Microwave Assisted Synthesis and Characterization of Induced Gellan Based Silver Nanocomposite Hydrogel

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Abstract. The current study deals with the synthesis, characterization of silver nanoparticles using gellan gum based silver nanocomposite materials using microwave radiation assisted method at room temperature. The resultant products have been confirmed to be Ag-Nanocomposite was carried out based on UV-Vis spectroscopy (440 nm), The UV-visible spectra showed that the characteristic of Ag nanoparticles surface Plasmon resonance (SPR) band exhibits an absorbance peak around at around 450 nm. The transmission electron microscope (TEM) images show that the formed nanoparticles were spherical in shape with smooth surfaces. The particle diameter was around 50-100 nm. Further the X-ray diffraction (XRD) analysis confirms the nanocrystalline phase of silver with face centered cubic (FCC) crystal structure and interesting results are discussed in this report.

INTRODUCTION

Metallic nanoparticles have attracted much attention in recent years due to their unique properties [1]. Among the noble metals, silver nanoparticles (AgNPs) are widely utilized in material science, physics and chemistry because of their particular optical, magnetic, electronic, and catalytic properties [2].AgNPs have been used for the determination of cyanide, thiocyanate and ammonia [3]. The synthesis of AgNPs in aqueous solutions is difficult due to the affinity of AgNPs to aggregateirreversibly. Recently, the microwave-assisted method was employed for the synthesis of the cellulose–silver nanocomposites, cellulose–carbonated hydroxyapatite nanocomposites, and cellulose–hydroxyapatite nanocomposites due to its unique effects such as rapid volumetric heating high reaction rate, short reaction time, enhanced reaction selectivity, and energy saving [4]. The polyol, such as EG, is a polar solvent which also has a reducing ability. The polyol process was applied for the large-scale synthesis of silver nanowires with uniform diameters. Microwave–polyol method has been widely utilized in the preparation of Ag nanoparticles using polyol as both reducing agent and solvent [5]. Moreover, microwave–polyol method also was used to the synthesis of nanocomposites [6].

In a present work have been developed polysaccharide based inorganic hydrogel and also present work explores the use of nano composite hydrogel which is prepared by using GG and (AAm-co-AMPS) by a green process. GG was chosen on the basis of its significant characteristics in biomedical fields. Structural, thermal and morphological studies of the hydrogel and their corresponding AgOnanocomposite hydrogel were carried out by using UV-visible spectroscopy and X-ray diffraction (XRD). The content and distribution of AgO nanoparticles in GG-graft-P(Aam-co-AMPS) hydrogel by thermogravimetric analysis (TGA), and transmission electron microscopy (TEM).

EXPERIMENTAL

Microwave Assisted Synthesis of GG-g-P(AMPS-AAM) hydrogel:Microwave assisted synthesis of GG-g-P(AMPS-AAM)hydrogels by using a free radical polymerization approach. 0.5g of GG was dissolved in 30 ml deionized water to form a viscous solution, 0.25g of AMPS and AAm monomers were added into it and stirred for some times, followed by addition of 1ml of 0.065 mol APS and MBA solutions into the reaction mixture. After thorough mixing, the solution was transferred to the reaction vessel (an open glass beaker), placed on the turntable of a domestic microwave oven and irradiated for a specific period under microwave power (80W) for 60 seconds. Then obtained gel was precipitated in acetone, filtered, purified by washing with methanol to remove residues of the unreacted monomers and cross-linking agents and finally dried in a vacuum oven at 50 °C until constant weight.

Preparation of GG-g-P(AAM-co-AMPS)-Ag nanohydrogel: Briefly, 0.5g of dry hydrogels were equilibrated in double distilled water for 48 h and the swollen hydrogel species were transferred in to a beaker containing 50 ml of $AgNO_3$ (10 mM) aqueous solution and then allowed to equilibrate for 24 h. During this equilibrium stage, the Ag^+ ions are being exchanged from solution to the GG-g-P(AAM-co-AMPS)hydrogel networks. The Ag^+ ions loaded GG-g-P(AAM-co-AMPS) hydrogels were wiped off using tissue paper and transferred in to a beaker containing 50 ml of TCS (10 mM) solution. The beaker was left in the refrigerator (4 °C) for 8 h in order to reduce the Ag^+ ions into AgOnano particles. The obtained hydrogel AgO nano particles was used for further studies.

UV–Visible absorption spectra of the hydrogels containing silver nanoparticles were recorded using UV-visible spectrophotometer (Shimadzu UV-1800, Japan) in the wavelength range 190 – 800 nm. Crystalline metallic silver nanoparticles were examined using an X-ray diffractometer (Rigaku Miniflex-II) operating at a voltage of 40 kV and current of 40 mA with CuKα radiation (λ=1.5406Å). The sample were scanned in the range 10-80° with a scanning speed and step size of 5°/min and 0.02°.The morphology of the GG-g-P(AMPS-c-AAM) and GG-g-P(AMPS-c-AAM)-Ag nano hydrogels were performed using transmission electron microscopy (TEM) which was performed at using JEOL JEM-2010 operated at an accelerating voltage of 200 keV.

The thermal properties of prepared Ag nanocomposite samples were studied using a TA-STD Q600 instrument under dry nitrogen atmosphere at the flow rate of 100mL/min. The samples were heated from room temperature to 700°Cat predetermined rate of 20°C/ min.

RESULTS AND DISCUSSIONS

The UV-Vis spectra of the GG-g-P(AMPS-AAM) hydrogel Ag nanocomposite. The Surface Plasmon resonance (SPR) bands of Ag nano-paricles in the hydrogel show different peak positions and peak widths with changing preparation time. Comparing with digital camera image for Ag nano-particles in the hydrogel, a blue shift is seen as the reaction time of Ag nanoparticles increase in hydrogl matrix. This result indicates that GG are good stabilizing agent for silver nano-particles. In addition, blue shifts and the narrower widths of the SPR bands confirm the smaller size and more uniform size distribution of silver nano-paricles by increasing reaction time of it in the hydrogel matrix [7].The mechanism of graft copolymerization of AMPS and AAm on biopolymers has been previously reported. The sulphate anion radicals (SO_4^{2-}) generated by the decomposition of APS act as chain carriers for graft copolymerization by creating GG macroradicals. However, in macromolecules like polysaccharides, rotation of the entire molecule is different and hence the microwave will be absorbed by the polar groups present (e.g.-OH groups on GG).
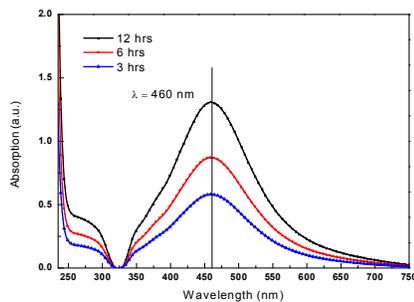

FIGURE 1. UV spectra of different time intervals of GG-g-P(AMPS-AAM)-Ag solution at 3 hrs, 6 hrs, and 12 hrs.
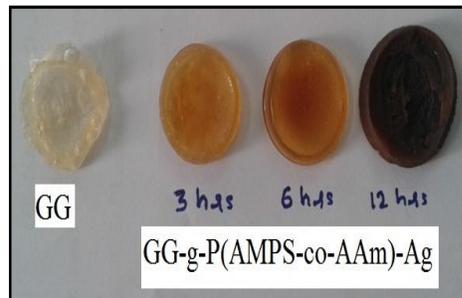

FIGURE 2. Photographic images of GG and nano composite hydrogel at different intervals of time.

The localized rotations of such groups lead to cleavage of bond leading to free macroradical sites on GG [8]. Finally, GG macroradicals and AMPS-AAm radicals are combined to form GG-g-P(AMPS-AAm) copolymer [9]. Therefore in this study, we have synthesized of Ag NPs in hydrogel as reported elsewhere [10].

In this experiment, the grafted hydrogels were allowed to swell in the AgNO$_3$ solutions and reduced with TSC solution throughout the gel networks. In detail, the P(AMPS-AAm) cross-linked networks act as reservoir for Ag$^+$ ion uptake and ions are anchored through carboxylic, amine and hydroxyl groups of biopolymers and thereby holds large amounts of Ag$^+$ ions in their network and facilitate the reducing process as well as helps in stabilization. The biopolymer in hydrogel networks arrests the agglomeration of Ag NPs. The Ag NPs synthesis in GG-g-P(AMPS-AAm) hydrogel networks is pictorially represented as reported [11]. It is quite interesting to point out that Ag NPs are strongly binding throughout the hydrogel networks as well as entrapped the NPs without releasing into the media. Analysis of the X-ray diffraction patterns is a suitable technique to identify the crystallinity of the inorganic polymer materials. The X-ray diffraction patterns of GG, GG-g-P(AMPS-co-AAm) and GG-g-P(AMPS-co-AAm)-Ag nanocomposite hydrogel were demonstrated in Figure 3.
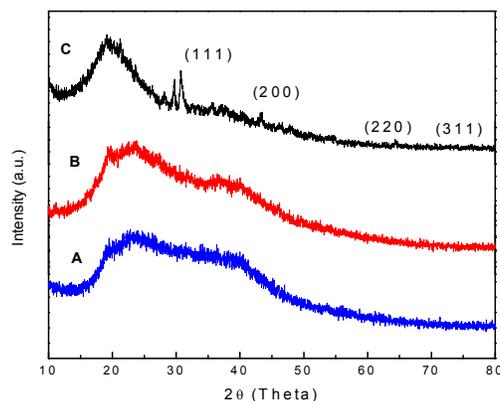

FIGURE 3. XRD patterns of (A) GG, (B) GG-g-P(AMPS-co-AAm), (C) GG-g-P(AMPS-co-AAm)Ag.

In Figure 3, it can be clearly seen that no diffraction peak was observed for the pure GG and GG-g-P(AMPS-co-AAm) hydrogel due to amorphous nature carbohydrate, while the AgO nanocomposite and GG-g-P(AMPS-co-AAm)Ag hydrogel showed intense diffraction peaks at $2\Theta=38.16, 44.26, 64.39$ and 74.40, corresponding to the reflections of crystal planes of (111), (200) and (311) respectively, of the face-centered cubic (fcc) structure of AgO. This face centered cubic structure indicates that the AgO nano particles were dispersed in the GG-g-P(AMPS-co-AAm) hydrogel [12].

TEM image demonstrates a highly uniform distribution of silver nanoparticles as shown in Figure 3. It is confirmed that the silver nanoparticles formed in the cross-linked network are spherical, highly dispersed, low nanometre in size. Moreover, the selected area electron diffraction (SAED) pattern of silver nanoparticles is clearly visible as three diffraction rings from the selected area of the TEM image and they are definitely attributed to the fcc structure of silver nanoparticles [13].
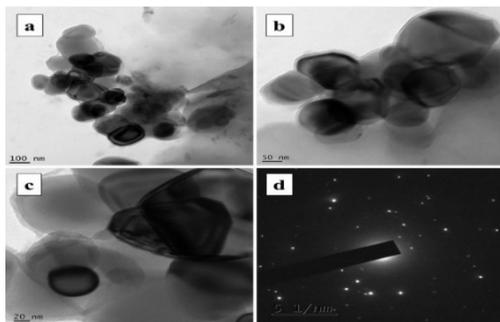

FIGURE 4. Transmission electron micrograph images of A) GG-g-P(AMPS-c-AAm)-Ag d) Typical SAEDofGG-g-P(AMPS-c-AAm)-Ag.
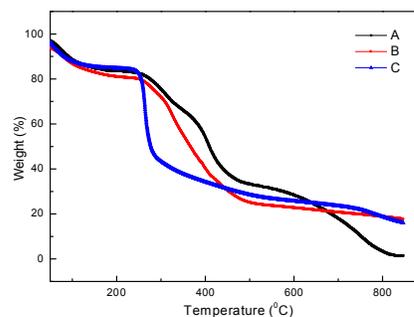
FIGURE 5. TGA patterns of (A) GG, (B) GG-g-P(AMPS-co-AAm), (C) GG-g-P(AMPS-co-AAm)Ag.

The brightest ring and the one closest to the centre is a combination of the (111)and (200)reflections. The second ring belongs to (222)reflection and the weakest third ring is due to either (420)and/or (422)reflections [14]. This clearly represents that highly dense GG-g-P(AMPS-co-AAm) hydrogel networks favour silver nanoparticle formation because that composition permits the establishment of inter- and intra-molecular attractions between the grafted hydrogel networks due to less free space in the hydrogel networks. The particle size is found between 20 and 50 nm.To investigate the thermal behaviour of the GG-g-P(AMPS-c-AAM) and GG-g-P(AMPS-c-AAM)-Ag hydrogels nanocomposite films, the analysis of thermogravimetric (TG) study was carried out. Thermograms obtained for the hydrogel nanocomposite are shown in Fig. 5 and exhibit three distinct regions. In the first region, starting from room temperature up to 200 °C, the weight loss could be attributed to the elimination of adsorbed water. The weight change was not significant and the sample was thermally stable. In the second region from 200 °C to 400 °C, the the hydrogel nanao composite film experienced a great weight loss because of the breakdown of side chain groups [15]. About 50% of the sample decomposed into volatiles. Another strong (the third region) weight loss of about 75% - 90% in the range 500–700 °C is attributed [16]. The hydrogel nanocomposites also exhibited three distinct regions with small variation in the decomposition temperature.

CONCLUSIONS

In this study, GG-g-P(AMPS-co-AAm) silver nanocomposite hydrogel were successfully synthesized through a green process (The silver nano particles were developed by reducing $AgNO_3$ solution with trisodium citrate in the GG-g-P(AMPS-co-AAm) hydrogel network). These synthesised composite were observed by UV-visible spectra at 424 nm. The synthesized silver nanoparticles were spherical in shape and their morphology was confirmed by TEM images. Further the X-ray diffraction (XRD) study reveals the nanocrystalline phase of silver with FCC crystal structure. From this investigation, silver nano particles were dispersed in the GG-g-P(AMPS-co-AAm)hydrogel and strong interaction was formed between the polymeric cross linked network and silver particles. From the TGA thermograms, it is noticed that the formed nanoparticles have not influenced the thermal properties of the nanocomposite film.

ACKNOWLEDGMENTS

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