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Protein mediated synthesis of gold nanobiocatalyst by microwave: A high efficient catalytic activity for the selective oxidation of benzyl alcohol

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ABSTRACT

A simple, proficient, one-pot green chemical method for the biosynthesis of gold nanoparticles (AuNPs) with protein egg albumin by microwaves, which produce novel gold nanobiocatalyst (AuNBC) and it was characterized by FT-IR, UV–vis, TEM and DLS, which exhibited excellent stability over a wide range of pH and temperature. The catalytic activity of the as-synthesized AuNBC was quantified by synthesizing sodium benzoate from the one-pot oxidation of benzyl alcohol using gold nanobiocatalyst under microwave heating, which was stronger than AuNPs prepared by conventional chemical methods. The protocol is environmentally benign with non-toxic reagents, high recyclability and high efficiency.

1. Introduction

Sodium benzoate is a type of salt, which is more likely to be chemically produced and used as preservative to foods such as soda, fruit juice, soya sauce, jams, jellies and other condiments, to inhibit decay. Since the early 1990s, benzoate has been widely used worldwide as a preservative due to its antimicrobial properties combined with its low toxicity and taste. There are some methods for the commercial preparation of sodium benzoate via the catalytic oxidation of toluene, which is achieved by heating a mixture of the substrates, cobalt acetate and bromide promoter in acetic acid to 250 °C at high pressure [1]. Even though, this process rises to problems such as difficult separation of products, waste generation, time consumption and corrosion of equipment. The requirement of expensive equipment also makes the cost of production very high and enormous amount of energy consuming operation under excessive conditions. Therefore, few attempts are being made to find environment friendly routes by performing the reaction under different conditions using a variety of solid catalysts, ionic liquids or supercritical fluids [2–5].

From recent years, nanoparticles synthesis and applications towards nanocatalyst have attracted a great deal of attention. Nanocatalysts are more efficient compared to heterogeneous catalysis and has recyclability, which is not possible in homogeneous catalysis [6–8], AuNPs as a nanocatalyst has been proven to be an excellent catalyst in many reactions, including both gas and liquid-phase oxidation [9–12]. The catalytic activity of gold is remarkably sensitive to many factors, such as the gold particle size effect [13,14], the preparation method [15], and the support effect [16]. Few researches have been made of bimetallic system based on gold for generation of the desired target molecules [17]. Recently, Dai et al. [18] reported synthesis of sodium benzoate using Au-Ag/TiO_2 catalysts. However, this process proceeds with disadvantages of higher time consuming, tough handling, toxic reagents and less ecofriendly. So, the manufacture of sodium benzoate from benzyl alcohol require significantly environmental-friendly process, non-toxic, and energy efficient towards the mild reaction condition and recyclability of catalyst, which will be conquer by highly efficient green route using biomolecule assisted synthesis of noble metal nanomaterials.

Within the past decade, green chemistry has attained the status of a major scientific discipline due to safer solvents, energy efficient which lead to the development of cleaner and more benign chemical processes [19,20]. Microwave assisted synthesis has been proven that most chemical transformations a significant energy savings with can be expected using microwaves, which drastically reduce reaction times, increase product yields, selectivity and enhance product purities by falling unwanted side reactions compared to conventional synthetic methods [21,22]. Significantly, biosynthetic routes generate negligible quantities of hazardous

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waste and consume far less energy than chemical synthesis routes which reduce the production cost of AuNPs.

Nowadays, bio mineralization processes exploit the specific interactions among biomolecular templates and inorganic materials, thus favouring controlled and efficient synthesis [23]. Previously, different types of micro-organisms, several biomolecule and green chemical methods for biosynthesis of gold or silver nanoparticles are also reported [24–31]. In comparison with traditional chemical synthesis, biomolecule assisted synthesis of noble metal nanomaterials have a number of advantages to other microorganisms. Since biomolecule assisted synthesis are carried out at room temperature and under aqueous conditions, energy input is reduced and the solvents or agents used are nontoxic factors that minimize environmental damage resulting higher yield of nanoparticles. Thus, the dissimilatory metal-reducing capability can be used for rapid and eco-friendly biosynthesis of metal nanoparticles [32].

In this study, we used cell-free *egg albumin* protein both as a reducing and a stabilizing agent for AuNPs synthesis. At this juncture, we account the egg albumin protein mediated green synthesis of gold nanocatalyst and catalytic application of this gold nanobiocatalyst (AuNBC) in the manufacture of sodium benzoate from benzyl alcohol which is significantly environmental-friendly process, non-toxic, and energy efficient one due to the mild reaction condition and recyclability of catalyst. To the best of our knowledge, no work has been reported on the synthesis of sodium benzoate using AuNBC elsewhere. Hence, in the present investigation, it was proposed to prepare gold nanocatalyst through green route and to apply this gold nanobiocatalyst for the synthesis of sodium benzoate from benzyl alcohol.

2. Materials and methods

All chemicals used are of analytical grade or of the highest purity available. $HAuCl_4{\cdot}3H_2O$, Egg albumin powder and the other pure chemicals and biochemical were purchased from Sigma Aldrich. Working standard solutions were prepared daily in deionised water. Ultrapure Millipore water was used in all AuNPs biosynthesis experiments. UV–vis absorption spectra were acquired on a Jasco V-570. IR spectra were measured with a Bruker Tensor-27. High resolution transmission electron micrograph (HR-TEM) was recorded by JEOL, JEM-2100 (200 kV). ^{1}H NMR was carried out using scanned on 400 MHz, FT-NMR Bruker Avance-400 in $CDCl_3$ (TMS for standard). DLS measurements were performed using Nanotrac (NPA 150/250). pH measurement was made by using model EQ-664 (Equip-tronics). Microwave synthesizer (CEM Discover) was used for the purpose of synthesis. The melting point was determined Shimadzu DSC 60 with a heating rate of 10.0 °C min^{-1}. ESI-Mass spectra were taken on a Shimadzu GCMS-QP 2000A.Gas chromatography (Shimadzu) and HPLC (Chrompack) was used to check the purity.

2.1. Synthesis of gold nanoparticles by protein white egg albumin

Prior to the synthesis of nanoparticles, all the glassware was washed with aqua regia (3:1 HCl–HNO_3) and then thoroughly rinsed with deionised water. Synthesis of gold nano-bio-conjugate (AuNBC) was carried out by microwave synthesizer under specific condition. The synthesis was carried out in a modified (CEM Discover) microwave using single mode and continuous power at 2.45 GHz. The reactions were carried out in sealed reaction vessel containing 3 ml of 0.60 mM $HAuCl_4$ solution, 2 ml white egg albumin protein (2 mg protein/ml) was mixed with 0.2 M sodium phosphate buffer (pH 7.0) with vigorous stirring and was heated at 80 °C at a power up to 50 W for 5 min. The solution changed from pale yellow to pink red to yield protein stabilized AuNPs with particle size of 39 ± 5 nm. On completion of the reaction, AuNBC were separated by centrifugation at 5000 rpm for 30 min. The solid particles were collected and dissolved in deionised water. For catalytic activity, AuNBC suspensions were separated by centrifugation. Pellets were collected, washed with ultra pure water to remove any unreacted gold and finally resuspended in ultra pure water.

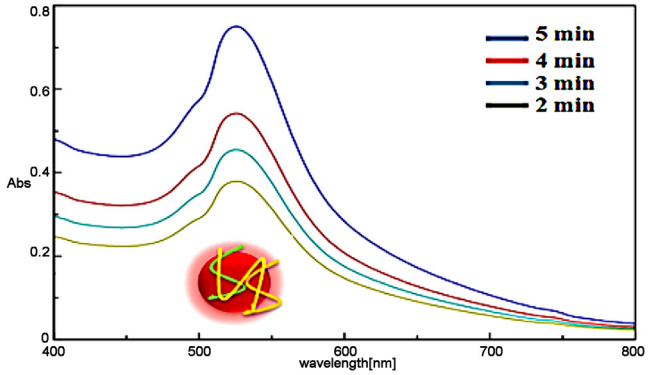

Fig. 1. UV–vis spectra of AuNPs synthesized by protein *egg albumin* at various times under microwave heating (reaction conditions: Temp. – 80 °C, P – 50 W, reaction time – 2–5 min).

2.2. Catalytic activity of AuNBC

The catalytic activity of AuNBC was studied using oxidation of benzyl alcohol as a model system and further it was carried out by microwave synthesizer. In a typical experiment, the reactions were carried out in dry 25 ml microwave reaction open vessel with air condenser equipped with a magnetic stir bar containing, 2 ml benzyl alcohol (1.5 M), 3 ml NaOH (0.1 M), 3.5 ml AuNBC (0.55 mM) and air as the oxidant under ambient pressure, stirred vigorously in a CEM microwave (90 °C, 80 W) for 8 min and kept for cooling. After that the reaction mixture was centrifuged to isolate the solid product and recrystallized with ethanol. White solid of sodium benzoate was obtained with high purity (>99%) checked using GC, HPLC and M.P. 302 °C using DSC experiment (Fig. S2, see ESI). In addition, the aqueous solution was acidified by HCl until the pH value was decreased to 3.0, the mixture was filtered and then white solid of benzoic acid was obtained with purity >99%, M.P. 122 °C and confirmed with GC and DSC respectively (Fig. S2 and S3, see ESI). Further, the remaining AuNBC catalyst was separated from the solid products using centrifugation and was reused.

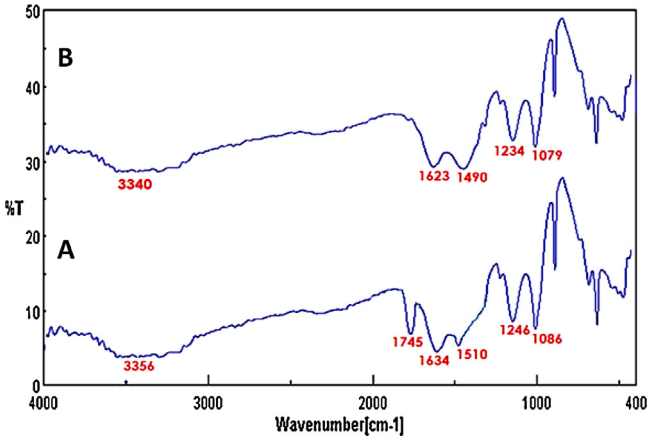

Fig. 2. FT-IR spectra of egg albumin protein before (A) and after (B) interaction with $HAuCl_4$.

3. Results and discussion

The physicochemical properties of the synthesized AuNBC were examined in detail by spectroscopic and microscopic techniques. Gold nanoparticles formation via egg albumin protein was indicated by the associated colour change of the reaction mixture. As the biosynthesis proceeds, the colour changes from light yellow to pale pink within approximately 3 min by microwave and finally to a dark red colour after 5 min. The spectra of the suspensions have a characteristic absorption maximum at 539 nm (Fig. 1), which is attributed to the surface plasmon resonance (SPR) band of the AuNBC. After this time, no further change in the spectrum was observed indicating that the precursors had been consumed. The microwave biosynthesized gold nanoparticles were very stable without obvious aggregation for more than 3 months, which undoubtedly evidence their high stability. This demonstrates that the interactions between Au^0 and the proteins neighbouring the nanoparticles are strong enough to put off aggregation.

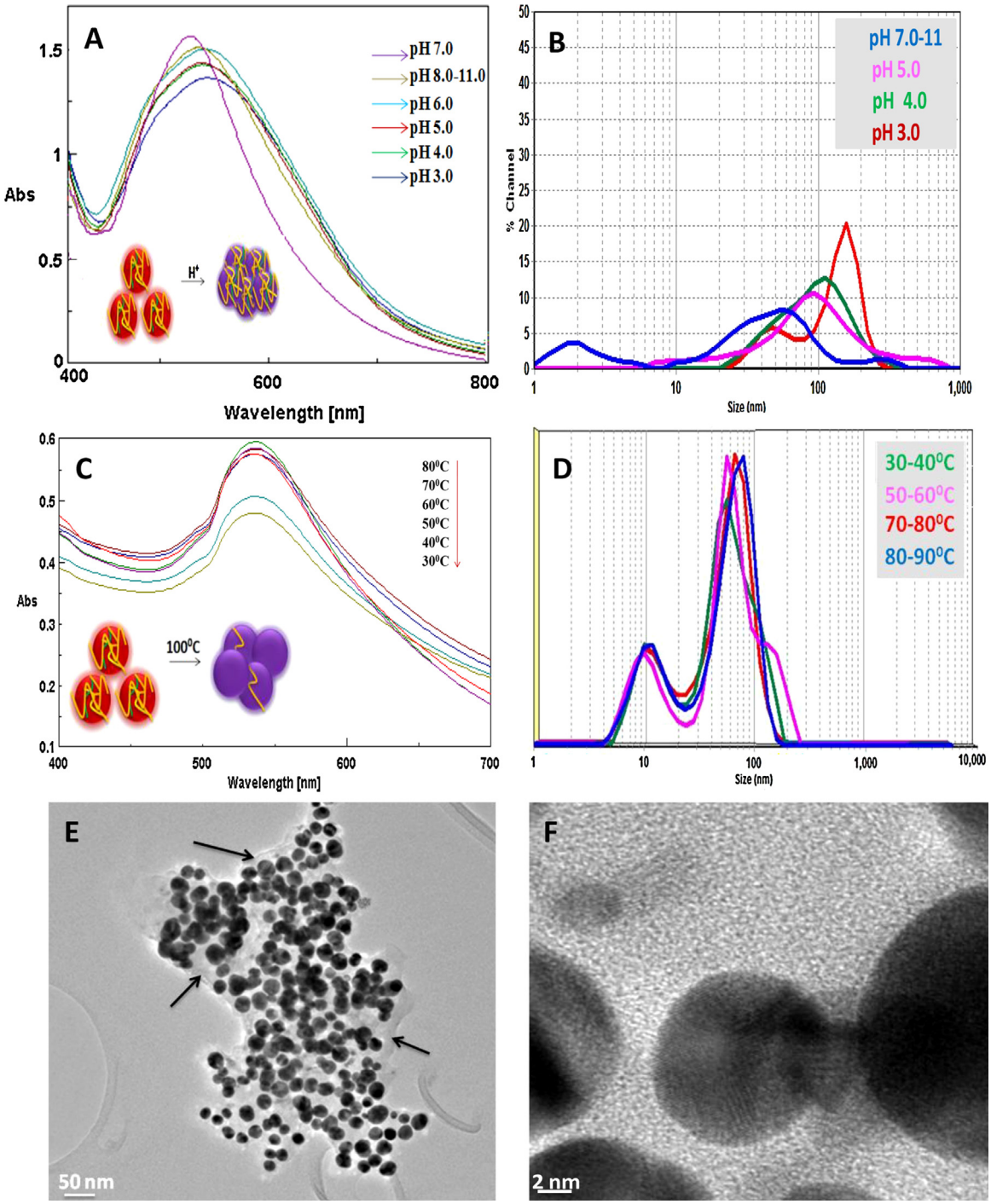

Fig. 3. Physicochemical interaction at AuNBC (A) UV–vis spectra and (B) DLS measurements of AuNBC suspension at different pH values. (C) UV–vis spectra and (D) DLS measurements of AuNBC suspension at different temperatures. (E and F) Low and high resolution TEM images of AuNPs synthesized by *egg albumin protein* (arrow indicates the protein layer).

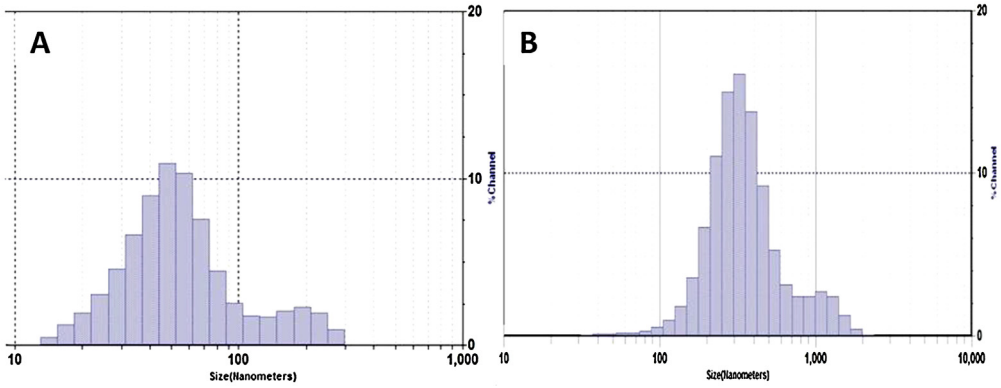

Fig. 4. Dynamic light scattering measurement of (A) as synthesized AuNBC and (B) AuNBC at 100 °C for 45 min (conditions: phosphate buffer (pH 7), Time – 2 min, 3.5 ml 0.55 mM AuNBC).

3.1. FT-IR analysis

The active site of protein involved in reduction of Au ions and AuNBC formation was investigated with Fourier transform infrared (FT-IR) spectroscopy. As is shown in Fig. 2A, the spectra record was carried out in the range of 400–4000 cm^{-1}. The strong peak was assigned at 3340 cm^{-1} (—OH stretch), 2934 cm^{-1} C—H stretching vibrations of methyl, methylene and methoxy groups of the proteins in the egg white extract. The peak located at 1623 cm^{-1} was assigned to the C=O stretching in carboxyl or C=N bending in the amide group, 1490 cm^{-1} of amide II (N—H) bonds of proteins, 1079 cm^{-1} of the C—O bond. The absorption band corresponding to the carboxyl groups disappeared and a new peak appeared at 1745 cm^{-1} on completion of the reduction process, indicating interaction of amino and carboxylate groups of the proteins with gold ions. Shifting of the P—O—C absorption at 1086 cm^{-1} and shifting up to 3396 cm^{-1}, 1634 cm^{-1}, 1510 cm^{-1}, 1246 cm^{-1}, shows phosphoprotein interaction with the AuNPs surface (Fig. 2B). This clearly indicates that carboxyl and amine groups of phosphor proteins are responsible for reduction and subsequent stabilization of AuNPs.

3.2. Effect of pH

The role of the surface charge of the protein on the stability of AuNBC was studied by changing the pH of the AuNBC suspension. The absorbance properties and the size distribution of AuNBC were then measured by UV–vis spectroscopy and DLS analysis, respectively. Fig. 3A shows that the SPR band of the AuNBC changes in the range of pH 3–11. The protein-capped AuNPs were stable at basic, neutral and slightly acidic conditions. However, on decreasing the pH of the suspension below 5.0, the absorbance of the SPR band at 539 nm decreases and at pH < 3.0 another poorly defined SPR band developed at about 583 nm. This SPR band red shifted on decreasing the pH values further. DLS measurements in Fig. 3B show that size of the nanoconjugate also increases on reducing the pH below 5. The average hydrodynamic diameter increased from 39 nm at pH 7.0 to 210 nm at pH 3.0.The pH induced aggregation of the nanoconjugate arises from protonation of protein carboxylate groups, of p$K \sim 5$, with consequent reduction in electrostatic repulsion. Additionally, the formation of intermolecular H-bonding between protonated functional groups of surface-bound protein molecules of different particles could also contribute aggregation. On increasing the pH of an aggregated suspension from 3.0 to 7.0 the SPR band blue-shifted to regain the original wavelength (see ESI, Fig. S1A) at 539 nm. These results suggest that an electrostatic mechanism is the main stabilization factor for AuNBC. Protein mediated nanoparticles synthesis was confirmed through TEM and HRTEM analysis. In Fig. 3E and F, micrographs recorded for sample after 5 min of reaction show that the size of the particles is 39 ± 5 nm. The as-synthesized AuNBC appeared well dispersed without agglomeration which is also confirmed by DLS measurement (Fig. 4A) and TEM analysis (Fig. 5A). The catalytic activity of our synthesized AuNBC shows higher rate constant (18 $mmol^{-1}$ min^{-1}) compared to other nanomaterials [32–40]. This suggests that protein bioconjugation retains most of the catalytic activity of spherical AuNPs providing an proficient green alternative to the conventional synthetic methodologies.

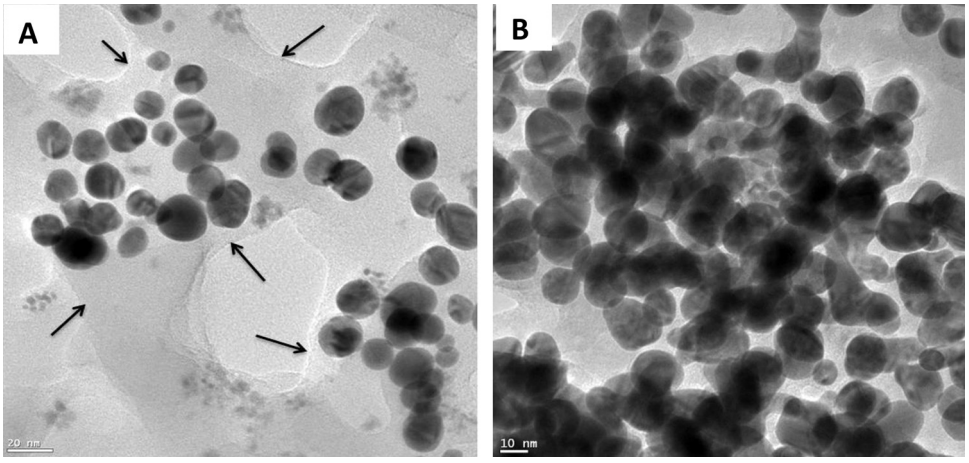

Fig. 5. TEM images of AuNBC (A) arrows indicate protein layer around nanoparticles and (B) at 100 °C for 45 min.

3.3. Effect of temperature on AuNBC and characterization by DLS, TEM, UV–vis spectrophotometry

The effect of temperature on the stability of the AuNBC was studied in the range of 30–90 °C. UV–vis spectroscopy (Fig. 3C) showed that the AuNBC are stable in this temperature range as the absorbance spectrum remains unchanged. DLS measurements also confirmed that AuNBC are colloidally stable within this temperature range. In fact, changing the temperature does not affect either the size or the surface charge (Fig. 3D) of the AuNBC. However, prolonged heating at 100 °C resulted in the agglomeration of nanoconjugate, as indicated by the broadening of the SPR band and also by DLS measurements (Fig. 4B). AuNBC aggregation, following heating at 100 °C for 45 min, was confirmed by TEM (Fig. 5B). As prior stated, it is well known that proteins are denatured at high temperature (see inset in Fig. 3C).

3.4. Oxidation of benzyl alcohol using AuNBC

We examined the activity of the AuNBC for the oxidation of benzyl alcohol using microwave heating under specific conditions (Fig. 6A). The AuNBC was added into the reaction mixture at 30 °C and then heated to 90 °C AuNBC to the reaction mixture. Interestingly, it is found that after 8 min, no benzyl alcohol was detected (Fig. 6B), which means that the benzyl alcohol was completely transformed into sodium benzoate. This conversion and purity has been shown by DSC experiment for melting point (see ESI, Fig. S2), GC and HPLC (see ESI, Fig. S3). The conversion of sodium benzoate has been further characterized with ESI-MS and ^{1}H NMR spectroscopic technique where ESI-MS spectra of sodium benzoate observed peak at $m/z = 145$ and ^{1}H NMR spectra shows the disappearance of proton at ($\delta = 8.63$, OH—; 4.16, CH_2—) of benzyl alcohol which confirmed the formation of sodium benzoate (See ESI, Fig. S4 and S5).

Thus, the conversions of benzyl alcohol are all 100%. Moreover, the as-prepared catalysts can be conveniently recycled with high stability. After the reaction, the catalyst was easily recovered by centrifugation. The best recovered AuNBC could be reused for more than six successive reactions without significant loss of the catalytic activity (Fig. 6C). The TON and TOF were calculated and found to be 2727 and 20454 h^{-1} respectively in required range. Sodium benzoate and benzoic acid can be easily separated out by adjusting the pH from 8.0 to 3.0 spontaneously. The as-obtained white product of sodium benzoate was obtained by simple evaporation of excess water and crystallization, while the as-obtained benzoic acid was collected by filtration, washed three times with deionized water, and dried in air. Finally, we have benchmarked the catalytic activity of the synthesized AuNBC with other nanomaterials. In order to compare the catalytic activity of the AuNBC to other AuNPs prepared by chemical methods. We found the rate constant values of AuNBC are much higher than those of reported various chemically prepared AuNPs (Table 1). We also performed the experiment to get

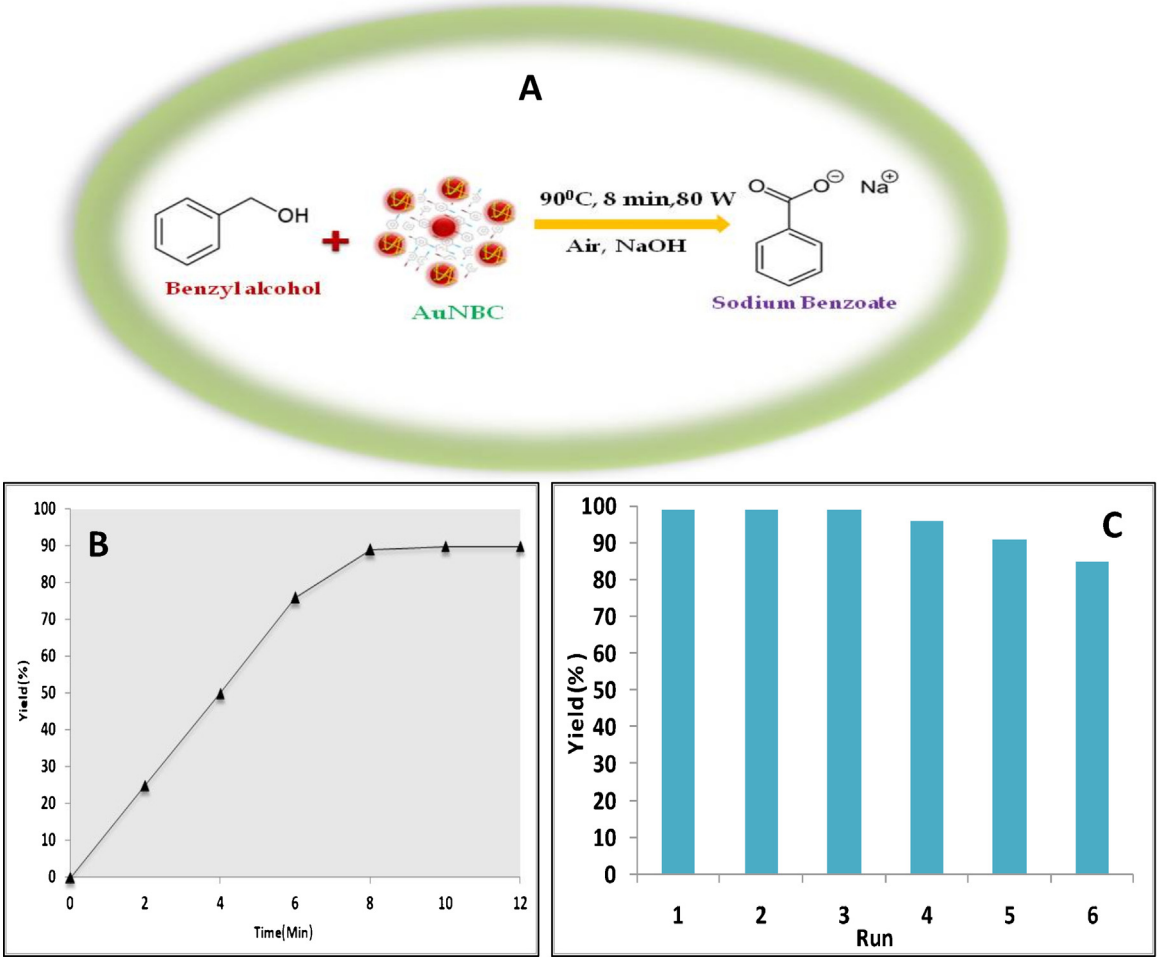

Fig. 6. Catalytic activity of AuNBC (A) benzyl alcohol oxidation under specific microwave heating. (B) Time course of the benzyl alcohol oxidation catalyzed by AuNBC. (C) Recyclability of AuNBC for synthesis of sodium benzoate (reaction conditions: Temp. – 90 °C, Time 8 min, P 80 W, 2 ml benzyl alcohol, 2 ml 0.1 M NaOH, 3.5 ml 0.55 mM AuNBC).

Table 1
Comparison of protein mediated gold nanobiocatalyst (AuNBC) with chemically synthesized AuNPs with rate constants.

Composition	Size	Rate constant
Seed-mediated synthesized AuNPs [37]	5–10 nm	9.6×10^{-1} mmol^{-1} s^{-1}
Gold nanoclusters stabilized by vinyl ether star polymers [38]	4–5 nm	6.2×10^{-2} mmol^{-1} s^{-1}
Silica-coated magnetite nanoparticles [39]	5.9 nm	5.8×10^{-1} mmol^{-1} s^{-1}
Au on nanosized NiO [40]	2–10 nm	4.30×10^{-1} mmol^{-1} s^{-1}
AuAg/TiO_2 [11]	10 nm	3.6×10^{-3} mmol^{-1} s^{-1}
AuNBC (presented study)	30–40 nm	18–26 mmol^{-1} min^{-1}

Table 2
Comparison of effect on alcohol oxidation with or without protein mediated gold nanobiocatalyst (AuNBC) under with or without microwave condition.

Effect on alcohol oxidation	Yield (%)
With microwave using AuNBC	<95%
Without microwave using AuNBC	>56%
Only with microwave	>8%

effect on alcohol oxidation with or without protein mediated gold nanobiocatalyst (AuNBC) under with or without microwave condition (Table 2) by comparing the considerable conversion, where with microwave using AuNBC gives the selectively sodium benzoate from benzyl alcohol with high yield (>95%).

4. Conclusion

In summary, we described a novel efficient protein egg albumin synthesized AuNBC with high stability for simple one-pot, green chemical methodology of sodium benzoate and benzoic acid from the green oxidation of benzyl alcohol using air as the oxidant under microwave heating with high yield. The catalytic activities of these AuNBC are significantly advanced which acquired more accessibility, stability and recyclability.

Supporting information

Supplementary materials of synthetic procedure associated with this article can be found, in the online version.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.08.022.

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