Electronic Supplementary Material (ESI) for RSC Advances

Aldol Condensation in PEG-400 catalyzed by Recyclable L-proline supported on nano gold surface

Ajeet Kumar[a], Manika Dewan,[a] Arnab De [b] Amit Saxena,[a] Swati Aerry,[a] and Subho Mozumdar[a*]

[a] Department of Chemistry, University of Delhi,Delhi-110007, India

[b] Department of Microbiology and Immunology, Columbia University Medical Center

* E-mail- subhoscom@yahoo.co.in.

GENERAL METHODOLOGY FOR THE SYNTHESIS OF CATALYST

A. Synthesis of Gold nanoparticles

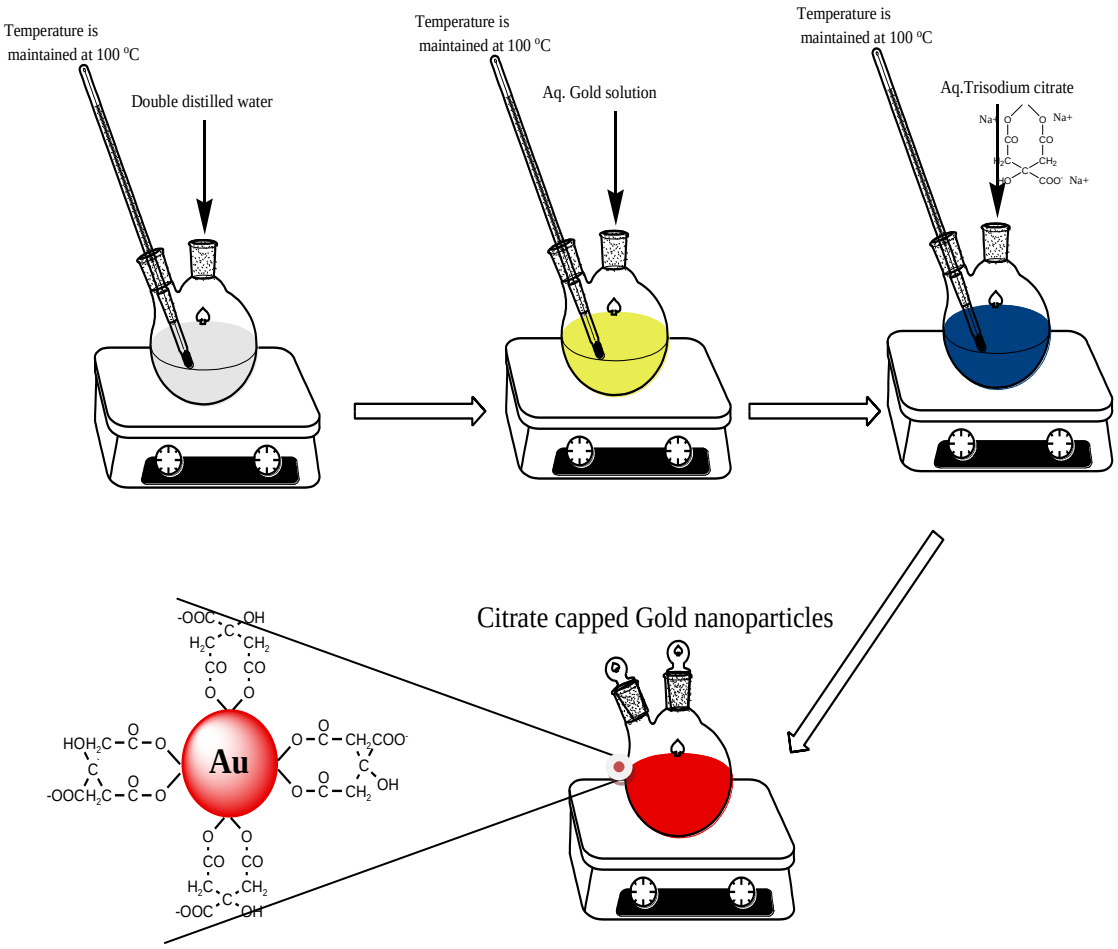
Au nanoparticles were synthesized using Turkevich approach with slight modification[19,20] (**Scheme 1)** as this is the most simple and versatile approach available in the literature for the synthesis of Au nanoparticles in aqueous solution.

In a 100 mL round bottom flask, 60 mL double distilled water was taken and allowed to boil using temperature controlled magnetic stirrer. Aqueous solution of aurochloric acid 1 mL (2 % w/v) was added and the reaction mixture was stirred for 1 min. 1 mL (5 % w/v) aqueous solution of tri-sodium citrate was added and the solution was allowed to stir vigorously for 20 min. After addition of tri-sodium citrate a blue color appeared followed by red wine optically clear homogeneous solution. This confirmed the formation of gold nanoparticles. The solution was cooled to room temperature and kept in a dry/cool place.

B. Protection of L-Proline

In a 100 mL round bottom flask 1:1 solution of water and dioxane (5 mL each) was taken. To this 1 mol L-Proline was added followed by addition of 4N NaOH (30 mL) solution with stirring. The reaction mixture was placed in ice-water so as to maintain a temperature of 3^{o}C - 5^{o}C. BOC-anhydride (1.2 mol) was added drop wise in a time span of one hour. The stirring was continued for 24 hrs. The reaction mixture was washed with diethyl ether (3x5 mL) upon completion of the extraction, the aqueous layer was treated with 1 N HCl to maintain a pH 2-3. The aqueous layer was extracted 2-3 times using

ethyl acetate. The solvent was removed under reduced pressure and purified by silica gel column chromatography.



Scheme 1: Synthesis of Gold nanoparticles.

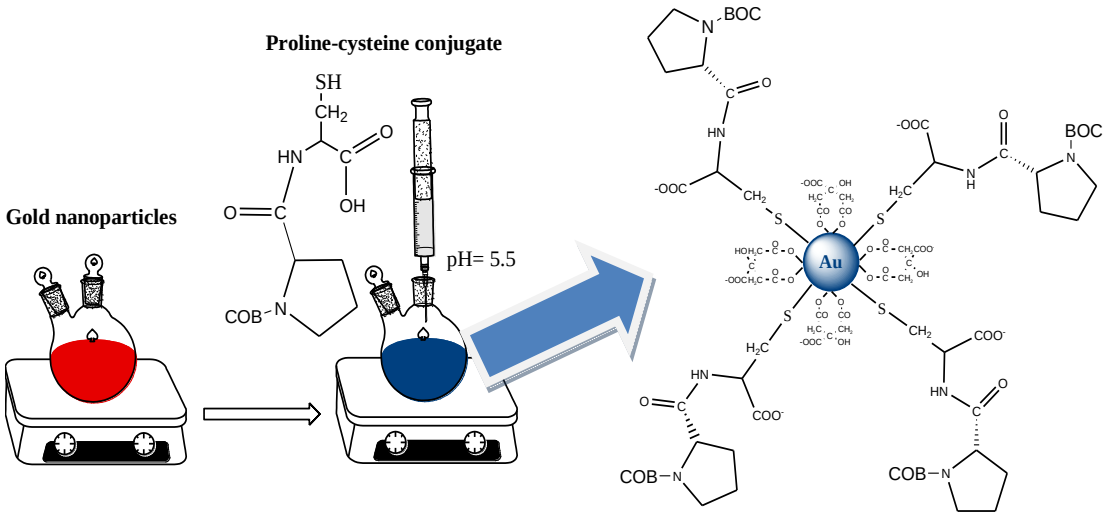
C. Binding of L-Proline with Cysteine

In a 50 mL round bottom flask containing 5 mL dichloromethane, 1 mol each of BOC L-Proline and L-Cysteine were added with stirring and the reaction mixture was maintained at 0°C - 5°C. Dicylohexyl carbodiimide (DCC, 1.2 mol) was added to the reaction mixture dropwise and stirring was continued for 18 hrs - 20 hrs. The reaction mixture was washed with 10% HCl and 10 % Na_2CO_3 followed by distilled water. The solvent was

removed under reduced pressure to obtain crude product which on crystallization using ethyl acetate gave DCC coupled BOC-proline-cysteine conjugate.

D. Immobilization of L-Proline-Cysteine conjugate on Au nanoparticles

BOC L-proline-Cysteine conjugate, prepared as described above, was added to the aqueous dispersion of Au nanoparticles at room temperature as shown in **Scheme 2.**



Scheme 2: Functionalisation of Proline on Gold nanoparticles with Cysteine as linker.

BOC L-Proline-Cysteine conjugated nanoparticles were separated from free proline-cysteine by centrifugation and washing. Attachment of BOC L-Proline-Cysteine on Au nanoparticles was confirmed by FT-IR, UV-visible spectroscopy, QELS, XRD and TEM of the conjugated nanoparticles.

E. Deprotection of L-proline-Cysteine conjugate

To a solution of BOC-Proline-Cysteine supported on Au nanoparticles (10 mmol) in CH_2Cl_2 (15 mL), TFA (1.5 mL) was added and the reaction mixture was stirred for 1 hr at room temperature. The excess solvent were removed under reduced pressure. The resulting oil was neutralized with saturated $NaHCO_3$ solution, extracted with CH_2Cl_2 (5×30 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product crystallized on standing.