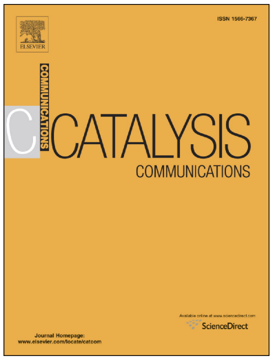

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Farhaz Liaquat Hussain, Mrinaly Suri, Ashutosh Namdeo, Geetika Borah, Dipanka Dutta, Tridip Goswami, Pallab Pahari

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A mild aerobic oxidation of benzyl alcohols and oxidative decarboxylation of phenylacetic acids by cellulose-supported Ag-Ag_2S nanoparticles

Farhaz Liaquat Hussain,[a] Mrinaly Suri,[a] Ashutosh Namdeo,[b] Geetika Borah,[c] Dipanka Dutta,[d] Tridip Goswami,[d] Pallab Pahari*[a]

[a]Applied Organic Chemistry Group, Chemical Science and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat, 785 006, Assam, India

Chemical Engineering group, Engineering Science and Technology Division, , CSIR-North East Institute of Science and Technology, Jorhat, 785 006, Assam, India

[c]Department of Chemistry, Dibrugarh University, Dibrugarh – 786004, Assam, India

[d]Cellulose Pulp & Paper Group, Material Science and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat, 785006, Assam, India

*Corresponding Author: Tel: +91-376-2372142, E-mail: ppahari@gmail.com

Abstract: Synthesis, characterization and catalytic activity of Ag-Ag_2S nanoparticles supported on environmentally benign cellulose matrix has been discussed. The nanoparticles carry out controlled oxidation of benzylic alcohols to aldehydes at room temperature. Same nanoparticles also carry out oxidative decarboxylation of phenylacetic acid and decarboxylation of mandelic acid derivatives to corresponding aldehydes under comparatively milder conditions. Stability and recyclability of the catalyst has been studied. The advantages of the catalyst developed in this work over other previous reports include room temperature or comparatively low temperature reaction, shorter reaction times, no requirement of stoichiometric oxidant or ligands, use of green solvents, functional group tolerance, and recyclability.

Keywords: heterogeneous catalysis; oxidation; oxidative decarboxylation; green chemistry.

1. Introduction

Application of nano-sized metals and composites as catalysts for various organic reactions has attracted a great attention for the researchers in the recent years [1,2]. Due to their very high surface area and reactive morphology, nano materials often act as superior catalysts compared to the larger sized counterparts [1-3]. Heterogeneous nature of the catalyst offer easy recyclability, and larger number of active sites provide better atom efficiency. Moreover, the size and shape of the nanoparticles control the catalytic activity leading to the scope of tuning the same catalyst for different reactions [4]. Although, number of reports are available for the use of nanomaterials for many different purposes, their application as recyclable heterogeneous catalysts in organic synthesis is still less explored.

Controlled oxidation of primary alcohol to aldehyde is one of the most important and fundamental reaction in organic chemistry [5]. A number of different oxidizing agents have already been developed for this purpose, including widely used DMSO/$(COCl)_2$ (Swern oxidation) [6], hypervalent iodine reagents [7], and different metal catalysts in combination with oxidants like peroxides, TEMPO, oxones etc. [8-11]. Although, these reactions are being extensively utilized, requirement of stoichiometric quantity of toxic and expensive reagents is the main drawback of the processes. In this situation, oxidation reaction using oxygen as the sole oxidant is becoming more useful, and accordingly, various transition metal catalyzed processes have been developed [12-14]. Unfortunately, these reported methods are not free from drawbacks like, requirement of harsh reaction conditions, high temperature, presence of toxic and costly metals and solvents, etc. Also the homogeneous catalysts used in many reactions are not recyclable. In this context, use of supported metal nanoparticles as recyclable heterogeneous catalysts is one of the prospective alternatives.

Stabilization of the metal nanoparticles using natural biopolymers like cellulose in place of different synthetic polymers is an emerging area of importance [15-17]. The highly oxygenated cellulose contains multiple hydroxyl groups that act as nucleation centre for the metals and provide necessary support for the stabilization of the nanoparticles. The materials prepared in this way show unique properties and find their application in diversified areas [15-18]. Recently, we have reported a process for the preparation of $Ag–Ag_2S$ nanoparticle supported in cellulose carrier and its application on the reduction of nitroaromatics [18]. We have also reported utilization of the cellulose-supported metal nanoparticles in different organic reactions [19]. In this report, we have shown that the cellulose-supported $Ag–Ag_2S$ nanoparticles is a very effective recyclable heterogeneous catalyst for carrying out selective oxidation of benzylic alcohols at room temperature. The same catalyst can also carry out oxidative decarboxylation of phenylacetic acids and decarboxylation of mandelic acids under microwave irradiation at moderate temperature (ca. 80 °C). It is to be noted that oxidation/dehydrogenation of alcohols using silver-based heterogeneous catalysts is well known in literature [20-24]. As a recent example, Hashemi reported a Ag(0) nanoparticle supported on silica-coated ferrite to carry out oxidant free dehydrogenation of alcohols under N_2-atmosphere in refluxing toluene [20]. Mitsudome reported similar reaction using hydrotalcite supported Ag(0) nanoparticle under argon atmosphere in *p*-xylene solvent at 130 °C [21]. Shimizu et al. [22] used alumina supported silver nanoparticle for oxidative dehydrogenation of alcohols using toluene as solvent under inert atmosphere at 100 °C. Millet et al. [23] used a Ag-catalyst for dehydrogenation of allyl alcohol to acrolein above 300 °C. Ivanovo, Chladek and few others used different silver catalyst for alcohol dehydrogenation [24]. However, most of those reactions require long reaction time (20-24 h), higher temperature and/or gaseous reaction conditions [20-24]. Report of aerial oxidation of alcohols at room temperature using heterogeneous recyclable silver catalyst is limited. Similarly, Ag-catalyzed decarboxylation reaction is well documented in the literature [25-28]. Starting from the pioneering work by Goosen et al. [25] and Larrosa et al. [26], the reaction was used by many different groups [27,28]. There are also a few reports of copper catalyzed oxidative decarboxylation reaction of phenyl acetic acid derivatives [29,30]. Most of these reactions typically rely on homogeneous catalysts. Also, the reactions require a very high temperature with long reaction time. In some cases, stoichiometric oxidants like, persulfates and amine ligands are also required. Although the synthesis of Ag-Ag_2S nanoparticles has reported earlier [18,31,32], their application as recyclable heterogeneous catalyst in organic synthesis is comparatively less [18]. Moreover, there is no report of studying the catalytic properties of Ag-Ag_2S nanoparticles towards oxidation and oxidative decarboxylation reactions so far.

2. Experimental

The Ag-Ag_2S nanoparticles supported on cellulose template was prepared in a simple one step co-precipitation using NaOH-urea-thiourea aqueous solution following an earlier reported procedure [18]. Details of the procedure of preparation of the nanoparticle, oxidation and decarboxylation reaction along with relevant reagents and instruments are given in the Electronic Supporting information (ESI).

3. Results and discussion

3.1. Characterization of cellulose-supported Ag-Ag_2S nanoparticles

Initially, powder X-ray diffraction was used to characterize the prepared Ag-Ag_2S nanoparticles (Fig. 1). Cellulose exhibits two main diffraction peaks corresponding to the 101 and 002 crystallographic planes at 2θ around 15.6° and 22.4°, respectively, characteristic of the cellulose crystalline phase of the fiber. After deposition of Ag-Ag_2S nanoparticles, the intensity of the basal reflection of the parent cellulose considerably decreases with the simultaneous appearance of three new diffraction peaks at 2θ values of 37.7, 43.8 and 63.7 corresponding to the (111), (200) and (222) planes of face center cubic (fcc) lattice of Ag(0) crystal along with the peaks due to Ag_2S. These values are in good agreement with the respective JCPDS card no. 65-8428 for Ag(0) and JCPDS card no. 65-2356 for Ag_2S. These results confirm the existence of metallic Ag and Ag_2S on cellulose templates, i.e. the formation of Ag-Ag_2S nanoparticles. The crystallite size has been calculated from XRD data based on the plane (111) at the 2θ value of 29.28 and using the Scherrer equation (shape factor K = 0.89). This was found to be in the range of 30 nm. This crystallite size corresponds to the volume-weighted average diameter.

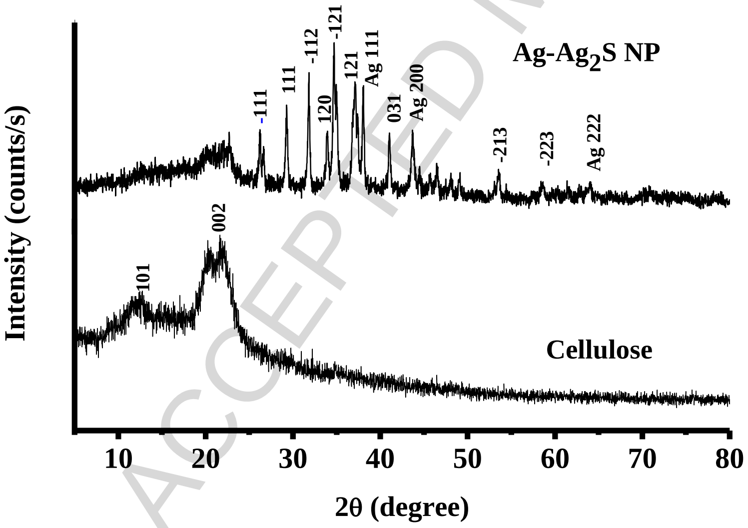


Fig. 1. Powder XRD pattern of cellulose-supported Ag-Ag_2S nanoparticles along with raw cellulose.

In the cross-sectional view of HRTEM image shown in Fig. 2, a small Ag particle can be visible like a dark spot in intimate contact with the Ag_2S sphere (faded portion). The inter-planer fringe spacing of about 0.238 nm on the dark spot agrees well with the (111) d-spacing of fcc Ag(0) crystal, while the d-spacing of about 0.30 nm on the faded area corresponds to (111) plane of monoclinic phase of Ag_2S crystal. The selected area electron diffraction (SAED) pattern, obtained by focusing the electron beam on the nanoparticles lying on the TEM grid, exhibits sharp diffraction which indicates crystalline nature of the structure. The particle size distribution calculated from TEM image (Fig. S2, ESI) shows narrow sized dispersion of the spherical shape nanoparticles on the support in the range of 8-29 nm, with a number average diameter of 16 nm (with standard deviation (SD) = 3.05) (Fig. S3, ESI). Further, we have converted number average diameter to surface-weighted diameter (~ 17 nm), which allows us to compare crystallite size with those obtained by chemisorption. Similarly, to compare with the crystallite size obtained by XRD, we have calculated the volume-weighted diameter (~18 nm). There are not many differences in the values obtained by the different methods due to the narrow crystallite size distribution as reflected from the value of standard deviation (SD). The active sites in the catalyst have also been quantified using TEM analysis. The calculation has been carried out by converting number average diameter to surface average diameter, which allows comparison of crystallite sizes by those obtained by chemisorption analysis [33]. The metal dispersion (Ds) has been calculated as 8% using surface weighted average diameter calculated from TEM [34].

EDX Spectra showed the presence of Ag, S, along with the C, O of the cellulose (Fig. S3, ESI). The elemental dot mapping images (Fig. S4, ESI) of the Ag-Ag_2S nanoparticles revealed the homogeneous distributions of the Ag and S throughout the surface of the cellulose fiber. An analysis through atomic absorption spectroscopy revealed the presence of silver metal in the catalyst as 1.5 wt%.

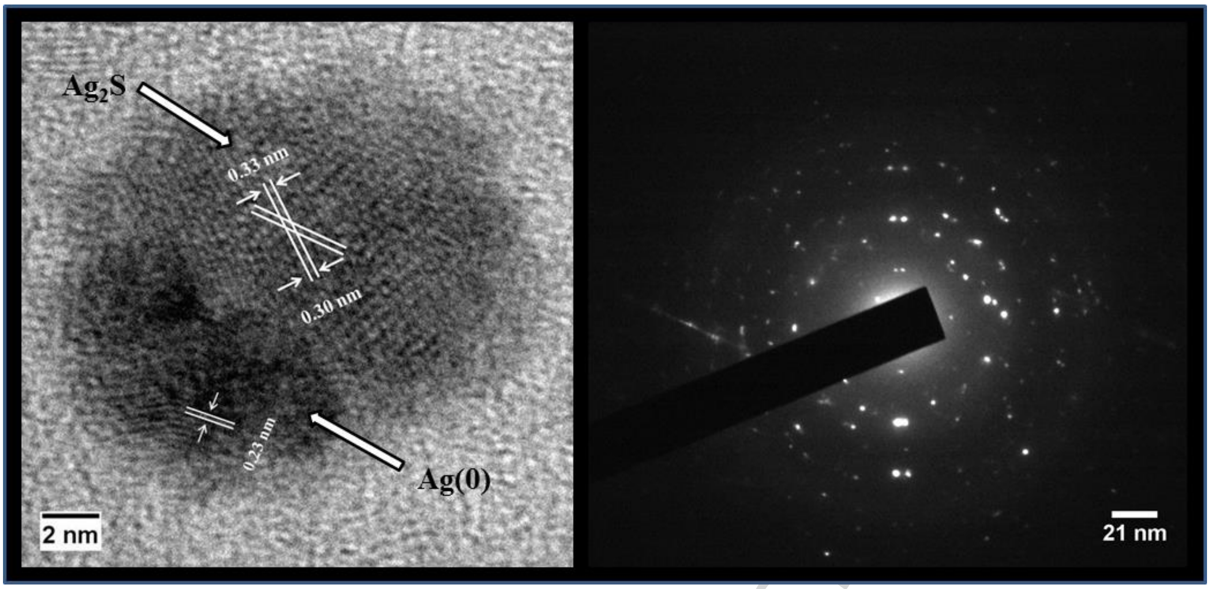


Fig. 2. HRTEM image with fringe spacing of Ag-Ag$_2$S nanoparticles along with SAED.

The oxidation state of the metals in Ag-Ag$_2$S nanoparticles can be observed by X-ray photoelectron spectroscopy (XPS) (Fig. 3). The raw XPS data were fitted with Gauss-Lorentz curve after subtraction of Shirley background using XPS 4.1 software [33]. During the fitting of Ag3d, the spin orbital separation was kept at 6 eV, while for S2p it was kept at 1.16 eV. After background correction the values of Ag3d appeared at 368.31 eV and 367.04 eV and that of S2p at 160.65 eV (Fig. 3 and S6). The values matched well with the standard Ag(0), Ag(I), and metal sulfide, respectively [31,35]. The percentage of Ag(0) and Ag(I) was also calculated from the XPS and found to be approximately 37 and 63%, respectively. Thermal stability of the prepared nanoparticle has been studied using thermo gravimetric analysis (TGA) (Fig. S7, ESI). The main degradation occurred between 200-600 °C for both the cellulose and the supported nanoparticles. The finding confirms that below 200 °C the prepared nanoparticle is sufficiently stable.

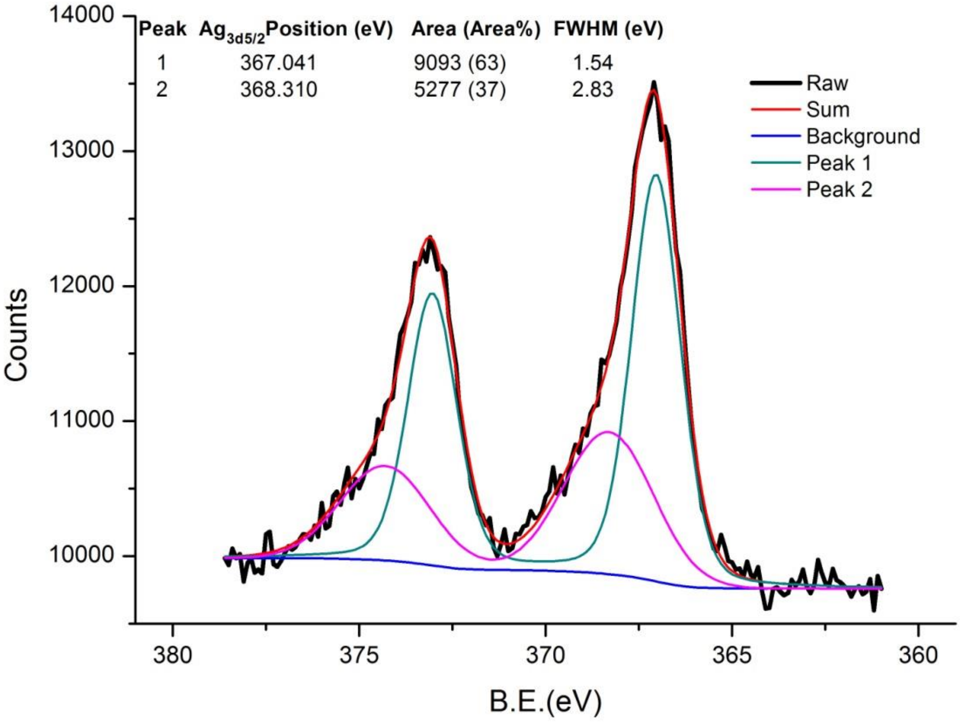


Figure 3. High resolution XPS spectra of Ag 3d.

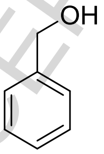
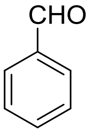
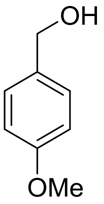
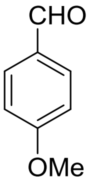
3.2. Catalytic activity of Ag-Ag_2S nanoparticles towards oxidation of benzylic alcohols

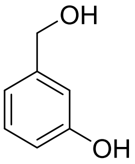
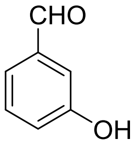
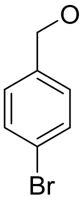
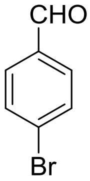
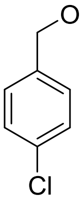
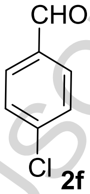
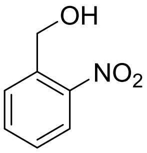
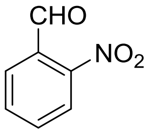
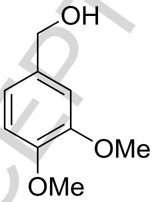
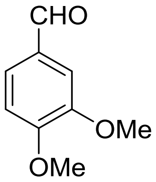
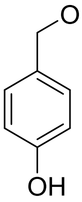
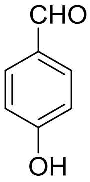
After synthesis and characterization, it was attempted to evaluate the activity of the Ag-Ag_2S nanoparticles as a heterogeneous catalyst towards oxidation of alcohols. Taking 4-nitrobenzyl alcohol as model substrate, a series of optimization reaction was carried out (Table S1, ESI). It was observed that selective and complete conversion of alcohol to aldehyde with an excellent isolated yield (82%) could be achieved by simply performing the reaction at room temperature under a bubbling oxygen balloon using acetonitrile as solvent. A blank reaction without catalyst did not show any detectable change in the starting material. Reactions were also performed in the presence of Ag_2S alone and a cellulose-supported Ag(0) catalyst. Both reactions did not show in detectable conversion of the starting material. To find out the efficiency of the catalyst, the rate of reaction in terms of turn over frequency

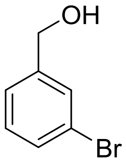
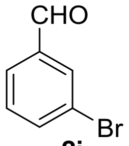
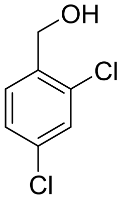
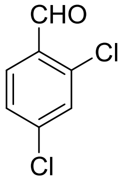
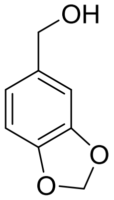
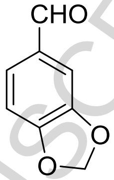
(TOF) has been calculated and found to be ~ 1.00 s^{-1} based on 30% conversion after 30 min of the start of reaction (See ESI for calculation).

The optimized reaction conditions were then applied to a number of different alcohols (Table 1). It was observed that the catalyst could oxidize different benzylic alcohols selectively to the corresponding aldehydes. Presence or absence of electron donating or withdrawing groups had almost no effect on the outcome and yield of the reaction. Sensitive groups like free hydroxyl and nitro were well tolerated under the reaction conditions. In no case over oxidation to benzoic acid was observed. The reaction was found to be selective towards oxidation of benzylic alcohols only. Aliphatic alcohols and secondary alcohols could not be oxidized under the reaction conditions. All the products were well characterized with ^{1}HNMR and ^{13}C NMR. Also, the melting points of the solid compounds were matched with the reported ones.

Table 1. Substrate scope of the catalyst towards oxidation of different benzylic alcohols[a].

Entry	Substrate	Product	Yield (%)[b]
1	 **1b**	 **2b**	80
2	 **1c**	 **2c**	75

3	 **1d**	 **2d**	78
4	 **1e**	 **2e**	70
5	 **1f**	 **2f**	77
6	 **1g**	 **2g**	65
7	 **1h**	 **2h**	74
8	 **1i**	 **2i**	82

9	 **1j**	 **2j**	70
10	 **1k**	 **2k**	79
11	 **1l**	 **2l**	60

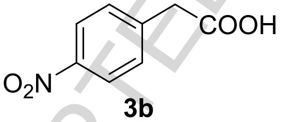
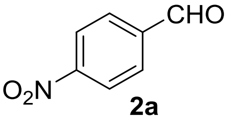
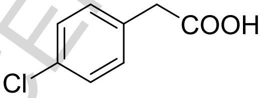
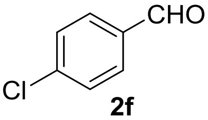
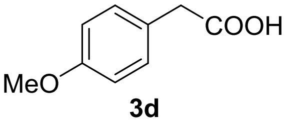
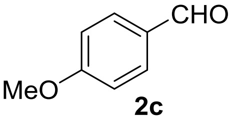
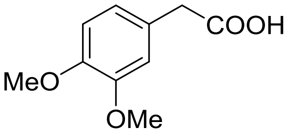
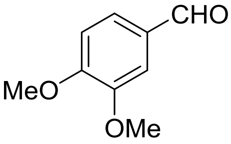
[a]Reaction conditions: Benzyl alcohol (1 mmol) and catalyst (15 mg) in acetonitrile (15 mL) were stirred at room temperature for 10 h; [b] yield refer to isolated compound after column chromatographic purification.

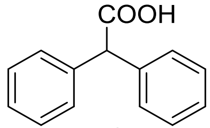
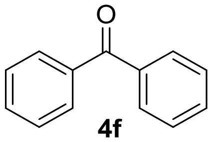
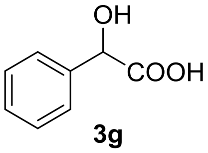
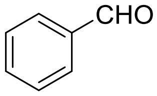
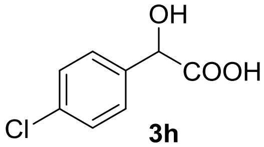
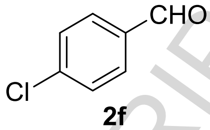
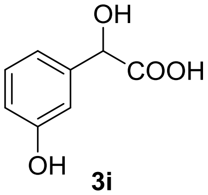
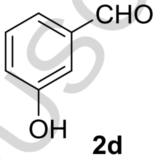
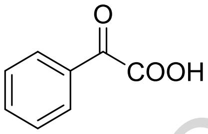
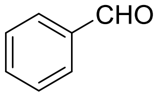
3.3. Catalytic activity of Ag-Ag_2S nanoparticles towards oxidative decarboxylation of phenyl acetic acid

To widen the scope of the application, Ag-catalyzed decarboxylation reaction was studied. Experiments showed that under microwave heating conditions the catalyst performed oxidative decarboxylation reaction of phenylacetic acid to benzaldehyde. Optimization experiments (Table S2, ESI) showed that the reaction could be carried out at a minimum temperature of 80 °C within very short reaction time (3 min) using either acetonitrile or water as solvent. A blank reaction test was also performed without the presence of catalyst to confirm the role of the catalyst.

Following the optimized reaction conditions, a number of different phenylacetic acid derivatives were studied. There was no considerable difference in yield with compounds having electron withdrawing (Entry 1 & 2, Table 2) and electron donating (Entry 3 & 4, Table 2) substituents. The decarboxylation of mandelic acid was also studied. It was observed that using the same reaction conditions, mandelic acid derivatives (Entry 6-8, Table 2) and phenylglyoxylic acid (Entry 9, Table 2) could also be decarboxylated to the corresponding benzaldehydes. In any case overoxidation of aldehyde to benzoic acid was not observed. Products were characterized with ^{1}HNMR and ^{13}C NMR and also by the comparison of physical data with the reported ones.

Table 2. Oxidative decarboxylation of different phenylacetic acid derivatives using cellulose supported Ag-Ag_2S nanoparticles [a].

Entry	Substrate	Product	Yield (%)
1	 **3b**	 **2a**	82
2	 **3c**	 **2f**	75
3	 **3d**	 **2c**	73
4	 **3e**	 **2h**	70

5	 **3f**	 **4f**	70
6	 **3g**	 **2b**	74
7	 **3h**	 **2f**	78
8	 **3i**	 **2d**	65
9	 **3j**	 **2b**	72

[a]Reaction conditions: phenylacetic acid (1 mmol) and catalyst (15 mg) in water (5 mL) was heated under microwave at 80 °C for 3 min; [b]yield refer to isolated compound after column chromatographic purification.

The recyclability of the catalyst in both oxidation and oxidative decarboxylation reactions was also investigated. For this experiment, the catalyst was recovered after reaction by simple filtration and then washed with corresponding solvents. After drying, it was reused directly in the next run. The results showed that the catalyst used in oxidation of alcohols remained almost equally active up to five consecutive reactions (Figure S7A, ESI). On the other hand, a minor decrease in activity of the catalyst used in oxidative decarboxylation was observed (Fig S7B, ESI). The Ag content in the recovered catalyst after the 3rd run was estimated by AAS and found to be almost same as that of the original. AAS of filtrate also showed only negligible amount of Ag. To check the heterogeneity of the catalyst, a filtration test was performed in which the oxidation of 4-nitrobenzyl alcohol was run for three hours and oxidative decarboxylation of phenylacetic acid was run for 1 min under optimized conditions. After that the catalyst was filtered out and the reactions were continued without catalyst. It was observed that the product ratio after the removal of the catalyst remained unchanged. The experiment confirmed that no leaching of any active species during the reaction occurred.

4. Conclusions

In summary, cellulose-supported Ag-Ag_2S nanoparticles has been prepared in a simple one step technique and characterized by PXRD, TEM and XPS analyses. The average size of the nanoparticles was found to be ~16 nm and it was distributed uniformly over the cellulose support. The prepared nanoparticle was found to be a very efficient catalyst for the oxidation of benzylic alcohols to corresponding aldehydes at room temperature. It was also effective for the oxidative decarboxylation of phenylacetic acids and decarboxylation of mandelic acids to aldehydes in a very short reaction time (3 min) at a temperature as low as 80 °C under microwave heating. The catalyst was also completely recyclable up to five consecutive reaction cycles. Use of green solvents like water and acetonitriles as reaction medium is another major advantage of the catalytic reaction. Although the exact mechanism of the reaction is not clear, inability of cellulose-supported Ag(0) and Ag_2S to carry out the reaction individually suggest that Ag-Ag_2S may be acting like Janus nanoparticles, which are known to have much better catalytic property compared to the individual components. Studies on the potential application of the catalyst towards other possible organic transformation are in progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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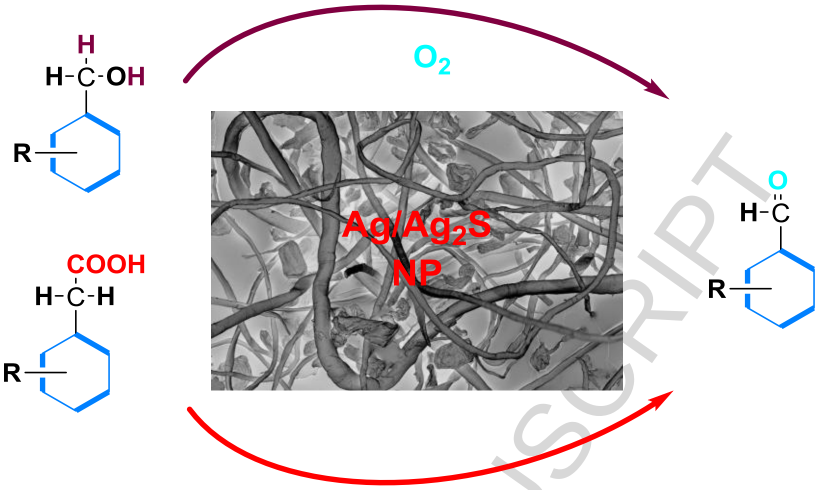
A mild aerobic oxidation of benzyl alcohols and oxidative decarboxylation of phenylacetic acids by cellulose supported Ag-Ag_2S nanoparticles

Farhaz Liaquat Hussain, Mrinaly Suri, Ashutosh Namdeo, Geetika Borah, Dipanka Dutta, Tridip Goswami, Pallab Pahari*



Graphical abstract

Highlights

- *Cellulose supported* Ag-Ag_2S *nanoparticles synthesized and characterized*
- *Prepared nanoparticles oxidize benzylic alcohols to aldehydes at room temperature*
- *It also decarboxylate phenylacetic acids to aldehydes*
- *Catalyst retains its activity even after five times of recycling*
- *Mostly green solvents like water and acetonitrile is used*