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AuPd bimetallic nanoparticles: Single step biofabrication, structural characterization and catalytic activity

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ABSTRACT

The room temperature biofabrication of AuPd-NPs using aqueous leaf extract of *Delonix regia* was reported. The nature, morphology and size of nanoparticles were analyzed using UV–visible spectroscopy, DLS, XRD, TEM and EDX techniques. Nearly spherical crystalline AuPd-NPs were synthesized within size range of 3–31 nm. Appearance of broad intense reflection at 39.29° position, nearer to the mean of Pd (40.26°) and Au (38.37°) reflections suggested fabrication of AuPd-NPs. Furthermore, as-formed AuPd-NPs showed recyclable catalytic efficiency towards the reduction of 3-nitroaniline and it remained at about 93% even after recycling for 5 consecutive cycles in terms of normalized activity parameter.

Introduction

Fabrication of bimetallic nanoparticles (NPs) is of recent research interest due to their bi-functional and synergistic properties [1,2]. As far as the technological and scientific aspect is concerned, the bimetallic NPs exhibit enhanced optical, catalytic, chemical, and biological properties compared to their monometallic counterparts [1,3,4]. Generally, bimetallic NPs are fabricated through chemical [2], electrochemical [5], thermolysis [6], sonochemical [7], and radiation-induced methods [8]. However, in spite of their extensive use, these techniques not only utilize toxic chemical reducing agents but also require expensive experimental setup. In addition, sometimes these methods face the problem of phase separation at atomic level, which leads to the formation of core–shell NPs [9]. Thus, the development of reliable eco-benign and economical methods for fabrication of alloy bimetallic NPs remains stills a challenge. Strategies to address rising environmental concerns through development of cost-effective, sustainable techniques by use of eco-friendly solvents and biodegradable polymers are the need of the day. Recently, intense research is focussed towards the biofabrication of NPs by exploiting natural resources viz. plants and microorganisms. This method is suitable for fabrication of biocompatible NPs for pharmaceutical and biomedical usage. The study on biofabrication of bimetallic NPs is less reported in the literature. So far very few studies are available for biofabrication of alloy type bimetallic NPs such as AuAg [10], AgPd [11], and AuPd [3].

In previous studies, our research group identified and fabricated monometallic NPs of different metals such as Au [12], Pd [13], Se [14], Pt [15], Ag [16], and SnO_2 [17] using different biological resources in aqueous medium. Here, for the first time, biofabrication of bimetallic alloy AuPd-NPs is carried out using aqueous leaf extract of *Delonix regia* (*D. regia*). Metal reducing potential of *D. regia* is already proved earlier for economical and eco-benign fabrication of monometallic palladium NPs [13]. Metal reducing potential of one other plant species of same genus is also reported earlier for fabrication of silver NPs [18]. Nature of biofabricated bimetallic NPs is evaluated using various characterization techniques viz. UV–visible spectroscopy, XRD, TEM, EDX coupled with SEM, DLS, and FTIR.

Nitro-aromatic compounds are, on average 500-times more toxic than their corresponding amino derivatives [19]. Degradation of these organic compounds is very difficult. However, the widespread use in the manufacture of drugs, rubber chemicals, explosives, insecticides and dyes leads to their continuous release into the environment. So discharge of nitro-aromatic compounds in water and environment is the matter of major concern for environment pollution nowadays. Application of biofabricated bimetallic NPs for the reduction of these nitro-aromatic compounds to less toxic amino analogues can pave a way for environmental remediation. The bimetallic NPs shows catalytic

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ability for a variety of reactions with superior activity and durability as compared to their monometallic counterparts [1,2]. In this study authors evaluated the catalytic potential of biofabricated NPs for the reduction of toxic nitro-organic pollutant 3-nitroaniline (3-NA). Kinetic evaluation of 3-NA reduction was carried out using different concentrations of AuPd-NPs (500–2000 μg) and at different reaction temperatures (10–50 °C). Recyclability study of AuPd-NPs catalysts was also carried out in a view of industrial importance.

Materials and methods

Materials

Gold-III-chloride–trihydrate ($HAuCl_4{\cdot}3H_2O$; 99%), palladium-II-chloride ($PdCl_2$; 99%), sodium borohydride ($NaBH_4$; 98%), and 3-NA ($C_6H_6N_2O_2$; 98%) were bought from HiMedia Laboratories Pvt. Ltd. Mumbai, India. All chemicals used for the study were of analytical grade and double-distilled deionized water was used for experiment. Leaves of *D. regia* were collected from the campus of Sardar Vallabhbhai National Institute of Technology, Surat, Gujarat, India.

Preparation of aqueous leaf extracts of D. regia

D. regia leaf extract was prepared according to the method reported earlier in literature [16]. 30 g of the fresh leaves of *D. regia* was heated with 120 mL of double-distilled water at 60 °C for 10 min. After that, the solution was filtered with Whatman filter paper no. 40. Filtrate was obtained as a clean light greenish-brown solution. This filtrate was used further for the biofabrication of bimetallic AuPd-NPs.

Biofabrication of AuPd-NPs

Biofabrication of bimetallic AuPd-NPs was initiated by the addition of a well-mixed aqueous solution (900 mL) of $HAuCl_4{\cdot}3H_2O$ (0.5×10^{-3} M) and $PdCl_2$ (0.5×10^{-3} M) to 100 mL of aqueous solution of *D. regia* leaf extract. This solution was kept in shaker at 500 rotation per minute (RPM) for 3 h at room temperature (RT) (28 ± 2 °C). Spontaneous reduction of salt solution was resulted in the fabrication of bimetallic AuPd-NPs. Monometallic NPs were also prepared for comparison purpose. Monometallic NPs were prepared by substituting the mixture of aqueous $HAuCl_4{\cdot}3H_2O$/$PdCl_2$ solution by individual salt solution of $HAuCl_4{\cdot}3H_2O$ and $PdCl_2$ in two separate experiments.

Quantification of total phenolic acid (TPA), total flavonoids (TF) and total protein (TP) in D. regia *leaf extract before and after bioreduction of salt solution ($HAuCl_4{\cdot}3H_2O$:$PdCl_2$)*

TPA, TF and TP contents of *D. regia* leaf extract before and after bioreduction of salt solution ($HAuCl_4{\cdot}3H_2O$:$PdCl_2$) was measured using three different colorimetric assays (i.e. Folin-Ciocalteu's colorimetric assay for TPA; aluminium chloride colorimetric assay for TF; Bradford protein assay for TP) following Dauthal and Mukhopadhyay [13]. Quantification of TPA, TF and TP was done on the basis of standard curve of gallic acid, quercetin and bovine serum albumin respectively. Results expressed in g of gallic acid equivalent per 100 g fresh weight (g GAE/100 g fw), g of quercetin equivalent per 100 g fresh weight (g QE/100 g fw) and g of bovine serum albumin equivalent per 100 g fresh weight (g BSAE/100 g fw).

Catalytic reduction of 3-NA using biofabricated AuPd-NPs

In a typical experiment, 3 mL of 3-NA (0.5×10^{-3} M) was mixed with aqueous solution of 0.12 mL $NaBH_4$ (1.0 M) in glass vial. 1 mg of AuPd-NPs was then added to above reaction mixtures with constant stirring at RT. UV–visible absorption spectra of reaction mixture were measured at every 1 min interval to observe the change in the reaction mixture. Blank reaction was also carried out for the reduction of 3-NA in the absence of catalyst. Catalyst concentration and reaction temperature dependent catalytic reduction were also carried out for kinetic evaluation of catalytic reduction. Furthermore, recyclability of biofabricated AuPd-NPs was tested for 5 consecutive cycles of catalytic reduction of 3-NA. To judge the recyclability of catalyst, AuPd-NPs were recovered from the reaction mixture by centrifugation at 20,000 RPM for 10 min, followed by washing with distilled water. Centrifuged AuPd-NPs were then dried in an oven at 60 °C for 2 h. Recycled catalytic used further for next catalytic run using same procedure. Catalytic potential of monometallic Au-NPs and Pd-NPs was also evaluated using above mentioned procedure.

Characterization

Absorbance behaviour of AuPd-NPs was recorded by UV–visible spectrophotometer (DR 5000, HACH, USA). *Z*-average and ζ potential distribution of the colloidal AuPd-NPs were determined by DLS (Zetasizer Nano ZS90, Malvern, UK). Size, morphology and selected area electron diffraction (SAED) pattern of biofabricated AuPd-NPs were analyzed using TEM (CM-200, Philips, UK). The composition of biofabricated NPs was identified by EDX (INCA X-sight, Oxford Instruments, UK) coupled with SEM (JSM-6380LV, JEOL, Japan). Structure of AuPd-NPs was determined by XRD (X'Pert Pro, PANalytical, Holland) equipped with Cu Kα radiation (45 kV, 35 mA). Identification of functional group of leaf extract responsible for metal ions reduction and stabilization of NPs was done by FTIR (Magna-550, Nicolet, USA).

Results and discussion

UV–visible analysis

UV–visible analysis was carried out to compare the absorbance behaviour of bimetallic NPs with individual monometallic NPs (Au-NPs and Pd-NPs) and also with their physical mixture (Fig. 1). UV–visible analysis of aqueous $HAuCl_4{\cdot}3H_2O$ salt solution initially showed absorption peak at 287 nm indicating the existence of Au^{3+} ions. Similarly $PdCl_2$ salt solution showed a strong absorption band at around 300 nm and a shoulder at 415 nm indicating the existence of Pd^{2+} ions in the mixture [13]. These peaks were due to charge transfer between the metal ions and corresponding ligands

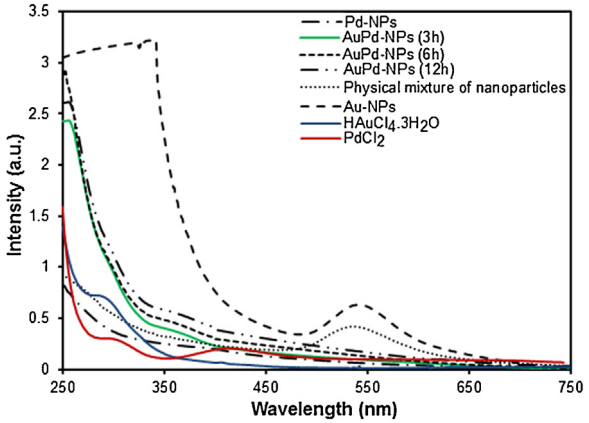

Fig. 1. UV–visible spectra of $HAuCl_4{\cdot}3H_2O$, $PdCl_2$, pure Au-NPs, pure Pd-NPs, physical mixture of monometallic NPs and bimetallic AuPd-NPs at 3 h, 6 h and 12 h of reaction time.