

Uniform silver nanoparticles on tunable porous N-doped carbon nanospheres for aerobic oxidative synthesis of aryl nitriles from benzylic alcohols

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Tunable N-doped carbon nanospheres from sucrose as carbon source and Tris(2-aminoethyl)amine (TAEA) as nitrogen source by a simple and easily reproducible method were prepared. It was demonstrated that the tunable N-doping of carbon spheres could be realized by altering the ratio of TAEA in the raw materials. The content of doped nitrogen, surface area, pore volume and pore size of carbon nanospheres were increased with the increasing of TAEA amount in the hydrothermal process. Prepared N-doped carbon nanospheres act as solid ligand for anchoring of Ag NPs which generated via chemical reduction of Ag ions. Benzylic alcohols and aldehydes were converted into the aryl nitriles by using Ag/N-CS-1 nanospheres as the catalyst and O₂ as the oxidant, efficiently. This catalyst was stable and could use for 6 successful runs.

KEYWORDS

Ag nanoparticles, aryl nitriles, porous nanocatalyst, tunable N-doped carbon spheres

1 | INTRODUCTION

Aromatic and aliphatic nitriles as a useful molecular scaffolds are an important part of pharmaceuticals, agrochemicals and fine chemicals. Up to now several nitrile-containing compounds were in clinical developments.^[1,2]

In organic synthesis, such nitrile-containing compounds can serve as essential precursors for the synthesis of various organic moieties such as heterocycles,^[3,4] esters, acids, amines, amides, tetrazoles, aldehydes and ketones.^[5,6] The Sandmeyer reaction^[7] and Rosenmund-von Braun reaction^[8] were used historically for the laboratorial and industrial synthesis of aryl nitriles which require stoichiometric amount of toxic HCN or metal cyanides and harsh reaction conditions with generation of significant amount of waste. Several reviews on cyanation reactions have been published in recent years.^[9-13] In the past decades, different transition metal-catalyzed protocols have been developed for the synthesis of aryl nitriles. Palladium, nickel and copper catalysts have shown to be

effective for cyanation of aryl halides and organometallic reagents.^[14] Various metal, metalloid-bound cyanide materials and nonmetallic “CN” units have been reported as CN precursors in the cyanation reactions. Recently, direct cyanation of aryl C-H bonds via transition metal-catalyzed process have been used as attractive method for the synthesis of organic nitriles.^[14] However, this method is limited to the electron-rich arenes. Toluene has been converted to benzonitrile via direct gas-phase ammoxidation process.^[15] Many transition metal-based catalytic green methods have been used for conversion of aldehydes, aldoximes, amides and carboxylic acids to the nitriles.^[16] Due to the use of toxic reagents, low yield of final products, organic wastes production, expensive catalytic systems and harsh reaction conditions in these methods the development of new synthetic pathways with milder reaction conditions is of significant interest. The oxidative synthesis of nitriles directly from various benzylic compounds, such as benzylic halides, alcohols, amines and azides with ammonia as a nitrogen source

instead of inorganic cyanides has also been reported with only water as byproduct. Also, some aryl nitriles have been synthesized via C-C double or triple bond cleavage method.^[17] Among the transition metal-catalyzed methods for cyanation reaction, dehydration of aldoximes or amides is a green method. The oxidative reaction directly from alcohols and ammonia is another green approach for aryl nitriles preparation which requires the use of stoichiometric amounts of oxidants and reagents.^[18,19] Several reagents such as I_2 , I_2 /DIH, I_2 /TBHP, $NiSO_4/K_2S_2O_8/NaOH$, $MnO_2/MgSO_4$, and $(Bu_4N)_2S_2O_8/Cu-(HCO_2)_2/Ni$ $(HCO_2)_2/KOH$ were reported in this regard.^[20] Inexpensive molecular oxygen or air as the sole oxidant was used in such transformation with benign byproducts (usually water). Based on literature, an easily prepared aluminum oxide-supported ruthenium hydroxide,^[21] $Ru(OH)_x/TiO_2$,^[22] manganese dioxide,^[23] $Cu/TEMPO$ ($TEMPO = 2, 2, 6, 6$ -tetramethylpiperidine-*N*-oxyl)/bipyridine,^[24] ligand free $Cu(II)/TEMPO$,^[25-27] ligand free $Fe/TEMPO$,^[28] nitrogen-doped graphene-layered cobalt or iron oxides,^[29] $La(OH)_3/Fe_3O_4$,^[30] and *O*-(4- CF_3 -benzoyl)-hydroxylamine organic acid^[31] were used as efficient catalysts for the synthesis of aryl nitriles directly from benzylic alcohols and ammonia in presence of O_2 . Some of these systems suffer from high reaction temperature or difficult purification and separation. Also, the formation of nitriles from aldehydes has been promoted with Ag nanoparticles and $K_4Fe(CN)_6$.^[32] Recently, we have used carbon as a support for generation of Cu and Au nanoparticles for organic functional group transformations, efficiently.^[33-35] In the last years, carbon with attractive properties such as porous structure, excellent electrical conductivity, and high stability find widespread applications as support in catalysts.^[36] The simplicity of synthesis of carbon nanospheres from inexpensive and available carbon sources (glucose or sucrose) is the one of the main advantages of this catalytic system. It is well known that structural modifications on the surface of carbon can effectively change the nature of the catalysts. Heteroatom doping strategy can control the intrinsic reactivity of the active metallic sites.^[37] Among different dopants, N is the most intensively investigated.

The synthesis of metal composites supported on N-doped carbon materials has been studied in recent years.^[38] These fascinating catalysts have been investigated in many industrial transformations such as oxidations, reductions, Fischer-Tropsch synthesis, and H_2 generation.^[39]

In this paper, we have prepared highly monodispersed, nitrogen-doped porous carbon nanospheres as a solid ligand for generation of Ag nanoparticles for oxidative synthesis of nitriles, for the first time, directly from alcohols and ammonia as nitrogen source.

Synthesis of carbon spheres and nitrogen doping was proceeded in one step via hydrothermal method. Generally, nitrogen doping provide basic properties, which can enhance the interaction between substrates and carbon surfaces.^[40,41] Also, nitrogen doping was able to increase the hydrophilicity of catalyst which led to the high dispersion ability of catalytic system in aqueous media.^[42] Tris(2-aminoethyl)amine as a high content nitrogen source and sucrose as an inexpensive carbon source were used for hydrothermal preparation of our catalyst. The Ag/N-doped carbon nanospheres empowers the synthesis of structurally diverse nitriles.

2 | EXPERIMENTAL

2.1 | Materials and apparatuses

Sucrose ($\geq 99.5\%$), $AgNO_3$ (99.9999% trace metals basis) and $NaBH_4$ (granular, 99.99% trace metals basis) were obtained from Aldrich and Tris(2-aminoethyl)amine (TAEA) was obtained from Fluka. All solvents were acquired from Merck (Mashhad, Iran). All chemicals were used as received without further purification.

For morphology study of the samples TEM and SEM experiments were conducted on a Leo 912AB microscope (Mashhad, Iran) operated at 120 kV and Leo 1450VP (Germany), respectively. The compositions of obtained samples were measured by the energy dispersive X-ray analysis (EDX). Powder XRD patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu KR radiation (40 kV, 30 mA). The percentage weight loss of shell and arginine was studied using TGA, (Mettler Toledo LF, Switzerland). FT-IR spectra were collected on a Nicolet Fourier spectrophotometer, using KBr pellets (Mashhad, Iran). A Hitachi U-3010 UV-Visible (Mashhad, Iran) spectrophotometer with a 1 cm path length quartz cuvette was used to identify the change in concentration over a wavelength range from 220 to 600 nm. Nitrogen adsorption-desorption isotherms were measured at 77 K using a Quantachrome adsorption instrument. Brunauer-Emmett-Teller (BET) and density functional theory (DFT) methods were used for the surface area determination and pore size evaluation. The content of Ag in the sample was confirmed by inductively coupled plasma/optical electron microscopy (ICP-OES). Raman spectroscopy was performed using a Bruker Senterra Raman microscope with an exciting laser wavelength of 785 nm and a resolution of 3 cm^{-1} . 1H and ^{13}C NMR spectra (Mashhad, Iran) were measured ($CDCl_3$) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively. A Benchtop centrifuge was used Max RPM (15000 min^{-1}) UNIVERSAL 320 (Germany).

2.2 | Preparation of tunable porous nitrogen-doped carbon spheres (porous N-CS-x)

Porous nitrogen-doped carbon spheres with tunable N content were synthesized as bellow: 8.77 mmol (3 g) sucrose was dissolved in 30 ml deionized water. Then, pH of the sucrose solution was adjusted by NaOH solution (0.5 M) to achieve the desired value of 12, and then 10 ml aqueous mixture of Tris(2-aminoethyl)amine (TAEA) was added into the solution. The weight of TAEA was selected as 3.4 mmol (0.5 g), 6.8 mmol (1 g) and 10.3 mmol (1.5 g) in 10 ml deionized water, respectively. Subsequently, the mixed solution was hydrothermal carbonized in a 50 ml Teflon-lined stainless steel autoclave by heating at 190 °C for 4 hr with a heating rate of 5 °C/min (45 ml of the mixed solution was transferred into the 50 ml capacity autoclave). After the hydrothermal treatment, the autoclave was left to cool to room temperature naturally, then the brownish-black product was collected by filtration and washed with hot water than with ethanol three times to remove residual organic contaminants. The final precipitate was dried in air at 80 °C overnight. The resulting samples were labeled as N-CS-x, where x represents the mass (0.5, 1 and 1.5 g, respectively) of TAEA. After that, for high surface area achievement, the above samples were pyrolyzed at 550 °C with the heating ramp rate of 5 °C/min under a nitrogen gas flow for 2 hr. The porous N-CS-x dark solids were purified in a 2 M HCl solution, rinsed with deionized water until neutral pH and dried at 80 °C overnight.

2.3 | Fabrication of the ag/N-CS-x nanocatalysts

100 mg of N-CS-x was dispersed in 50 ml of deionized water by ultrasonic dispersion for 15 min. Then, 10 ml of AgNO₃ (10 mg/ml) was added to the N-CS-x dispersion

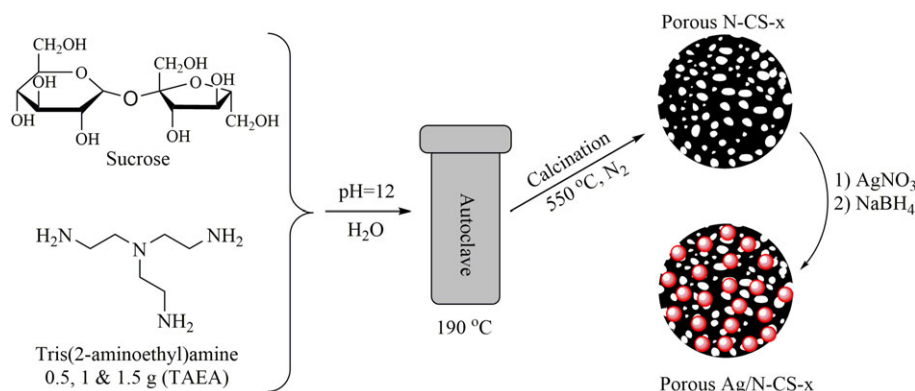
mixture and re-dispersed for another 10 min. For generation of Ag nanoparticles (Ag NPs) onto the surface of N-CS-x, 10 ml of 0.1 M aqueous solution of NaBH₄ was dropped to the above mixture, followed by stirring at room temperature for 6 hr. The Ag/N-CS-x nanocatalysts were then collected by centrifugation and washed with hot water and ethanol three times before drying at 80 °C overnight.

2.4 | The ag/N-CS catalyzed direct oxidative synthesis of nitriles from primary alcohols

Primary alcohol (1 mmol), Ag/N-CS (3 mol%), EtOH (3 ml), and NH₃(28%) (equiv. NH₃/alcohol = 2.4) were refluxed under O₂ balloon. After the completion of the reaction which was monitored by thin layer chromatography (TLC), the catalyst was filtered, washed with ethanol, aqueous solution of NaOH and water. The catalyst was then dried at 80 °C in oven. The final products were purified by a silica gel column chromatography and then characterized by Mass spectra, ¹H and ¹³C NMR spectra.

3 | RESULTS AND DISCUSSION

The Ag nanoparticles (NPs) immobilized porous N-CSs were synthesized in two step. At first step, porous N-doped CSs were prepared hydrothermally with sucrose as inexpensive carbon source and TAEA as nitrogen source. At second step, Ag NPs were generated via chemical reduction of loaded Ag ions onto the surface of N-CSs to achieve final Ag/N-CS-x nanocatalysts. It was demonstrated that the tunable N-doping of carbon spheres could be realized by altering the ratio of TAEA in the raw materials. Thus, different amount of TAEA was used in first step (0.5, 1 and 1.5 g) which obtained catalysts were named N-CS-0.5, N-CS-1 and N-CS-1.5. Scheme 1 illustrates a schematic diagram for preparation of Ag/N-CS-x.



SCHEME 1 Schematic illustrate of the porous Ag/N-CS-x

The final compositions of obtained samples were shown in Table 1 (Based on CHN). The results showed that when the amount of TAEA was increased in the catalyst synthesis steps, the content of doped nitrogen was also increased. In order to demonstrate the porous structure of synthesized samples, the BET (Brunauer-Emmett-Teller) adsorption measurements were carried out. The Surface area, pore size and pore volume of samples were increased simultaneously with TAEA amount. Difference between these parameters for N-CS-1 and N-CS-1.5 were not considerable. Therefore the N-CS-1 was chosen as final support for generation of Ag NPs. Based on ICP-

TABLE 1 Elemental compositions of the samples after doping

Sample	C ^b (wt%)	N ^b (wt%)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Ag ^a (wt%)
N-CS-0.5	71.56	25.11	355.1	1.38	0.142	2.1
N-CS-1	60.02	37.24	457.2	2.39	0.225	7.6
N-CS-1.5	58.83	39.35	461.7	2.51	0.232	7.9

^aThe content of Ag was measured after Ag ions loading and chemical reduction process for each sample by ICP-OES analyzes.

^bBased on CHN analyze.

OES analyzes the content of Ag in Ag/N-CS-1, Ag/N-CS-1.5 and Ag/N-CS-0.5 nanocatalysts were 7.6 wt%, 7.9 wt% and 2.1 wt%.

The morphologies of the N-CS-1 and Ag/N-CS-1 were characterized by TEM and SEM analyzes. As shown in Figure 1a, The N-CS-1 show nanospheres structure. As exhibits in Figure 1b, SEM image of the obtained sample N-CS-1 possesses nice spherical shape and good dispersity and homogeneity. The diameter of the N-CS-1 is in the range of 50–150 nm. After chemical reduction of loaded Ag ions the uniformly dispersed Ag NPs onto the surface of porous N-CS-1 were observed with particles size below 5 nm (Figure 1c). Figure 1d shows the EDX analyzes of Ag/N-CS-1 with elemental composition of the C, N, O, and Ag, and the catalyst is composed of N-doped carbon spheres and Ag NPs.

In order to get further information about the crystalline structure of the N-CS-1 and Ag/N-CS-1 nanospheres, XRD patterns and Raman spectra were used. As shown in Figure 2a, the XRD pattern of N-CS-1 exhibit two weak diffraction peaks at around 25° and 43°, which can be attributed to the (002) and (100) diffraction peaks of the graphitic and disordered structure, respectively. Low intensity of these peaks revealed that has low crystallinity

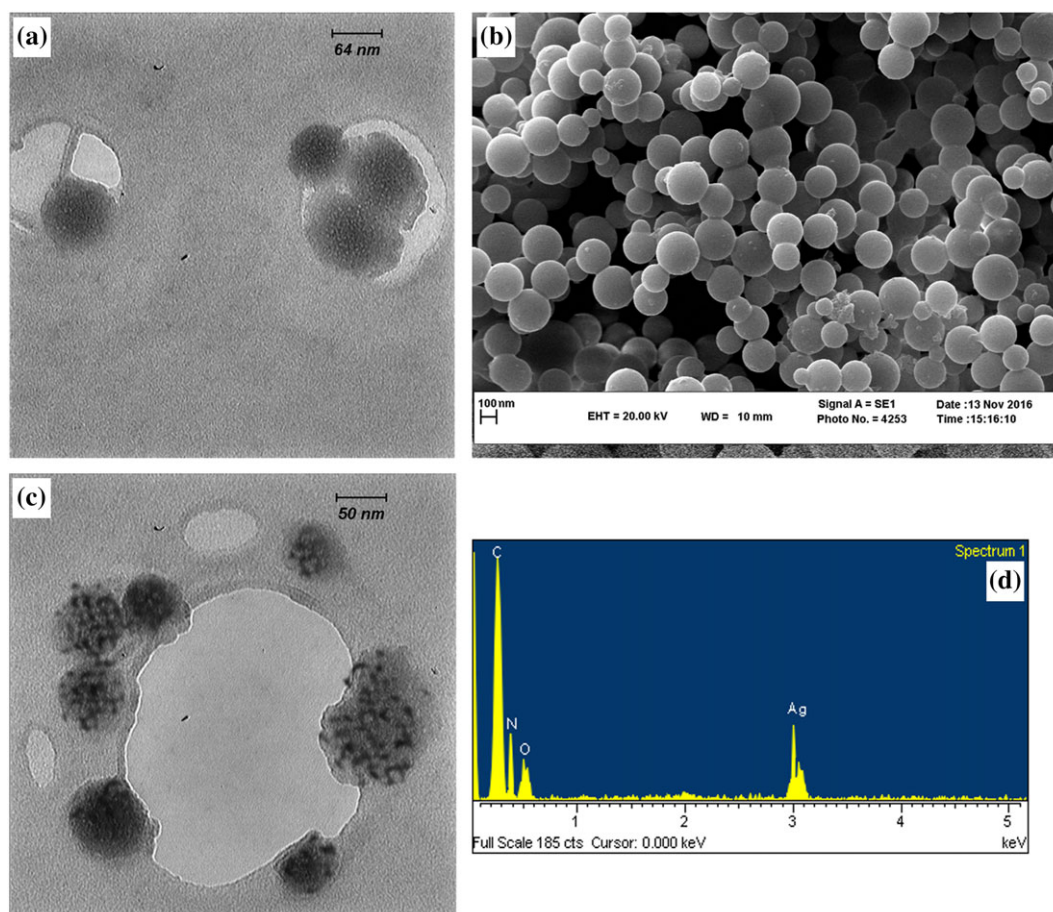


FIGURE 1 a) TEM and b) SEM images of N-CS-1 nanospheres. c) TEM and d) EDX of Ag/N-CS-1

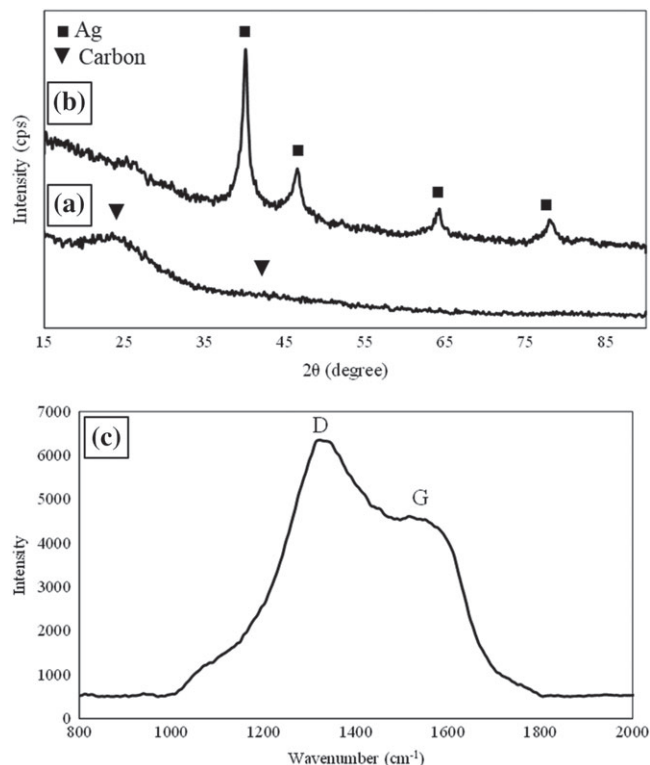


FIGURE 2 a) XRD pattern of N-CS-1 and b) XRD pattern of Ag/N-CS-1. c) Raman spectra of N-CS-1

and disorder structure of N-CS-1^[43] This characteristic peak was also observed in XRD pattern of Ag/N-CS-1, indicating that support is successfully carbonized (Figure 2b). Also, Four characteristic diffraction peaks of Ag NPs at 2θ angles of 38.1° , 44.3° , 64.4° , and 77.4° , corresponding to the reflections of (111), (200), (220) and (311) crystalline planes are consistent with those found in the JCPDS database (PDF No. 65-3107). These results show that Ag NPs were generated successfully onto the N-doped porous carbon spheres.^[44] The average crystalline size of Ag NPs calculated by the Scherrer equation is about 4.5 nm from the broadness of the (111) peak. Two broad peaks at 1321 cm^{-1} and 1580 cm^{-1} corresponding to the disordered (D) band and graphite (G) band were appeared in the Raman spectroscopy of the N-CS-1 (Figure 2c). The I_D/I_G of N-CS-1 is more than one, indicating the high disorder structure of support.^[45]

After successful characterization, the catalytic activity of prepared Ag/N-CS-1 evaluated in aerobic oxidative conversion of alcohols and aldehydes to nitriles. Conversion of benzyl alcohol to benzonitrile was studied as a model reaction in presence of ammonia under oxygen atmosphere. After 1 hr of beginning of the model reaction, different parameters were considered for optimization of reaction condition (Table 2). At the outset, the catalyst amount was studied in the model reaction. The best result was observed when 3 mol% of Ag/N-CS-1 with

TABLE 2 Optimization of reaction conditions^a

		1a:NH ₃ (equiv.)	Yield 1b (%) ^b		
Entry	Cat. (mol %)	Solvent	T (°C)	1a:NH ₃ (equiv.)	Yield 1b (%) ^b
1	Ag/N-Cs-1 (6)	CH ₃ CN	82	1:1	73
2	Ag/N-Cs-1 (3)	CH ₃ CN	82	1:1	71
3	Ag/N-Cs-1 (1)	CH ₃ CN	82	1:1	35
4	Ag/N-Cs-1 (3)	CH ₃ CN	60	1:1	61
5	Ag/N-Cs-1 (3)	CH ₃ CN	40	1:1	26
6	Ag/N-Cs-1 (3)	DMSO	189	1:1	85
7	Ag/N-Cs-1 (3)	DMF	153	1:1	86
8	Ag/N-Cs-1 (3)	1,4-Dioxane	101	1:1	86
9	Ag/N-Cs-1 (3)	Toluene	110	1:1	60
10	Ag/N-Cs-1 (3)	EtOH	78	1:1	84
11	Ag/N-Cs-1 (3)	H ₂ O	100	1:1	40
12	Ag/N-Cs-1 (3)	EtOH	78	1:1.2	87
13	Ag/N-Cs-1 (3)	EtOH	78	1:1.8	90
14	Ag/N-Cs-1 (3)	EtOH	78	1:2.4	94
15	–	EtOH	78	1:2.4	–
16 ^c	N-CS-1	EtOH	78	1:2.4	–
17 ^d	AgNO ₃	EtOH	78	1:2.4	–
18	Ag/non-N doped-Cs	EtOH	78	1:2.4	35 ^e

^aReaction condition: **1a** (1 mmol), catalyst (Ag: 3 mol% with respect to **1a**), NH₃ (2.4 mmol), and solvent (3.0 ml) under an O₂ balloon at reflux for 1 hr.

^bisolated yield.

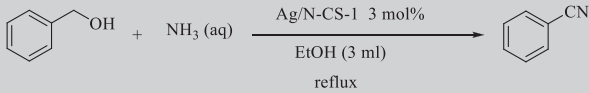
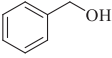

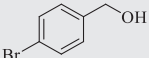
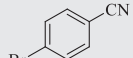
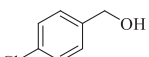
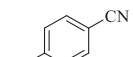
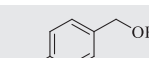
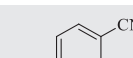
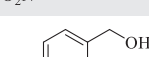
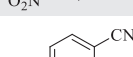
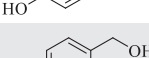
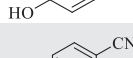
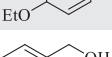



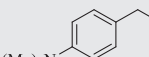
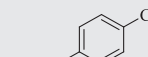
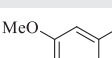
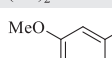
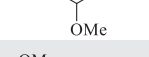
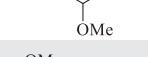
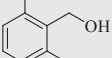

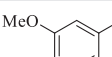

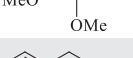

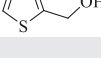

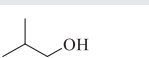

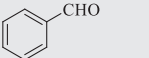
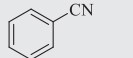
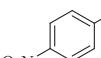

^c0.1 g of catalyst.

^d3 mol% of AgNO₃.

^eYield after 24 hr.



respect to the benzyl alcohol was used at reflux condition (Table 2, entries 1–3). The effect of lower reaction temperature on the yield of the final product was also studied. However, lower yield was obtained when reaction temperature was decreased to 60 °C and 40 °C (Table 2, entries 4–5). Dimethyl sulfoxide (DMSO), DMF (*N,N*-dimethylformamide), 1,4-Dioxane, toluene, EtOH, and H₂O were used as reaction solvents. The model reaction in polar solvents gave better yields than CH₃CN (Table 2, entries 6–11). Due to the low solubility of ammonia in toluene, the reaction was proceeded in extended time. Based on these results, EtOH was chosen as green solvent for model reaction. By increasing the equivalent of ammonia, the model reaction was proceeded in shorter reaction time and higher yield of benzonitrile was achieved (Table 2, entries 12–14). Control experiments revealed that Ag/N-Cs-1 nanocatalyst is

TABLE 3 Scope of the Ag/N-Cs-1 catalyzed direct conversion of benzyl alcohols to nitriles^a

Entry	Substrate	Time (h)	Product	Yield (%)
				
1		2		94
2		2		94
3		2		93
4		2.5		90
5		2.5		91
6		1.5		96
7		2		94
8		2.5		95
9		2		90
10		3		88
11		2		93
12		3		89
13		3		91
14		24	–	0
15		24	–	0
16		1		96
17		1.2		91
18		1		96
19		1.5		94

(Continues)

TABLE 3 (Continued)

Entry	Substrate	Time (h)	Product	Yield (%)
20		1.5		93

^aReaction conditions: benzyl alcohol (1 mmol), aqueous NH₃ (2.4 equiv.), Ag/N-Cs-1 (3 mol%), EtOH (3 ml) under O₂ balloon at reflux.

essential for this conversion. In the absence of any catalyst the reaction did not proceed. The same results were achieved when N-CS-1 and AgNO₃ was used as reaction catalyst (Table 2, entries 15–17). For comparison, Ag/non-N doped carbon nanospheres were synthesized via same procedure without N-doping step. The content of Ag for the synthesized Ag/non-N doped carbon nanospheres were measured by ICP. Based on ICP the content of Ag was 0.3 wt%. The model reaction was carried out with this catalyst at optimized reaction condition. In comparison with Ag/N-CS-1 nanospheres, Ag/non-N doped carbon nanospheres showed lower yield even after 24 hr (Table 2, entry 18).

The scope and generality of the present Ag/N-Cs-1-catalyzed reaction with regard to various kinds of structurally diverse primary alcohols based on the optimized conditions was examined. Ag/N-Cs-1 revealed high catalytic activities for the transformation of benzilic and heteroatom-containing alcohols, as summarized in Table 3. The conversion of benzyl alcohols contain electron-donating as well as electron-withdrawing groups, efficiently proceeded to afford the corresponding substituted benzonitriles with excellent yields (90–96%, Table 3, entries 1–11). Multi substituted benzyl alcohols

were also converted to the corresponding nitriles in high yields. This observation showed that the position of substituents on benzyl alcohol did not much affect the reaction (Table 3, entries 9–11). Also, heteroatom containing alcohols were converted into the corresponding nitriles in high yields (Table 3, entries 12 and 13). Aliphatic primary alcohols could not be converted to the desired products in this catalytic system (Table 3, entries 14 and 15). In addition, Ag/N-Cs-1 nanocatalyst showed high catalytic activity for the oxidative conversion of various aldehydes including benzilic and heteroatom containing in the presence of ammonia (Table 3, entries 16–20). Also, formation of benzaldehyde in the early stages of the model reaction was observed (monitored by TLC) which followed by the formation of benzonitrile. These results are similar to the previously reported mechanism for this reaction. It can be concluded that Ag/N-Cs-1 catalyzed direct conversion of alcohols to the nitriles possibly proceeds through three steps: 1) the aerobic oxidative dehydrogenation of alcohols to aldehydes, 2) the Dehydrative condensation of the aldehydes and ammonia into imines, and 3) the aerobic oxidative dehydrogenation of the imines to produce the corresponding nitriles.^[13]

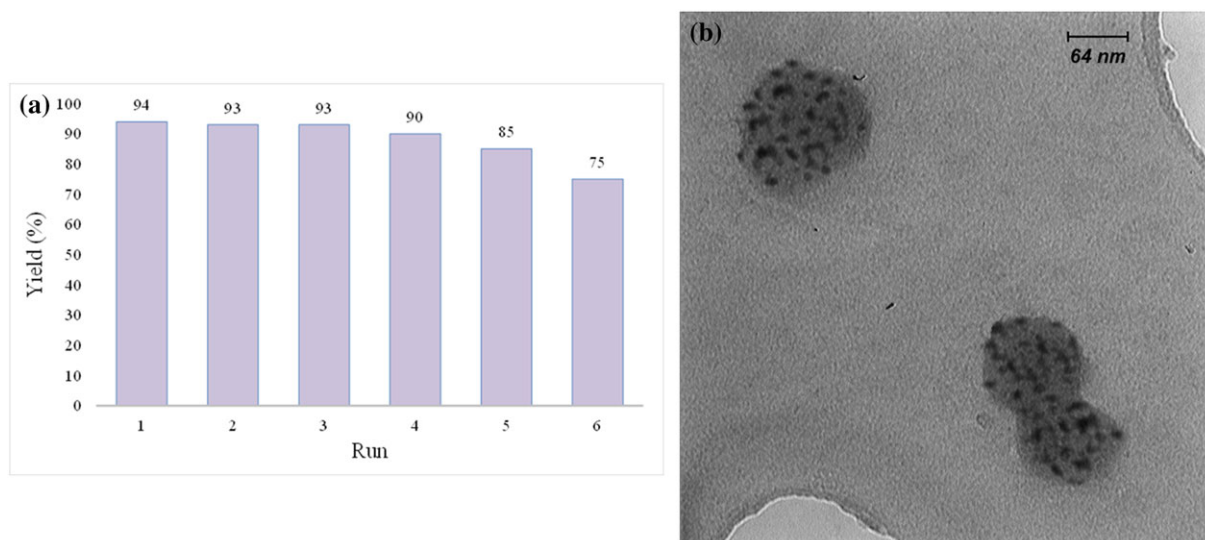


FIGURE 3 a) Recycling study for Ag/N-Cs-1 catalyzed oxidative synthesis of benzonitrile, b) TEM of catalyst after 6 runs

Recovery and reusability of Ag/N-CS-1 nanospheres was investigated in the model reaction. After completion of the reaction which was monitored by TLC, Ag/N-CS-1 nanospheres was filtered simply, washed with aqueous NaOH, ethanol and hot water. Obtained catalyst was then dried at 70 °C for 4 hr. The catalyst was used at least in 6 successful runs (Figure 3a). Based on ICP-OES results the Ag content of Ag/N-CS-1 after 6 successful runs was 7.2 wt%. This result indicates that about 0.4 wt% of Ag NPs were leached after 6 recycle which is a very small amount. The TEM image of catalyst was measured after 6 runs (Figure 3b). No aggregation of nanoparticles or integrity of carbon nanospheres was observed. Probably the observed decrease in activity of catalyst was due to the catalyst poisoning.

4 | CONCLUSION

To sum up, in the present study we synthesized Tunable N-doped carbon nanospheres from sucrose as carbon source and TAEA as nitrogen source by a simple and easily reproducible method. The content of doped nitrogen, Surface area, pore volume and pore size of carbon spheres were increased with the increasing of TAEA amount in the hydrothermal process. Prepared N-doped carbon spheres can act as solid ligand for immobilization of Ag NPs. It was found that benzylic alcohols and aldehydes could be easily converted into aryl nitriles by using Ag/N-CS-1 nanospheres as the catalyst and O₂ as the oxidant.

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