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A simple approach for facile synthesis of Ag, anisotropic Au and bimetallic (Ag/Au) nanoparticles using cruciferous vegetable extracts

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ABSTRACT

We present a simple and straightforward approach for the synthesis and stabilization of relatively monodisperse Ag, Au and bimetallic (Ag/Au) nanoparticles by using cruciferous vegetable (green/red) extracts by simply adjusting the pH environment in the aqueous medium. The vegetable extracts act both as reducing and capping agents. The monometallic and bimetallic nanoparticles of Ag and Au so obtained were characterized by UV–visible spectroscopy, X-ray diffraction (XRD), dynamic light scattering (DLS) and transmission electron microscopy (TEM). It is shown that red cabbage extract can be used for the preparation of anisotropic Au nanoparticles. The formation of Au anisotropic nanoparticles was found to depend on a number of environmental factors, such as the pH of the reaction medium, reaction time, and initial reactant concentrations. Additionally, it is shown that these extract-stabilized Au and Ag nanoparticles can be used as a seed for preparation of bimetallic Au/Ag nanoparticles. For bimetallic alloy nanoparticles the absorption peak was observed between the two maxima of the corresponding metallic particles. The surface plasmon absorption maxima for bimetallic nanoparticles changed linearly with increasing Au mole ratio content in various alloy compositions. It has been shown that the formation of hollow Au spheres depends on the experimental conditions.

1. Introduction

Over the past decade synthesis of nanoparticles has been paid wide attention in the emerging areas of nanoscience and technology as particles in the nanoregime show different properties as compared to the bulk [1]. Various chemical routes for the synthesis of particles have been attempted [1]. Recently, attempts have been made to synthesize particles using plant extracts [2–4]. Among various metal-nanoparticles, gold and silver nanoparticles are of particular interest to applications that leverage on their strongly size- and shape-dependent properties [1,5,6]. Hence, attempts have been made to use various methods to synthesize anisotropic nanoparticles [1,5,6].

The properties of metal alloy nanocrystals are different from those of monometallic nanocrystals [7]. They are particularly important in the field of catalysis since they often exhibit better catalytic performance than their monometallic counterparts [7]. The bimetallic nanoparticles may be fabricated as alloy nanoparticles where the two constituent metals are mixed at the atomic level or as core/shell nanoparticles where the two components are separated by distinct phase boundaries [8,9]. It is known that bimetallic nanoparticles with the same overall composition but different composition distributions can exhibit different properties [8,10] for the two extremes of alloy (maximally mixed) and core/shell (minimally mixed) particles.

Preparation of bimetallic nanoparticles from metal salts can be divided into two groups: coreduction and successive reduction of two metal salts. Metal alloy nanocrystals are generally prepared by the coreduction process of the metal ions [11]. Successive reduction is usually carried out to prepare "core–shell"-structured bimetallic nanoparticles. The deposition of one metal on preformed monometallic nanoparticles of another metal seems to be very effective. For this purpose, however, a second metal must be deposited on the surface of the preformed particles, and the preformed monometallic nanoparticles should be chemically surrounded by the deposited element [12].

Recently, galvanic replacement reactions (transmetallation reactions) involving sacrificial metal nanoparticles and suitable metal ions have been employed by various groups [13,14] for the synthesis of hollow/porous metal [13] and metal alloy [11] nanostructures in aqueous [13] and organic environments [15,16]. Galvanic replacement reactions are single-step reactions that utilize the differences in the standard electrode potentials of various elements, leading to deposition of the more noble element and dissolution of the less noble component. The electroless nature of galvanic replacement reactions provides them the unique and significant advantage of simplicity.

Cruciferous vegetable (green/red) extracts contain sulforaphane, isothiocyanates, indoles, and natural chemicals that stimulate the production of cancer-fighting enzymes and are also rich in vitamin

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C [17]. Recently, we have reported the free radical reactions with the extract of green and red cabbages [18]. It has been shown that the high reactivity of the red cabbage extract is due to the high contents of phenols [18]. As phenols play a significant role in the reduction of metal ions [19], thus, there exists a possibility that extracts can play a role in the reduction of metal ions. In this study a simple synthetic route to form gold nanotriangles, Ag nanoparticles and alloy using a single step room-temperature reduction of aqueous salts of corresponding metals by cabbage extracts is presented. The reduction of metal ions is fairly rapid, occurs readily in solution, and results in a high density of extremely stable Ag, Au and bimetallic (Ag/Au) nanoparticles. The Ag nanoparticles though predominantly spherical in shape but with Au nanoparticles different morphologies were obtained. Experimental conditions such as the aging time of the cabbage extract, pH of the reaction medium, reaction time, and initial reactant concentrations, were systematically varied to arrive at the optimal growth conditions for the generation of nanoparticles. It is worth noting that there are several significant merits in the current synthesis strategy. First, the extracts can act both as a reducing agent and a capping agent for the generation of Ag, Au and bimetallic nanoparticles upon the addition of basic aqueous solution; second, the highly stable Au, alloy, and especially Ag nanoparticles could be achieved by simply adjusting the pH environment in the system. Additionally, one may separate the extract from Ag nanoparticles by utilizing phase-transfer reaction [20,21] in consideration of weak hydrogen-bonding interactions between the extract and the surface of the nanoparticles.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$) (BDH, India), tetrachloroauric(III) acid ($HAuCl_4$) (Aldrich), sodium hydroxide (BDH, India), gelatin (BDH, India), polyvinylpyrrolidone (PVP) (M_w 40,000) (Sigma), chloroform (Spectrochem, India) and cetyltrimethylammonium bromide (CTAB) (Sigma) were used as received. All solutions were prepared just before the experiments and kept in the dark to avoid any photochemical reactions. Water purified through a Millipore system was used.

2.2. Preparation of cabbage extracts

Green and red cabbages were purchased from an Indian grocery market. Cabbage extracts were prepared by soaking 100 g of washed, dried and finely chopped green/red cabbage (*Brassica oleacea* var. *capitata*) vegetables in 100 mL of methanol for 24 h at room temperature then decanted and stored in a refrigerator at 4 °C. Cabbage extracts were covered with aluminum foil to avoid any photochemical reactions.

2.3. Methods for the preparation of nanoparticles

For the preparation of metal nanoparticles 0.05–0.50 mL of extract in methanol was taken and dried over a weighing paper. The dried amount was dissolved in 10 mL of water. Detailed preparation is mentioned while discussing the results. The results are repeated with different extracts, prepared taking fresh green and red cabbages, and found to be reproducible within ±10%.

2.4. Characterization

Absorption measurements were carried out on a Chemito spectrascan UV 2600 spectrophotometer. The spectra were recorded at room temperature using a quartz cuvette. Dynamic light scattering experiments were done on a Malvern 4800 Autosizer employing a 7132 digital correlator. The intensity correlation function was analyzed by the method of cumulants using the mean and variance of the distribution on the fitted variable. The diffusion coefficient (D) of the particle is related to the average decay rate (Γ) of the correlation function by $\Gamma = Dq^2$ where q is the magnitude of the scattering vector (given by $q = \frac{4n}{}$ sin/2, where λ is the wavelength of light; n is the refractive index and θ is the scattering angle). The mean hydrodynamic coefficient of the particles was obtained from the diffusion coefficient using the Stokes–Einstein relationship. The light source was an Ar^+ ion laser operated at 514.5 nm and a scattering angle $\theta = 90°$. Crystallographic information about the samples was obtained from powder X-ray diffraction (XRD). X-ray diffraction patterns were taken using a Phillips Analytical (PW 1729) diffractometer employing Cu K_α radiation (1.5406 Å). Samples for transmission electron microscopy (TEM) were prepared by putting a drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. The excess solvent was removed by using a filter paper, and letting the solvent evaporate at room temperature. TEM characterization was carried out using a Phillips CM 200 electron microscope. Particle sizes were measured from the TEM micrographs and calculated by taking the average of at least 100 particles.

3. Results and discussion

3.1. Synthesis of Ag nanoparticles using green/red cabbage extracts

Addition of Ag^+ ions (5×10^{-4} M $AgNO_3$) to the green/red cabbage extract (1.10 mg/mL) under ambient conditions showed a very slow formation of Ag nanoparticles. The surface plasmon absorption band was broad and the Ag nanoparticles formed were not stable and precipitated in 2 days (Fig. S1). The flocculation appeared to accompany the Ag^+ reduction, which might be due to insufficient extract as the protecting agent. Hence, to increase the stabilizing power of the cabbage extracts, firstly, in one set the concentration of the cabbage extracts was increased from 1.10 mg/mL to 3.30 mg/mL keeping the Ag^+ concentration constant and in the second set Ag^+ concentration was increased to 1×10^{-3} M. Both sets gave similar results as mentioned above. Secondly, without increasing the concentration of cabbage extracts, the pH of the solution was increased in steps. It was noticed that as the pH of the solution increased the tendency of aggregation decreased, and finally no visible flocculation appeared in the pH window 10.0–11.4. To see the effect of concentration of cabbage extract and Ag^+ on the formation and stabilization of Ag nanoparticles in the pH window 10.0–11.4, an aqueous solution of 1×10^{-3} M $AgNO_3$ and 3.30 mg/mL of cabbage extracts was taken. Even at high concentrations, we achieved Ag nanoparticle formation and stabilization. It was noticed that on increasing the pH of the reaction mixture the rate of reduction of Ag^+ ions increased and exhibited a strong surface plasmon absorption band. The particles so formed were stable for more than a month. A representative UV–visible absorption spectrum of the aqueous solution containing 1.10 mg/mL green/red cabbage extract and 5×10^{-4} M $AgNO_3$ at pH 10.7 is shown in Fig. 1. It can be noticed from Fig. 1 that in the red cabbage extract the reduction is faster than the green cabbage extract as the optical absorbance is higher just after addition of the extract. However, once the particles formed they act as catalyst and the final absorbance yield is almost similar in both the cases. The other significant difference is observed in the width of the surface plasmon absorption band in the case of green and red cabbage extracts. Hence, the size and shape of the Ag nanocrystals were examined through dynamic light scattering (Fig. S2), XRD (Fig. S3), and TEM measurements (Fig. S4). In the XRD pattern, obtained for Ag nanoparticles, a number of Bragg reflections were observed that may be indexed on the basis of the FCC structure of Ag. The XRD pattern thus clearly shows that the Ag nanoparticles formed by the reduction of Ag^+ ions by green cabbage and red cabbage extracts are crystalline in nature. Dynamic light scattering experiments showed that the size