Comparison of galvanic displacement and electroless methods for deposition of gold nanoparticles on synthetic calcite

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Abstract. Gold nanoparticles have been deposited on synthetic calcite substrate by galvanic displacement reaction and electroless deposition methods. A comparative study has shown that electroless deposition is superior compared to galvanic displacement reaction for uniform deposition of gold nanoparticles on calcite. Characterization of the samples, prepared by two different deposition methods, was carried out by X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy (FE–SEM) and diffuse reflectance spectroscopy (DRS) measurements. FE–SEM studies prove that smaller nanoparticles of gold are deposited uniformly on calcite if electroless deposition method was employed and DRS measurements show the characteristic surface plasmon resonance of gold nanoparticles.

Keywords. Calcite; gold nanoparticles; electroless deposition; galvanic displacement reaction.

1. Introduction

Gold nanoparticles deposited on various substrates have been widely used as active catalysts, e.g. for the oxidation of alcohols, epoxidation of alkenes, CO oxidation, selective O_2 reduction, etc. (Schimpf *et al* 2002; Choudhary *et al* 2005; Hughes *et al* 2005). Gold nanoparticles are very stable which makes them poor in catalysis but deposited gold nanoparticles possess better catalytic activity. The deposited gold nanoparticles are also efficient catalysts in pollution control, chemical sensing and fuel cells (Moshfegh 2009). Gold nanoparticles deposited on substrates possess wide range of applications in the field of biological sensing and surface enhanced Raman scattering (Evans *et al* 2007; Batista *et al* 2009). Au nanoparticles deposited substrates have also been used for studying substrate based fluorescence enhancement (Goldys and Xie 2008). Gold nanoparticles have been deposited on different substrates by various physical and chemical methods. A brief review on the reported methods for the deposition of gold nanoparticles on different substrates is given below.

Gold nanoparticles have been deposited on roughened surfaces of CaF_2 by glancing angle deposition (Evans *et al* 2007). Polycarbonate membranes (PCM) of various pore sizes have been used as templates for the deposition of Au nanoparticles (Batista *et al* 2009). The deposition of gold

nanoparticles on carbon nanotubes has been done by a direct deposition method (Zhang *et al* 2009). Microwave assisted and thermal decomposition methods have been reported for the deposition of gold nanoparticles on different substrates (Xue *et al* 2001; Raghuveer *et al* 2006). Homogeneous deposition–precipitation has been used to deposit gold nanoparticles on MgO, CaO, BaO, SrO_2, Al_2O_3, Ga_2O_3, In_2O_3 and other transition and rare earth metal oxides (Choudhary and Dumbre 2009; Choudhary *et al* 2009). Gold nanoparticles have been deposited on highly oriented pyrolytic graphite (Limat *et al* 2009) and Cu_2O and ZnO single crystal planes by electrochemical deposition (Read *et al* 2009). Gold nanolayers have been deposited on polymers such as polytetrafluoroethylene (PTFE) and polyethyleneterephthalate (PET) films by sputtering (Slepicka *et al* 2009). Deposition of gold nanoparticles on monolayer graphene epitaxied SiC (0001) substrate has been reported (Premlal *et al* 2009). Au nanoclusters have been deposited on CeO_2 nanorods and CeO_2 nanoparticles by deposition precipitation (Huang *et al* 2009).

Mercaptopropyltrimethoxysilane (MCPTMS) functionalized indium tin oxide electrode has been coated with gold nanoparticles by an electrochemical method (Dai and Compton 2006). Au nanoparticles have been deposited on the surface of sodium trititanate nanotubes by an ion-exchange method (Tsai *et al* 2009). Gold nanoparticles have been deposited on *p*-type Si (100) surface by an electrochemical method (Fang *et al* 2007). Gold nanoparticles have been deposited on sapphire substrate (0001 plane) by pulsed laser deposition (PLD) (Kukreja *et al* 2008). Photo-induced chemical method has been employed for the deposition of gold nanoparticles on GaAs and InP (Dmitruk *et al* 2008).

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Au nanoparticles have also been deposited on submicronsized polystyrene spheres by surface modification followed by electroless plating (Kobayashi *et al* 2007).

The reported methods consist of complicated and expensive procedures for the deposition of gold nanoparticles on the substrates. In the present study, a simple method for the deposition of gold nanoparticles on a cheaper substrate such as calcite has been reported. A comparison of electroless deposition and galvanic displacement methods has also been carried out. Apart from gold chloride, remaining chemicals used throughout the procedure are economical and non-hazardous.
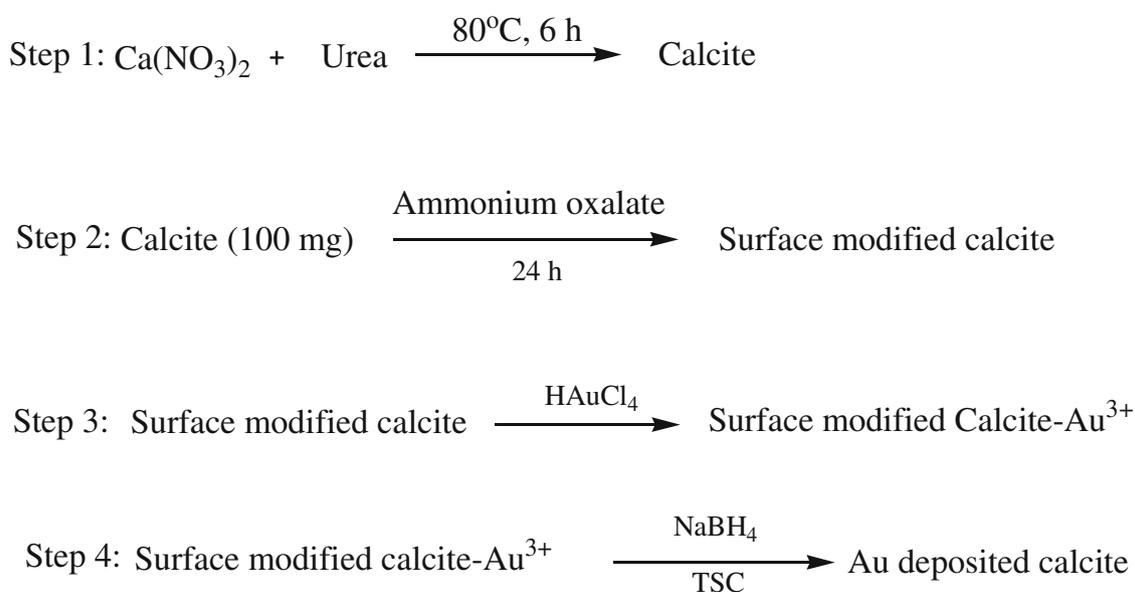
2. Experimental

All the chemicals used throughout the experiments were of analytical grade. Millipore® water was used for making aqueous solutions. Synthesis of calcite and its surface modification with ammonium oxalate was based on reported literature (Srikanth and Jeevanandam 2009). Gold nanoparticles were deposited on calcite by two different methods: electroless deposition and galvanic displacement reaction. The electroless deposition was carried out on the surface modified calcite using silver nitrate and formaldehyde (Chou and Ren 2000). In the galvanic displacement reaction, silver nanoparticles deposited calcite, prepared by a previously reported method (Srikanth and Jeevanandam 2009), was used and the silver nanoparticles were galvanically displaced with gold nanoparticles (Liu and Yang 2006). More details on the deposition experiments are as follows.

For the electroless deposition (scheme 1), calcite was synthesized by homogeneous precipitation using urea and calcium nitrate and calcite was subsequently surface modified with ammonium oxalate. Then, about 10 mL of 5 mM aqueous gold chloride solution was mixed with 100 mg of the surface modified calcite and stirred for 2 h at room temperature. The sample was washed with water and ethanol followed by drying inside a drying cabinet. The colour of the sample turned from white to light yellow indicating that gold ions are attached to the surface modified calcite. The gold ions were then reduced using 10 mM aqueous sodium borohydride solution (10 ml) in the presence of tri-sodium citrate (0·1 g) (Jana *et al* 2001). During the reduction, yellow coloured sample turned into pink. The electroless deposition experiments were carried out for different time intervals (30, 90, 180 min) at room temperature.

For the galvanic displacement reaction, initially, the Ag nanoparticles deposited calcite was prepared. Then, about 100 mg of silver nanoparticles deposited calcite was taken and to it 5 mM aqueous gold chloride solution (10 ml) was added. The contents were kept for equilibrium at room temperature up to 12 h under stirring. The products collected were washed and dried in an oven and the samples obtained were black in colour. The nomenclature of various samples, prepared in the present study, is given in table 1.

Among various colours which are light of a particular wavelength, a material with black colour absorbs light of different wavelengths especially in the visible region of the spectrum. In the present study, there are two phases in the coating; one is metallic and another one is non-metallic oxide phase. The high reflectivity of the metals is due to high skin effect where electromagnetic radiation cannot penetrate far into the metal because of the high electron density. In the present system, yellow colour is due to the presence of gold ion. Both pink and black coloured calcite samples contain

Step 1: $Ca(NO_3)_2$ + Urea $\xrightarrow{80^{\circ}C,\ 6\ h}$ Calcite

Step 2: Calcite (100 mg) $\xrightarrow[24\ h]{\text{Ammonium oxalate}}$ Surface modified calcite

Step 3: Surface modified calcite $\xrightarrow{HAuCl_4}$ Surface modified Calcite-Au^{3+}

Step 4: Surface modified calcite-Au^{3+} $\xrightarrow[\text{TSC}]{NaBH_4}$ Au deposited calcite

Scheme 1. Steps involved in electroless method for deposition of gold nanoparticles on calcite.

gold, C and O. Here, gold is the metallic phase; calcite and oxalate are the non-metallic phases. Further, particle or crystallite size also affects the reflectivity of electromagnetic radiation. The contradictory observation, in the present study, is that the bigger particle sized gold produced by the displacement reaction shows black colour. This means that there may not be continuous gold distribution. If this is so, the light can penetrate far into the calcite leading to more absorbance.

2.1 *Characterization*

Powder XRD patterns were obtained using a Brucker AXS D8 powder diffractometer operating with CuK_α radiation (40 kV, 45 mA, $\lambda = 1.5406$ Å) with a $0.02°$ step scan per min. The diffraction patterns obtained were compared with the reference JCPDS files. SEM images were obtained using a FEI Quanta 200F microscope operating at an accelerating

Table 1. Nomenclature of the gold deposited calcite samples prepared.

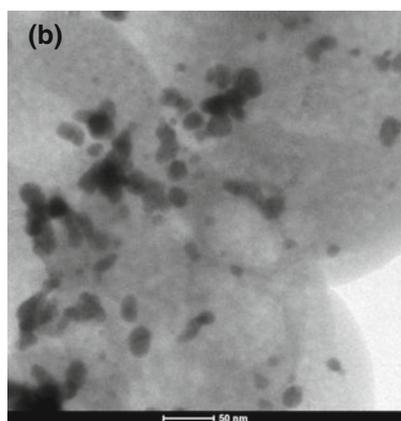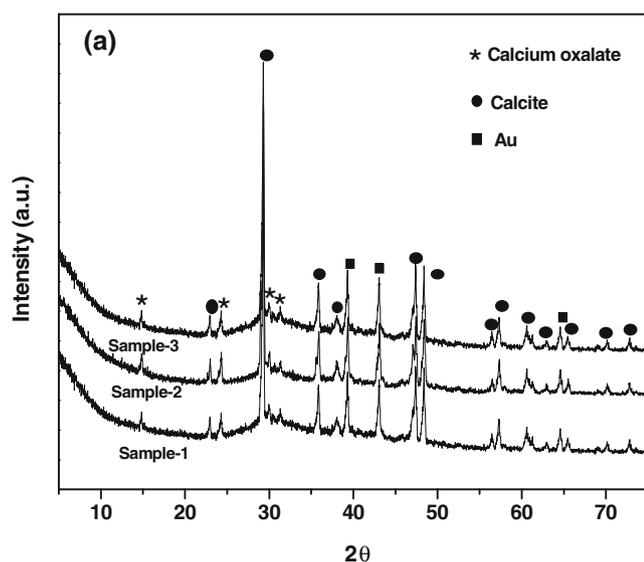| Sample	Preparation method	Experimental details
Sample 1	Electroless deposition	Reduction time, 30 min
Sample 2	Electroless deposition	Reduction time, 90 min
Sample 3	Electroless deposition	Reduction time, 180 min
Sample 4	Galvanic displacement reaction	Equilibrium time, 1 h
Sample 5	Galvanic displacement reaction	Equilibrium time, 12 h

Figure 1. (**a**) XRD patterns and (**b**) TEM image of gold deposited calcite samples prepared by electroless deposition.
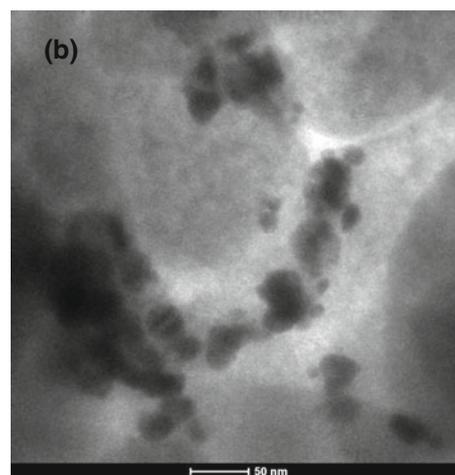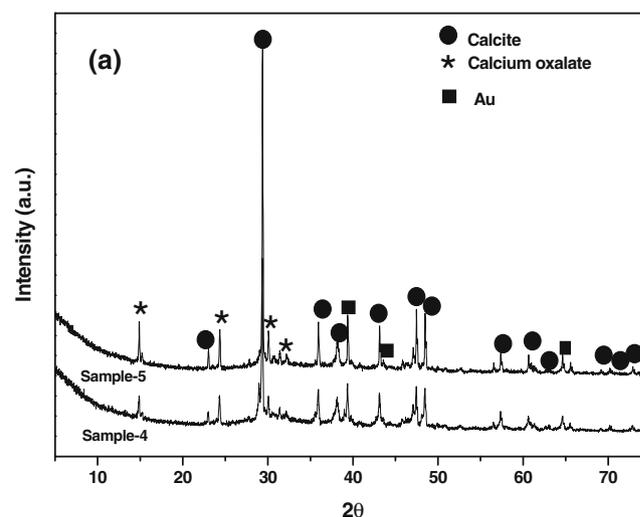

Figure 2. (**a**) XRD patterns and (**b**) TEM image of gold deposited calcite samples prepared by galvanic displacement.

voltage of 20 kV. TEM images were recorded using a TEC-NAI G^2 instrument operating at 200 kV. The powder samples were dispersed in ethanol, sonicated for a few min and then one drop each was allowed to dry in air on carbon coated copper grids. To study the surface plasmon resonance of Au nanoparticles deposited on calcite, a Shimadzu® UV-3600 UV-Vis-NIR spectrophotometer was used along with an integrated sphere (ISR-3100). About 50 mg of the gold deposited calcite samples were mixed with about 3 g of $BaSO_4$ (reference). The powders were packed in the sample holder and the reflectance spectra were recorded in the 200–800 nm wavelength range.
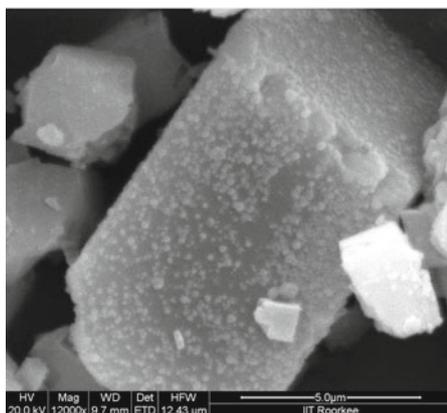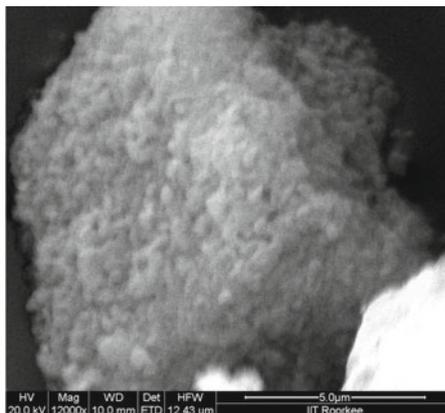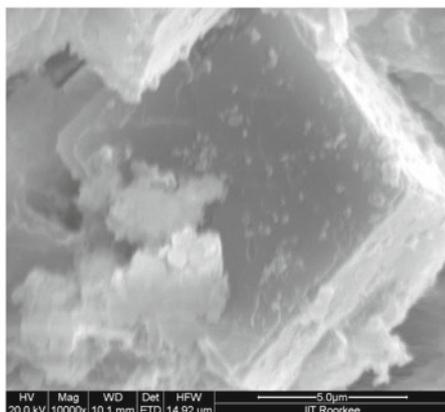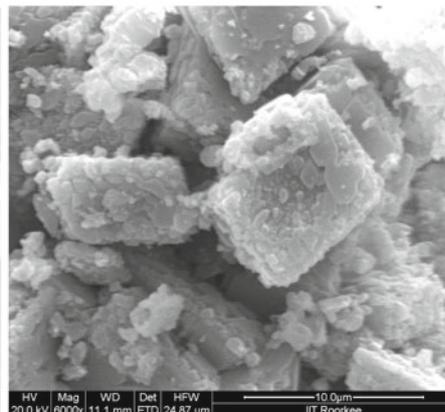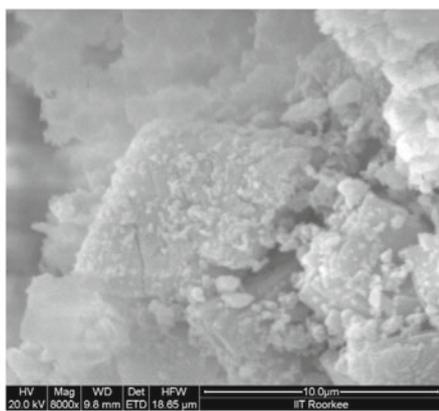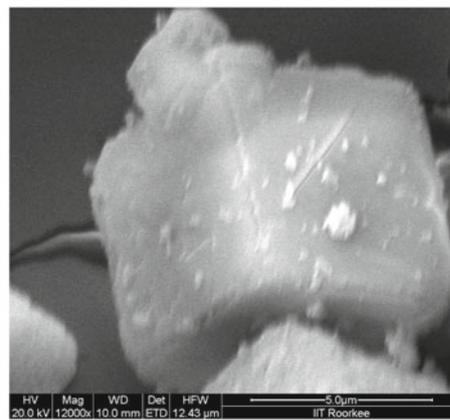

Figure 3. FE–SEM images of gold deposited calcite samples.

Table 2. Mean particle size of gold in Au-deposited calcite samples.

Sample	Mean size (nm)	Standard deviation (nm)
Sample 1	149	25·0
Sample 2	363	23·0
Sample 3	283	26·0
Sample 4	404	31·0
Sample 5	329	18·9

3. Results and discussion

3.1 *X-ray diffraction and TEM analysis*

The powder diffraction patterns for the deposition of gold nanoparticles on calcite substrate by electroless deposition are shown in figure 1. The diffraction patterns show peaks due to calcite (JCPDS File No. 85-0849), calcium oxalate monohydrate (JCPDS File No. 77-1160), and gold (04-0784); during the surface modification with ammonium oxalate, part of the calcite is converted into calcium oxalate (Srikanth and Jeevanandam 2009). The crystallite size of gold, calculated for the three samples prepared
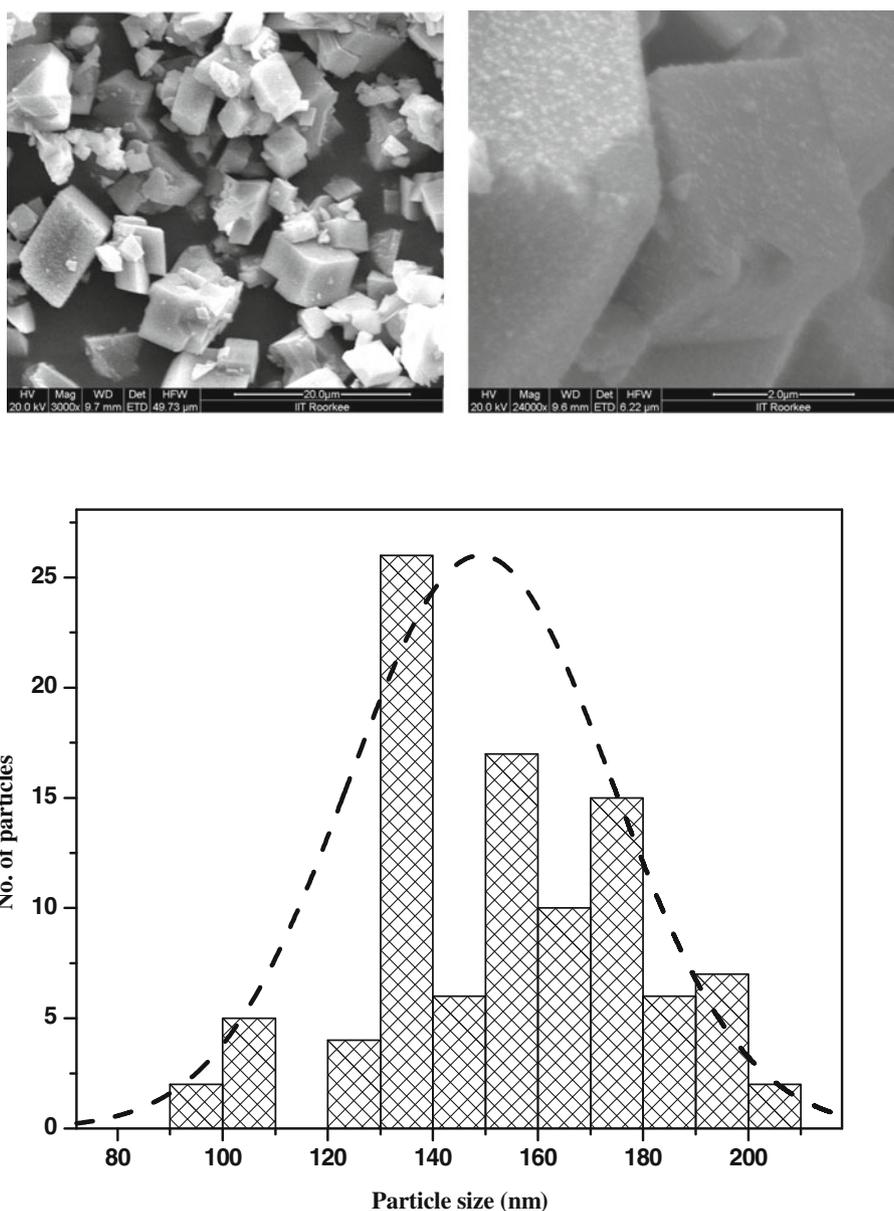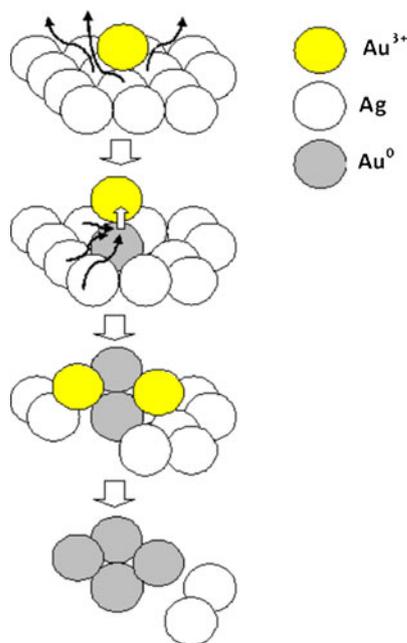

Figure 4. FE–SEM images of gold nanoparticles deposited calcite, prepared by electroless deposition (sample 1), under two different magnifications. The particle size histogram is also shown.

by electroless deposition using Debye–Scherrer's formula, was found to be about 38 nm. This is in good agreement with the particle size (∼37 nm) obtained by TEM measurements (figure 1b, sample 1). Figure 2 represents XRD patterns for the gold deposited calcite, prepared by galvanic displacement reaction (samples 4 and 5). The characteristic peaks of gold (111), (200) and (220) are again found in addition to those due to calcite and calcium oxalate monohydrate. The crystallite size of the gold nanoparticles from XRD measurements was found to be around 70 nm. TEM image (figure 2b, sample 5) shows gold nanoparticles with size ranging from about 35 to 70 nm.

3.2 *FE–SEM, EDXA and UV-Vis spectroscopy results*

The morphology of calcite on deposition of gold nanoparticles was studied by FE–SEM analysis (figure 3).

Scheme 2. Pictorial representation of growth of gold particles in displacement reaction. Arrows indicate oxalate groups.

From the FE–SEM images it is clear that gold nanoparticles are deposited on the surface of calcite by both the methods. The mean particle size of gold obtained from the FE–SEM images are given in table 2. For the gold deposited calcite samples prepared by electroless deposition, the mean particle size of Au varies from about 150 to 360 nm. In the case of samples prepared by galvanic displacement, the mean particle size varies between about 280 and 400 nm. Moreover, electroless deposition leads to the formation of uniform, smaller and well separated gold nanoparticles (e.g. sample 1) compared to the galvanic displacement reaction (e.g. sample 5). FE–SEM images recorded under different magnifications for a sample prepared by electroless deposition (sample 1, figure 4) show that the sample consists of gold nanoparticles with uniform size (mean particle size = 149 ± 25 nm) on the calcite.

The galvanic displacement reaction leads to the formation of bigger Au nanoparticles (about 280 to 400 nm) on calcite, and the standard deviation is similar to the samples which were prepared by electroless deposition method. During the galvanic displacement reaction, when displacement of silver with gold takes place, there is no control on the size of the deposited Au nanoparticles, which results in a bigger particle size. From FE–SEM results (figure 3 and table 2), it is also clear that, among the 30, 60 and 90 min electroless deposition time intervals, 30 min is the best for the uniform deposition of gold nanoparticles; longer deposition time leads to an increase in the Au particle size. Also, the surface modification of calcite with ammonium oxalate is important for the successful electroless deposition of Au nanoparticles. If surface unmodified calcite is employed, it leads to poor deposition of Au nanoparticles (figure 3, sample 6).

In the ammonium oxalate treatment of calcite, one end of oxalate is attached with calcite while the other end is free for the formation of either Ag^+ or Au^{3+} compound of oxalate. The Ag^+ ions per unit area are more than the number of Au^{3+} since Au^{3+} requires three oxalate end groups for its settlement. In other words, the availability of gold atoms must be lower than the availability of silver atoms per unit area
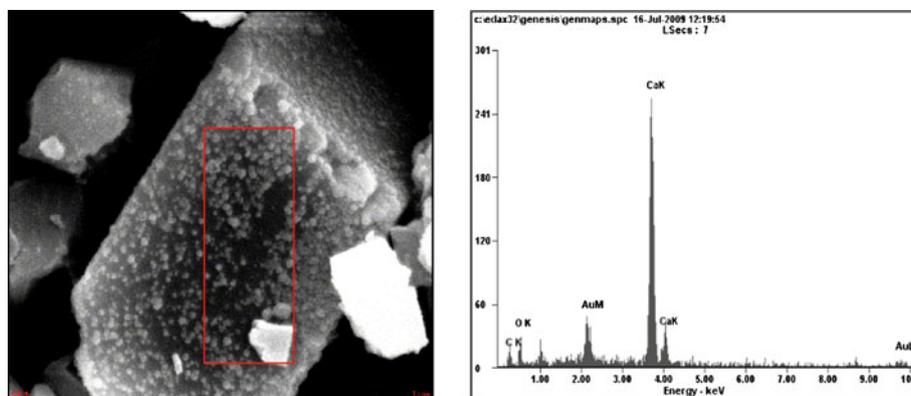

Figure 5. Typical EDXA data of gold deposited calcite (sample 1).

of calcite. Further, the reaction centres in gold containing calcite are less than that on the silver containing calcite. Upon reaction with sodium borohydride, in the presence of sodium citrate, the reduction of each Au^{3+} takes place with the borohydride oxidation. Hence there is no chance for the growth of gold on gold. Whereas, in the displacement reaction, the Au^{3+} ions are first adsorbed over a silver atom and three such adjacent silver atoms are involved in the reduction of an Au^{3+} ion into gold. Here, there is a chance for the adsorption of Au^{3+} ion on already deposited gold atoms which are in contact with silver atoms. The electron transfer may take place from silver atom to Au^{3+} through gold atom. This kind of reduction of Au^{3+} on gold leads to the growth and finally bigger particle size of gold. A pictorial representation of the growth of gold particles in the displacement reaction is shown in scheme 2.

The presence of gold on the surface of calcite was supported by EDXA results too (figure 5). The image mapping for different elements supported the presence of Ca, C, O and Au in the samples. The solution pH determines the reaction type which may lead to the deposition of boron along with the metal (Mallory and Hajdu 1990). The pH during electroless deposition of gold was 7·2. In the present study, from EDX analysis, boron could not be detected. This indicates the absence of boron in the products within the detection limit of the EDX analysis. The atomic percent of gold deposited in all the samples prepared by two methods is nearly the same, about 3 atom % (see table 3). However, advantage of the electroless deposition is the formation of smaller, uniform Au nanoparticles on calcite. Yet another important characterization technique for the gold deposited calcite samples is diffuse reflectance spectroscopy (DRS). The surface plasmon resonance band, observed at about 520 to 550 nm in all the gold deposited calcite samples prepared by the two methods (figure 6), indicates the presence of gold nanoparticles on calcite.
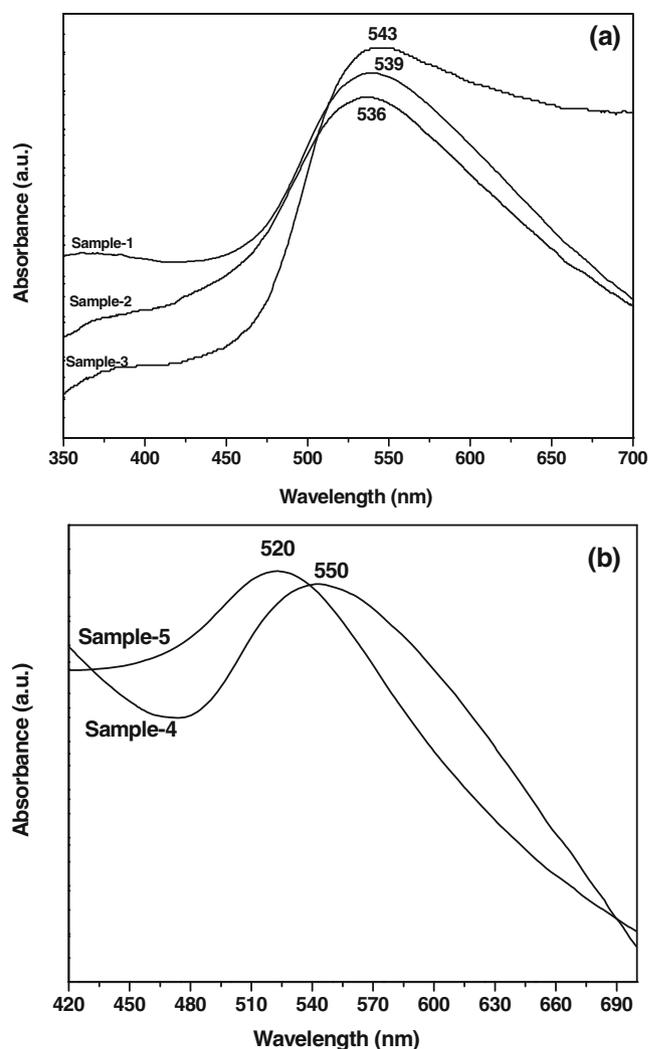

Figure 6. UV-Vis spectra of gold deposited calcite samples prepared by (**a**) electroless deposition and (**b**) galvanic displacement reaction.

3.3 *Proposed mechanism for deposition of gold nanoparticles*

The proposed mechanism for the deposition of Au nanoparticles on calcite by electroless deposition and galvanic displacement methods is shown in scheme 3. In the case of electroless deposition, the surface modification of calcite with ammonium oxalate makes the surface of calcite attached

Table 3. Atomic percent of elements present in gold deposited calcite samples.

Sample	% Ca	% C	% O	% Au
Sample 1	27·1	22·8	43·3	02·8
Sample 2	21·3	31·7	45·6	03·4
Sample 3	18·9	30·6	48·4	03·8
Sample 4	23·1	27·4	46·0	03·6
Sample 5	27·2	28·2	40·4	04·3

with negative oxalate groups and the Au^{3+} ions attach to these negative oxalate groups. The reduction with sodium borohydride, in the presence of tri-sodium citrate which acts as a capping agent, leads to the deposition of Au nanoparticles on calcite. An electroless deposition experiment performed using surface unmodified calcite led to a poor deposition of Au nanoparticles on calcite (see figure 3, sample 6). This proves that surface modification is necessary for uniform deposition of gold nanoparticles. In the galvanic displacement reaction, the replacement of Ag by Au is based on their reduction potentials. The standard reduction potential for Ag^+/Ag system is $+ 0·767$ V, while that for Au^{3+}/Au is $+ 0·995$ V. Due to the higher reduction potential of Au^{3+}/Au system, the Au^{3+} ions are reduced to Au on calcite with the concomitant oxidation of Ag to Ag^+.

$$AuCl_4^- + 3Ag \rightarrow Au + 3AgCl + Cl^-.$$
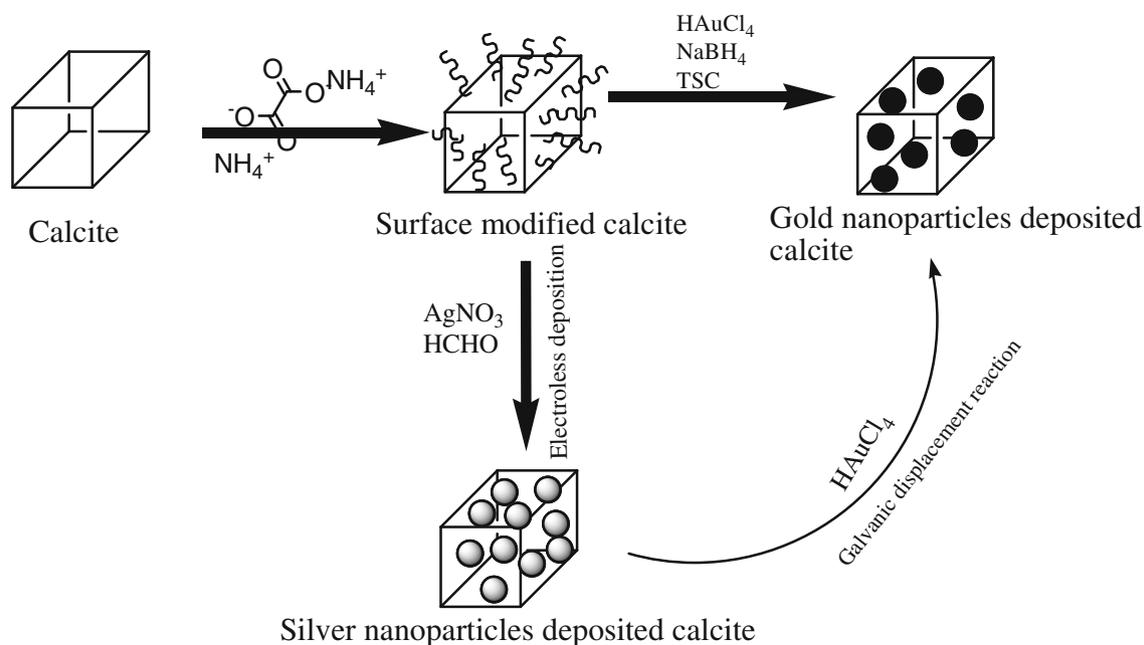
Scheme 3. Proposed mechanism for deposition of Au nanoparticles on calcite.

4. Conclusions

Gold nanoparticles have been deposited on synthetic calcite using two different methods: electroless deposition and galvanic displacement reaction. Electroless deposition is better for a uniform deposition of smaller Au nanoparticles on calcite compared to the galvanic displacement reaction. The present method is simple, economical and may be extended to other substrates with possible applications in catalysis, optoelectronics, sensors, etc.

Acknowledgements

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