

Antibacterial activity of Ag–Au alloy NPs and chemical sensor property of Au NPs synthesized by dextran

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ABSTRACT

Gold and silver–gold alloy nanoparticles with mean diameter of 10 nm and narrow size distribution were prepared by reduction of the correspondent metal precursors using aqueous dextran solution which acts as both a reducing and capping agent. The formation of nanoparticles was characterized by UV–vis spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD) and dynamic light scattering (DLS). The silver and gold nanoparticles exhibited absorption maxima at 425 and 551 nm respectively; while for the bimetallic Ag–Au alloy appeared 520 nm in between them. TEM images showed monodispersed particles in the range of 8–10 nm. The crystallinity of the nanoparticles was assured by XRD analysis. DLS data gave particle size distribution. The dextran stabilized Au nanoparticles used as a colorimetric sensor for detection and estimation of pesticide present in water. The dextran stabilized Ag–Au alloy nanoparticles exhibited interesting antimicrobial activity against bacteria at micromolar concentrations.

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1. Introduction

The particles having a diameter of 1–100 nm range can be defined as nanoparticles. The study of particles of nanoscale dimensions has drawn much attention due to the size-dependent novel properties. Nanoparticles have received a vast attention and provided a lot of opportunities of new applications to the researchers in many areas. Both nanoscience and nanotechnology has gained tremendous importance due to their unique and remarkable properties, such as electronic, electric, optic, catalytic, mechanical, heat transfer, sensor, conductivity, antimicrobial, etc. (Devi, Pal, & Shah, 2007; Cha, Kang, Kim, & Lee, 2007). These properties can be used for the advancement of modern technologies. Metal nanoparticles are typically utilized in industry and many applied fields (Silvert & Tekaiia-Elhissen, 1995; Carotenuto, Nicolais, & Pepe, 2000; Jang et al., 2003). In accordance with the demands of industry, a variety of synthetic approaches have been used to synthesize

these types of nanoparticles. The typically classified methods for preparing nanoparticles are chemical reduction (He, Qian, Yin, & Zhu, 2002), photochemical reduction (Kohon, Kondow, Maluné, & Takeda, 2000; Hunng et al., 1996), reverse micelles process (Liu, Xie, & Ye, 2006; Giorgio, Maillard, & Pileni, 2002), microwave dielectric heating reduction (Dave, Kapoor, Mukherjee, & Patel, 2005), ultrasonic irradiation (Aruna, Gedanken, Jeevanandam, Koltypin, & Salkar, 1999), radiolysis (Belloni, Lampre, Mostafavi, & Soroushian, 2005), solvothermalysis (Banaś, Starowicz, & Stypuła, 2006), and green synthesis of metal salts (Mollick et al., 2012). The prepared nanoparticles using such route must have good dispersibility and thermal stability which are considered to be very important factors for industrial applications. High cost, low yield of products and the controlling of size are major difficulties in the sol–gel and micro-emulsion method (Cui, Dong, Li, & Wang, 2001; Bassner & Klingenberg, 1998; Patakfalvi & Dékány, 2002). Due to the deterioration of their chemical and physical properties, the nanoparticles get aggregated easily even when they are stored at room temperature. Utilization of reducing cum protecting molecules or organic capping molecules to the as synthesized nanoparticles is the significant synthetic approach of stable nanoparticles synthesis without aggregation problem (Murphy et al., 2005; Hunt, Ohde, & Wai,

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2001; Bandow, Maeda, Nagata, & Okitsu, 1996; Gao, Lu, & Zhao, 2003). Polymers are often employed as templates or stabilizers to provide the formed metallic and bimetallic nanoparticles with excellent stability and desirable properties for various applications (Li et al., 2007; Ballauff, Drechsler, Lu, & Mei, 2006; Hu, Liu, Wu, & Zhang, 2012; Yuan et al., 2012; He, Li, & Li, 2009). Amongst the widely used polymers, polyamidoamine, dextran are synthetic macromolecules with well controllable particle size, inner cavity and surface functional groups (Fréchet & Tomalia, 2001; Trollsås & Hedrick, 1998). These unique structural characteristics make them ideal templates or stabilizers to form many dendrimer-based nanocomposites. The polymer-entrapped metal nanoparticles (PENPs) with smaller core size can be synthesized via the chemical reduction method, whereas polymer-stabilized metal nanoparticles (PSNPs) with a larger metal size are able to form by the slow reduction method. The polymer templating or stabilization approaches have been utilized to create Ag PENPs (Baker, Lee, & Shi, 2008), Ag PSNPs (Liu et al., 2010), Au PSNPs (Baker, Chen, Shi, Van Antwerp, & Wang, 2009), Au PENPs (Wang et al., 2011; Peng et al., 2012), Au–Ag alloy PENPs or PSNPs or other inorganic nanoparticles (Liu et al., 2012).

The management of microbial infections constitutes a serious concern of modern societies, where the appearance and development of resistance to conventional antibiotics are a major healthcare issue. The development of novel antimicrobials is, therefore, absolutely mandatory for preventing and controlling microbial infections in the future. The antimicrobial properties of silver have been known since ancient times, and in the last few years much attention has been given to the antimicrobial effect of silver nanoparticles. Moreover, several salts of silver and their derivatives are commercially manufactured as antimicrobial agents (Daima, Jain, Kachhwaha, & Kothari, 2009; Sondi & Salopek-Sondi, 2004; Lin, Sharma, & Yngard, 2009; Saha et al., 2010; Acharya, Chattopadhyay, Patra, Sarkar, & Saha, 2011). Moreover, several salts of gold and their derivatives are also commercially manufactured as antimicrobial agents (Krutyakov, Kudrynskiy, Lisichkin, & Olenin, 2008; Hernández-Sierra et al., 2008). In small concentrations, both gold and silver are safe for human cells, but lethal for bacteria and viruses. Reduction of the particle size of the materials is an efficient and reliable tool for improving their biocompatibility that can be achieved using nanotechnology. So now-a-days, the use of silver and gold alloy as an antimicrobial agent was developed (Baptista, Santos, & Queiroz, 2012) which gave us a promising approach in the field of nanobiotechnology. Further polymer coated nanoparticles were tested against different bacterial species to evaluate their antimicrobial efficacy. The antibacterial activities of silver nanoparticles are well established and several mechanisms for their bactericidal effects have been proposed (Maity et al., 2012).

In this context, we have proposed a single-step method for rapid preparation of Ag–Au alloy and Au nanoparticles by using dextran as a reductive and protective agent to achieve size controllable nanoparticles, in order to attain good stability. Although few reports are available on the antimicrobial effects of alloy nanoparticles, we have studied the antimicrobial properties of the dextran stabilized Ag–Au alloy nanoparticles and found a significant effect as bactericidal agent against five bacteria. The dextran stabilized Au nanoparticles have been used as colorimetric sensor for detection and estimation of pesticide present in water.

2. Materials and methods

2.1. Materials

Silver nitrate (AgNO_3 , Merck, Mumbai, India) and Tetrachloroauric (III) acid (HAuCl_4 , Sigma–Aldrich, Steinheim, Germany)

were used as the metal precursor to prepare the Ag, Au, Ag–Au nanoparticles. Sodium hydroxide (NaOH , Merck, Mumbai, India) was used to enhance the reaction rate of silver nanoparticles formation. Dextran T40 (Pharmacia, Sweden) was used as a reducing agent and stabilizing agent to prevent aggregation of nanoparticles. All the chemicals were used of analytical grade and used without any further purification. Triple distilled water was used throughout the total experiments.

2.2. Preparatory method

All glassware was cleaned with chromic acid and then tap water in a bath. The cleaned glassware was rinsed first thoroughly with triple distilled water and then acetone prior to use. A stock solution of 5% dextran was prepared by dissolving the dextran in triple distilled water. Silver nitrate solution (0.001 M) was prepared by adding AgNO_3 in triple distilled water. Then, the silver nitrate solution was mixed with the dextran solution (1:9) followed by the addition of 0.4 ml of a very diluted solution of sodium hydroxide (0.001 M) at room temperature. The transparent colorless solution was converted to the characteristic pale yellow color, indicating the formation of silver nanoparticles. Tetrachloroauric acid solution (0.001 M) was prepared by adding HAuCl_4 in triple distilled water. Then, the tetrachloroauric acid solution was mixed with dextran solution (1:9) at room temperature. The transparent colorless solution was converted to the characteristic violet color, indicating the formation of gold nanoparticles. The Ag–Au bimetallic (1:1) nanoparticles were prepared by mixing an aqueous tetrachloroauric acid solution with pre-prepared Ag nanoparticles at room temperature. The pale yellow colored solution was converted to the characteristic deep violet color, indicating the formation of Ag–Au bimetallic nanoparticles.

2.3. Assay for antimicrobial activity of silver-gold nanoparticles against microorganisms

The silver–gold alloy nanoparticles in sterilized distilled water were tested for their antibacterial activity by the agar diffusion method. Four bacterial strains, *Bacillus subtilis* [MTCC 736], *Bacillus cereus* [MTCC 306], *Escherichia coli* [MTCC 68] and *Pseudomonas aeruginosa* [MTCC 8158] were used for this analysis. These bacteria were grown on liquid nutrient agar media (HiMedia Laboratories Pvt. Ltd., Mumbai, India) for 24 h prior to the experiment, and were seeded in agar plates by the pour plate technique. One cavity was made using a cork borer (10 mm diameter) at the center of the agar plate and were filled with the silver gold alloy nanoparticle solution (0.1 mg/ml) and then incubated at 37 °C for 24 h. Simultaneously; the control sets (only sterile water and the plant extract) were maintained at the same experimental condition. Every experiment was repeated three times.

2.4. Estimation of methyl parathion

Ten milliliters of the as-prepared dextran coated Au nanoparticles were used to detect and estimate the methyl parathion. Five hundred microliters of a solution containing different concentrations of methyl parathion was added to the above Au nanoparticles sol. The concentration of methyl parathion in the Au nanoparticles solution was varied from 100 to 500 ppm. The mixture was heated at 80 °C temperature for 5 min with continuous stirring. The deep reddish-violet color changed into deep yellowish. The colour change from deep reddish-violet to deep yellowish was probably due to the catalytic hydrolysis reaction of methyl parathion in the presence of Au nanoparticles which produced 4-nitrophenolate and sodium di-O-methyl thiophosphonate. Sodium di-O-methyl thiophosphonate helped in aggregation of gold nanoparticles that was

the reason behind colour change of the sol. The intensity of the yellowish colour gradually increased with the increase of methyl parathion.

2.5. Instrumentation and measurements

The formation of gold nanoparticles and silver–gold alloy nanoparticles were characterized by Ultraviolet–visible (UV–vis) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) and dynamic light scattering (DLS).

2.6. UV–vis absorption spectroscopy

Silver and gold are inorganic species, while showing characteristic absorption that can be identified qualitatively by UV–vis absorption spectroscopy. UV–vis spectra were recorded in the range between 200 and 700 nm using a Shimadzu UV 1800 spectrophotometer. The absorption of the prepared colloidal solutions was obtained by measuring in a quartz cuvette with 1 cm optical path length.

2.7. TEM

The size, shape, morphology and particle distribution can be recognized by Transmission electron microscopy. The images of transmission electron microscopy (TEM) were collected using TEM, JEOL JEM 2010 (Japan) running at 100 kV. The liquid sample was sonicated very well; a 5 μ l aliquot is placed on a hydrophilic carbon coated copper grid and the excess solution was removed by tissue paper and allowed to air dry at room temperature overnight.

2.8. XRD

The crystallinity and phase composition of metallic and bimetallic nanoparticles were investigated using PANalytical, XPERT-PRO diffractometer (Netherlands) operated at 40 kV, 30 mA, with graphite monochromatized Cu K_{α} radiation of wavelength $\lambda = 1.5406 \text{ \AA}$ and nickel filter. The XRD pattern was recorded in the 2θ range from 0° to 90° at scanning step of every one unit.

2.9. DLS

Dynamic light scattering (also known as photon correlation spectroscopy or quasi-elastic light scattering) is a technique in physics which is used to determine the size distribution profile of small particles in suspension. Light scattering technique was performed in Malvern Zetasizer ZS 90 with He–Ne laser.

3. Results and discussion

Dextran polysaccharide (also well known as polyglucin) is a water soluble linear biopolymer composed of repeated monomeric glucose units with a predominance of 1,6- α -D-glucopyranosyl linkages. It has wide range of applications in food, medical related areas and biological functions. An implementation of dextran as a protecting agent for the synthesis of metal nanoparticles was reported in various works. In our synthetic procedure, this polysaccharide has a dual role as a reducing and stabilizing agent in the synthesis of metallic (Au) and bimetallic (Ag–Au) alloy nanoparticles in aqueous solution at room temperature.

3.1. UV–vis spectroscopic analysis

UV–vis absorption spectrometry is used to characterize the formed Au nanoparticles and Ag–Au alloy nanoparticles. The typical surface plasmon resonance (SPR) band at 425 and 551 nm

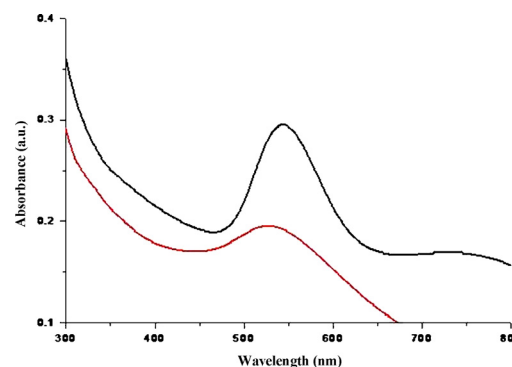


Fig. 1. UV–vis spectroscopy of Au (black) and Ag–Au alloy (red) nanoparticles.

indicates the formation of monometallic Ag and Au nanoparticles. The absorption maximum of bimetallic Ag–Au alloy nanoparticles is observed at 520 nm (Fig. 1). It is also observed that only one absorbance peak is obtained for the bimetallic nanoparticle solution. The bimetallic Ag–Au alloy nanoparticles formation is confirmed from the fact that the absorption spectra shows only one plasmon band instead of two individual bands for Ag and Au monometallic nanoparticles (Ahmad, Khan, Kumar, Sastry, & Senapati, 2005; Mendoza-Álvarez, Nolasco-Hernández, Pal, Pescador-Rojas, & Sánchez-Ramírez, 2008). If the particles are not alloy particles then the nanoparticles give rise to two characteristics surface plasmon absorption bands due to separate gold and silver nanoparticles. This absorption spectroscopic data suggests that the simultaneous reduction of Ag^+ and Au^{3+} ions in aqueous dextran solution produces the bimetallic alloy nanoparticles. This was further confirmed by the TEM images described below.

3.2. TEM studies

While the absorption spectroscopy provide strong evidence of the formation of nanoparticles and their growth kinetics, the TEM study helps to elaborate the morphology of size and shape of the resultant nanoparticles. The typical TEM images of Au monometallic and bimetallic Ag–Au alloy nanoparticles are shown in Fig. 2 and Fig. 3 respectively. It is clear from the TEM images that the gold nanoparticles are spherical in shape and the size is 8–10 nm. The sizes of silver–gold alloy nanoparticles are larger. The bigger size of the bimetallic nanoparticles compared to the monometallic nanoparticles due to the larger space is needed for the crystal structure through complex formation. The lattice fringes in the TEM images and the typical selected area electron diffraction (SAED) pattern with circular rings corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes show that the Au monometallic and Ag–Au bimetallic alloy nanoparticles obtained are highly crystalline in nature. These results are in strong agreement with the UV–vis spectroscopic data discussed previously.

3.3. EDX measurement

The elemental analysis of monometallic and bimetallic alloy nanoparticles is performed using the energy dispersive X-ray (EDX) analysis on the TEM. The EDX spectrum of the Au and Ag–Au alloy nanoparticles prepared by dextran as a reducing and protecting agent are shown in Figure S1. The peaks are around 2.2 keV for Au nanoparticles and 2.2 and 3.1 keV for Ag–Au alloy nanoparticles due to the corresponding binding energy of Au and Ag elements, respectively. Also, the peak near 1.0 and 8.9 keV belong to C, and Cu is observed and ignored. The carbon and copper peaks response is due to the TEM holding grid. Obviously, no other peak is detected throughout the scanning range of binding energies. This

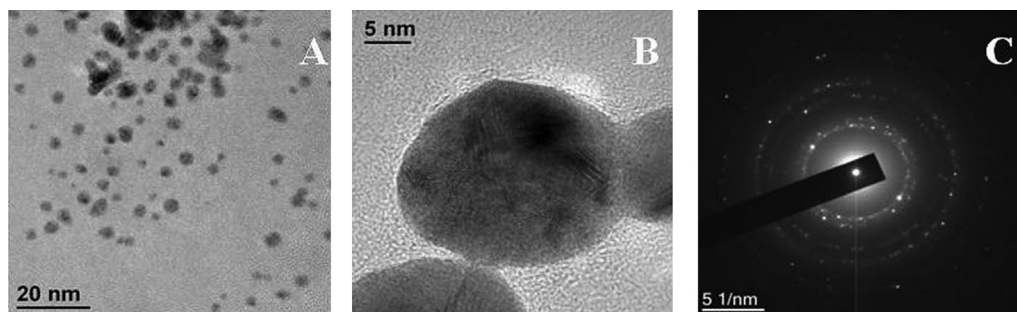


Fig. 2. TEM images of Au nanoparticles: (A) widely dispersed; (B) single particle; and (C) SAED pattern.

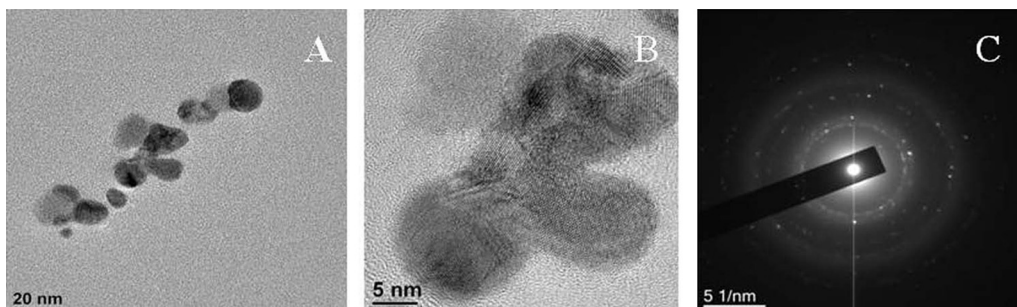


Fig. 3. TEM images of Ag–Au alloy nanoparticles: (A) widely dispersed; (B) single particle; and (C) SAED pattern.

result reveals that the as-synthesized Au and Ag–Au alloy nanoparticles are highly pure.

3.4. XRD studies

The crystallinity and crystal structure of Au nanoparticles and Ag–Au alloy nanoparticles are examined by XRD analysis. The XRD pattern of the nanoscale Au and Ag–Au alloy particles are shown in Fig. 4. The characteristic peaks at 2θ degrees of 38.2607, 44.3657, 64.7927, 77.9267 and 81.7877° are assigned to the reflections of corresponding (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes, respectively of Au nanoparticles. The characteristic peaks at 2θ degrees of 32.2457, 46.3457, 64.5287, 76.8707 and 85.7147° are assigned to the reflections of corresponding (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes, respectively of Ag–Au alloy nanoparticles. This observation confirms that the as-synthesized Au and Ag–Au alloy nanoparticles are in the face centered cubic (fcc) structure. In addition to the Bragg peaks representative of fcc silver nanoparticles, additional and unassigned peaks are also observed suggesting that the crystallization of reducing and capping agent occurs on the surface of the nanoparticles (Bankura et al., 2012). The Ag and Au have very similar lattice parameters: the lattice constants are

4.0862 Å (Ag) and 4.07825 Å (Au) (Alqudami, Annapoorni, Govind & Shivaprasad, 2008). XRD patterns show smaller difference for the Au and Ag–Au alloy nanoparticles samples due to the close lattice constants of Ag and Au.

3.5. DLS study

The narrow particle size distribution of nanoparticles was characterized by DLS study. Population of nanoparticles was observed with an average size of 10–12 nm of Au and Ag–Au alloy nanoparticles respectively in Figure S2. The population of particles with a larger diameter may result from the presence of free dextran chains or containing aggregated metal nanoparticles embedded in the dextran matrix (Domingos, Eising, Fort, & Signori, 2011). Although the peaks corresponding to the large scale structures are the most intense, the number of aggregates is very low, as confirmed by their negligible presence in the TEM images. It may be noticed that the size of dextran stabilized Ag–Au alloy nanoparticles measured by TEM is smaller than that measured by DLS. Such types of anomaly in size are due to the sample preparation, because TEM imaged the dry particles whereas DLS detected the hydrated ones due to polymer in aqueous solutions (Liu et al., 2013).

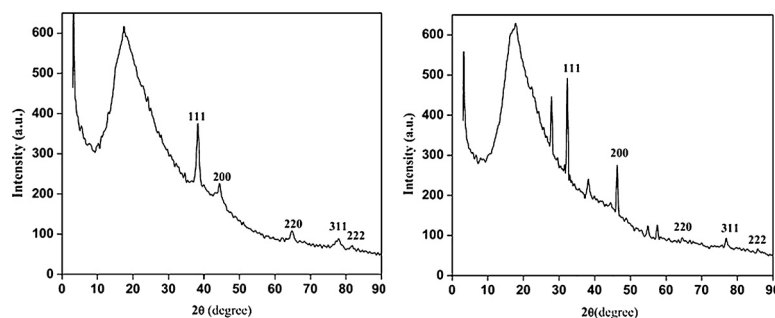


Fig. 4. XRD patterns of (A) Au nanoparticles and (B) Ag–Au alloy nanoparticles.

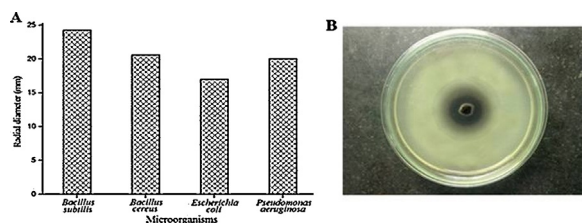


Fig. 5. (A) Radial diameter of inhibitory zone by silver–gold alloy nanoparticles (0.1 mg/ml) against different Microorganisms; and (B) Digital photograph of the antibacterial activity of silver–gold alloy nanoparticles showed against *Bacillus subtilis* in petri plates by cup plate method.

3.6. Antimicrobial activity against microorganism

The silver–gold alloy nanoparticle solution exhibited excellent antibacterial activity against the bacteria, *Bacillus subtilis*, *Bacillus cereus*, *Escherichia coli* and *Pseudomonas aeruginosa* by showing the clearing zones around the holes with bacteria growth on petri plates by the cup plate method (Mondal et al., 2013). The radial diameter of the inhibiting zones of *Bacillus subtilis*, *Bacillus cereus*, *Escherichia coli* and *Pseudomonas aeruginosa* are 24, 21, 17, and 20 mm, respectively is due to the silver–gold alloy nanoparticle. At the same time the control sets did not show any inhibition zone against these bacteria (data not shown). Silver–gold alloy nanoparticles at the concentration of 0.1 mg/ml showed a range of specificity towards its antimicrobial activity (Fig. 5A). These nanoparticles reveal higher antibacterial activity against *Bacillus subtilis* (Fig. 5B), and *Bacillus cereus* whereas intermediate reactivity is revealed against *Escherichia coli*, and *Pseudomonas aeruginosa*. The antibacterial activity of silver–gold alloy nanoparticle sample is better than Au nanoparticles reported earlier (Kaittanis, Nath, Perez, & Tinkham, 2008) but not as good as that of dextran coated silver nanoparticles (Bankura et al., 2012). Results are mean of three separate experiments, each in triplicate. This design of a silver–gold alloy nanoparticle synthesis has great potential due to its antibacterial activity.

3.7. Colorimetric sensor property studies

The pesticide methyl parathion is chosen because it is a highly neurotoxic agricultural chemical that is used extensively worldwide to control a wide range of insect pests. Its residue in the soil causes pollution in the environment and poses a risk to human health. The sensor properties were studied by examining the UV–vis spectral change due to the addition of methyl parathion in the ppm level. The sensor property was examined with as prepared Au nanoparticles. Methyl parathion was added to the Au nanoparticles solutions by varying concentration of pesticide from 100 to 500 ppm and corresponding changes of absorption coefficients were observed. When methyl parathion was added in the as prepared Au nanoparticles, we observed a new peak at around 400 nm in addition to the peak found at 545 nm. More interestingly, an increase of the absorbance at 400 nm, the newly found peak, was observed when the concentration of methyl parathion increased from 100 to 500 ppm (Fig. 6A).

The newly found peak might be due to the 4-nitrophenolate ions which are produced by hydrolysis of methyl parathion. The catalytic hydrolysis reaction of methyl parathion in the presence of Au nanoparticles produces 4-nitrophenolate and sodium di-O-methyl thiophosphonate (Barman, Laha, & Maiti, 2013). The literature survey confirms that the 4-nitrophenolate ion shows a characteristic absorption peak at 400 nm (Wu & Chen, 2012). The increase in the concentration of methyl parathion in the mixture quantitatively increases the amount of the 4-nitrophenolate ions in the medium which are reflected in the absorption spectra (Fig. 6B).

A calibration curve between absorption coefficients of 400 nm peak versus concentration of methyl parathion pesticide can help to estimate quantitatively the presence of methyl parathion in a sample at ppm level (Fig. 6C). This calibration curve enables the indirect quantitative measurement of methyl parathion by estimating the 4-nitrophenolate ions present in the medium. The corresponding decrease in the absorption peak at 545 nm suggests that the Au nanoparticle capped with dextran hydrolyzed produces sodium di-O-methyl thiophosphonate. The broadening of the 545 nm peak in the presence of methyl parathion confirms the catalytic hydrolysis.

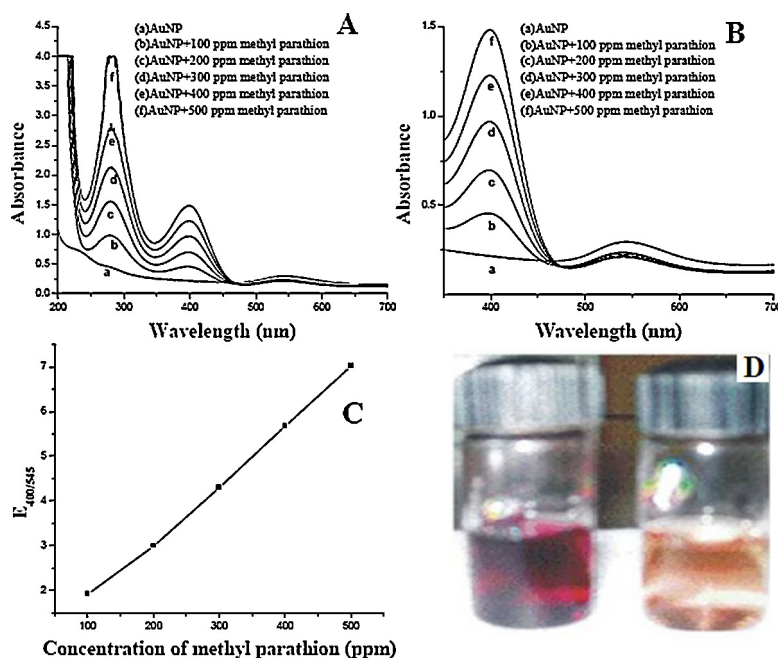


Fig. 6. (A) UV–vis spectra of Au nanoparticles and Au nanoparticles with various concentrations of methyl parathion 100–500 ppm; (B) Corresponding changes of absorption coefficients of 400 nm with various concentrations of methyl parathion; (C) Calibration curve between absorption coefficients of 400 nm peak versus concentration of methyl parathion; and (D) Digital photographic images of color changes due to addition of methyl parathion.

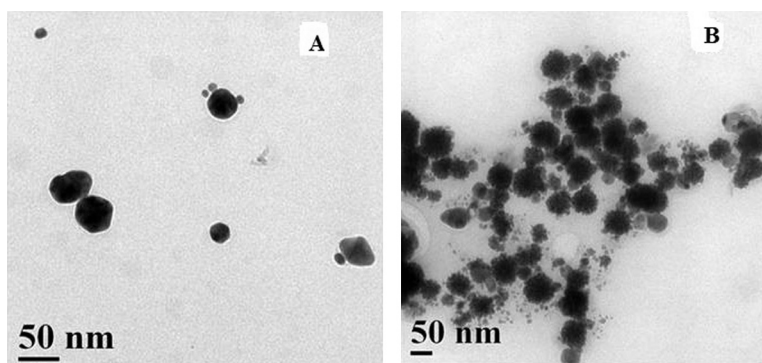


Fig. 7. TEM images of Au nanoparticles (A) as synthesized (B) restructuring of Au nanoparticles after addition of methyl parathion.

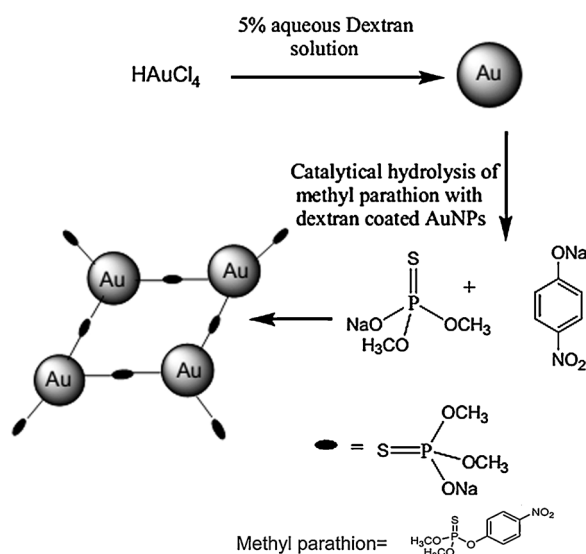


Fig. 8. Strategy for the formation of GNP and catalytic hydrolysis of methyl parathion as well as aggregation of GNP.

The TEM image of Fig. 7 is due to the Au nanoparticles with methyl parathion in presence of dextran. It appears the restructuring of Au nanoparticles after the addition of methyl parathion is due to agglomeration of particles. It may be the surface of the Au nanoparticles that forms an Au–S coordination bond, as the sol is being heated after the addition of methyl parathion and some hydrolyzed product sodium di-O-methyl thiophosphonate get adsorbed on the Au surface. Its adsorption on the Au nanoparticles surface lowers the surface charge, and thus, they agglomerate and particle branching is observed (Fig. 8).

4. Conclusions

We have developed a simple, safe, one-step and eco-friendly preparatory method of Au and Ag–Au alloy nanoparticles using aqueous dextran solution as a reducing and stabilizing agent at room temperature. The nanoparticles produced are highly stable and show no aggregation. The dextran stabilized Au nanoparticles have been used as a colorimetric sensor for detection and estimation of pesticide present in water. The prepared silver–gold alloy nanoparticles have significant antibacterial activity against different types of bacteria. Application of alloy nanoparticles based on these findings may lead to valuable discoveries in various fields such as medical devices and antimicrobial agents.

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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.carbpol.2014.02.047>.

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