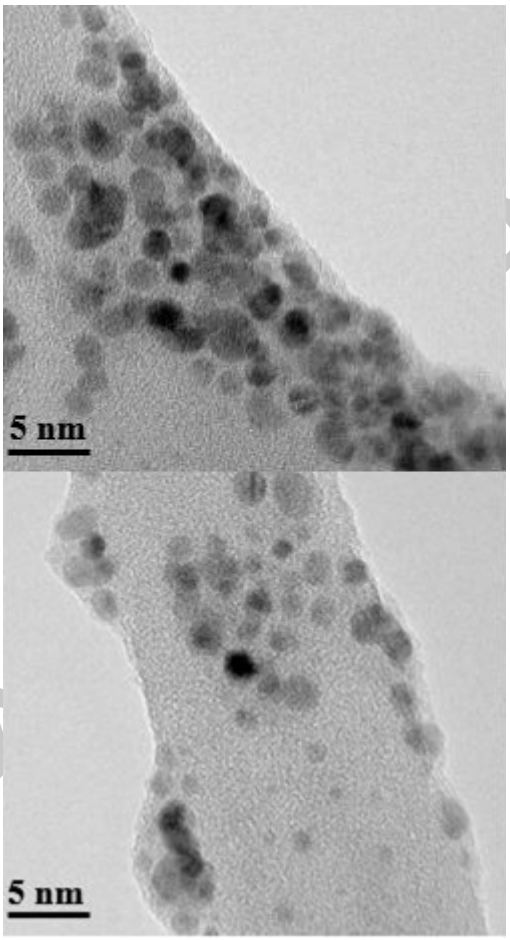


Figure 14. TEM images of reused catalyst after 6 th catalytic cycle.

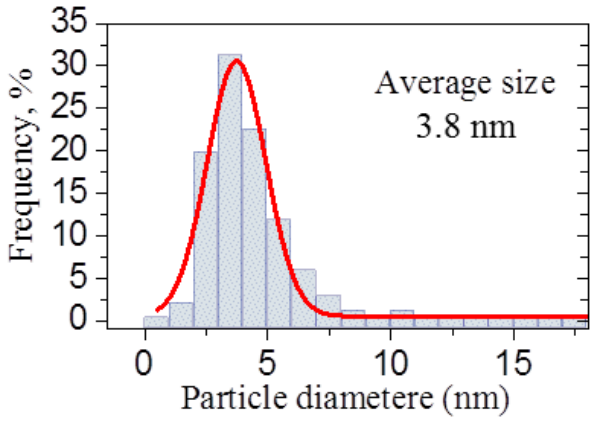


Figure 15. Distribution diagram of Au nanoparticles in reused catalysis after 6th catalytic cycle.

Conclusion

In summary, we have developed a highly active, resistant, chemoselective and recoverable creatine modified starch supported gold catalyst for the reductions of nitroaromatic compounds. Using this green catalyst, a wide range of substrates was successfully reduced to the corresponding amines under mild conditions. In particular, the performance of the catalyst was fully retained during its employment in several catalytic batches, and it is possible to recover it up to twelve times without decreasing its catalytic activity. This catalyst is much more appropriate than creatine-free starch@Au catalyst and starch-crt@Au, in terms of Au loading during its preparation, activity and recyclability with lower Au leaching during the recycling process.

3. Experimental

3.1. General remarks.

All materials were purchased from Sigma-Aldrich, Across and Merck Millipore. Reactions were monitored by GC in a Varian CP-3800 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively on a Bruker Avance HD apparatus in DMSO-d_6 and $CDCl_3$. FT-IR studies of samples were performed using a FT-IR spectrophotometer Bruker vector 22, by preparing their KBr pellets from 400 to 4000 cm^{-1}. The TEM and SEM mapping images were captured with EOL JEM-2010 and Hitachi S3000N respectively. XPS analyses were performed using a K-Alpha spectrometer. The weight loss of samples was measured using a thermogravimeter NETZSCH STA 409 under an O_2 flow rate of 20 $ml.min^{-1}$ with a heating rate of 10 °C·min^{-1} from 30 to 800 °C. Digital images of the samples were acquired with Hitachi S4160 FE-SEM apparatus operating at 20 kV. X-Ray diffraction (XRD) was recorded using Philips X'Pert Pro instrument.

3.2. Procedure for the preparation of starch@Cl

Starch (3.6 g) was sonicated in dry toluene (30 mL) for 20 minutes and then (3-chloropropyl)triethoxysilane (10.4 mmol, 2.5 mL) was added. The resulting mixture was refluxed at 110 °C under argon atmosphere for 24 h. Then, the white suspension was separated by centrifugation, washed with ethyl acetate (3×10 mL) and dried in an oven at 60 °C.

3.3. Procedure for the preparation of functional starch@crt

The starch@Cl (2.5 g) was added to a flask containing xylene (15 mL) and the mixture was sonicated for 10 min. Then, creatine (11.4 mmol, 1.5 g) and Et_3N (23 mmol, 3.2 mL) were added and the mixture was stirred at 130 °C for 24 h. Next, white solid was separated by centrifugation washed with water (3×10 mL) and ethyl acetate (3×10 mL) and dried in the oven at 60 °C.

3.4. Procedure for the preparation of starch-crt@Au

Starch@crt (1 g) was added to flask containing H_2O (10 mL) and the resulting mixture was sonicated for 10 min. Then, aqueous $NaAuCl_4.2H_2O$ solution (0.027 mmol, 11 mg in 2 mL H_2O) was added slowly. Afterwards, aqueous $NaBH_4$ (1 mmol, 37 mg in 1 mL H_2O) were added slowly during 5 min and the resulting mixture was stirred for 24 h at room temperature. Then, the solid was separated by centrifugation, washed with H_2O (10 mL) and ethyl acetate (3×5 mL) and dried in an oven at 70 °C. The loading of Au was determined using atomic absorption spectroscopy (AAS) to be 0.0198 mmol/g indicating that a 73.3% of Au was successfully loaded.

3.5. General procedure for the reduction of nitro aromatic using starch-crt@Au

To a flask containing nitroarene (0.5 mmol), starch-crt@Au (0.1 mol%, 25 mg) and $NaBH_4$ (2.5 mmol, 45 mg), 2 mL of H_2O:EtOH (1:1) was added. Reaction mixture was stirred at room temperature for the appropriate reaction times (see Tables 2 and 3). Progress of the reactions were monitored by GC, TLC and or ^1H NMR. After completion of the reaction, the crude product was extracted with ethyl acetate (3×5 mL). The solvent was evaporated and the residue was purified using column or plate chromatography.

3.6. Procedure for the preparation of starch@Au

A solution of starch (1 g) in H_2O (10 mL) was sonicated for 10 min. Then, a solution of $NaAuCl_4.2H_2O$ (0.027 mmol, 11 mg in 2 mL H_2O) was added slowly. Then, $NaBH_4$ (1 mmol, 37 mg in 1 mL H_2O) were added slowly during the 5 min and resulting mixture was stirred for 24 h at room temperature. Afterwards, the solid was separated by centrifugation, washed with H_2O (5 mL) and ethyl acetate and dried in the oven at 70 °C. The loading of Au was found to be 0.011 mmol/g (using AAS) indicating that a 42% of Au was successfully loaded.

3.7. General procedure for the reduction of nitro aromatic using starch@Au

A solution of H_2O:EtOH (1:1) (2 mL) was added to a flask containing nitroarene (0.5 mmol), starch-crt@Au (0.1 mol%, 45 mg) and $NaBH_4$ (2.5 mmol, 94 mg). The reaction mixture was stirred at room temperature for appropriate reaction times and the progress of the reactions were monitored by GC, TLC and or ^1H NMR. After completion of the reaction, the crude product was extracted with ethyl acetate (3×5 mL). The solvent was evaporated and the residue purified using column or plate chromatography.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 97021804) for support of this work. We also gratefully acknowledge financial support from the Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013-43446-P and CTQ2014-51912-REDC), the Spanish Ministerio de Economía, Industria y Competitividad, Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU) (projects CTQ2016-76782-P and CTQ2016-81797-REDC), the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante.

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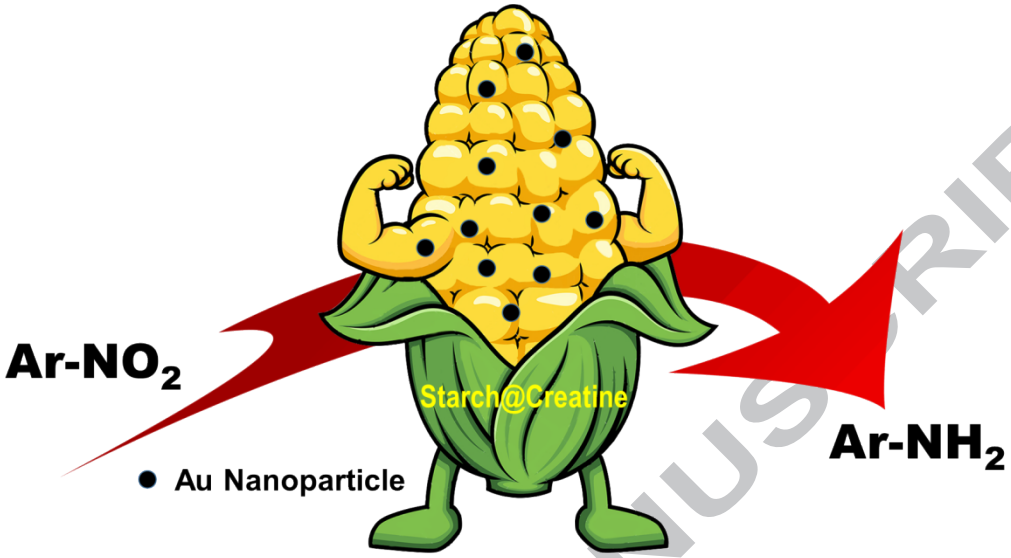
Graphical Abstract



Research Highlights

A novel and green gold catalyst was prepared by simple method.

This material showed high catalytic activity for selective reduction of nitroarenes.

The catalyst recycled for several runs.

Fresh and reused catalysts were fully characterized.