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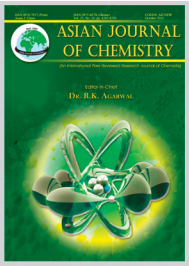

Synthesis of Silver Nanoparticles Doped in the Zeolite Framework

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In this article, synthesis of silver nanoparticles doped in the zeolite type A, at room temperature and in the absence of any additive reagents has been considered. This synthesized sample showed considerably antibacterial activity which was proved against gram-negative bacteria (*i.e. Escherichia coli* and *Shigella dysentriae*) and gram positive (*i.e., Staphylococcus aureus* and methicillin-resistant *Staphyloccus aureus*) by disk diffusion method using Mueller-Hinton agar at different sizes of silver nanoparticles.

Key Words: Synthesis, Silver, Nanoparticles, Zeolite.

INTRODUCTION

Currently, the use of nanoparticles (NPs) and related component through their usage in different industrial and agricultural aspects, dramatically has been developed[1-3]. It has proved that the properties of compound in the nano dimension are completely different with the accepted properties of bulky sized structure of them. Among the investigated nanoparticles, the use of transition metals are much more attractive because of their unique and indispensable physicochemical properties[4]. Silver has broad applications in the clothing, catalysis dentistry, medicine, mirrors, optics, photography, electronics and food industries[5,6]. Furthermore, introducing of single nanoparticles into other substrates lead to novel nanocomposites. There are variety of nanoparticles classification including metal/polymer, metal/metal, metal/metal oxides, metal/clay and metal zeolite[7,8]. Properties of single constituent, particle size, shape and surface interaction role over on the properties of nanocomposites. The most important strategy for reaching to nano dimension is discovering of appropriate nanosized framework that fully supports the growth of silver nanoparticles inside themselves. Among the mentioned frameworks, zeolite showed the best results and following our investigation we introduced the frame properties of zeolite for supporting and controlling of nano sized silver.

EXPERIMENTAL

For the preparation of Ag/zeolite nanocrystals, the silver contents of the sample were 0.5 (S1), 1.0 (S2), 2.0 (S3), 3.0 (S4), 4.0 (S5). At the beginning of the reaction, constant amounts of zeolite, were suspended in different volumes of 4.6×10^{-4} M $AgNO_3$ solution and stirred for 4 h at 40 ºC to achieve the $AgNO_3$/zeolite suspensions and make sure of cation exchange accomplishment. A freshly prepared $NaBH_4$ (1.84×10^{-2} M) solution was added to the Ag^+/zeolite suspensions at room temperature under mixing condition to obtain a constant $AgNO_3/NaBH_4$ molar ratio (1:3) and mixing was continued for 1 h and resulted suspensions were filtered by büchner funnel then washed by distilled water three times and dried overnight at 50 ºC.

RESULTS AND DISCUSSION

Zeolite was selected as the framework for supporting and controlling of the nanosized particles of silver. Trial of different reducing agents candidates $NaBH_4$ which showed the best result on the mentioned condition. According to the following proposed equation, silver nanosized particles were grown inside the zeolite pores.

$$Ag^+/zeolite + BH_4^- + H_3O \rightarrow Ag/zeolite + B(OH)_3 + 3.5H_2\uparrow$$

As illustrated in Fig. 1, the solution of $AgNO_3$/zeolite was colourless but by adding of reducing agent, it turned to different range of brown. This phenomena proved the generation of crystalline structure of synthesized silver nanoparticle samples.

Fig. 2, indicates the XRD patterns of zeolite and Ag/zeolite nanocrystals (S1-S5) in the wide angle range of 2θ ($5° < 2\theta < 80°$) that indicates the formation of synthesized Ag nanoparticle as a crystalline structure.

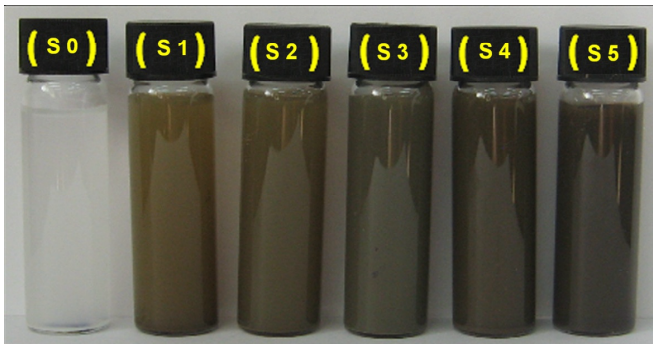


Fig. 1. Different range of Ag^+/zeolite solution before and after addition of $NaBH_4$

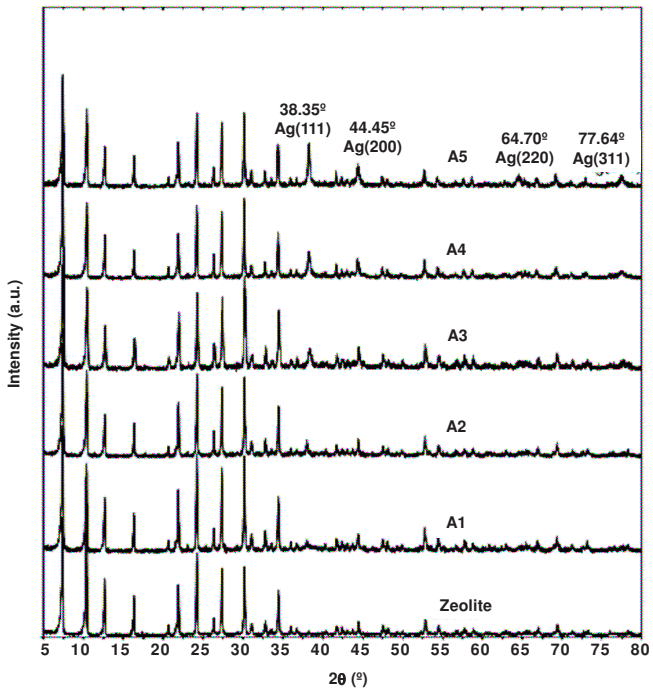


Fig. 2. Powder X-ray diffraction of patterns of zeolite and silver/zeolite nanocomposites

The TEM images (Fig. 3) only shows the silver nanoparticles average sized, but it is not able to illustrate clearly the exact dimension od synthesized silver in the zeolite framework.

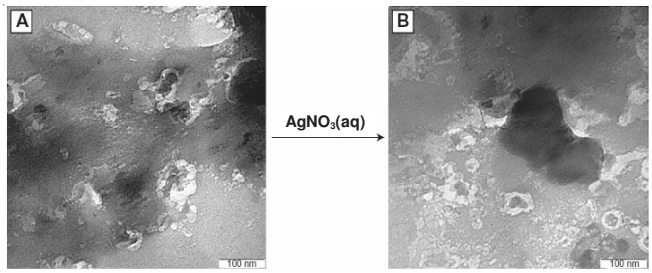


Fig. 3. Transmission electron microscopy images of A) zeolite and B) zeolite after impregnation with aqueous $AgNO_3$ ($AgNO_3$/zeolite [S0])

The bar chart of particle size indicates the mean diameters of nanoparticles ranged in 2.0-3.5 nm. As has been illustrated, the first sample shows the least deviation from the averaged size. This diversion from the mean diameter of nanoparticles is increased dramatically as the concentration was raised (Fig. 4).

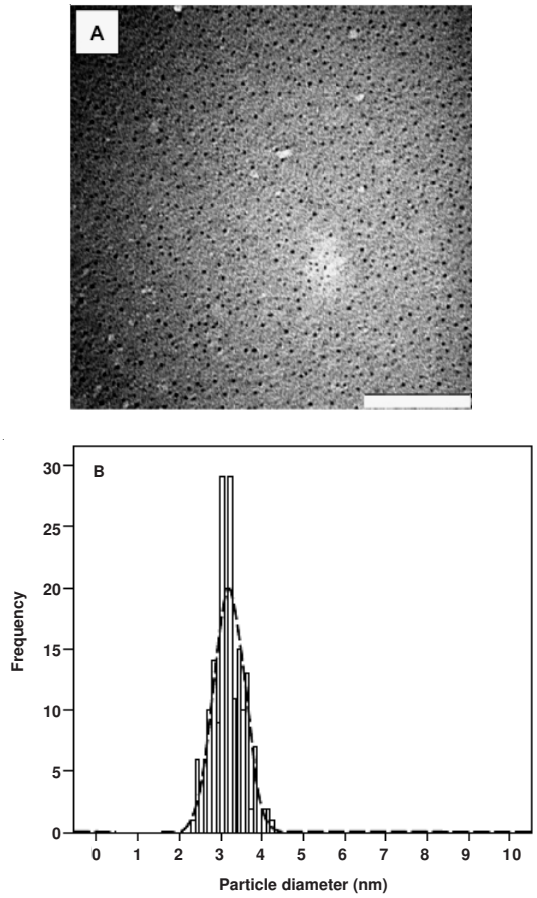
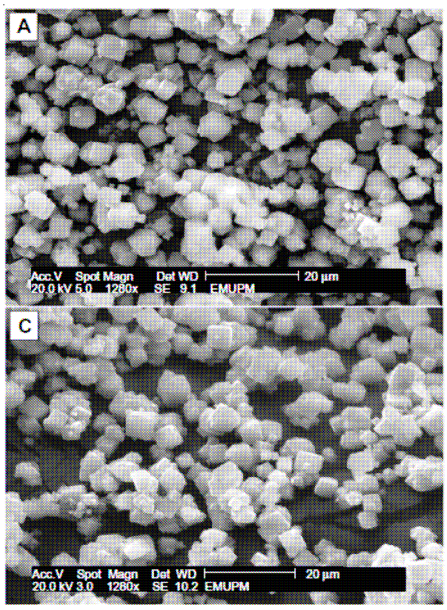


Fig. 4. Transmission electron microscopy images and corresponding particle size distribution of silver/zeolite nanocomposites

SEM images (Fig. 5) indicates no different structure between the initial zeolite and Ag/zeolite nano particles at different concentration. Additionally, EDXRF spectrum confirms the presence of silver element doped inside of zeolite framework.



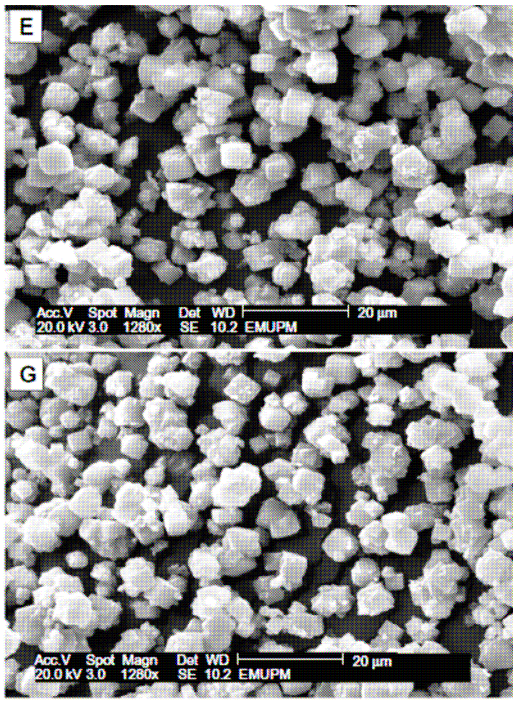


Fig. 5. Scanning electron microscopy micrographs and energy dispersive X-ray fluorescence spectrometer spectra, respectively, for the zeolite (A, B) and silver/zeolite nanocomposites (A2 1.0% [C, D]

FT-IR spectra don't show any palpable difference among the initial zeolite and silver doped zeolites[9,10]. The antibacterial studies illustrated the same inhabitation zone test for $AgNO_3$/zeolite and silver/zeolite nanoparticles against gram positive and gram negative *B. cereous* and *E. coli*, respectively. Maximum access of bacteria nuclear cells relating to greatest surface area of nanoparticles lead to efficient increase of antibacterial properties in all silver/zeolite nanoparticles that can be assumed because of gradually releasing of silver ions in the case of bacteria, silver contiguity.

It can be calculated that as the size of silver nanoparticles is increased by growth of silver loaded in the zeolite framework, its antibacterial activity remains completely impervious.

Conclusion

Ultimately, in this survey, we showed the frame properties of zeolite for controlling and supporting of silver nanoparticles that can be used as a prospective candidate of different nanosized structures. This procedure presents significant mechanism for synthesizing and size controlling of nanoparticles that is indispensible for its antibacterial feature. According to nanosized dimension of particles which were controlled by isometric cavities of zeolite framework, this method can be developed for pharmacological investigation in immediate future and advanced for multifarious elements including transition metals and their alloys.

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