

Green synthesis of gum-acacia assisted gold-hydroxyapatite nanostructures – Characterization and catalytic activity



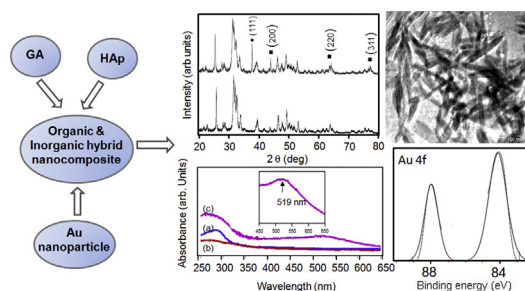
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HIGHLIGHTS

- We report low cost, low temperature synthesis of HAp by using natural polysaccharide.
- As-synthesized HAp under different parameters is characterized by various techniques.
- The gold nanoparticles (3–13 nm) appear to be uniformly dispersed in the HAp matrix.
- As-synthesized products are organic-inorganic hybrid nanocomposites proved by TGA.
- As synthesized product is explored for catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a facile and green synthetic protocol for the synthesis of Gum Acacia assisted hydroxyapatite (GA-HAP) nanostructures and *in-situ* reduced gold nanoparticles in GA-HAP (GA-HAP-Au) by controlling size and shape using gum acacia (GA) is reported. GA acts both as crystal growth modifier for HAp particles and as a reducing agent for the synthesis of gold nanoparticles (3–13 nm). The HAp nanoparticles were prepared from cheap chemicals, orthophosphoric acid and calcium chloride at mild reaction conditions by chemical precipitation method. This protocol is monitored and studied to understand the various morphologies of HAp nanostructures at different reaction conditions. The interaction of carboxylate group of glucuronic acid present in GA with HAp particles regulates the nucleation and crystal growth of the formed nanoparticles. As-synthesized products were well characterized by various techniques and the catalytic activity of GA-HAP-Au is explored for the hydrogenation of nitrobenzene to aniline formation under gas phase reaction.

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1. Introduction

Hydroxyapatite [HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] has been investigated as a potential heterogeneous catalyst for various chemical reactions such as dehydrogenation, epoxidation, removal (deprotection) of

N-benzyloxycarbonyl groups, racemization of alcohols, Knoevenagel condensation, Diels–Alder, aldol condensation reactions and oxidative cleavage of alkenes [1–9]. Yamaguchi et al. reported apatite as a catalyst for the partial oxidation of alcohols in the liquid phase, employing oxygen as an oxidant [10]. On the other hand, it has received great attention as an excellent candidate for biomedical applications, owing to its outstanding biocompatibility [11–13]. Properties such as bioactivity, solubility, fracture

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toughness, superior ion-exchange capacity and thermal stability can be modified by controlling the particles size and shape during the synthesis process [14]. Therefore, it is of great importance to develop synthesis methods aiming to control the particle size, morphology and chemical composition of HAp particles.

To date, a variety of methods have been reported for the preparation of HAp nanostructures following different methods such as mechanochemistry [15], hydrothermal [16], microwave irradiation [17–19] ultrasonic irradiation [20], solvothermal [21], chemical precipitation [22] and other techniques [23–31]. Amongst the various synthetic routes, the most popular and widely used technique for the synthesis of HAp nanostructures is chemical precipitation, due to the great control over HAp grain size and the relatively large amount of the product formed at mild temperatures [30]. In this method, the grain size of the synthesized HAp is greatly influenced by experimental conditions such as pH, temperature, concentration of the modifiers, addition rate of precursor, stirring rate, time and presence of impurities. Although precipitation occurs at room temperature, there is a necessity to raise the temperature in order to accelerate the formation of HAp nanoparticles, thereby reducing the reaction time [32]. Hence, this method is versatile and economical as it can be used to prepare HAp particles with an aid of simple chemicals.

It is well established that organic modifiers are widely used in the morphology and size-controlled synthesis of inorganic materials. In view of this, synthesis of HAp crystallites, using several organic modifiers, such as ethylene glycol [33], CTAB [34], amino acids, EDTA, mixed Tween-80 and polyoxyethylene [35] are widely reported. Other than these, surfactants, proteins and polymers have also been commonly used for guiding the synthesis of nanosized HAp for biological applications [36]. HAp-polymer composites such as HAp-gelatin, HAp-collagen, HAp/collagen-alginate, HAp-polypropylene [37] and HAp-chitosan are reported in the literature [38]. In an earlier work from our group, modified chitosan (carboxymethyl chitosan (CMCh)) was used to synthesize HAp by coprecipitation method that resulted in the formation of novel nanocomposite [39]. The development of facile, green, surfactant-free, HAp nanostructure with uniform size distribution by controlling the growth and the morphology still remains a challenge. In this regard, in the present work we have employed Gum Acacia both as a crystal growth modifier and reducing agent. Gum Acacia (GA) is a natural gum exudate, highly branched, extracted from acacia Senegal tree. It is a mixture of calcium, magnesium and potassium salt of a polysaccharide acid and composed of carbohydrate moieties (*galactopyranose*, *arabinopyranose*, *arabinofuranose*, *rhamnopyranose*, *glucopyranosyl uronic acid* and *4-O methyl glucopyranosyl uronic acid*) with a small portion of hydroxyproline rich protein [40]. It is a good emulsifying, stabilizing and dispersing agent due to electrostatic interactions between negatively charged groups from GA and positive sites on the oxide surface [39,41]. Our previous studies on GA explain the basic structure as well as good reducing and stabilizing properties in formation of metal nanoparticles [42,43].

Supported gold nanoparticles have potential applications as heterogeneous catalysts and are widely exploited [44]. Haruta et al. demonstrated that gold nanoparticles dispersed on metallic oxides, show high catalytic activity for CO oxidation [45]. In addition, Au/Ca₁₀(PO₄)₆(OH)₂ catalysts have been found to be excellent for various organic reactions such as water–gas shift reaction, wet oxidation of organic compounds, oxidation of silanes to silanols, deoxygenation of epoxides to alkenes and direct tandem synthesis of imines and oximes [46–51]. The high catalytic activity of supported gold particles has been accredited to quantum size effects, particle size, morphology and its oxidation state [52].

Herein, we report a green and facile method for size-controlled

synthesis of HAp nanocrystals by chemical precipitation method using natural polysaccharide – Gum Acacia (GA) that acts both as crystal growth modifier and reducing agent at mild reaction conditions. The present protocol is extended to synthesize hydroxyapatite-supported gold nanoparticles (GA-HAp-Au) and explore the catalytic activity for the hydrogenation of nitrobenzene to aniline under gas phase reaction.

2. Experimental procedure

2.1. Preparation of catalysts

Analytical pure calcium chloride and orthophosphoric acid were used as starting materials. 1 M calcium chloride was dissolved in 20 ml of homogenized GA solution to form uniform suspension. To the above solution 20 ml of 0.6 M phosphoric acid was added drop wise (ratio Ca/P 1.67, characteristic of calcium hydroxyapatite) and the pH of the solution was adjusted to 10 by adding sodium hydroxide under vigorous stirring, resulting in a milky white suspension. Later the suspension was sonicated for 10 min and then transferred to a 100 ml round bottom flask, and stirred for 24 h at 80 °C. Similar experiments were carried out for the synthesis of GA-HAp-Au catalyst. Required amount of HAuCl₄·3H₂O was dissolved in distilled water and added as a precursor to GA-HAp mixture during the reaction procedure to obtain GA-HAp-Au catalysts with 1 and 5 wt % of metallic gold. Finally, the mixture was centrifuged, washed with distilled water and ethanol till it reaches neutral pH and then dried at 60 °C for 4 h for further characterization.

2.2. General procedure for the catalytic activity of the GA-HAp-Au catalyst for hydrogenation of nitrobenzene

A down flow fixed bed reactor operating at atmospheric pressure and made of Pyrex glass was used for testing the catalysts for hydrogenation of nitrobenzene. About 100 mg of the catalyst, diluted with double the amount of quartz grains was packed between the layers of quartz wool. The upper portion of the reactor was filled with glass beads that serve as pre-heater for the reactants.

Prior to introducing the reactant with a syringe pump (B-Braun perfusor pump, Germany) the catalyst was pre-reduced in purified hydrogen flow (60 mL/min) at 230 °C for 3 h, so that the reduced surface contains Au⁰ stabilized on the support surface. After the reduction, the reactor was fed with nitrobenzene at 230 °C (WHSV = 36.12 h⁻¹; H₂/Nitrobenzene = 4; Residence time: 0.0276 h). The reaction products were analyzed by HP-6890 gas chromatograph equipped with a HP-5 capillary column with a flame-ionization detector (FID). The products were also identified using HP-5973 quadrupole GC-MSD system using HP-1MS capillary column.

2.3. Characterization techniques

The synthesized Gum Acacia assisted hydroxyapatite (GA-HAp) and in-situ reduced gold nanoparticles in GA-HAp (GA-HAp-Au) nanostructures were well characterized by ultraviolet–visible–diffused reflectance (UV–Vis–DRS) spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, BET surface area, pore size distribution and thermogravimetric analysis (TGA). The structural properties of the obtained products were recorded using a Rigaku X-ray powder diffractometer (Cu radiation, $\lambda = 0.1546$ nm) running at 40 kV and 40 mA (Tokyo, Japan). TEM images were observed on TECNAI FE12 TEM instrument operating at 120 kV using SIS imaging software.

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