Facile and Green Synthesis of Carboxy Methyl Cellulose Stabilized Bio-Functionalized Gold Nanoparticles and Its Catalytic Activity

Abstract:

Gold nanoparticles (AuNP's) are synthesized in sustainable green method using Carboxy Methyl Cellulose (CMC) and employed as catalyst in the reduction of p-nitro aniline with $NaBH_4$ to p-phenylene diamine. It is observed that the speed of reaction was fast due to their size, as particle size decreases surface area increases. It is also observed that the rate of reaction is fast with comparison with the other catalyst. This is because the nanoparticles have more effective surface area and posses less steric hindrance with p-nitro aniline and $NaBH_4$ when compared to nanoparticles due to their shape. The recyclability of nanoparticles shows it is potential recyclable catalyst for industrial applications.

Key Words: Green synthesis, gold nanoparticles, CMC, catalytic reduction, potential recyclable

Introduction:

Noble metal nanoparticles are attracting a great deal of researchers' attention due to their unique properties and perspectives of implementation in different fields. The areas of application of noble metal nanoparticles are extremely diverse. The possibilities of using noble metal nanoparticles as the agents for targeted delivery of drugs in living organisms, in photodynamic therapy of cancerous tumors, in the treatment of skin diseases, as biocidal disinfectants, as auxiliary materials in the imaging of affected tissues, in catalysis, as well as in other areas are being actively studied. The outstanding susceptibility of noble metal nanoparticles optical spectra to the tiny changes in the surrounding media electrodynamic properties facilitates the development of the chemical and biological sensors on their basis.

Noble metals are used to improve the characteristics of photodetectors and solar panels [1]. Nanostructures of noble metals are actively used as elements for the development of metamaterials [2]. Some efforts have been made to use them in nonlinear optics: for the second harmonic generation [3], for the terahertz radiation generation [4], as well as for studying of the hybrid states, such as plexitons (plasmon-excitons). Nanoparticles of noble metals were used to modify photo-induced changes in molecular layers [5], and also as optical nano antennas serving to change the rate of radiation processes [6].

Among different noble metal nanoparticles, Gold nanoparticles (AuNP's) have been widely employed in bio-nanotechnology based on their unique properties and multiple surface functionalities. The ease of AuNP's functionalization provides a versatile platform for nano-biological assemblies with oligo-nucleotides [7] antibodies [8], and proteins [9].

Bio-conjugates of AuNP's have also become promising candidates in the design of novel biomaterials for the investigation of biological systems [10]. The versatility of AuNP's has provided useful materials for a range of biomedical applications. In diagnostics, the binding event between the analytes and the AuNP's can alter the physicochemical properties of AuNP's such as surface plasmon resonance, conductivity, and redox behavior, leading to detectable signals [11]. AuNP's also serve as practical platforms for therapeutic agents, with their high surface area allowing a dense presentation of multifunctional moieties (e.g., drugs [12] and targeting agents [13]). Hence, researchers focused on easy and simple methods to achieve monodispersed and low dimensional nanoparticles. In this context, the present paper describes the synthesis of gold nanoparticles stabilized by Carboxy Methyl Cellulose (CMC) biopolymer and fructose as reducing agents. This method provides an amicable protocol to produce gold nanoparticles by controlling the size and shape.

Materials and Methods:

Chloroauric acid ($HAuCl_4$), Fructose and CMC were obtained in pureform from Sigma–Aldrich (USA) and are utilized as received. The acquired nanostructures were characterized by means of Transmission Electron Microscope (TEM), x–ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FT–IR). TEM, selected area electron diffraction pattern (SAED) and energy dispersive x-ray (EDX) data were obtained on an FEI Technai G2 S–Twin. For TEM analysis, a few drops of the Au colloidal samples dispersion onto the carbon coated copper TEM grid and dried overnight. XRD measurements were performed on a Bruker's AXS Model D8 Advance powder x-ray diffractometer instrument operated with Cu Kα radiation as the x-ray source (λ= 1.54 Ao). The FT–IR spectra were collected on the Nicolet 5700 Thermo scientific instrument with the samples as KBr pellets.

Preparation of Au nanostructures:

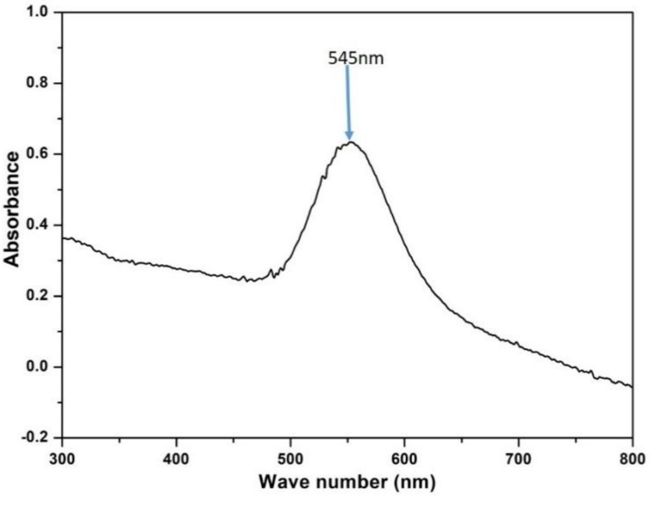
To synthesize Au nanoparticles, 2 mL of 0.01 M $HAuCl_4$ aqueous solution was added to the mixture of 2 mL of 1% fructose and 98 mL of 0.1 wt% CMC aqueous solution containing beaker at room temperature. For synthesizing self-assembled Au nanoparticles chain structures, the amount of CMC was 0.5 wt%.

Catalysis of *p*-Nitroaniline reduction:

0.6906 gm of *p*-Nitroaniline and 0.189 gm of $NaBH_4$ were dissolved in 50 ml of deionized water. Then from this 400µl of each $NaBH_4$ and *p*-Nitroaniline solutions were dissolved in 3200µl of deionized water. This is the main basic reaction mixture. Take 1500µl of this reaction mixture into the cuvette which was dissolved in the 1500µl of deionized water. To this add 0.05gm of the prepared nanoparticles as the catalysts to the reaction. Now observe the reaction path of this reaction by using the UV-Visible Spectroscopy.

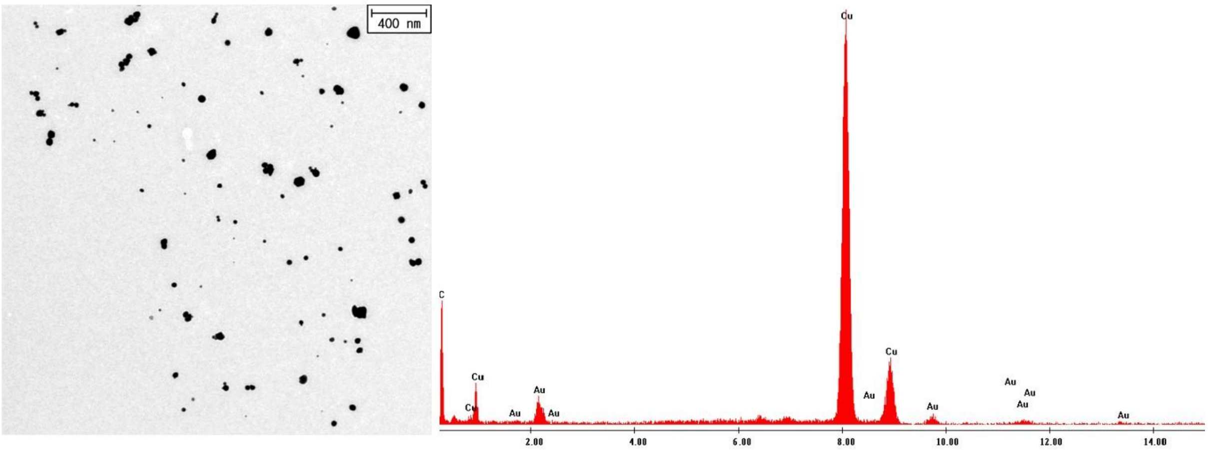
Results and Discussions:

The UV-Vis spectrum of the as prepared nanoparticles showed that the characteristic peak 545 nm, which initially attested the formation of low dimensional gold nanoparticles and it is presented in figure-1. Typically, maximum SPR absorption wavelength (λm) of GNPs is size and shape. This result motivated us to further characterize the samples in detail.



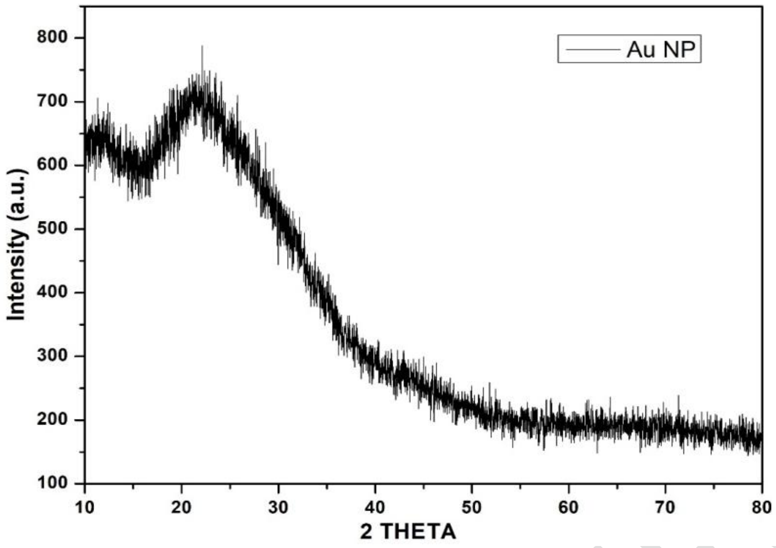
Figue-1: UV−visible spectra for Gold Nanoparticles

The characteristic features from HR-TEM confirm the crystallinity of the as prepared Au nanoparticles and the mono-dispersion of Au nanoparticles, as shown in Figure-2. The EDAX spectrum confirmed the purity and no other particles were presented in the material. These results comply with the previous UV–Vis results, in which the bigger size of particles was formed due to low value of the polarity index of reaction medium that consequent the growth of particles and assembly caused by the highly extended CMC polymer chain in low polarity indexed solvent. However, the Au nanostructures prepared from the use of 0.5% CMC, the spherical nanoparticles with an average diameter of ~15 nm tend to linear assembling and form chain like structures, which was observed in Figure-2. At high amount of CMC (0.5%), the number of CMC molecules anchoring to the surface of Au particles is increased.



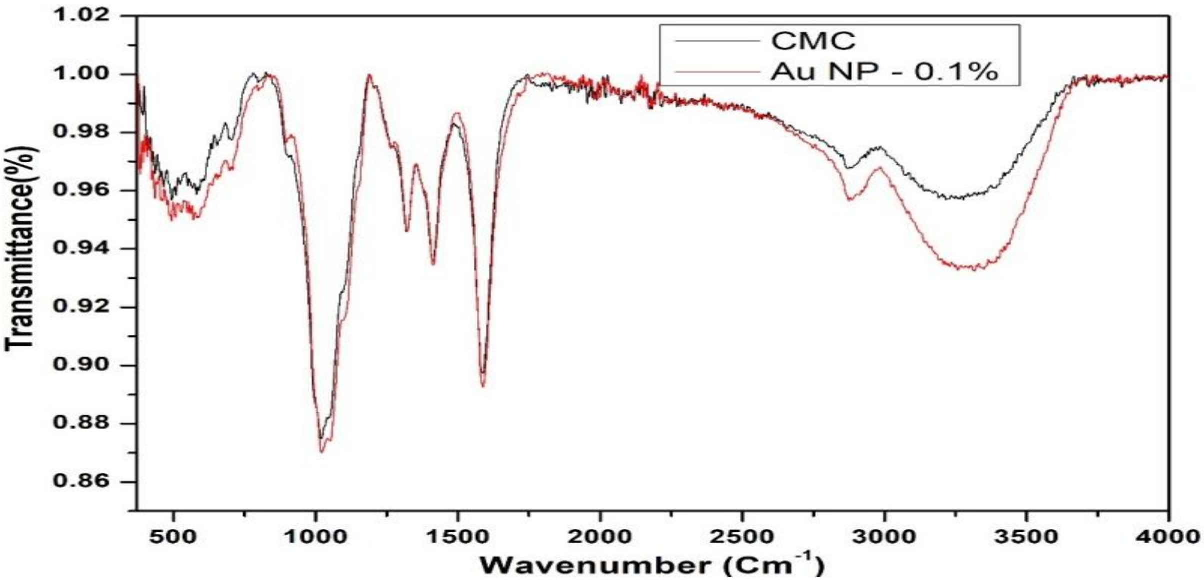
Figue-2: HR-TEM confirmation of crystallinity of the prepared Au nanoparticles and the mono-dispersion with EDAX spectrum confirm the purity

Therefore, the discrete Au nanoparticles directed to assembling in the linear way and form nanoparticle chain like structures via non-covalent interactions formed between the CMC molecules present on the surface of Au particles. The XRD spectrum of the synthesized nanoparticles was presented in figure-3. The results showed that the peak at 2 theta 28.2 represent the characteristic (111) phase of the fcc structure. The spectra confirmed the formed nanoparticles are in crystalline phase with an average crystalline size of 14.6 nm.



Figue-3: XRD spectrum of the synthesized CMC stabilized nanoparticles

The FT–IR spectrum of CMC stabilized Au nanoparticles (Figure-4) showed some shifts corresponding to stretching vibration of –OH functional group from 3265 to 3420 cm^{-1}, asymmetric stretching vibration of –COO– from 1588 to 1603 cm^{-1}, symmetric stretching vibration of –COO– from 1411 to1418 cm^{-1}, in–plane vibration of –OH from 1320 to 1331 cm^{-1} and stretching vibration of C–O–C from 1020 to 1060 cm^{-1}. These observations suggest that the prepared Au nanoparticles are stabilized through the interaction of both the –COO– (carboxylate) and -OH (hydroxyl) functional groups in CMC molecules.

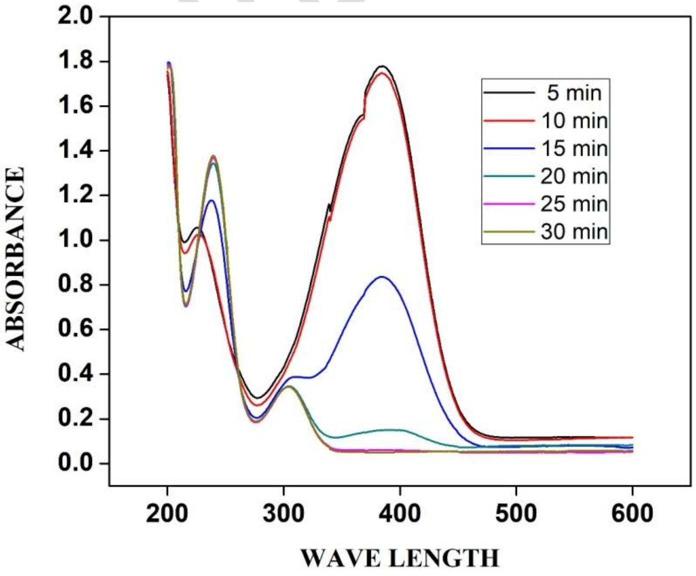


Figue-4: FT–IR spectrum of CMC stabilized Au nanoparticles

Catalytic studies:

Figure-5 shows the reduction of p-nitroaniline in the presence of gold nanoparticles formed from CMC stabilization was monitored in real time by UV−visible spectroscopy. A blank experiment was carried out for the reduction of p-nitroaniline with $NaBH_4$ in the absence of gold nanoparticles. There is a very slow decrease in the characteristic absorbance of p-nitroaniline at 378 nm after 24 h. The reaction was performed in the presence of gold nanoparticles where the absorbance peak at 378 nm showed a progressive decrease, a shifting of the absorbance peak at 223 nm, and the appearance of a new absorption peak at 303 nm. This result indicates that the gold nanoparticles were accelerating the reduction of p-nitroaniline into p-phenylenediamine in the presence of $NaBH_4$. The reduction rates of this reaction can be considered to be independent of the concentration of $NaBH_4$ since this reagent was used in large excess with respect to p-nitroaniline. Therefore, this chemical reduction follows first-order kinetics.

Figure-6 shows the reusable catalytic properties of the metal nanoparticles obtained from use of 0.5% CMC. It is found that, after 6 recycling reactions, the p-Nitroaniline still can be converting to p-phenylenediamine in the presence of $NaBH_4$ with a conversion rate reaching ~85%. Thus, the metal nanoparticles synthesized are potent recyclable nanocatalyst for the industrial applications.



Figue-5: Reduction of p-nitroaniline in the presence of gold nanoparticles formed from CMC stabilization

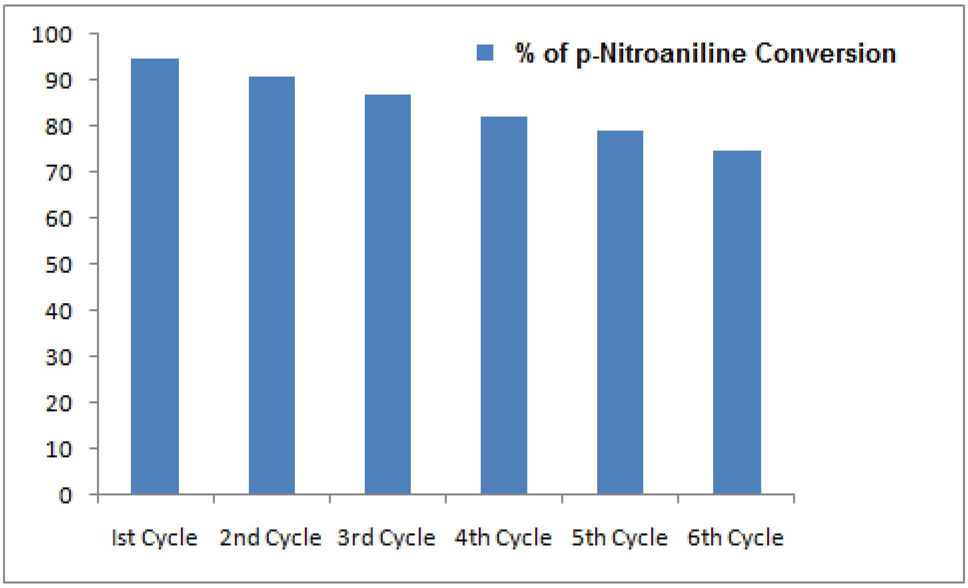


Figure-6: Recyclability of the Gold nanoparticles obtained as a catalyst for the reduction of p-nitroaniline with $NaBH_4$.

Conclusion:

Gold nanoparticles (AuNP's) were used as an eco-friendly catalyst in a green approach format in water at room temperature to accomplish an efficient chemoselective reduction of p-Nitroaniline. The product of this chemical reduction, p-phenylenediamine, is an attractive intermediate in the preparation of polymers, hair dyes, and rubber products. Hence, there is a great demand to develop efficient catalysts for this chemical reduction of p-nitroanilines. The reactions are worth repeating, since they are reusable and high yielding (around 95 percent).

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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