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Green synthesis of polysaccharide/gold nanoparticle nanocomposite: An efficient ammonia sensor

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ABSTRACT

A low cost eco-friendly method for the synthesis of gold nanoparticles (AuNPs) using guar gum (GG) as a reducing agent is reported. The nanoparticles obtained are characterized by UV–vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Based on these results, a potential mechanism for this method of AuNPs synthesis is discussed. GG/AuNPs nanocomposite (GG/AuNPs NC) was exploited for optical sensor for detection of aqueous ammonia based on surface plasmon resonance (SPR). It was found to have good reproducibility, response times of ~10 s and excellent sensitivity with a detection limit of 1 ppb (parts-per-billion). This system allows the rapid production of an ultra-low-cost GG/AuNPs NC-based aqueous ammonia sensor.

1. Introduction

Nowadays, demands for robust ammonia sensing systems are increasing (Timmer, Olthuis, & Van Der Berg, 2005). Particularly, detection systems for continuous monitoring (Masserini & Fanning, 2000) are needed because ammonia is toxic to many aquatic organisms even in very low concentrations. One of the industrial gases of interest is ammonia in the form of ammonium hydroxide because of its toxic and polluting nature. Large quantities of ammonia are released in the farming industries and also produced in the chemical industry for fertilizers or in refrigeration systems. Leakage of ammonia can lead to life-threatening situations. The safe allowed limit in which people can work is 20 ppm (parts-per-million). High concentrations (500 ppm or more) of ammonia can lead to severe burns on skin, eyes, throat, or lungs causing permanent blindness and lung disease (De la Hoz, Schueter, & Rom, 1996). There is considerable interest in measuring the amount of ammonia in the human body, as it can be an indicator of disorder or diseases like kidney and liver malfunction, asthma, diabetes, cancer, and ulcers (Ament et al., 1999; Narasimhan, Goodman, & Patel, 2001).

Ammonia sensors based on ZnO, In_2O_3 and SnO_2 nanostructures have been demonstrated (Rout, Hegde, Govindraj, & Rao, 2007). Films from conjugated polymers such as polyaniline have also been used to detect ammonia by changes of their conduction properties (Koul, Chandra, & Dhawan, 2001). The major drawbacks associated with these sensors are their operation at high temperatures and sophisticated instrumentation along with the detection limit. Room temperature ammonia sensors remain an area of continuous interest. It has been shown that β-Fe_2O_3 NPs can be used for the detection of aqueous ammonia at room temperature (Rahman, Jamal, Khan, & Faisal, 2011). Silver nanoparticles (AgNPs) as ammonia sensor in 1–50 ppm have been reported (Pandey, Goswami, & Nanda, 2012). It has been seen that the detection of ammonia can be based on position and amplitude of the surface plasmon resonance (SPR) band change with ammonia concentration.

Green synthesis of AuNPs by using hydroxyl propyl cellulose, fungal proteins of *Coriolus versicolor* and by leaf extract of *Dalbergia sissoo* has already been reported (Abdel-Halim & Al-Deyab, 2011; Sanghi & Verma, 2010; Singh, Baboota, Naik, & Singh, 2012). But the synthesis of AuNPs by using guar gum (GG) has not yet been reported so far. GG is a naturally occurring plant polysaccharide produce in abundance. India generates about 80% of the world's total GG production. It is easily available, non-toxic, eco-friendly, biodegradable and cost effective. GG is also a renewable and abundantly available industrial polysaccharide material having backbone of β-D-(1→4) mannopyranosyl units with α-D-galactopyranosyl units as side chains. Many modified GG-silica nanocomposites are known to act as efficient heavy metals adsorbents or as efficient flocculants (Singh, Pandey, Singh, & Sanghi, 2009; Tiwari, 2010, 2011; Tiwari, Mishra, Kobayashi, & Turner, 2012).

We have for the first time reported the green synthesis of AuNPs using aqueous solution of polysaccharide *Cyamopsis tetragonaloba* commonly known as GG from plants as reducing agent. Here the main efforts are focused on synthesis, characterization and application in detecting the aqueous ammonia concentration in liquid

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phase by monitoring the absorbance spectra. Sensitivity, stability and reproducibility studies reveal excellent properties that can be explored as ammonia sensor for practical applications at room temperature. Our main focus has been ammonia detection at sub-ppm level.

2. Experimental

2.1. Materials

Gold (III) chloride hydrate ($HAuCl_4{\cdot}3H_2O$, 99.9%) purchased from Aldrich (USA) and used without further purification. GG and sodium hydroxide was purchased from Merck, Germany. All aqueous solutions were made using ultrahigh de-ionized (DI) water purified using a Mill-Q Plus system (Millipore Co.).

2.2. Preparation of GG/AuNPs NC using GG

All glassware used was cleaned in a bath of freshly prepared aqua regia solution (HCl:HNO_3, 3:1), and rinsed thoroughly with H_2O prior to use. For the synthesis of AuNPs, a stock solution of 10 mm was prepared by adding gold (III) chloride hydrate in DI water. Then, the gold (III) chloride hydrate solution was mixed with GG solution followed by the addition of few drop of very dilute solution of sodium hydroxide (0.01 M) at room temperature. Then, the solutions were stirred gently at the desired temperatures (80 °C) for 160 min to yield AuNPs. Here the yellow color solution was converted to the characteristics pink-red color solution indicating the formation of GG/AuNPs NC. It was observed that the aqueous solution of AuNPs was stable for more than eight months at room temperature.

2.3. Characterization of synthesized GG/AuNPs NC

The nanostructured materials are characterized by X-ray diffraction (XRD) using Bruker D8 Advance powder diffractometer operating in the reflection mode with CuKα radiation. The size of the NPs were determined with transmission electron microscope (TEM) using a TECHNAI T20 microscope operating at 200 kV equipped with an EDS (energy dispersive spectrum) detector. UV–vis spectroscopy was used to ensure the formation of NPs.

3. Results and discussion

3.1. UV–vis and TEM analysis of GG/AuNPs NC

It is well known that the optical properties of AuNPs depend strongly on the size, shape, interactions between the nanoparticles and their adsorbed species on the surface of the nanoparticles. Fig. 1A shows the UV–vis spectra of the GG/AuNPs NC formed at different molar concentrations of $HAuCl_4{\cdot}3H_2O$. In this experiment, AuNPs synthesized under conditions of lower concentration of $HAuCl_4{\cdot}3H_2O$ (1 mM), GG (2.5%, w/v) gave a brown suspension (a), whereas at higher molar concentration of gold salt (10 mM) the suspension was purple red (b). The color of the gold colloid arises because of the SPR absorption of AuNPs (Mulvaney, 1996). The sample solutions of AuNPs prepared here show an intensive SPR band around 539 nm. In general, the AuNPs often show an intense SPR band from 500 to 600 nm at the UV–vis (Szunerits & Boukherroub, 2006). According to the reported literature, the position of SPR absorption of AuNPs depends on their size and shape as well as their surrounding medium (Prasad, Stoeva, Sorensen, & Klabunde, 2003; Rechberger et al., 2003).

The formation of AuNPs was evidenced with the change in color of the solution after addition of gold salt from the yellowish to pink red color solution. The formation of GG/AuNPs NC was monitored through UV–vis spectrophotometer at time intervals from 10 to 160 min (Fig. 1B). The intensity of the peak increases gradually with increase of time. The spectrum obtained at 160 min shows the absorption maximum as 539 nm.

The UV–vis absorption spectra of AuNPs prepared using GG in different concentrations (0.125–3.5%, w/v), at initial pH of 8 and temperature of 80 °C for 160 min was measured. It was found that there is a gradual increase in the absorption intensity, by increasing the GG concentration up to 3.5% (w/v). It is worthy of mention here that the least amount of GG in the reaction medium (1%, w/v) is enough for full reduction of the Au^{3+} to Au^0 nanoparticles.

Investigation of the morphologies of the as-prepared GG/AuNPs NC was performed using TEM (Fig. 2A). NPs with spherical shapes are observed in Fig. 2A. The EDS equipped with TEM instrument confirms the presence of Au in the sample (Fig. 2B). A high-resolution TEM (HRTEM) image (shown in Fig. 2C) with clear lattice fringes having a *d*-spacing of 0.23, 0.20 and 0.14 nm reveals that the fcc crystal lattice with (1 1 1), (2 0 0) and (2 2 0) planes (JCPDS 46-1045). Fig. 2D shows the selected area electron diffraction (SAED) pattern of AuNPs. The clear lattice fringes in high resolution TEM image and the typical SAED pattern with bright circular rings correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes. Fig. 2E shows the particle size distribution histograms of AuNPs formed after 160 min. The average particle size is found to be ~6.5 nm.

3.2. XRD studies

The XRD spectrum, for the synthesized GG/AuNPs NC is presented in Fig. 2F. It shows intensive characteristic peaks of metallic Au. Four main characteristic peaks for gold at 38.35, 44.36, 64.73 and 77.63 corresponding to Miller indices (1 1 1), (2 0 0), (2 2 0) and

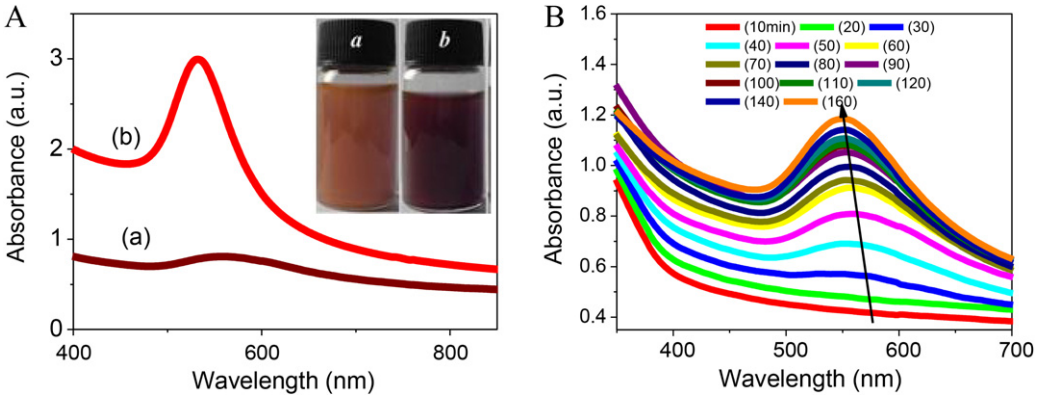

Fig. 1. (A) UV–vis spectra of AuNPs formed at different molar concentration (a) 1 mM; (b) 10 mM of $HAuCl_4$. (B) UV–vis spectra at different time interval.