RESEARCH PAPER

Green Synthesis of Ag Nanoparticles Immobilized on Graphene for the Selective Oxidation of Alcohols

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ABSTRACT

In this work, we were synthesized 5%Ag/Graphene nanocomposites via an easy and green route. The as-prepared nanocatalysts were characterized by XRD, SEM, TEM, EDX and EDX mapping. The catalytic activity of 5%Ag/Graphene nanocomposite with H_2O_2 was examined in numerous alcohols oxidation reaction. To achieve the best conversion of the benzyl alcohol, different parameters such as the amount of nanocatalyst, oxidant type, solvent and amount of oxidant were examined. The results showed that the reaction time for alcohols with a substituent in the para position is shorter and a higher conversion of alcohols is obtained with these substrates. This nanocomposite can be efficiently recovered and reused five times without significantly loss in catalytic activity. Recoverability of the nanocatalyst, short time, high conversion, eco-friendly and economical are some advantages of this reaction. A hot filtration test was determined that 5%Ag/graphene nanocomposite operates heterogeneously in the oxidation reaction. Due to the high value of green syntheses in the last decade, we used pomegranate juice as a reducing agent. Pomegranate juice was used not only as a reducing agent but also as a surfactant. On the other hand, hydrogen peroxide was used as a non-toxic and green oxidizing agent.

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INTRODUCTION

Oxidation reactions are one of the most significant reactions in organic chemistry and provide significant route for the preparation and correction of functional groups [1]. In synthetic organic chemistry, selective oxidation of alcohols is investigated as one of the most important and fundamental chemical reactions for the large–scale preparation of industrial compounds such as aldehydes and ketones. These related carbonyl compounds can be used to prepare pharmaceuticals, insecticides, cosmetics, dyes, agricultural chemicals, etc [2,3]. Generally, the oxidation of alcohols has been carried out using of toxic and corrosive oxidants such as ammonium permanganate, pyridinium chlorochromate (PCC), chromium trioxide, pyridinium dichromate (PDC), tert-butyl hydroperoxide, $KMnO_4$, ClO_2, H_5IO_6 and NaClO, etc. which are not only hazardous and expensive reagents, but also causes economic and environmental problems because of the production of large amounts of toxic by-products [4-6]. Thus, utilization of stable, clean and economic oxidizing reagent for this reaction could

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be an attractive challenge in this regard. H_2O_2 is attractive as a cheap, safe, readily available and environmentally friendly oxidant for producing active oxidation species in aqueous solution, with water as the byproduct [7]. In addition, it has been made clear that, reactions in H_2O can facilitate availability to various reactivity and selectivity methods compared with those observed in current organic solvents because of its significant physical and chemical properties [8].

Although, in previous research, different catalytic systems have been suggested for improving the chemical transformation of alcohols to aldehydes, the development of new effective oxidation reactions as heterogeneous systems in terms of economic and environmental reasons would be very valuable [9-12].

Graphene, a new 2-dimensional carbon substance, has attracted a lot of attention as optimal supporting substances because of its unique electronic, physical and chemical properties [13-15]. In recent years, various graphene-based nanocomposites, comprising different metal oxides and nanoparticles such as Ag, Au, Pt, Pd and TiO_2, have started to become a new field of nanoscience and nanotechnology [16-20]. The synergy of Ag nanoparticles and graphene, leads to some superior catalytic, optical and electronic properties. Therefore, substances with improved performance may be produced and used in applications, such as catalysis, sensors, antimicrobial coating etc. [21-24].

Due to the high conductivity, powerful ultraviolet-visible absorption ability and catalytic reactivity, the Ag nanoparticles have been used in many area, such as electronic devices, surface enhanced Raman scattering, biomarkers [25, 26]. There are several reports regarding the synthesis methods of silver/graphene nanocomposites in the literature [27-29]. However, all the methods require complex processes, long reaction times and $NaBH_4$ as a reductant, which is highly toxic [30]. According to the limited reasons, it is still necessary to develop a simple, efficient and green method to fabricate silver/graphene nanocomposites. Herein, we utilized pomegranate juice as a natural reductant to synthesize Ag/graphene nanocomposite. This research shows a green and economic method for the synthesis of Ag/graphene nanocomposite. Pomegranate juice is a potential source of anthocyanin. Anthocyanins are pigments found in red fruits. Pomegranate juice was used as reducing agent for reduce Ag^+ to Ag.

Based on our findings in previous works on the synthesis and application of heterogonous catalysts in organic reactions, [31-36] in this research, we designed, prepared, and characterized Ag nanoparticles supported on graphene and then employed as a stable and efficient heterogeneous catalyst for oxidation of alcohols.

MATERIALS AND METHODS

Materials and Characterization

All chemicals employed were of analytical grade, were used as received without any further purification, and were obtained from Merck. Pomegranate juice was obtained from Shiraz in Iran. X-ray powder diffraction (XRD) patterns of the samples were recorded using a Bruker Advance D8 Diffractometer with Cu Kα radiation (λ=0.154 nm). Chemical analysis of the samples was done by energy dispersive X-ray (EDX) analysis joined to a Philips XL 30 scanning electron microscope. The SEM measurements were performed on a Holland Philips XL30 microscope. Transmission electron microscopy (TEM) measurements were performed on a LEO 912 AB TEM operated at 120 kV. Products of these oxidation reactions were analyzed by GC (Shimadzu 8A) and were identified by GC-MS (Finnigan TSQ-7000).

Preparation of catalysts

Preparation of graphene oxide

Graphene oxide (GO) was prepared according to an improved Hummer method [37], using graphite powder as the starting material. In a typical procedure, 3 g of graphite powder, 18 ml of HNO_3 (67 wt%), and 46 ml of H_2SO_4 (98 wt%) were mixed and strongly stirred with magnetic stirring in the range of 0–5 °C for 15 min in a 500 ml reaction flask immersed in an ice-water bath. Then 6 g of $KMnO_4$ was gradually added with continuous stirring to the above solution within 15 min. After this, the obtained solution was stirred continuously for 2 h in an ice-water bath and maintained the temperature in the range of 10–15 °C, and then the resulting solution was stirred continuously at 35 °C for 30 min. Subsequently, 138 ml of distilled water was gradually added to the suspension for 10 min, and then the temperature was maintained in the range of 95–98 °C for 30 min. Afterwards, the obtained solution was diluted by 200 ml of warm distilled water (40 °C) and treated with 18 ml of H_2O_2 (30%) to reduce remaining permanganate to soluble manganese ions. Finally, graphene oxide was obtained after centrifugal separation, washed with distilled water and thoroughly dried in a vacuum oven at 60 °C for 24 h.

Preparation of Ag/graphene nanocomposites

Ag/graphene nanocomposites were synthesized by reducing silver ions and graphene oxide simultarieously. In a typical procedure, 0.1 g of prepared graphene oxide was dispersed in deionized water (50 ml) by ultrasonication for 30 min to synthesize a stable graphene oxide suspension. An aqueous solution of $AgNO_3$ was added slowly to the resulting suspension with magnetic stirring for 30 min. Then 50 ml pomegranate juice was gradually added into the above mixture. The resulting mixture was stirred for 12 h. The reduction of Ag from Ag^+ to Ag^0 was confirmed by the darkening of the mixture. The black solid precipitates were filtered, washed with deionized water and ethanol for several times. Finally, the as-prepared nanocomposites were dried in a vacuum at 60 °C for 48 h.

Experimental procedure

First, benzyl alcohol (1 mmol) and H_2O_2 (3 mmol) were dissolved in 2 ml H_2O, subsequently, 0.05 g catalyst (5%Ag/graphene nanocomposite) was added, and the mixture was stirred continuously at 80 °C. The progress of the reaction was followed by TLC. After the completion of the reaction, the resulting mixture was cooled down to room temperature, and the nanocomposite was filtered by centrifugation and washed with solvent for several times. The product was extracted from the reaction mixture by using ethyl acetate and subjected to GC analysis.

RESULTS AND DISCUSSION

Characterization of the catalysts

The structural and morphological information of the synthesized compound was investigated using different standard physicochemical techniques such as XRD, TEM, FE−SEM, EDX, and EDX mapping. The crystalline structure of graphene oxide

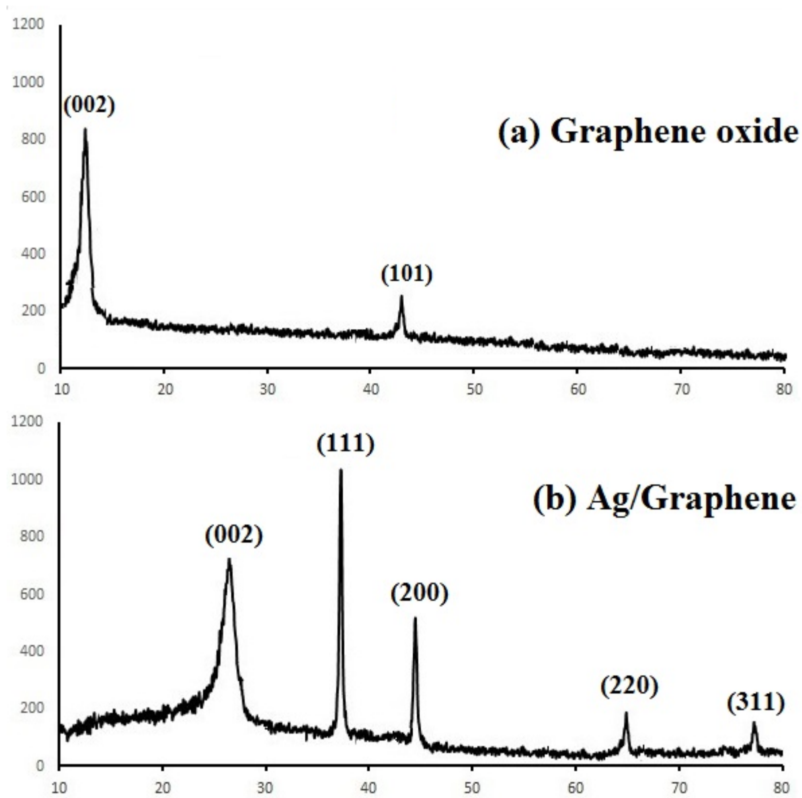


Fig. 1. XRD patterns of graphene oxide (GO) (a), 5%Ag/graphene nanocomposite (b).

(GO) and 5%Ag/graphene nanocomposite was determined using XRD analysis, and the diffraction patterns are illustrated in Fig. 1. As shown in Fig. 1a, graphene oxide display a sharp diffraction peak at 2θ=11.9° and a very low intensity peak near 2θ=41.9° which are corresponding to (002) and (101) crystal planes respectively [30]. However, the Ag/graphene nanocomposite prepared by ultrasound irradiation, revealed this diffraction peak to disappear and a new broad scattering peak

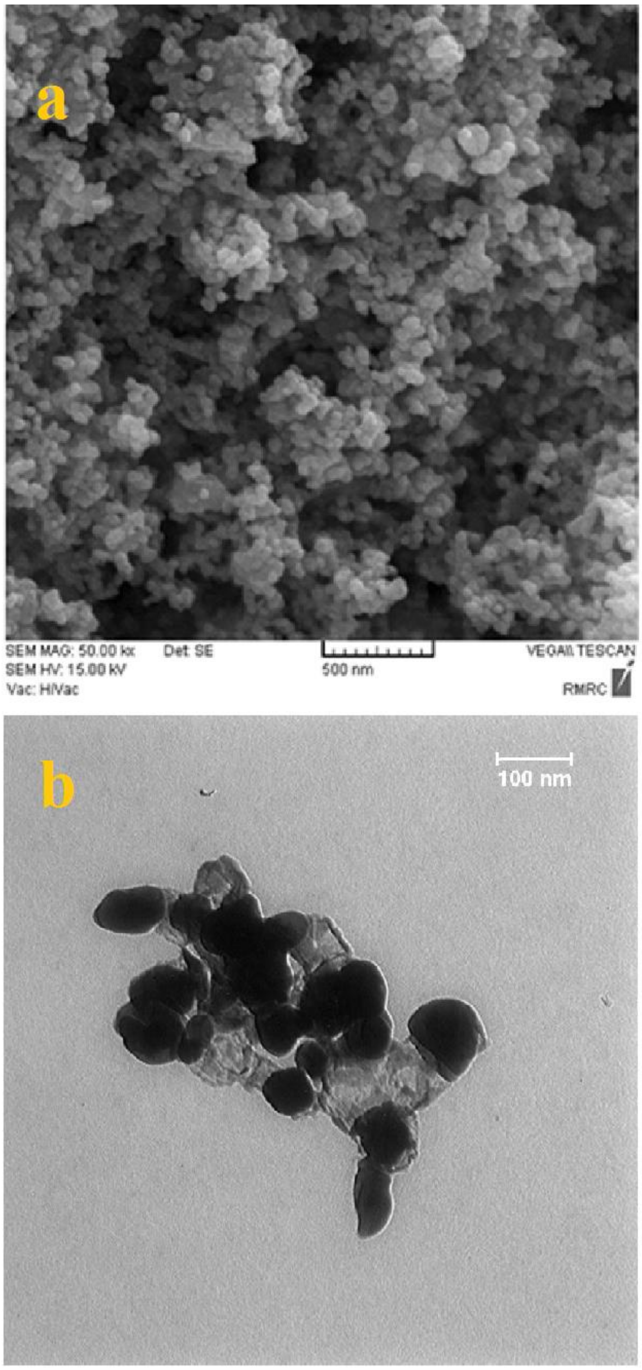


Fig. 2. FE-SEM image of 5%Ag/graphene nanocomposite (a), TEM image of 5%Ag/graphene nanocomposite.

appears at a 2θ value of 26.8 corresponding to the (002) plane as shown in Fig. 1b. This indicates that the reduction of the oxygen functional group has occurred in the graphene oxide structure. In the pattern of 5%Ag/graphene nanocomposite, the intense four main diffraction peaks at 2θ=38.1°, 44.4°, 64.8° and 77.8° which are corresponding to (111), (200), (220) and (311) diffraction peaks of the face-centered cubic silver crystal, which is in agreement with the reported data (JCPDS File No, 04-0783). The results indicate the Ag/graphene nanocomposite to be successfully prepared with pomegranate juice as green reductant. It was suggested that graphene oxide (GO) and Ag ions have been reduced to graphene and Ag nanoparticles.

The surface morphology and particle size of 5%Ag/graphene nanocomposites were investigated using SEM and TEM analyses (Fig. 2). As shown SEM image, spherical morphology with an average diameter of about 50-60 nm for nanocomposite was obtained (Fig. 2a). Also, from

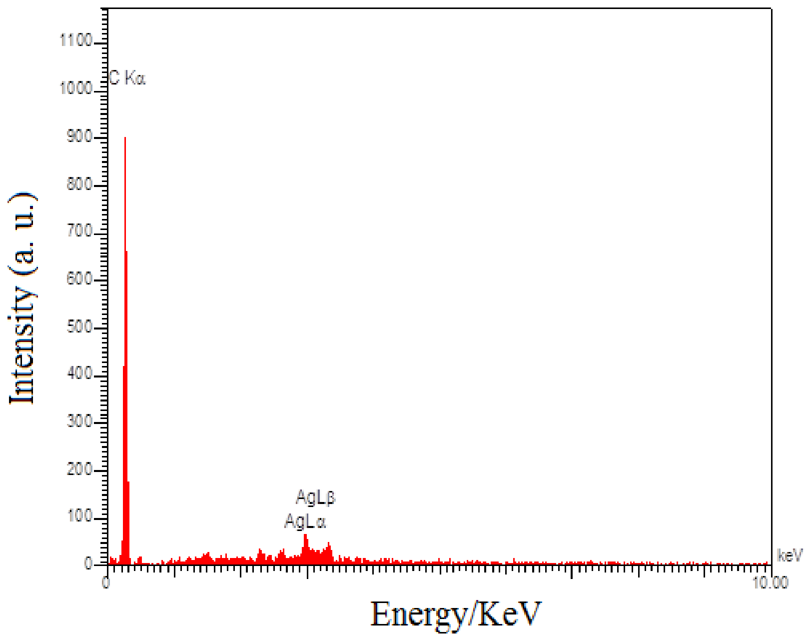


Fig. 3. EDX analysis of 5%Ag/graphene nanocomposite.

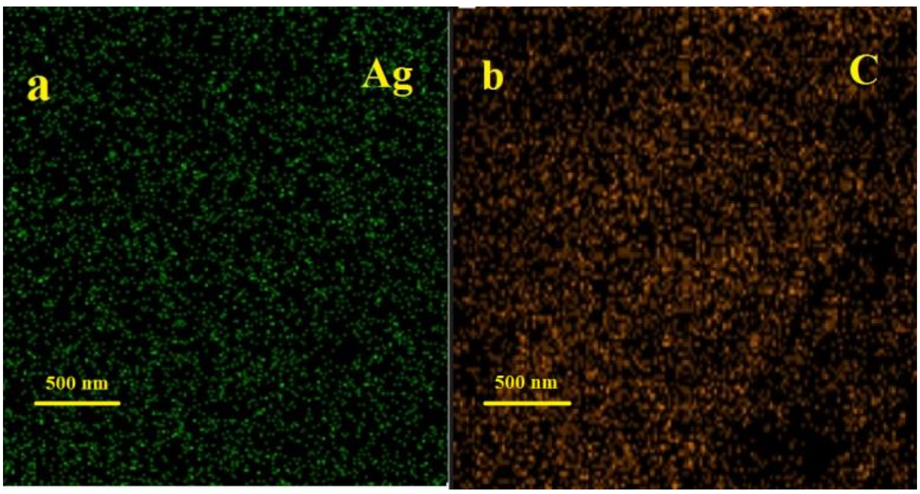


Fig. 4. EDX elemental maps of 5%Ag/graphene nanocomposite.

the resulting TEM image, spherical nanoparticles with fairly uniform shape and size were showed (Fig. 2b).

The elemental analysis of 5%Ag/graphene nanocomposite was carried out using Energy dispersive X-ray analysis (EDX) that is presented in Fig. 3. The presence of peaks corresponding to expected elements of C, and Ag in the structure confirmed the successful preparation of 5%Ag/graphene nanocomposite. In addition, the elemental mapping results of the synthesized nanocomposite revealed that C, and Ag was uniformly distributed throughout the structure (Fig. 4).

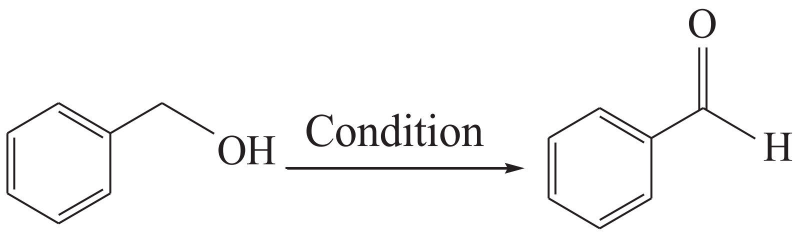


Fig. 5. Oxidation reaction of benzyl alcohol with 5%Ag/graphene nanocomposite as catalyst in various condition.

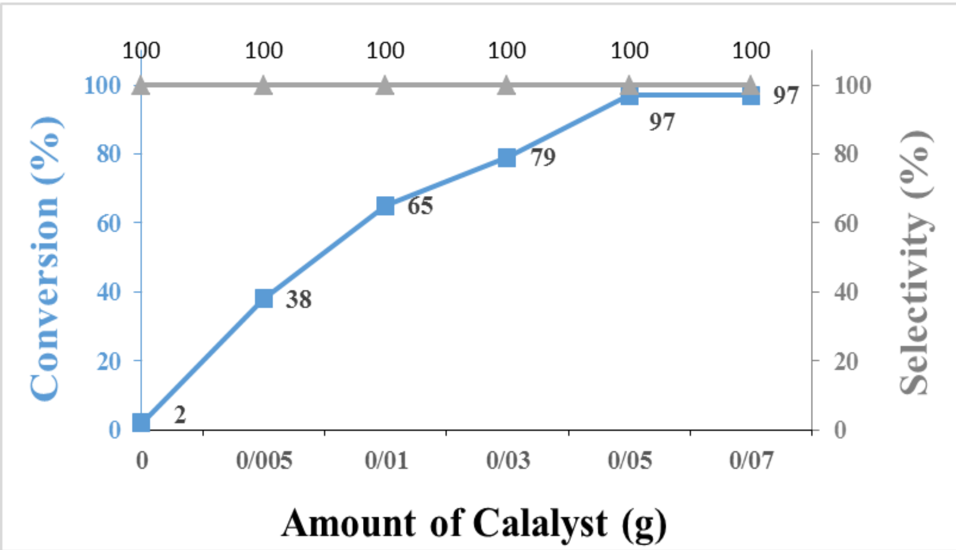


Fig. 6. Effect of catalyst amount on oxidation reaction of benzyl alcohol, Reaction conditions: benzyl alcohol (1 mmol), H_2O_2 (3 mmol), water (2 ml), Temp: 80 °C, Time: 5 h.

Table 1. Effect of solvents in the oxidation reaction of benzyl alcohol [a].

Entry	Solvent	Conversion (%)	Selectivity (%)
1	toluene	74	100
2	acetonitrile	94	100
3	n–hexane	64	100
4	chloroform	52	100
5	water	97	100

[a] Reaction conditions: benzyl alcohol (1 mmol), 0.05 g catalyst, H_2O_2 (3 mmol), Time: 5 h, Temp: 80 °C.

Catalytic oxidation of benzyl alcohol

The catalytic activity of the as synthesized 5%Ag/graphene nanocomposite has been studied for the oxidation reaction of alcohols. Initially, to optimize reaction condition for the oxidation of alcohols, benzyl alcohol was chosen as a model substrate, and the oxidation reaction was carried out in various conditions with 5%Ag/graphene nanocomposite as catalyst and hydrogen peroxide as oxidant (Fig. 5).

Based on the obtained results in absence of any catalyst a negligible conversion was observed after 5 h. Furthermore, the amount of the catalyst was studied. With increasing, the amount of the catalyst to 0.05 g an enhancement in the conversion of the benzyl alcohol was seen (Fig. 6), which proved the high influence of the presence of catalyst in the reaction. The results show that the best conversion was obtained when 0.05 g of catalyst was used. In values higher than 0.05 g no significant effect was seen on the conversion of benzyl alcohol, but in amounts less than 5%Ag/graphene nanocomposite showed lower conversion of benzyl alcohol at the same reaction conditions. Conversion and selectivity were determined by GC.

To choose the best solvent, we used five solvents includes toluene, acetonitrile, chloroform, n-hexane and water (Table 1). The obtained results demonstrated that water and

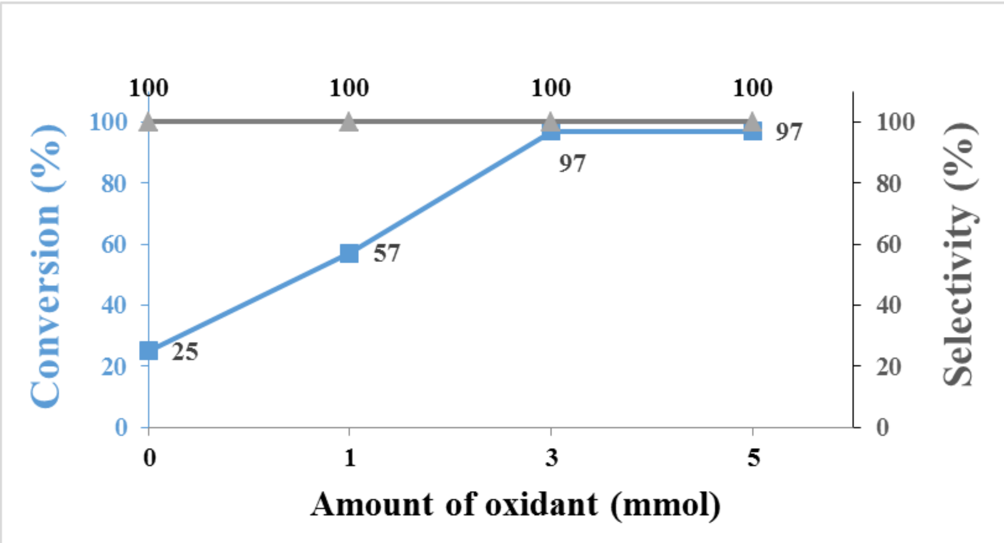


Fig. 7. The effect of the amount of oxidant in the oxidation reaction of benzyl alcohol. Reaction conditions: benzyl alcohol (1 mmol), 0.05 g catalyst, water (2 ml), Time: 5 h, Temp: 80 °C.

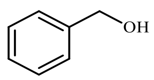
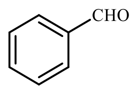
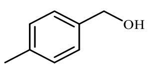
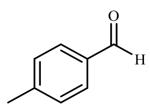
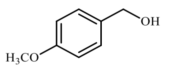
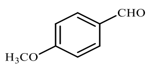
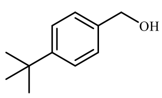
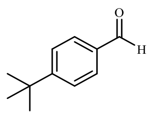
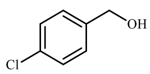
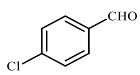
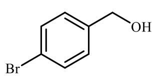
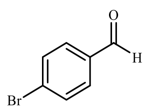
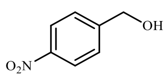
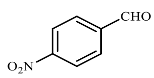
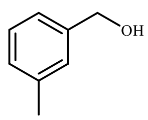
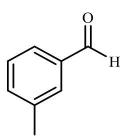
Table 2. Oxidation of benzyl alcohol with 5%Ag/graphene nanocomposite in the presence of various oxidants [a].

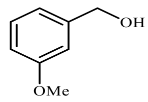
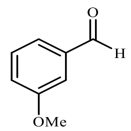
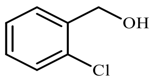
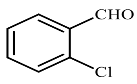
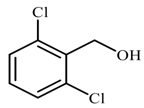
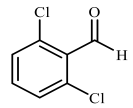
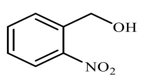
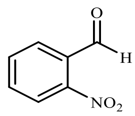
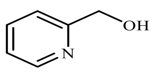
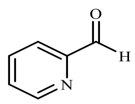
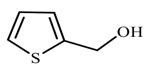
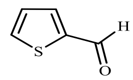
Entry	Oxi(	Tir	Conversi	Selectivit benzaldehy	Selectivity to benzoic acid (%)
1	TB		97	68	32
2	H_2		97	100	0
3	Ph		87	89	11

[a] Reaction conditions: benzyl alcohol (1 mmol), 0.05 g catalyst, oxidant (3 mmol) and water (2 ml), Temp: 80 °C.

acetonitrile were better than toluene, chloroform and n-hexane. After 5 h, the model reaction in water was effectively complete with 97% conversion for benzyl alcohol. Acetonitrile with high dielectric constant facilitates the clash and contact of oxygen source, benzyl alcohol, and nanocomposite, that increase the adsorption of reactants on nanocomposite surface and as a result, obtained the better conversion as compared with the other solvents. In relation to chloroform, lone pair of electrons on chlorine binds to the sites nanocomposite, and thereby lower yield was

Table 3. Catalytic activity evaluation of the 5%Ag/graphene nanocomposite for the oxidation reaction of alcohols with H_2O_2 under optimal reaction conditions [a].

Entry	Substrate	Product [b]	Time (min)	Conversion (%)	Ref
1			300	97	32
2			180	96	32
3			240	95	32
4			300	95	39
5			360	80	32
6			360	78	40
7			360	36	32
8			240	78	40

9			240	77	39
10			360	45	41
11			360	34	41
12			360	18	41
13			240	95	39
14			300	87	39

[a] Reaction conditions: alcohol (1 mmol), 0.05 g catalyst, water: (2 ml), H_2O_2 (3 mmol), Temp: 80 °C.
[b] Selectivity of product: 100% aldehyde

obtained. The lower yield obtained with n-hexane and toluene (non-polar solvents) is due to the low solubility of the oxidant in these solvents and as a result, adsorbed solvent molecules occupy part of the active sites of the nanocomposite.

To study the oxidant effect, the oxidation reaction was performed in the presence of various oxidants including hydrogen peroxide (H_2O_2), TBHP (tert-buthyl hydrogen peroxide), and PhIO (iodosyl benzene) that was prepared according to the literature [38]. In these experiments, TBHP showed conversion of 97% with 68% selectivity for benzaldehyde in 4 h (Table 2, entry 1), benzoic acid is a by-product of over-oxidation. With H_2O_2, benzaldehyde was produced in 97% conversion and 100% selectivity after 5 h (Table 1, entry 2). 87% conversion and 89% selectivity for benzaldehyde in 5 h was obtained by PhIO (Table 1, entry 3). Therefore, the highest conversion and selectivity of benzaldehyde was achieved with H_2O_2 and was chosen as the optimal oxidant.

Afterward, the effect of the amount of H_2O_2 (0 mmol, 1 mmol, 3 mmol, and 5 mmol) on the catalytic efficiency of 5%Ag/graphene nanocomposite was investigated. The results are depicted in Fig. 7. Benzyl alcohol as a reactant was slightly oxidized to the main product in the absence of H_2O_2. The conversion of benzyl alcohol enhances significantly with increasing the amount of H_2O_2, whereas the selectivity of benzaldehyde remains constant. With growing the amount of oxidant, more than 3 mmol did not have any remarkable impact on the conversion of benzyl alcohol.

To evaluate the efficiency and the performance of 5%Ag/graphene nanocomposite for the oxidation reaction of the alcohols, numerous substituents (e.g., chloro, nitro, methyl, and methoxy) in the aromatic ring were considered. The results shown in Table 3 (Entries 1-14) clearly indicated that electronic effects, steric hindrance, and the position of substituent groups play an important role in the oxidation reaction of various alcohols.

Substituted benzyl alcohols bearing electron-donating groups such as OCH_3 and CH_3 were significantly converted into its corresponding aldehydes with high conversion (Table 3, Entries 2–4). The compounds with electron-withdrawing groups such as Cl, Br, and NO_2 were also oxidized selectively and converted into the desirable products in lower conversion because of the lower electron density on the aromatic ring (Table 3, Entries 5–7). However, the results showed that benzyl alcohols containing substituents at the 4-para position of the aromatic ring compared to the substituents at the 2-ortho and 3-meta position of the ring transformed to the desirable products

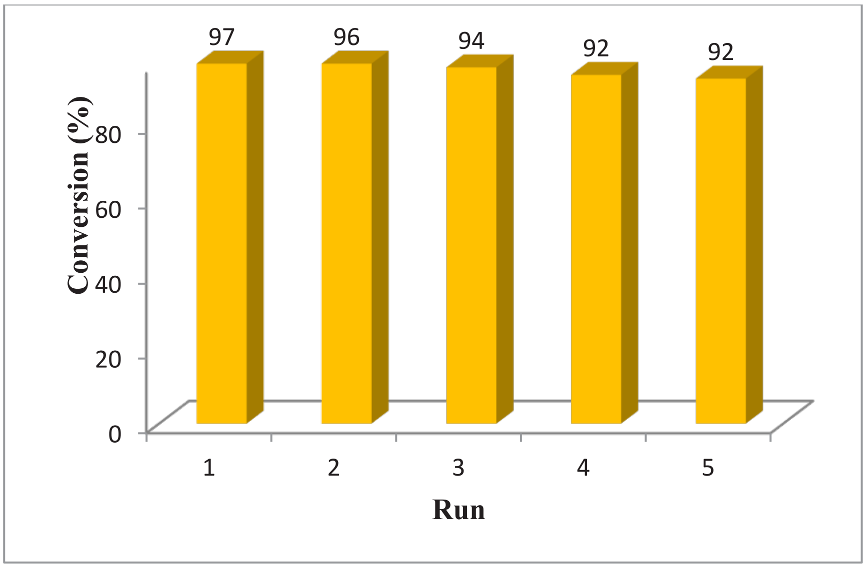


Fig. 8. Recyclability of 5%Ag/graphene nanocomposite in the oxidation reaction of benzyl alcohol.

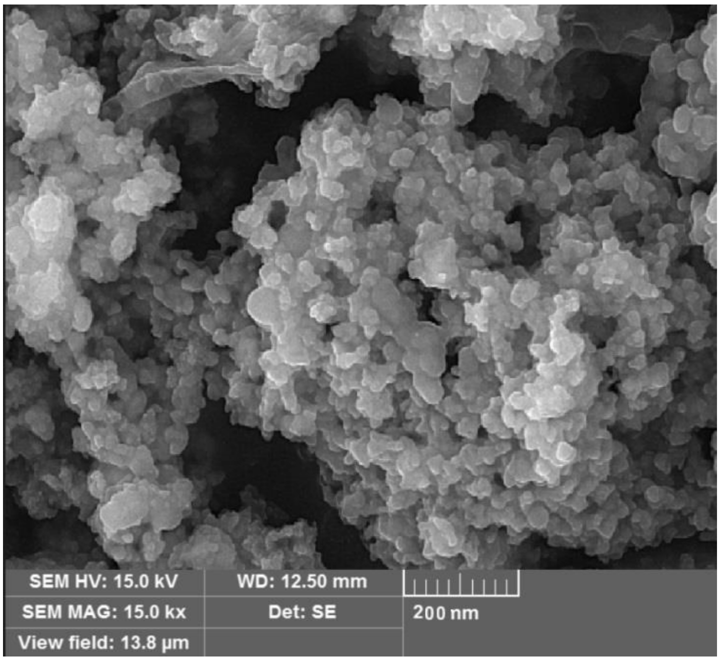


Fig. 9. SEM of 5%Ag/graphene nanocomposite after 5 cycles.

in higher yield (Table 3, Entries 8−12). Additionally, heteroaromatic alcohols was successfully oxidized to desired products and gave the corresponding aldehydes in high conversion (Table 3, Entries 13, 14).

A hot filtration test was performed in the oxidation reaction of alcohols to distinguish whether 5%Ag/graphene nanocomposite act as a heterogeneous catalyst. For this purpose, after 50% progress of reaction, nanocomposite was removed from the reaction mixture and reaction was continued without nanocomposite for 5 h. The GC results demonstrated that in the absence of 5%Ag/graphene nanocomposite as catalyst, the oxidation reaction was completely stopped. Therefore, according to the results, it was determined that 5%Ag/graphene nanocomposite operates heterogeneously in the oxidation reaction.

Reusability is of remarkable specifications of a heterogeneous catalyst that should be studied. For this purpose, the reusability of 5%Ag/graphene nanocomposite was assessed for the oxidation reaction of benzyl alcohol under optimized conditions (Fig. 8). After the completion of the reaction, the catalyst was divided from the reaction mixture, thoroughly washed with distilled water, and then dried in the oven. Nanocomposite can

Table 4. Comparison of the activity of 5%Ag/graphene nanocomposite with some previous catalytic systems in the oxidation reaction of benzyl alcohol.

Entry	Reaction Condition	Time (h)	Conversion (%)	Selectivity of benzaldehyde (%)	Ref
1	Triple−shell hollow $CuNiFe_2O_4$ spheres, H_2O, 80 °C, H_2O_2	4	98	100	32
2	MnO_x/HAP−10, toluene, 80 °C, O_2	2	48	97	40
3	2%V_2O_5/STO, acetonitrile, 80 °C, TBHP	3	70	88	41
4	5%Co_3O_4/HCS_5, DMF, 110 °C, O_2	8	50	63	42
5	Pd/$Co(OH)_2$, Solvent−free, 160 °C, O_2	4	33	80	43
6	Au/TiO_2, Solvent−free, 80 °C, TBHP, MW irradiation	1	69.3	99.1	44
7	$La_{0.9}Ce_{0.1}CoO_3$, toluene, 88 °C, O_2	1	95	95	45
8	5%Ag/graphene nanocomposite, water, 80 °C, H_2O_2	5	97	100	This work

HAP: Hydroxyapatite

be reused at least five times without observation of remarkable loss in its catalytic efficiency and conversion.

The SEM image of the reused catalyst after the 5th run (Fig. 9) demonstrated no significant changes compared to the fresh catalyst, and the nanocomposites are still nearly spherical.

The catalytic efficiency of 5%Ag/graphene nanocomposite was compared with that of other literature reported catalysts toward the oxidation reaction of alcohols. It was demonstrated that 5%Ag/graphene nanocomposite is the most favorable catalyst for the oxidation of benzyl alcohol, leading to the formation of products in good selectivity and high conversion (Table 4).

CONCLUSION

In this present study, we have successfully synthesized and employed highly efficient, stable, non-toxic and environmentally benign supported silver nanoparticles on graphene as a nanocatalyst in the alcohols oxidation reaction with H_2O_2. This nanocomposite oxidizes a wide range of alcohols under mild conditions and produces of the corresponding aldehydes with excellent selectivity. Moreover, the nanocomposite could be facilely separated from the reaction residue and reused in five successive cycles without significant loss of catalytic activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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