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Controlled silver nanoparticles synthesis in semi-hydrogel networks of poly(acrylamide) and carbohydrates: A rational methodology for antibacterial application

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ABSTRACT

In the present study, we report the preparation of semi interpenetrating hydrogel networks (SIHNs) based on cross-linked poly (acrylamide) prepared through an optimized rapid redox-solution polymerization with *N*,*N*′-methylenebisacrylamide (MBA) in presence of three different carbohydrate polymers, namely gum acacia (GA), carboxymethylcellulose (CMC) and starch (SR). Highly stable and uniformly distributed silver nanoparticles have been obtained with hydrogel networks as nanoreactors via in situ reduction of silver nitrate ($AgNO_3$) using sodium borohydride ($NaBH_4$) as reducing agent. The formation of silver nanoparticles has been confirmed with ultraviolet visible (UV–vis) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analyses. Thermogravimetric analysis (TGA) provides the amounts of silver nanoparticles exist in the hydrogel networks. Transmission electron microscopy (TEM) results demonstrate that acacia employed hydrogels have regulated the silver nanoparticles size to 2–5 nm where as CMC and starch composed hydrogel networks result in a heterogeneous size from 2 to 20 nm. The preliminary antibacterial activity performed to these hydrogel–silver nanocomposites.

1. Introduction

In recent years, the study and preparation of inorganic particles on the nanometer scale has attracted considerable interest from both fundamental and applied research (Bajpai, Mohan, Bajpai, Tankhiwale, & Thomas, 2007). It is recognized that the physical and mechanical properties of nanosize particles differ from those of macroscopic material. Precious metal nanoparticles are mainly utilized in solving the problems of water purification, catalysis and hydrogen storage. A wide range of applications have been found for metal nanoparticles in catalysis (Biffis, Orlandi, & Corain, 2003; Daniel & Astrue, 2004), electronics (Kiesow, Morris, Radehaus, & Heilmann, 2003), sensors and high density information storage (Ross, 2001; Vaseashta & D-Malinovska, 2005), luminescence devices (Colvin, Schlamp, & Alivisatos, 1994), photonics (Xu, Zhang, Paquet, Lin, & Kumacheva, 2003), pharmaceuticals, biotechnology and medicine (Xu, Zeng, Lu, & Yu, 2006).

Generally metal nanoparticles agglomerate due to high active surface area. To stabilize and control the nanoparticles structures various surfactants, polymers, dendrimers, biological templates, and biomacromolecules were used (Bajpai et al., 2007; Chen & Hsieh, 2002; Chen, Serizawa, & Akashi, 1999; Esumi, Isono, & Yoshimura, 2004; Esumi, Suzuki, Yamahira, & Torigoe, 2000). Biological systems form sophisticated mesoscopic and macroscopic structures with tremendous control over the placement of nanoscopic building blocks within extended architectures (Mandal, Phadtare, & Sastry, 2005). The concept of green nanoparticles preparation was promoted by Raveendran et al. (Raveendran, Fu, & Wallen, 2003) in which β-D-glucose act as reducing agent and starch played stabilizer role. In another study, silver nanoparticles were prepared with carbohydrate polymer, carboxymethyl cellulose sodium (CMCNa) that effectively works as both reducing and stabilizing reagent (Chen, Wang, Zhang, & Jin, 2008). Mono-disperse self assembly of ordered arrays of platinum nanoparticles were successfully prepared in presence of sodium carboxymethyl cellulose (Liu, Sutton, & Roberts, 2007). Nanoparticles (CdS) were synthesized through a simple and "green" route using starch as a capping agent (Wei, Kang, & Mu, 2004). Starch acted both as reducing and stabilizing agent in the production of silver nanoparticles (10–34 nm) in an autoclave reaction at 15 psi, 121 °C for 5 min which are highly stable in aqueous solution over a period of three months (Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006). Hollow silver nanospheres were fabricated using mercapto modified starch as a template (Wang & Chen, 2007). In addition, several approaches have been carried out to prepare silver

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nanocomposites with well-defined size and morphology (Zhang, Zhang, Wang, Chen, & Lei, 2001; Zhao et al., 2005).

Among the recognized novel approaches, hydrogel or macroscopic gels have been used as promising templates or nanopots to prepare nanoparticles that brought a concept for newer composite/hybrid materials (Mohan, Lee, Premkumar, & Geckeler, 2007). The available free-network spaces between hydrogel networks reserve to grew and stabilize the nanoparticles. In detail, in-situ reduction of metal ions and stabilization of particles can be explained as (a) first metal ions are anchored by functional groups of hydrogel networks and major amounts of metal ions are entrapped in the free-network spaces of hydrogels, (b) then reduction process takes place where sodium borohydride ($NaBH_4$) or some reducing agents employed for this purpose, (c) the formed particles are well stabilized by the hydrogel network chains (Wang, Flynn, & Langer, 2004). The formed nanoparticles in their network effectively inhibit the aggregation for longer periods and can be extracted into water whenever they are required for usage. Moreover, these nanocomposite systems are highly suitable for bio-medical applications because of their good bio-compatibility over biological molecules, cells, tissues, etc. Another advantage of this method is that we can control overall size and morphology of the nanoparticles by changing its functionality and cross-linking points. Poly(vinylpyrrolidone) (PVP) based poly(acrylamide) (PAM) semi-IPN hydrogels network also used to stabilize the silver nanoparticles (Murthy, Mohan, Varaprasad, Sreedhar, & Raju, 2008). A series of antibacterial superabsorbents containing silver hydrogel nanocomposites were successfully prepared by inverse suspension polymerization (Lee & Huang, 2007).

By considering the importance of hydrogel networks as effective carriers for nanosystems and natural polymers (carbohydrates) such as starch, carboxymethylcellulose, acacia, as prepolymer renewable materials with hydrophilic nature for anchoring/reduction of metal ions and stabilization, prompted us to draw a new idea in which semi-IPN hydrogels prepared in presence of prepolymers that would be better choice to cook metal nanoparticle in their networks. For this purpose, the combination of poly(acrylamide) hydrogel and carbohydrates systems are selected because of their more relevance for pharmaceutical and biomedical applications.

2. Materials and methods

2.1. Materials

Acrylamide (AM), carboxymethylcellulose (CMC), starch (SR), gum acacia or acacia (GA), ammonium persulphate (APS) were supplied by S.D. Fine Chemicals (Mumbai, India) and used as received. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), *N*,*N*′-methylenebisacrylamide (MBA), *N*,*N*,*N*′,*N*′′-tetramethylethylenediamine (TEMED) were received from Aldrich Chemical Company Inc. (Milwaukee, WI, USA) and used without further purification. Double (DB) distilled water was used for the preparation of any solutions in this study.

2.2. Preparation of semi-IPN hydrogels

Poly(acrylamide) semi-IPN hydrogels were prepared by polymerizing 1 g of AM dissolved in 6 ml of distilled water with different carbohydrates of various concentration of GA, CMC, and SR in presence of a cross-linker (MBA) and initiating system (APS/TEMED). Polymerizations were performed in 100 ml beakers at room temperature. The polymerization reactions for all the ratios became gels within 1 h of reaction time and the gel codes are listed along with composition information in Table 1.

2.3. Preparation of semi-IPN hydrogel–silver nanocomposites

To prepare semi-IPN hydrogel–silver nanocomposites, accurately weighed dry semi-IPN hydrogels were equilibrated with water for 3 days and these semi-IPN hydrogels were transferred to another beaker containing 50 ml of 5 mM $AgNO_3$ aqueous solutions, allowed to equilibrate for 1 day. Here, most of the silver ions are exchanged from solution into hydrogel networks by anchoring through –COOH, –$CONH_2$, –OH groups of hydrogel chains and rest of metal ions were occupied in free-network spaces of hydrogels. These silver salt loaded semi-IPN hydrogels were finally transferred into a beaker containing 50 ml of 10 mM $NaBH_4$ aqueous solution and allowed for 2 h to reduce the silver ions into silver nanoparticles. The obtained silver nanoparticles in the semi-IPN hydrogels are often termed in the forthcoming sections as semi-IPN hydrogel–silver nanocomposites (SIHSN). The resulting nanocomposite is termed SIHSN-GA, SIHSN-CMC, and SIHSN-SR for semi-IPN hydrogels when they were prepared with gum acacia, carboxymethylcellulose and starch.

2.4. Swelling studies

The same weights of dried semi-IPN hydrogels were equilibrated in distilled water at 25 °C for 3 days. Swollen semi-IPN hydrogels were treated first with $AgNO_3$ and then with $NaBH_4$ solutions as explained in the experimental section. The swelling ratio (Q) of the gels was calculated from equation: $Q = W_e/W_d$, where W_e is the weight of water in the swollen hydrogel and W_d is the dry weight of the pure hydrogel.

2.5. Characterization

FTIR spectra of semi-IPN hydrogels and SIHSNs were recorded with a Thermo Nicolet Nexus 670 spectrophotometer (Washington, USA). UV–vis spectra of SIHSNs (10 mg in 1 ml of distilled water) were carried out on a Shimadzu 160A UV spectrophotometer (Kyoto, Japan). For this, grinded samples (10 mg/ml) were stored for 10 days to leach out silver nanoparticles into water (medium) and then performed the measurements. X-ray diffraction measurements for SIHSNs were recorded using a Rikagu diffractometer (Cu radiation, $\lambda = 0.1546$ nm) running at 40 kV and 40 mA (Rikagu, Japan). The thermal stabilities of these nanocomposites were evaluated using Mettler Toledo 851e thermal system (Zurich, Switzerland) at a heating rate of 10 °C/min under nitrogen atmosphere (flow rate, 10 ml/min). Transmission electron microscopy (TEM) images for these nanocomposites were recorded using a Tecnai F 12 transmission electron microscope operating at an acceleration voltage of 15 kV. For TEM measurements, samples were prepared by dropping 10–20 μl of finely grinded semi-IPN hydrogel silver nanocomposite dispersions on a copper grid and dried at room temperature after removing excess solution using filter paper.

2.6. Antibacterial activity

To carry out the antibacterial activity for these nanocomposites, nutrient agar medium was prepared by using peptone (5.0 g), beef extract (3.0 g), and sodium chloride (NaCl) (5.0 g) in 1000 ml distilled water and the pH was adjusted to 7.0 and agar (15.0 g) was added to the solution. The agar medium was sterilized in a conical flask at a pressure of 15 lbs for 30 min. This nutrient agar medium was transferred into sterilized petri dishes in a laminar air flan. After solidification of the media, bacillus culture was streaked on the solid surface of the media. To this inoculated petri dish, one drop of gel particle solution (20 mg/10 ml distilled water) was added using 50-μl tip and incubated for 2 days at 37 °C in the incubation chamber.

Table 1
Synthetic parameters and components involved in the preparation of PAM hydrogel and semi-IPN-hydrogels[a]

PAM hydrogel					
Code		AM (g)		MBA ($\times 10^{-3}$ mM)	
PAM		1 g (14.26 mM)		6.48	
PAM/GA semi-IPN hydrogels		PAM/CMC semi-IPN hydrogels		PAM//SR semi-IPN hydrogels	
Code	GA (g)	Code	CMC (g)	Code	SR (g)
GA1	0.10	CMC1	0.10	SR1	0.10
GA2	0.15	CMC2	0.15	SR2	0.15
GA3	0.20	CMC3	0.20	SR3	0.20
GA4	0.25	CMC4	0.25	SR4	0.25
GA5	0.5	CMC5	0.5	SR5	0.5

[a] AM, [14.26 mM]; APS, [2.192×10^{-3} mM]; TEMED, [8.6×10^{-5} mM]; temperature, 25 ± 1 °C; and time, 24 h.

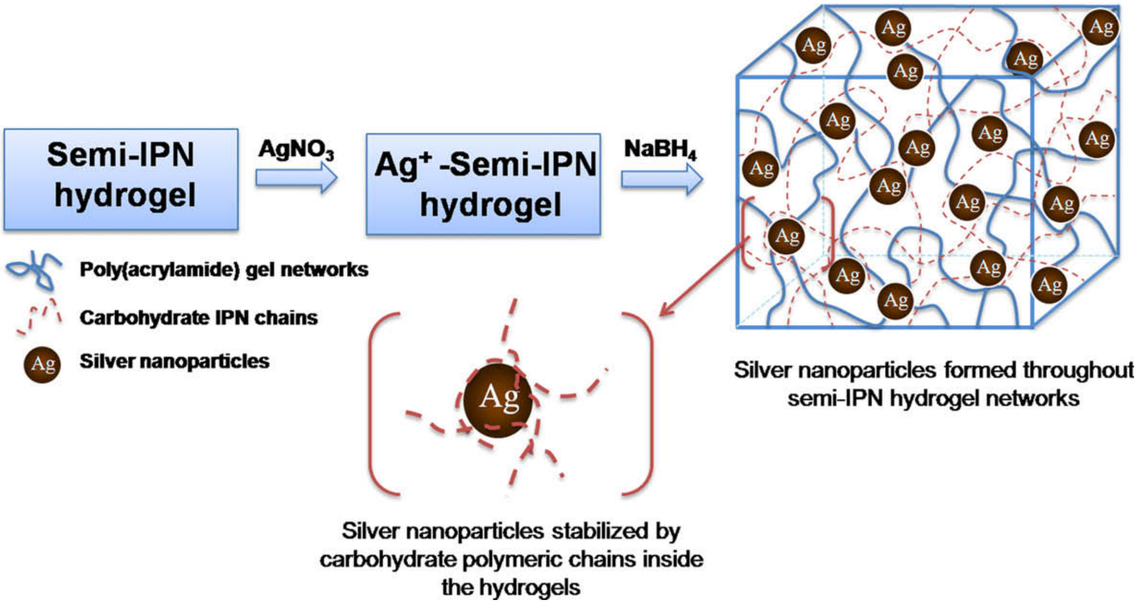
3. Results and discussion

The concept of producing nanoparticles in the networks of hydro-, micro-, and nanogel systems was recognized as most important approach due to its direct applicability in various biomedical applications and in this way a number of composite systems were evaluated (Bajpai et al., 2007). Following to the extension to the hydrogel–metal nanocomposites, recently semi-IPN hydrogels based on poly(acrylamide) hydrogels/poly(vinylpyrrolidone) networks have been used successfully to produce silver nanoparticles (Murthy et al., 2008). Moreover, no reports have been found in the literature that semi-IPNs can be effectively employed to generate the nanoparticles in their networks (Thomas, Namdeo, Mohan, Bajpai, & Bajpai, 2008). At this junction, we have explored to design semi-IPN hydrogels employing acacia, carboxymethylcellulose, and starch carbohydrate polymers which are renewed materials to enhance the reduction potential/anchoring ability and stabilization of the formed nanoparticles (Goia & Matijevic, 1998; Magdassi, Bassa, Vinetsky, & Kamyshny, 2003; Mohan, Raju, Sambasivudu, Singh, & Sreedhar, 2007; Raveendran, Fua, & Wallen, 2006). In any conventional hydrogel networks processes the available functional groups and cross-link density decides the stability of nanoparticles.

Therefore, in this study, we have developed smaller size and finer distribution of silver nanoparticles in semi-IPN hydrogel networks composed of poly(acrylamide) with GA/CMC/SR carbohydrate polymeric chains. The advanced feature of this methodology is that the nanoparticles simply prepared at room temperature in presence of green stabilizers. In these experiments, the semi-IPN hydrogels were allowed to swell in the $AgNO_3$ solutions and reduced with $NaBH_4$ throughout the gel networks. In detail, the PAM cross-linked networks act as reservoir for metal ions uptake and the ions are anchored through carboxylic, amide, and hydroxyl groups of carbohydrate polymers and thereby holds large amounts of metal ions in their network and facilitate the reducing process as well as helps in stabilization. The carbohydrate polymers in hydrogel networks arrest the agglomeration of silver nanoparticles. The concept of silver nanoparticles synthesis in semi-IPN hydrogel networks is schematically presented in scheme 1. It is quite interesting to point out that silver nanoparticle are formed exclusively inside the hydrogel networks and no particles formation is observed in the surrounding medium, that strictly confirm that hydrogel networks are binding to the silver ions as well as storing the nanoparticles without releasing into the media.

3.1. Swelling capacity

The basic feature of hydrogel is that it can absorb and hold huge amount of water/ solvent in its network structures and release over a period of time (usually from weeks to months). This special property is very important not only to load the metal ions and formation of metal nanoparticles from reduction reaction, but also for its future studies including antibacterial activity or wound healing, and for any biomedical applications. Hence, we have chosen carbohydrate polymers (GA, CMC, and starch) to improve swelling



Scheme 1. Synthesis of silver nanoparticles throughout semi-IPN hydrogel networks.

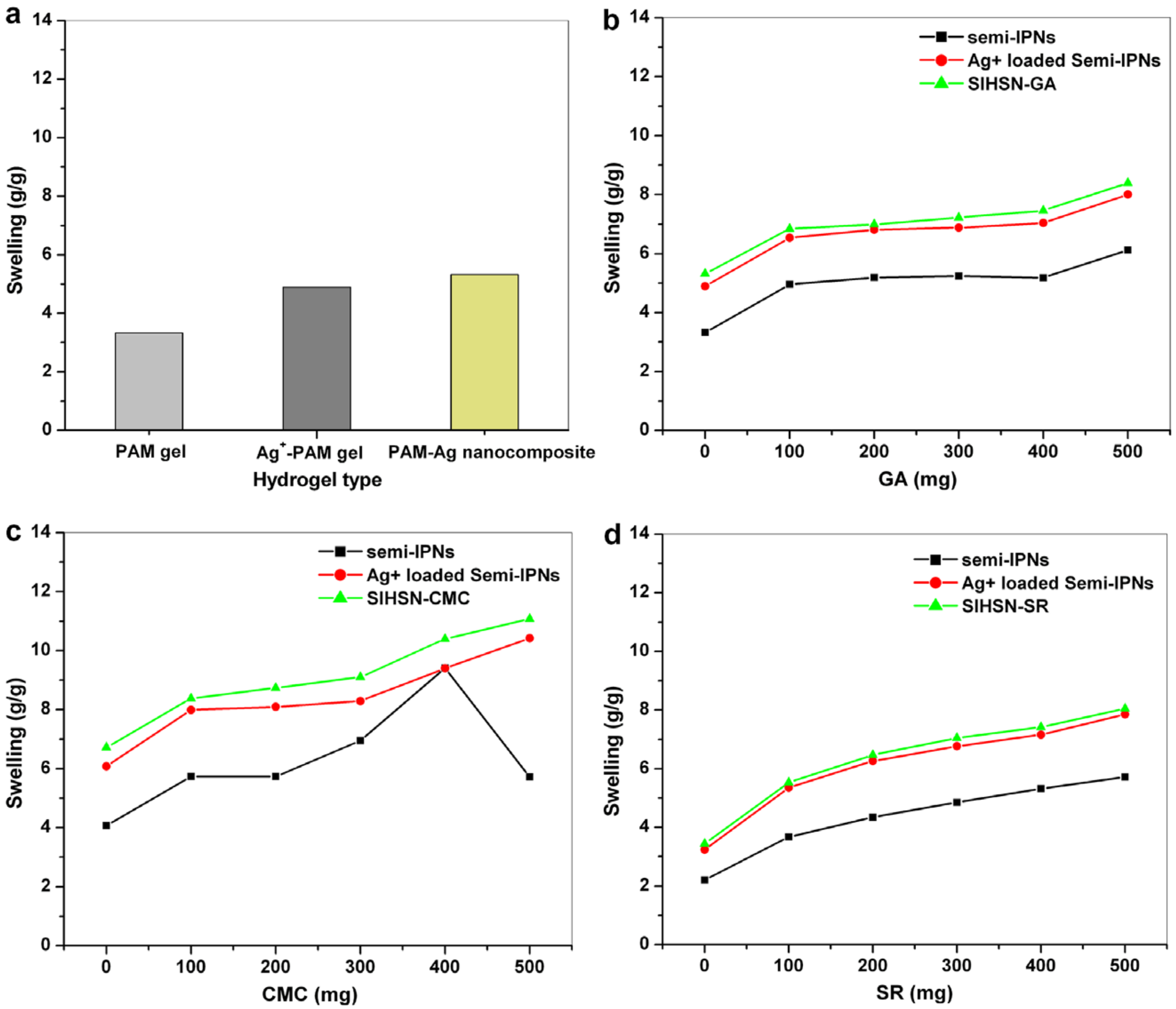


Fig. 1. Swelling behavior of (a) PAM, Ag$^+$-loaded PAM and PAM-Ag nanocomposites; (b–d) semi-IPN hydrogels, Ag$^+$ loaded semi-IPN hydrogels, and SIHSNs; prepared at AM = [14.26 mM]; MBA = [6.48 × 10^{-3} mM]; APS = [2.192 × 10^{-3} mM]; TEMED = [8.6 × 10^{-5} mM].

capacity of poly(acrylamide) hydrogels at a given concentration of cross-linker, which can also serve as green stabilizers and for biocompatibility.

PAM hydrogels swelling capacity before and after addition of silver salt and formation of silver nanoparticles was shown in Fig. 1a. It is confirmed to continued improvement in the swelling capacity. The swelling capacities of PAM semi-IPN hydrogels composed of different amounts (100–500 mg) of GA, CMC and SR are shown in Fig. 1b–d, respectively. With increase of carbohydrate polymer content the semi-IPN hydrogels swelling has capacity improved. This is because of more hydrophilic polymeric chains were entrapped in the hydrogel networks which assist to improve swelling characteristic of gel systems. At all the compositions of semi-IPNs, compared to SR, the GA and CMC contained gel networks showed higher swelling capacity (CMC > GA > SR semi-IPN hydrogels). An improved absorption capacity with CMC and GA semi-IPN hydrogels observed due to more hydrophilic chains or hydration of functional groups on the polymeric chains (–OH) and (–COOCH$_3$Na) (Berlin, Anderson, & Pallansch, 1973; Chen, Liu, & Tan, 2008). Overall, the swelling capacity of GA contained IPN hydrogels are close to CMC based IPN hydrogels. It was known that polar head groups of polymeric chains such as hydroxyl, thiol, amine, and nitrile groups have a high affinity for salts (Mbhele et al., 2003; Porel, Singh, Harsha, Narayana Rao, & Radhakrishnan, 2005; Prasad, Mehta, Meena, & Siddhanta, 2006). After treating the semi-IPN hydrogels with silver salts, the silver ions loaded through the gel networks which are responsible to cause repulsion of networks, ultimately leads to an improved swelling behavior of hydrogel systems. It is quite uniform for all the semi-IPN hydrogel systems as found in our previous studies (Murthy et al., 2008). Further increase in swelling capacity was recognized after addition of reducing agent (NaBH$_4$) to silver ions loaded semi-IPN hydrogels. This pattern of swelling is reasonable because once the silver nanoparticles are formed inside the network/throughout the gel networks overall porosity of system increased which allow for more number of water molecules inside the gel. The other reason can be that the formed particles have different sizes and different surface charges in the gel networks that cause absolute expansion of the networks. Interestingly, similar swelling characteristics were achieved for poly(acrylamide)/poly(vinylpyrrolidone) semi-IPN hydrogel networks (Murthy et al., 2008). In contrast, it was noticed in our previous study with poly(*N*-isopropylacrylamide-*co*-sodium acrylate) hydrogels a slight decrement in their swelling characteristic after addition of $NaBH_4$. It not only depends on the cross-link density/networks but also on the nature of networks (Mohan et al., 2007). The order of swelling capacity for various gel systems followed as, semi-IPN hydrogel–silver nanocomposites >Ag^+ loaded semi-IPN hydrogels >semi-IPN hydrogels (Fig. 1). Moreover, semi-IPN hydrogels swelling capacity had not changed much after incorporation of silver salts and formation of silver nanoparticles in the gels (Fig. 1a–d).

3.2. UV–vis spectra

The formation of silver nanostructures in the entire semi-IPN hydrogel networks can be expected in our current strategy because the silver salts loaded in semi-IPN hydrogels are readily reduced by $NaBH_4$ which immediately turn into an opaque brown color. It represents that the particles were entrapped inside the networks through strong localization and stabilization established from the carbohydrate polymers. On the other hand, linear polymeric chains promote the stabilization of particles by the adsorption of polymeric chains on their surface via bonding with the –COOH, –OH, $–NH_2$, –CONH, etc. functional groups of polymers (Scheme 1). The existence of silver nanoparticles in the gel networks is tested by UV–vis spectral analysis. Fig. 2a–d, illustrates the absorption peaks for semi-IPN hydrogel–silver nanocomposites in the 380–500 nm wavelength range in UV–vis spectra that are assigned to silver nanoparticles which arose from the surface plasmon resonance (SPR).

To determine the reduction and stabilization efficiency of silver nanoparticles by hydrogel networks, we have evaluated UV–vis study for all SIHSNs. A significant improvement in the absorption peaks at ~416 nm (0.197–0.84) and ~408–416 nm (0.13–0.78) noticed for SIHSN-GA and SIHSN-CMC series indicating that with increase of CMC and GA content from 100 to 500 mg facilitate in holding large number of silver ion which were further reduced to silver nanoparticles (Fig. 2a and b). In the previous study of polyethyleneimine, silica, and poly(methylmethacrylate-*co*-butyl acrylate-*co*-acrylic acid) terpolymer microgel embedded silver nanoparticle (2–5 nm) exhibited the same range of absorption bands (Dai & Bruening, 2002; Wang & Asher, 2001; Xu et al., 2003). Whereas, SIHSN-SR series showed random change in the region of 416 nm (Fig. 2c). Initial concentration of SR produced a significant plasmon resonance peak (0.31) but further increase in SR (150–250 mg) might be causing to hold silver nanoparticles without releasing into the media (highly cross-linked networks) (0.19–0.21) which restricts the particles release into the media. But, with 500 mg SR, again increased absorption peak (0.43) could

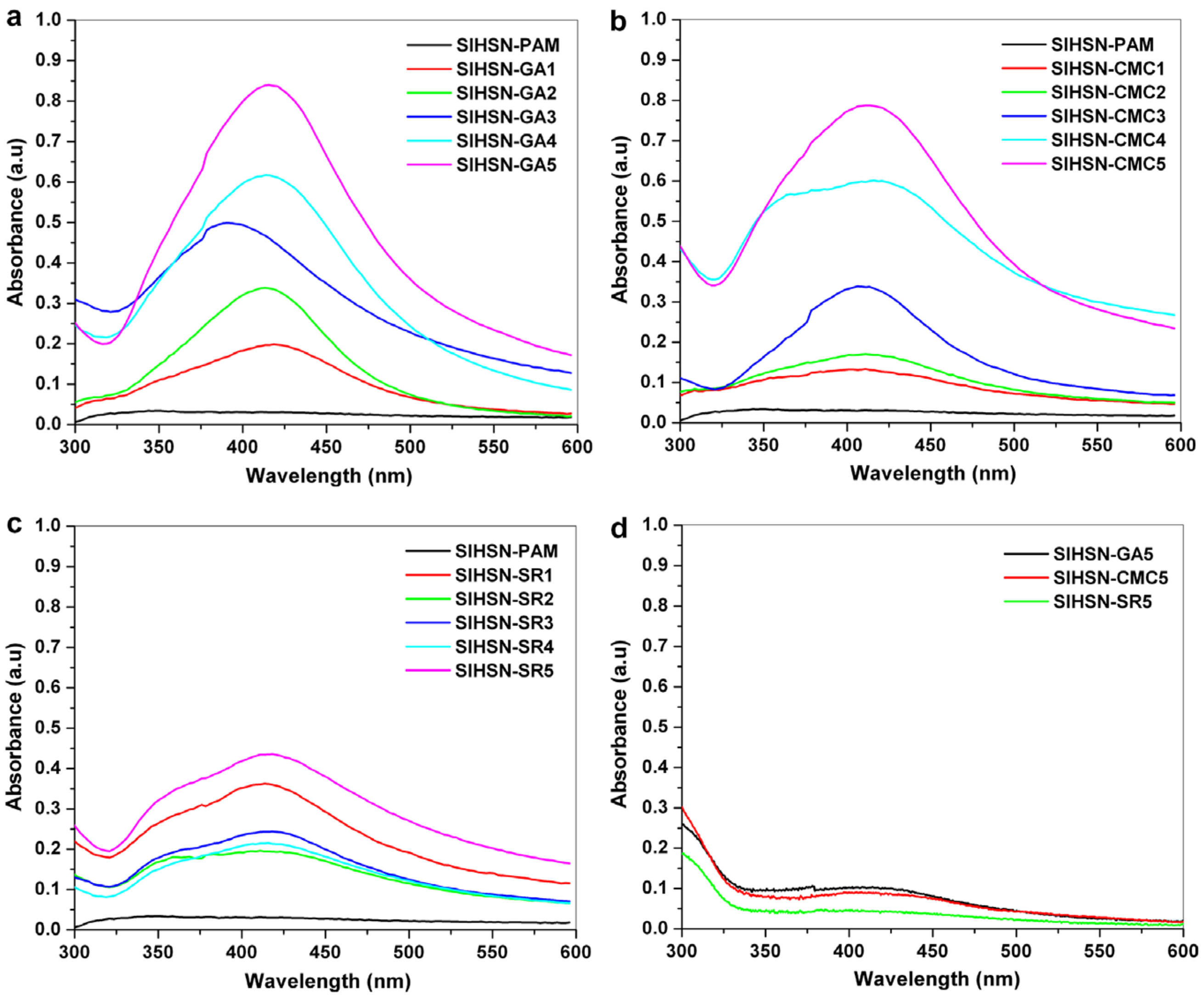


Fig. 2. UV spectra of SIHSNs for (a) SIHSN-GA1 to SIHSN-GA5 (b) SIHSN-CMC1 to SIHSN-CMC5, (c) SIHSN-SR1 to SIHSN-SR5, and (d) SIHSNs without employing reducing agent, $NaBH_4$.

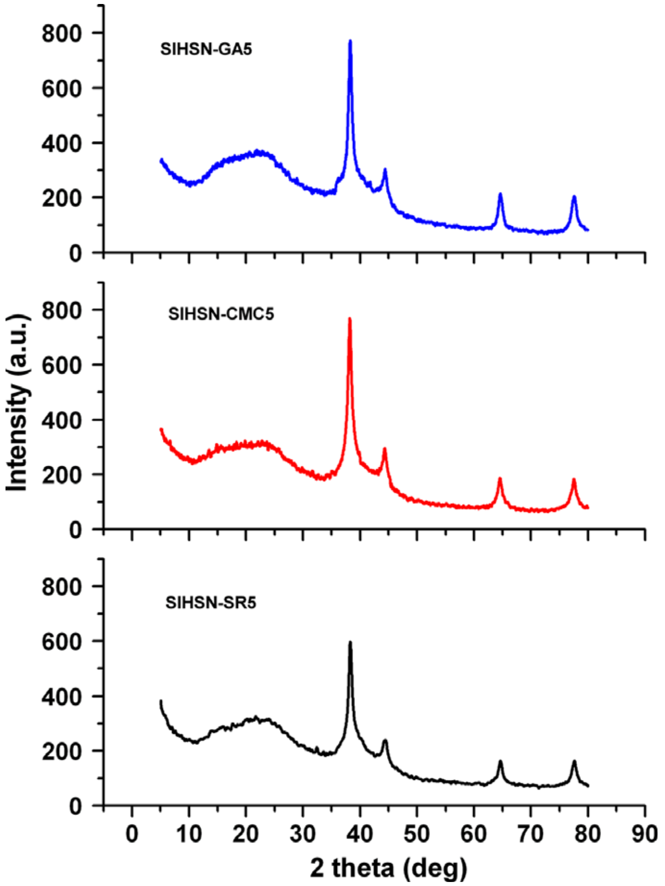


Fig. 3. XRD patterns of semi-IPIN hydrogel–silver nanocomposites prepared using with CMC (500 mg) (CMC5); GA (500 mg) (GA5); and SR (500 mg) (SR5).

be due to soluble starch contents in the systems. From this study, we can speculate that GA and CMC series (SIHSN-GA1 to SIHSN-GA5) and (SIHSN-CMC1 to SIHSN-CMC5) provides enough space to synthesize more nanoparticles in their networks than in SR series.

Since all the absorption peaks are remarkably similar for all the semi-IPN hydrogel–silver nanocomposites (Fig. 2a–c) suggesting that silver nanoparticle embedded in the gel networks are very similar in their size and morphology (Ho, Tobis, Sprich, Thomann, & Tiller, 2004). Further, it clearly confirms that no aggregations or cluster formation of silver particles because of complete absence of peaks or tails at 560 nm (Murphy & Jana, 2002).

Moreover, we have also achieved here that without employing any reducing agent ($NaBH_4$) the absorption peaks are seen at 411 nm in UV–vis spectra, for all the series of SIHSNs but their peak heights are very low (<0.15) (Fig. 2d). In general, carbohydrate polymers themselves works as reducing agents for producing metal nanostructures. In the present case, it did not occur because carbohydrate polymer chains are buried in the gel networks and all the silver salts have more interaction with acrylamide main gel networks and free networks. Considering this point, we have a plan for our future study to develop few functional silver nanocomposite systems without employing reducing agents to control the silver particles.

Table 2
FTIR spectra of GA, CMA, SR, semi-IPN hydrogels, and SIHSNs

Code	–OH and –NH	>C=O	–C–O–C–
PAM	3430	1664	–
GA	3424	1644	1120
PAM/GA5 semi-IPN hydrogel	3426	1655	1120
SIHSN-GA5	3426	1649	1120
CMC	3432	1603	1122
PAM/CMC5 semi-IPN hydrogel	3441	1653	1122
SIHSN-CMC5	3430	1655	1122
SR	3534	1656	1122
PAM/SR5 semi-IPN hydrogel	3454	1657	1123
SIHSN-SR5	3444	1637	1123

3.3. X-ray diffraction

Fig. 3 illustrates the X-ray diffraction patterns of SIHSNs. A common broad diffraction peak 2θ can be seen at 20° due to the amorphous nature of poly(acrylamide) hydrogel and carbohydrate polymers. This was confirmed with our previous reports on poly(*N*-isopropylacrylamide) and poly(acrylamide) gels. The diffractogram of semi-IPN hydrogel–silver nanocomposites are assigned to diffractions at 2θ values of about 38°, 44°, 65°, 78° to the brags reflections of (111) (200) (220) and (311) plane of face centered cubic (fcc) structure of silver nanoparticles. Sharp and intense peaks represent to highly crystalline silver nanostructures formed in semi-IPN nanocomposites (Biffis et al., 2003).

3.4. FTIR spectra

FTIR spectral details of GA, CMC, and SR polymers; their semi-IPN hydrogels and SIHSNs were provided in Table 2. Poly(acrylamide) (PAM) hydrogel exhibited broad bands at 3430 and 1664 cm^{-1} due to amide groups stretching of poly(acrylamide) chains (Murali Mohan, Murthy, Rao, Sreeramulu, & Mohana Raju, 2005). The bands at 3424, 3432 and 3454 cm^{-1} are corresponding to hydrogen bonded (bridged) hydroxyl groups of GA, hydroxyl and carboxyl groups of CMC, and hydroxyl groups of starch polymer chains (Biswal & Singh, 2004; Mohan et al., 2007; Murthy, Murali Mohan, Sreeramulu, & Mohana Raju, 2006). The stretching vibration of ester groups of GA, CMC and SR are observed at 1644, 1603, and 1655 cm^{-1}. After making semi-IPN hydrogels using GA, CMC, and SR the peak positions increased considerably, ie., 3424, 1644 to 3426, 1655 cm^{-1} for PAM/GA semi-IPN hydrogels; 3432, 1603 to 3441, 1653 for PAM/CMC semi-IPN hydrogels; and 3534, 1656 to 3454, 1657 cm^{-1} for PAM/SR semi-IPN hydrogels. Similarly, significant changes were observed for SIHSNs due to Ag nanoparticles interaction with hydrogel networks (peaks were shifted to lower wavenumbers). Therefore, we can confirm the presence of silver nanoparticles in the hydrogel networks.

3.5. Morphology studies

It is possible to obtain silver nanoparticles inside PAM hydrogel networks but the amount of particles (number of particles) are less as observed in TEM image (Murthy et al., 2008). The particle size can be achieved between 10 and 15 nm. A recent study also suggests that PAM hydrogel can act as nanocarriers for silver nanoparticles (∼5 nm) but the population of particles is less. Therefore, it is important to construct favorable hydrogel networks that can improve the efficacy of silver nanoparticles formation inside their networks. In this route a number of hydrogel systems were evaluated (Thomas et al., 2008). To solve these problems a simple system based on poly(*N*-isopropylacrylamide-*co*-sodium acrylate) (PNIPAM-*co*-SA) (Mohan et al., 2007) was proposed for ∼3 nm silver nanoparticles.

The smallest particles of 10 nm were obtained with PEI-MA/HEM networks with 2.5 wt.% PEI networks where decrement in the PEI networks to 0.6–1.2 wt.% leads to increased in size to 20–50 nm (Ho et al., 2004). Microgel systems are feasible to get Pd par-

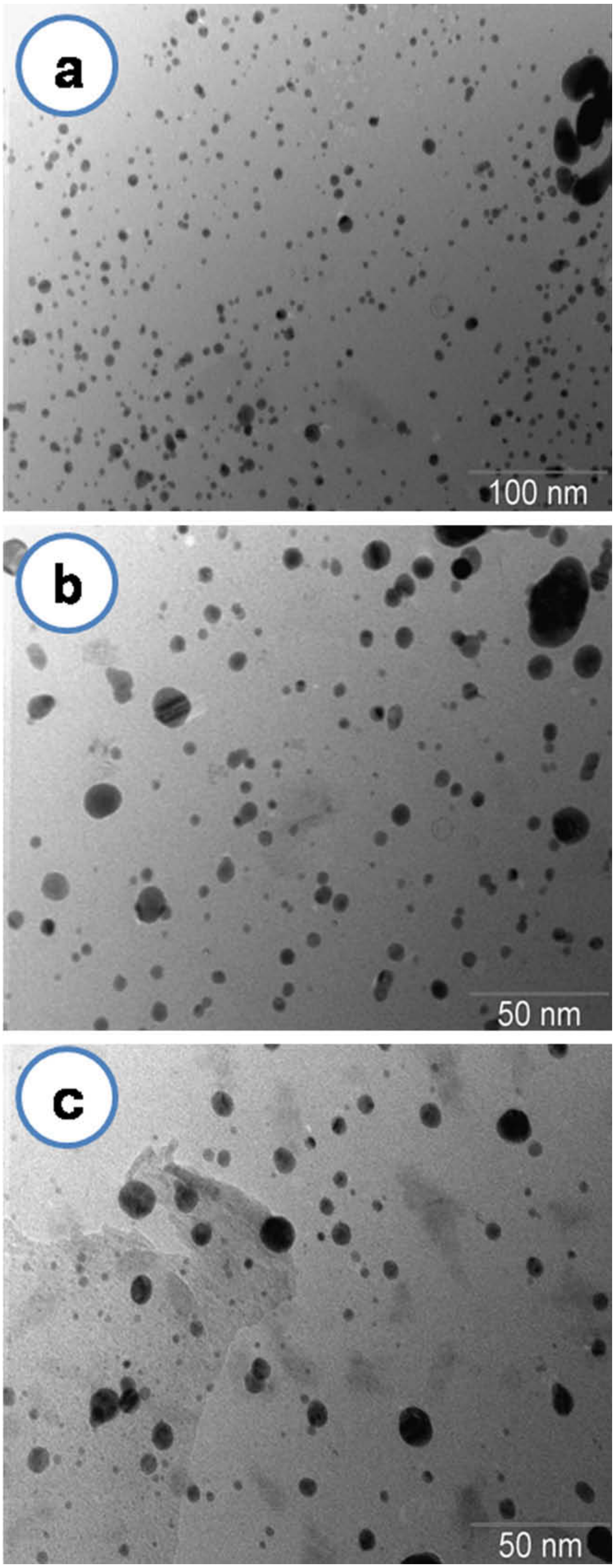


Fig. 4. Transmission electron micrograph images of (a) SIHSN-GA5, (b) SIHSN-CMC5 and SIHSN-SR5.

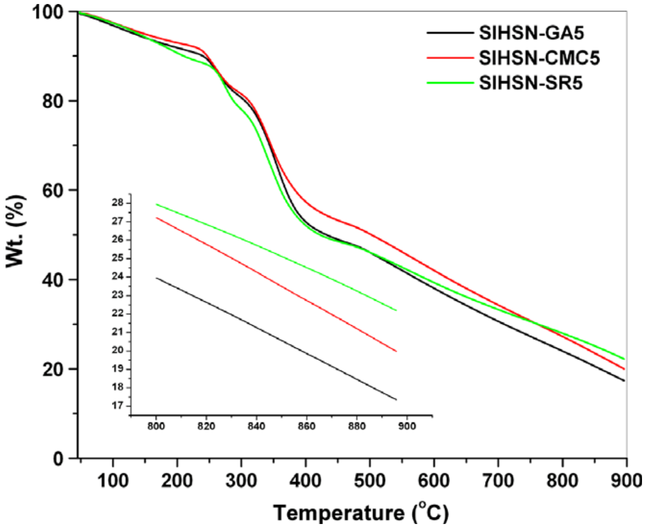


Fig. 5. Thermograms of SIHSN-GA5, SIHSN-CMC5, and SIHSN-SR5.

ticle sizes from 3.1 to 8.9 nm (Biffis et al., 2003). PNIPAM cross-linked with MBA and *N*,*N*′-cystaminebisacrylamide (CBA) hydrogels proposed to control the Au particles size <5 nm (Wang et al. (2004). To obtain low nanoparticles size by gel networks as templates one must select microgel systems such as poly[(*N*-isopropylacrylamide)-*co*-(acrylic acid)-*co*-(2-hydroxyethyl acrylate)] (Zhang, Xu, & Kumacheva, 2004), and poly(vinylcaprolactam-*co*-acetoacetoxyethylmethacrylate) (VCL/AAEM) microgels (Pich, Karak, Lu, Ghosh, & Adler, 2006) which are required additional controlled synthetic routes of gels.

In contrast, we propose here that the carbohydrate polymers can control the size of particles through their networks. Fig. 4 showed typical TEM images of silver nanoparticles extracted from SIHSNs (1 mg/ml for a day), which facilitate excellent stability to the nanoparticle throughout the network structure through amide, hydroxyl, and carboxyl groups of the polymeric chains. SIHSN-GA5 contains smaller particles (2–5 nm) (Fig. 4a) than SIHSN-CMC5 (Fig. 4b) and SIHSN-SR5 (Fig. 4c) 2–20 nm. It reveals that GA polymeric chains controls to lower particle size due to effective reduction and stabilization characteristics. The obtained particles size is even lower than GA polymer used to produce silver nanoparticles (Mohan et al., 2007). The size control capacity relay on the presence of functional groups: acacia (3, –OH groups in each repeating unit), CMC (2, –OH and 1, –COOH groups in each repeating units) and starch (2 –OH groups).

3.6. Thermal stability

Fig. 5 illustrates the thermograms of semi-IPN hydrogel–silver nanocomposites composed with GA (500 mg), CMC (500 mg), and SR (500 mg). These SIHSNs exhibit excellent thermal stability. It is noted as three degradation steps and only 45% weight loss below 460 °C. Thermal stability of SIHSN-GA5 represents higher thermal stability than SIHSN-CMC5 and SIHSN-SR5, due to the presence of more amount of silver nanoparticles formation inside the SIHSN-GA5 nanocomposite.

3.7. Antibacterial activity

Now a day's nanotechnology has expanded its applications in biomedical field including fighting and preventing of diseases using atomic scale functional materials. Interestingly, silver nanoparticles have been considered to increase the resistant strains of bacteria to the most potent antibiotics. A recent study indicates that the bactericidal effect of silver nanoparticles mostly depends on the size of particles and the smaller is the better ie., 1–10 nm

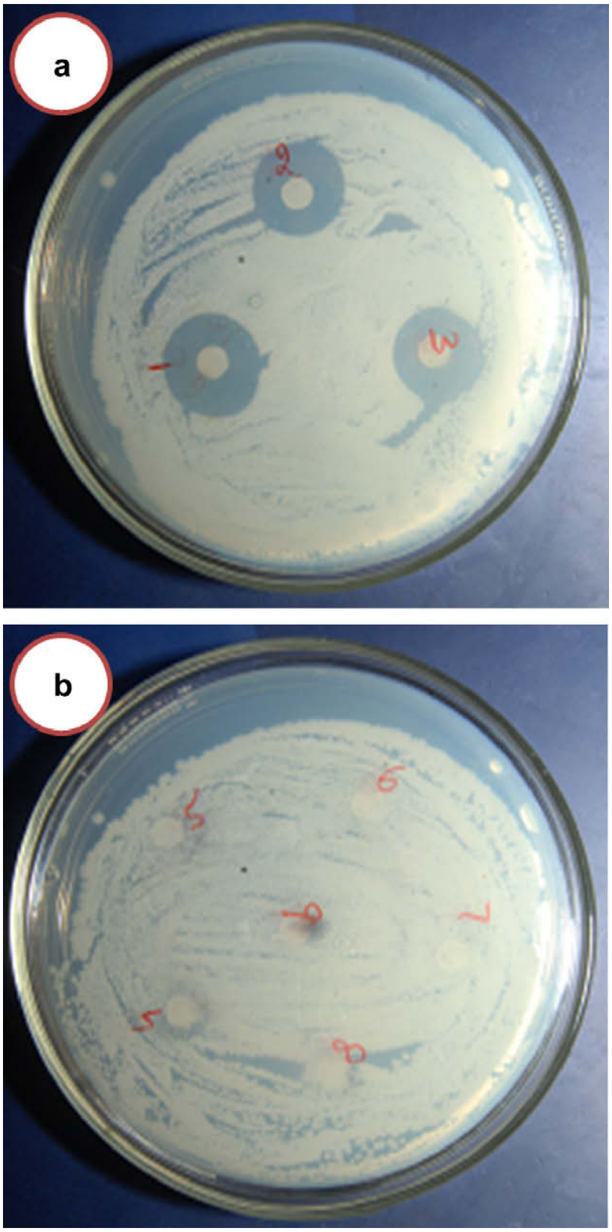


Fig. 6. Antibacterial effect of (a) (1–3) are SIHSN-GA5, SIHSN-CMC5, and SIHSN-SR5; (b) (4–6) Ag^+-loaded PAM/GA (500 mg), Ag^+-loaded PAM/CMC (500 mg), and Ag^+-loaded PAM/SR (500 mg); and (7–9) PAM/GA (500 mg), PAM/CMC (500 mg), and PAM/SR (500 mg) semi-IPN hydrogels.

which have a direct interaction with the bacteria (Morones et al., 2005). Fig. 6 exhibited the antibacterial property of semi-IPN hydrogel–silver nanocomposites. The antibacterial activity is resulting mainly due to the release of silver nanoparticles from the SHISNs. The inhibition area follows in an order: SHISN-GA5 (1.8 cm) > SHISN-CMC5 (1.6 cm) > SHISN-SR5 (1.5 cm). This behavior is expected because smaller sized silver nanoparticles (2–5 nm) in SHISNs are responsible to kill more number of *Escherichia. coli*. On the other hand, due to lower release or higher crosslinking network of SHISN-SR5 has shown comparatively lower effect on *E. coli*. Similar results were noticed in the case of (PNIPAM-*co*-SA) hydrogel–silver nanocomposites where lower sized Ag nanoparticles had great impact than other formulations (Mohan et al., 2007). The Ag^+-loaded semi-IPN hydrogels showed a mild effect on *E. coli* but semi-IPN hydrogels did not show any effect on *E. coli*.

4. Conclusions

In conclusion, we have demonstrated that controlled sized silver nanoparticles were synthesized inside the semi-IPN hydrogel templates that contain different carbohydrate polymeric networks. UV–vis spectral study illustrates an increased reduction of silver ions due to contribution by GA polymeric chains. TEM images indicate that gum acacia (GA) contained semi-IPN hydrogels produced well defined silver nanoparticles than other semi-IPN hydrogels. Thermal analyses further confirm that SIHSN-GA has higher number of particles. More importantly, these semi-IPN networks also showed conversion of few silver ions into silver nanoparticles without using reducing agent. All SIHSNs exhibited similar antibacterial activity against *E. coli*. Future directions include controlling the particle size and structure by standardizing semi-IPN hydrogel networks.

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References

Bajpai, S. K., Mohan, Y. M., Bajpai, M., Tankhiwale, R., & Thomas, V. (2007). Synthesis of polymer stabilized silver and gold nanostructures. *Journal of nanoscience and nanotechnology, 7*, 2994–3010.

Berlin, E., Anderson, B. A., & Pallansch, M. J. (1973). Water sorption by dried dairy products stabilized with carboxymethyl cellulose. *Journal of Dairy Science, 56*, 685–689.

Biffis, A., Orlandi, N., & Corain, B. (2003). Microgel-stabilized metal nanoclusters: Size control by microgel nanomorphology. *Advanced Materials, 15*, 1551–1555.

Biswal, D. R., & Singh, R. P. (2004). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers, 57*, 379–387.

Chen, D-H., & Hsieh, C-H. (2002). Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions. *Journal of Materials Chemistry, 12*, 2412–2415.

Chen, Y., Liu, Y., & Tan, H-M. (2008). Preparation of macroporous cellulose-based superabsorbent polymer through the precipitation method. *Bioresources, 3*, 247–254.

Chen, C-W., Serizawa, T., & Akashi, M. (1999). Synthesis and characterization of poly(*N*-isopropylacrylamide)-coated polystyrene microspheres with silver nanoparticles on their surfaces. *Langmuir, 15*, 7998–8006.

Chen, J., Wang, J., Zhang, X., & Jin, Y. (2008). Microwave-assisted green synthesis of silver nanoparticles by carboxymethyl cellulose sodium and silver nitrate. *Materials Chemistry and Physics, 108*, 421–424.

Colvin, V. L., Schlamp, M. C., & Alivisatos, A. P. (1994). Light-emitting-diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature, 370*, 354–357.

Dai, J., & Bruening, M. L. (2002). Catalytic nanoparticles formed by reduction of metal ions in multilayered polyelectrolyte films. *Nanoletters, 2*, 497–501.

Daniel, M. C., & Astrue, D. (2004). Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews, 104*, 293–346.

Esumi, K., Isono, R., & Yoshimura, T. (2004). Preparation of PAMAM- and PPI-metal (silver, platinum, and palladium) nanocomposites and their catalytic activities for reduction of 4-nitrophenol. *Langmuir, 20*, 237–243.

Esumi, K., Suzuki, A., Yamahira, A., & Torigoe, K. (2000). Role of poly(amidoamine) dendrimers for preparing nanoparticles of gold platinum and silver. *Langmuir, 16*, 2604–2608.

Goia, D. V., & Matijevic, E. (1998). Preparation of monodispersed metal particles. *New Journal of Chemistry, 22*, 1203–1215.

Ho, C. H., Tobis, J., Sprich, Ch., Thomann, R., & Tiller, J. C. (2004). Nanoseparated polymeric networks with multiple antimicrobial properties. *Advanced Materials, 16*, 957–961.

Kiesow, A., Morris, J. E., Radehaus, C., & Heilmann, A. (2003). Switching behavior of plasma polymer films containing silver nanoparticles. *Journal of Applied Physics, 94*, 6988–6990.

Lee, W-F., & Huang, Y-C. (2007). Swelling and antibacterial properties for the superabsorbent hydrogels containing silver nanoparticles. *Journal of Applied Polymer Science, 106*, 1992–1999.

Liu, J., Sutton, J., & Roberts, C. B. (2007). Synthesis and extraction of monodisperse sodium carboxymethylcellulose-stabilized platinum nanoparticles for the self-assembly of ordered arrays. *Journal of Physical Chemistry C, 111*, 11566–11576.

Magdassi, S., Bassa, A., Vinetsky, Y., & Kamyshny, A. (2003). Silver nanoparticles as pigments for water-based ink-Jet inks. *Chemistry of Materials, 15*, 2208–2217.

Mandal, S., Phadtare, S., & Sastry, M. (2005). Interfacing biology with nanoparticles. *Current Applied Physics, 5*, 118–127.

Mbhele, Z. H., Salemane, M. G., van Sittert, C. G. C. E., Nedeljkovi, J. M., Djokovi, V., & Luyt, A. S. (2003). Fabrication and characterization of silver-polyvinyl alcohol nanocomposites. *Chemistry Materials, 15*, 5019–5024.

Mohan, Y. M., Lee, K., Premkumar, T., & Geckeler, K. E. (2007). Hydrogel networks as nanoreactors: A novel approach to silver nanoparticles for antibacterial applications. *Polymer, 48*, 158–164.

Mohan, Y. M., Raju, K. M., Sambasivudu, K., Singh, S., & Sreedhar, B. (2007). Preparation of acacia-stabilized silver nanoparticles: A green approach. *Journal of Applied Polymer Science, 106*, 3375–3381.

Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramírez, J. P., & Yacaman, M. J. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology, 16*, 2346–2353.

Murali Mohan, Y., Murthy, P. S. K., Rao, K. M., Sreeramulu, J., & Mohana Raju, K. (2005). Swelling behavior and diffusion studies of high-water-retaining acrylamide/potassium methacrylate hydrogels. *Journal of Applied Polymer Science, 96*, 1153–1164.

Murphy, C. J., & Jana, N. R. (2002). Controlling the aspect ratio of inorganic nanorods and nanowires. *Advanced Materials, 14*, 80–82.

Murthy, P. S. K. ., Mohan, Y. M., Varaprasad, K., Sreedhar, B., & Raju, K. M. (2008). First successful design of semi-IPN hydrogel–silver nanocomposites: A facile approach for antibacterial application. *Journal of Colloid and Interface Science, 318*, 217–224.

Murthy, P. S. K., Murali Mohan, Y., Sreeramulu, J., & Mohana Raju, K. (2006). Semi-IPNs of starch and poly(acrylamide-*co*-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation. *Reactive and Functional Polymers, 66*, 1482–1493.

Pich, A., Karak, A., Lu, Y., Ghosh, A. K., & Adler, H-J. P. (2006). Preparation of hybrid microgels functionalized by silver nanoparticles. *Macromolecular Rapid Communications, 27*, 344–350.

Porel, S., Singh, S., Harsha, S. S., Narayana Rao, D., & Radhakrishnan, T. P. (2005). Nanoparticle-embedded polymer: In situ synthesis free-standing films with highly monodisperse silver nanoparticles and optical limiting. *Chemistry Materials, 17*, 9–12.

Prasad, K., Mehta, G., Meena, R., & Siddhanta, A. K. (2006). Hydrogel-forming agar-graft-PVP and kappa-carrageenan-graft-PVP blends: Rapid synthesis, and characterization. *Journal of Applied Polymer Science, 100*, 3654–3663.

Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely "green" synthesis and stabilization of metal nanoparticles. *Journal of American Chemical Society, 125*, 13940–13941.

Raveendran, P., Fua, J., & Wallen, S. L. (2006). A simple and green method for the synthesis of Au, Ag, and Au–Ag alloy nanoparticles. *Green Chemistry, 8*, 34–38.

Ross, C. A. (2001). Patterned magnetic recording media. *Annual Review of Materials Research, 31*, 203–235.

Thomas, V., Namdeo, M., Mohan, Y. M., Bajpai, S. K., & Bajpai, M. (2008). Review on polymer, hydrogel and microgel metal nanocomposites: A facile nanotechnological approach. *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry, 45*, 1079–1119.

Vaseashta, A., & D-Malinovska, D. (2005). Nanostructured and nanoscale devices, sensors and detectors. *Science and Technology of Advanced Materials, 6*, 312–318.

Vigneshwaran, N., Nachane, R. P., Balasubramanya, R. H., & Varadarajan, P. V. (2006). A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch. *Carbohydrate Research, 341*, 2012–2018.

Wang, W., & Asher, S. A. (2001). Photochemical incorporation of silver quantum dots in monodisperse silica colloids for photonic crystal applications. *Journal of American Chemical Society, 123*, 12528–12535.

Wang, L., & Chen, D. (2007). A facile method for the preparation of hollow silver spheres. *Materials Letters, 61*, 2113–2116.

Wang, C., Flynn, N. T., & Langer, R. (2004). Controlled structure and properties of thermoresponsive nanoparticle–hydrogel composites. *Advanced Materials, 16*, 1074–1079.

Wei, Q., Kang, S-Z., & Mu, J. (2004). "Green" synthesis of starch capped CdS nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 247*, 125–127.

Xu, Z. P., Zeng, Q. H., Lu, G. Q., & Yu, A. B. (2006). Inorganic nanoparticles as carriers for efficient cellular delivery. *Chemical Engineering Science, 61*, 1027–1040.

Xu, S., Zhang, J., Paquet, C., Lin, Y., & Kumacheva, E. (2003). From hybrid microgels to photonic crystals. *Advanced Functional Materials, 13*, 468–472.

Zhang, J., Xu, S., & Kumacheva, E. (2004). Polymer microgels: Reactors for semiconductor, metal, and magnetic nanoparticles. *Journal of American Chemical Society, 126*, 7908–7914.

Zhang, Z., Zhang, L., Wang, S., Chen, W., & Lei, Y. (2001). A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. *Polymer, 42*, 8315–8318.

Zhao, X., Ding, X., Deng, Z., Zheng, Z., Peng, Y., & Long, X. (2005). Thermoswitchable electronic properties of a gold nanoparticle/hydrogel composite. *Macromolecular Rapid Communications, 26*, 1784–1787.