

# Preparation of Acacia-Stabilized Silver Nanoparticles: A Green Approach

Y. Murali Mohan,<sup>1\*</sup> K. Mohana Raju,<sup>1</sup> K. Sambasivudu,<sup>1</sup> Satyendra Singh,<sup>2</sup> B. Sreedhar<sup>2</sup>

<sup>1</sup>Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515003, India

<sup>2</sup>Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

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**ABSTRACT:** We report a facile approach for the spontaneous formation of silver nanoparticles in the presence of gum acacia polymer (a natural polymer) without the addition of any typical reducing agent under mild conditions. Silver nanoparticles (~ 5 nm) have been obtained by the mixing of equal amounts of 0.5 wt % aqueous solutions of acacia and silver nitrate. The formation of silver nanoparticles has been confirmed with ultraviolet-visible, Fourier transform infrared, X-ray diffraction, and X-ray photoelectron spectroscopy analyses. Gum acacia polymeric chains

promote the reduction process and act as good stabilizers over 5 months. To confirm the formation and stabilization of the nanoparticles, a transmission electron microscope has been employed. The advantage of this methodology is that it is possible to prepare silver nanoparticles without any organic solvents or reducing agents. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3375–3381, 2007

**Key words:** gels; hydrogels; nanotechnology; networks; stabilization

## INTRODUCTION

Nanoparticles display exclusive spectroscopic, electronic, and chemical properties that arise from their smaller size and large specific surface area, which differ appreciably from those of bulk materials.<sup>1</sup> A wide range of applications have been found for nanoparticles in catalysis,<sup>2</sup> electronics,<sup>3</sup> sensors, high-density information storage,<sup>4</sup> photoluminescence and electroluminescence devices,<sup>5</sup> photonics,<sup>6</sup> pharmaceuticals, and biotechnology and medicine.<sup>7</sup> Because of the multitude of their potential applications, the synthesis of nanoparticles with a narrow size distribution is one of the most important and never-ending challenges.<sup>8</sup> The success of nanomaterials relies not only on the size and shape-controlled distribution but also on the preparative routes. Regardless of the preparative method, metal nanoparticles have the tendency to form large clusters or aggregates that lead to precipitation. Chemical reduction is one of the better strategies for generating uniform particles with a narrow size distribution via microemulsion,<sup>9</sup> coprecipitation,<sup>10,11</sup> carbon nanotube,<sup>12</sup> and polymer protection<sup>13–15</sup> methods.

In contrast to simple organic templates, biological macromolecules,<sup>16,17</sup> block copolymers,<sup>18,19</sup> dendrimers,<sup>20–22</sup> liquid crystals,<sup>23</sup> latex particles,<sup>24</sup> mesoporous inorganic materials,<sup>25</sup> microgels,<sup>26</sup> and hydrogels<sup>27,28</sup> have been employed as templates for producing well-dispersed nanoparticles.

Most frequently, polymers are being used in the chemical synthesis of nanoparticles renowned as steric stabilizers or capping agents.<sup>1,2</sup> Poly(ethylene glycol)s can act as both media and reducing agents for metal ions.<sup>29</sup> In particular, poly(vinyl pyrrolidone) (PVP) is considered a model protecting material, and interestingly, very recent studies have revealed that PVP can be used for the controlled synthesis of colloidal and triangular silver nanoparticles in a single step without any reducing agent.<sup>30,31</sup> Hussain et al.<sup>32</sup> proposed a successful synthetic methodology for the production of precise silver and gold nanoparticles using sodium acrylate and poly(sodium acrylate) without any reducing agent. Ershov and Henglein<sup>33</sup> reported that silver ions could be reduced competently with aqueous solutions of poly(sodium acrylate) or partly carboxylated polyacrylamide. In this process, the reducing agent is the hydrated electron generated  $\gamma$ -radiolytically or with hydrogen. It has been demonstrated that the ultraviolet (UV) irradiation of an alcohol–water solution of silver perchlorate in the presence of poly(sodium acrylate) forms quite stabilized silver nanoclusters.<sup>34</sup> Sukhorukov et al.<sup>35</sup> examined a photoinduced reduction of silver in which the formation of nanoparticles was controlled to occur only inside

Correspondence to: K. M. Raju (kmmohan@yahoo.com) or B. Sreedhar (sreedhar0508@yahoo.co.in).

\*Present address: University of Nebraska Medical Center, Department of Pharmaceutical Sciences, College of Pharmacy, Omaha, Nebraska 68198-6025.

polyelectrolyte poly(styrene sulfonate) capsules. Using a microwave irradiation method, Yamamoto et al.<sup>36</sup> produced triangular silver nanoplates through the reduction of silver nitrate ( $\text{AgNO}_3$ ) in aqueous solutions of PVP.

In the early days of colloid science, plant extracts and gums were used routinely for stabilizing colloidal metal dispersions.<sup>37</sup> In that category, gum arabic or gum acacia is a well-known polysaccharide with a high molecular weight that can be derived from the acacia tree. In fact, the ancient Egyptians widely used this natural polymer as an adhesive for mineral pigments in paints and for the flaxen wrappings used to embalm mummies and so on.<sup>38</sup> Moreover, gum acacia polymer has been employed for solid-liquid dispersion applications.<sup>39</sup> This natural polymer is extensively used in confectioneries and soft drink processing because it has an inherent ability to emulsify and stabilize a flavoring oil dispersed in an aqueous medium. This natural polymer not only is very low cost and abundantly available in nature but also has excellent emulsifying and surface-active properties, which would be beneficial for the design of metal nanoparticles. Therefore, we explored a simple and green approach to the spontaneous formation of silver nanoparticles without any reducing agent, using gum acacia as a reducing and stabilizing agent.

## EXPERIMENTAL

### Materials

$\text{AgNO}_3$  (analytical-reagent-grade) was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI), and gum arabic (gum acacia; dried) was obtained from S.D. Fine Chemical (Mumbai, India). Double-distilled water was used for the preparation of acacia and  $\text{AgNO}_3$  solutions.

### Preparation of the silver nanoparticles

Silver nanoparticles were prepared by the addition of a gum acacia solution to an  $\text{AgNO}_3$  solution and stirring for a few minutes until the gum acacia dissolved completely. Different compositions with various concentrations of gum acacia (0.1–0.5 wt %) and  $\text{AgNO}_3$  (0.1–0.5 wt %) solutions were prepared and allowed to stand for 24 h to obtain silver nanoparticles.

### Characterization

IR spectra of acacia and acacia–silver particles were recorded with a Thermo Nicolet Nexus (Washington, USA) 670 spectrophotometer. Ultraviolet–visible (UV–vis) spectra were carried out on a Citra (Mel-

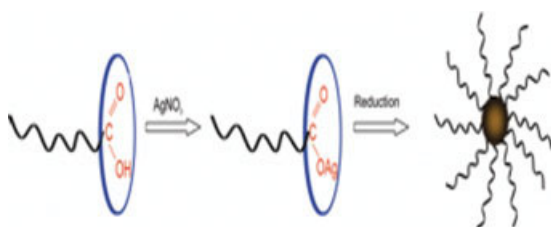
bourne, Australia) 10e UV–vis spectrophotometer. X-ray diffraction (XRD) measurements were recorded with a Rigaku diffractometer (Tokyo, Japan) (Cu radiation,  $\lambda = 0.1546$  nm) running at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis (Manchester, UK) 165 instrument. Transmission electron microscopy (TEM) images were recorded with a Tecnai (Phillips, Oregon, USA) F 12 transmission electron microscope. TEM samples were prepared by the dispersion of 2–3 drops of an acacia–silver nanoparticle solution on a copper grid and dried at room temperature after the removal of excess solution with filter paper.

## RESULTS AND DISCUSSION

Recent studies have focused on the synthesis of metal nanoparticles with polymeric templates in the absence of typical chemical reducing agents.<sup>29–35</sup> In addition to the established strategies, we have employed here a simple and highly facile template-based methodology to prepare silver nanoparticles with gum acacia polymer without the addition of any reducing agent. The most advanced feature of this methodology is that we can prepare the nanoparticles at room temperature. Although poly(ethylene glycol) is able to show reducing and stabilization activity, it requires higher temperatures (e.g., 80–110°C) to make nanoparticles.<sup>29</sup> In this study, upon the addition of silver salt to gum acacia solutions, we have observed a change in the color of the reaction mixture from yellow to gray or brown with time. This is a basic indication of the formation of silver nanoparticles. However, no change in the color of the solution after 24 h of reaction indicates that most of the  $\text{Ag}^+$  ions have converted into Ag nanoparticles.

Scheme 1 shows a schematic illustration of the preparation of silver nanoparticles. Initially, silver cations ( $\text{Ag}^+$ ) are mixed with an aqueous acacia polymer solution, in which the ion-exchange process occurs, and the glycoprotein carboxylate group ( $-\text{COOH}$ ) of gum acacia is converted into  $-\text{COOAg}$ . In a later stage, these silver ions, attached to carboxylate groups, are converted into silver nanoparticles in an *in situ* manner and subsequently stabilized by the gum acacia polymer chains. A detailed description is given in the following sections.

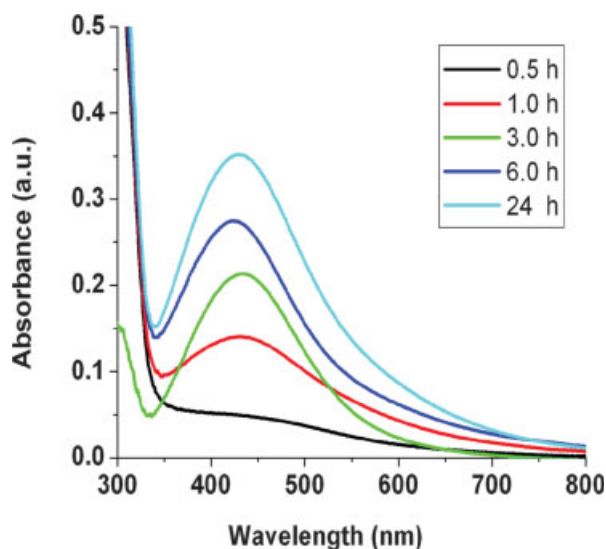
It has been clearly reported in several previous studies that the absorption peaks in the 380–500-nm wavelength range in UV–vis spectra can be assigned to silver nanoparticles because of the surface plasmon resonance of silver nanoparticles.<sup>40</sup> We monitored the time evaluation of UV–vis absorption spectra for the samples ( $[\text{AgNO}_3] = 0.5$  wt % and  $[\text{acacia}] = 0.5$  wt %) at different intervals to evaluate the



**Scheme 1** Schematic illustration of the synthesis of silver nanoparticles with the acacia polymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

formation of the silver nanoparticles. Figure 1 shows the experimental UV-vis spectra of the formed silver nanoparticles. It reveals that the reduction starts during the initial stages of the reaction, and nanoparticle formation can be observed after 30 min and is almost complete after 24 h of reaction. As the time progress, the intensity of the surface plasmon absorption at 420 nm increases and remains unchanged above 24 h, but there is no tilting of the peak position. This confirms that the reduction potentiality increases with time.

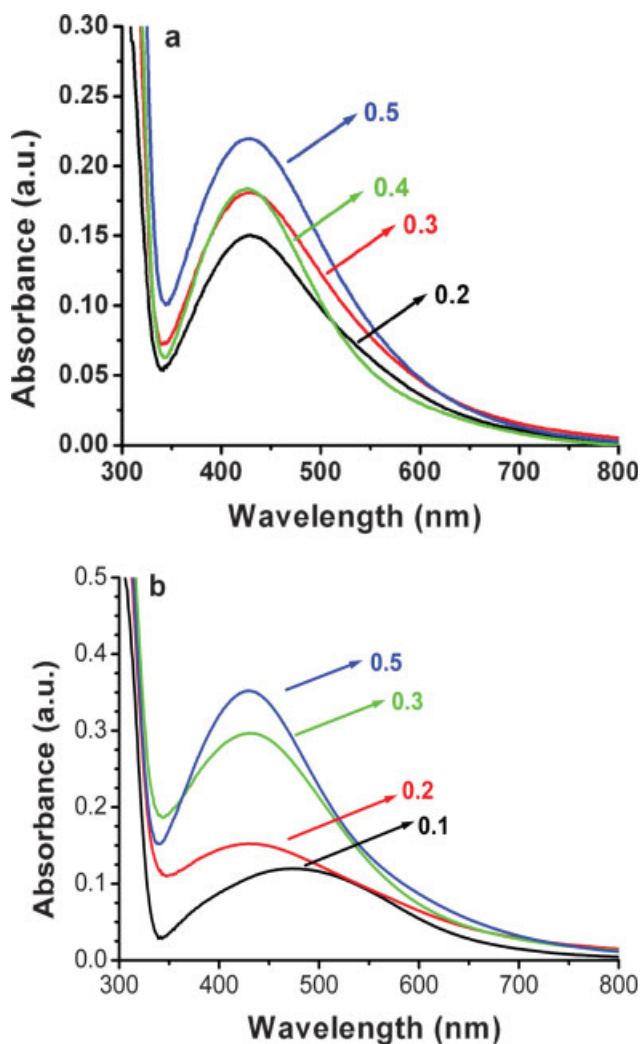
To determine the reduction efficacy of  $\text{Ag}^+$ , we have evaluated various concentrations of the acacia polymer and  $\text{AgNO}_3$ , and their respective UV-vis spectra are presented in Figure 2. Significant information drawn from the UV-vis results illustrates that with an increase in the silver salt or polymer concentration in the preparation, there is a considerable improvement in the reduction efficacy. In all the UV-vis spectra, the fact that no peaks can be



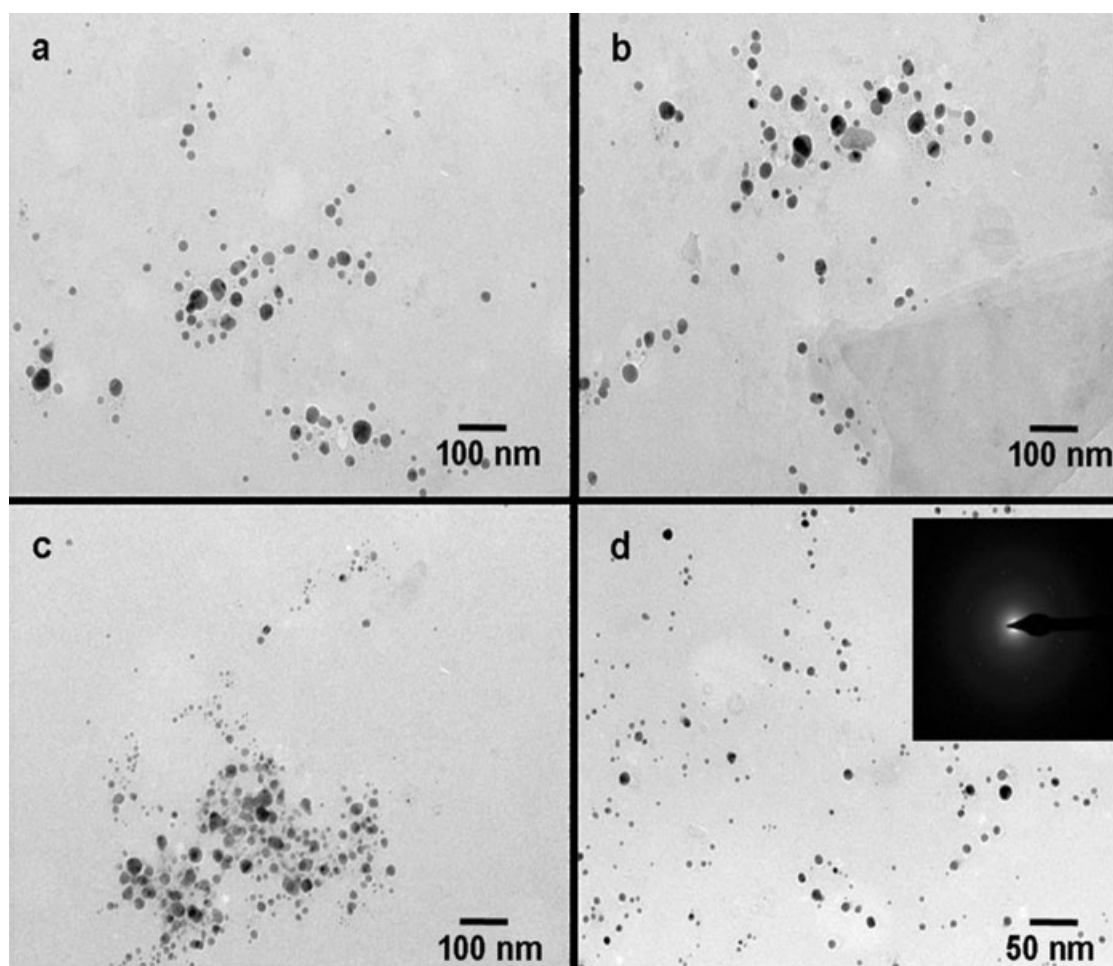
**Figure 1** UV-vis spectra of nanoparticles at different times. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

observed at 335 or 560 nm confirms the complete absence of  $\text{Ag}$  nanoparticle aggregation or  $\text{Ag}_n$  cluster formation.<sup>40(b,c)</sup> In other words, the nanoparticles that form in this reaction are highly dispersed in nature. The remarkable stability (no aggregation) of the nanoparticles was noticed in this investigation even after 5 months at room temperature.

The TEM results shown in Figure 3 firmly demonstrate that the higher amounts of the acacia polymer used in the formulation have a great influence on the size of the silver nanoparticles that form. The size of the silver nanoparticles decreases from  $18.04 \pm 1.91$  to  $5.21 \pm 0.30$  nm as the acacia concentration is varied from 0.1 to 0.5 wt % at a constant reducing agent ( $\text{AgNO}_3$ ) concentration of 0.5 wt %. This reveals that  $[\text{AgNO}_3] = 0.5$  wt % and  $[\text{acacia}] = 0.5$



**Figure 2** UV-vis spectra: (a) an acacia concentration of 0.3 wt % and different concentrations of  $\text{AgNO}_3$  and (b) an  $\text{AgNO}_3$  concentration of 0.5 wt % and different concentrations of acacia. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



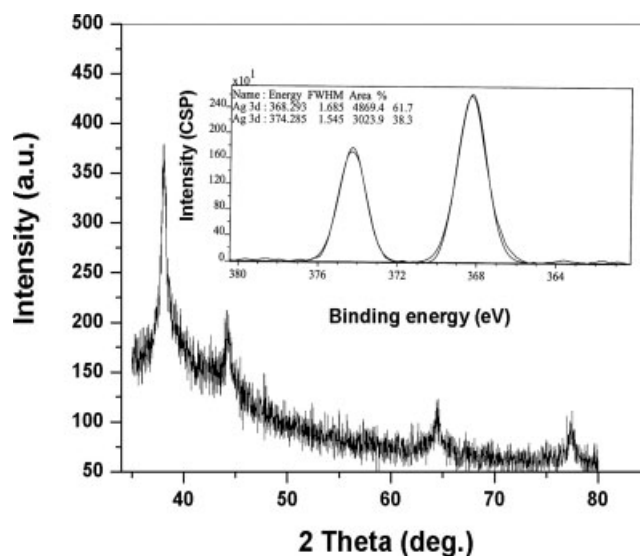
**Figure 3** TEM images for  $18.04 \pm 1.919$ ,  $17.54 \pm 0.6395$ ,  $14.81 \pm 1.152$ , and  $5.21 \pm 0.30$  nm silver nanoparticles prepared with an  $\text{AgNO}_3$  concentration of 0.5 wt % and different concentrations of acacia: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.5 wt %.

wt % in aqueous media constitute a good composition for obtaining  $\sim 5$  nm-silver nanoparticles. A completely different methodology, based on bulk thermosensitive hydrogel nanotemplates, provides silver nanoparticles 3 nm in size,<sup>41</sup> but this approach involves several steps, including the synthesis of a hydrogel, metal salt incorporation, and a reduction process. This investigation has been successful in obtaining nanoparticles in a single step.

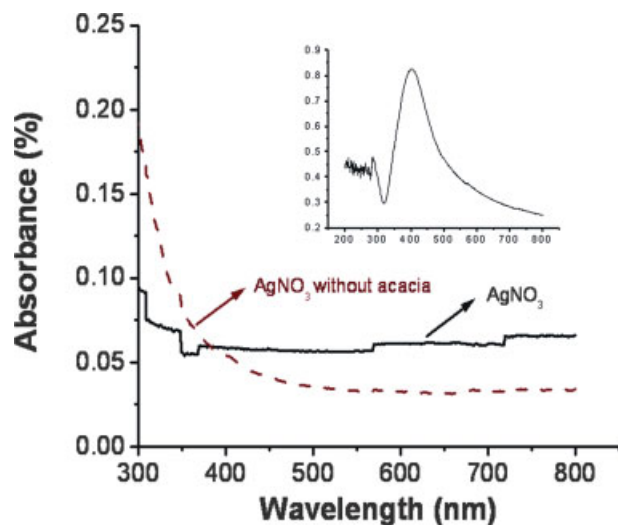
The nature of the silver formed in this approach has been evaluated with XRD and XPS methods. The XRD profile presented in Figure 4 exhibits characteristic peaks at scattering angles ( $2\theta$ ) of 38.06, 44.22, 64.48, and 77.32 corresponding to scattering from the (111), (220), (220), and (311) planes, respectively. These diffraction peaks firmly represent a face-centered cubic structure of crystalline silver nanoparticles.<sup>42</sup> Moreover, the high-resolution narrow XPS scans of the  $\text{Ag}^0$  stage (3d5/2) show a binding energy peak at 368 eV, which clearly supports the formation of silver nanoparticles<sup>43</sup> (Fig. 4, inset).

In this facile approach, we describe in detail the reduction process because most of the reports reveal

that polymeric chains stabilize the nanoparticles but may not assist in the reduction process. The acacia polymer is made of both a high-molecular-weight



**Figure 4** XRD spectrum and XPS of silver nanoparticles.



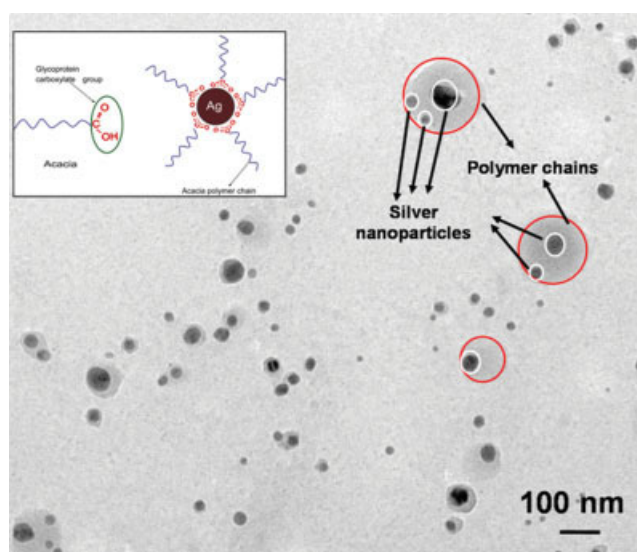
**Figure 5** UV spectra of  $\text{AgNO}_3$  solutions with and without the acacia polymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

glycoprotein containing 90% carbohydrates and a low-molecular-weight heterogeneous polysaccharide with a huge number of hydroxyl and carboxyl groups in the polymer chains. How does the acacia polymer work in the reduction process? We suspect that the reduction process takes place through the hydroxyl groups of the acacia polymer, and in fact, it is widely acceptable that the hydroxyl groups of poly(ethylene glycol) or ethylene glycols are effective reducing agents.<sup>29</sup> The hydroxyl groups of the polymer chains reduce the silver metal ( $\text{AgNO}_3$ ) to silver nanoparticles through the oxidation mechanism.<sup>44</sup> Washio et al.<sup>30</sup> reported for the first time that even residual hydroxyl end groups present on PVP chains exhibit prospective reducing properties. To prove this nature, we monitored the UV-vis spectra of  $\text{AgNO}_3$  solutions without the acacia polymer and with the acacia polymer. In Figure 5, without the acacia polymer, the  $\text{AgNO}_3$  solution does not show any absorption peak, and the  $\text{AgNO}_3$  solution remains in its  $\text{Ag}^+$  stage, whereas in the presence of the acacia polymer,  $\text{AgNO}_3$  converts into silver nanoparticles, which can be clearly observed at  $\sim 420$  nm (Fig. 5, inset). Therefore, it clearly shows that the acacia polymer helps in the reduction of  $\text{AgNO}_3$ .

Usually, the stability of metal nanoparticles is attributed mainly to the adsorption of the polymeric chains onto the crystalline planes of the nanoparticles. The intramolecular and intermolecular association of the acacia polymer leads to the formation of hydrogen bonds, which are ultimately responsible for network formation within the polymeric chains, and these networks provide nanoscopic domains in which the nanoparticles can grow like

hydrogel network systems.<sup>40,45</sup> The stabilization phenomenon has been observed clearly with a TEM experiment. Figure 6 displays a typical TEM image of the silver nanoparticles obtained with  $[\text{AgNO}_3] = 0.5$  wt % and  $[\text{acacia}] = 0.3$  wt % (a negatively stained sample in which we can also observe the polymer structure). It appears that the silver nanoparticles are encapsulated by the acacia polymeric networks or silver-acacia core-shell structure. The formed acacia polymer networks facilitate the excellent stability of the nanoparticles through electrostatic and steric effects and the carboxylate groups of the polymeric chains (Fig. 6, inset), which further promote the stabilization of silver nanoparticles. Because of the complexation ability of the polymer with silver metal nanoparticles through the carboxyl-functional groups of the polymeric chains and networks, they surround and protect the particles over longer periods.

On the other hand, a strong physical adsorption of the acacia polymer onto the surface of the silver nanoparticles is also an indication of better stabilization. The Fourier transform infrared (FTIR) spectrum of the acacia-silver nanoparticle system clearly reveals the adsorption of acacia polymer chains onto silver nanoparticles by the presence of an additional peak at  $1601\text{ cm}^{-1}$  [ $-\text{COO}^-$  group attached to silver particles; Fig. 7(b)]. This peak is completely absent for the pure acacia polymer [Fig. 7(a)]. Furthermore, the variations in the shape and peak position of the  $-\text{OH}$  and  $-\text{COOH}$  groups at  $3450\text{ cm}^{-1}$  occurred because of the contribution toward the reduction and stabilization processes.



**Figure 6** TEM image of acacia-silver nanoparticles (negatively stained with uranyl acetate). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

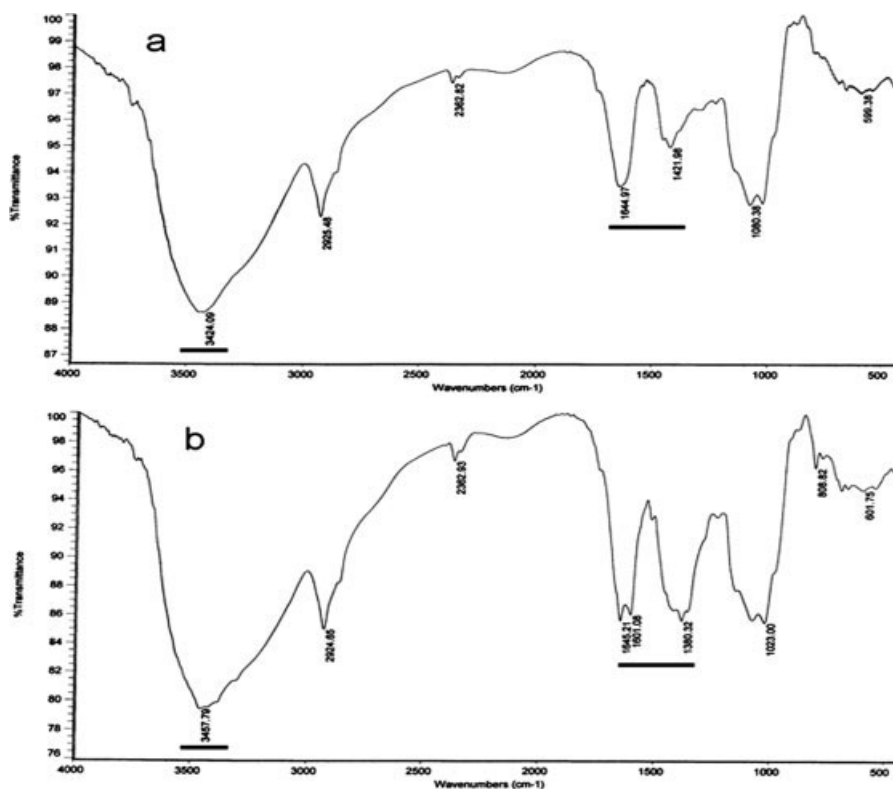


Figure 7 FTIR spectra of (a) acacia and (b) acacia–silver nanoparticles.

## CONCLUSIONS

We have developed a highly facile, simple, cost-effective, and green approach to the preparation of silver nanoparticles without the use of any reducing agent in the presence of the acacia polymer. Acacia has acted as a reducing agent and stabilizer in this investigation. The acacia composition with respect to  $\text{AgNO}_3$  allows good control over the size of the silver nanoparticles. The formation of silver nanoparticles by acacia polymer networks has been proved with various techniques such as FTIR, UV–vis, XRD, XPS, and TEM. The formed silver nanoparticles are stable for 5 months. This methodology can also be adapted to the preparation of other metal nanoparticles.

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