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A RAPID SIMPLE ROUTE FOR SYNTHESIS OF NANOSIZED SILVER BY CHEMICAL PHOTOREDUCTION METHOD U

as poster/oral presentation.

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A RAPID SIMPLE ROUTE FOR SYNTHESIS OF NANOSIZED SILVER BY CHEMICAL PHOTOREDUCTION METHOD USING POLYOXOMETALATE

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ABSTRACT

Synthesis of nanosized silver particles by chemical reduction using polyoxometalate ($H_3PW_{12}O_{40}$), formaldehyde as a reductant agent and PVP (polyvinyl-pyrrolidone) as a stabilizer was performed. Effects of several processing variables such as quantities of acidic solution, irradiation time and also protective agents were investigated. The products were mainly characterized for their particle size distribution to provide information on the optimal conditions of synthesis and sufficient stability against coagulation. Also, silver nanoparticles were characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD).

It is shown that increasing $H_3PW_{12}O_{40}$ amount and irradiation time and also decreasing PVP as stabilizer, increase the size of synthesized nanoparticles. Our results indicated that for 0.01M silver nitrate solution, the addition of PVP/$AgNO_3$ ratio to 4 and quantity of $H_3PW_{12}O_{40}$ to 0.03g would produce silver colloids having sizes between 2 to 20 nm. The synthesized nanoparticles by this method are free from any metal ion contamination and suitable for use in semiconductor industry.

INTRODUCTION

Metal nanoparticles have been extensively investigated in recent years due to their unusual physical and chemical properties, which largely differ from their bulk properties. Several methods have been used to prepare silver nanoparticles, including chemical and physical methods [1]. Among them, the chemical reduction of silver ions in the presence of a protecting agent is the most common way [2]. The unique properties of polyoxometalates such as strong Bronsted acidity, high hydrolytic stability (pH=0–12), high thermal stability, operating in pure water without any additive, corrosiveness, safety and greenness [3-5], motivate us to exploit them as suitable reagents for synthesis of silver nanoparticles in a chemical reduction method.

Although in most cases, Ag NPs were synthesized in the presence of bases, such as sodium hydroxide, sodium carbonate, pyridine, and triethylamine [2], we tried to investigate the replacement of bases by acids.

The objective of this article was to use Keggin type polyoxometalate ($H_3PW_{12}O_{40}$) in chemical photoreduction reaction for synthesize of silver nanoparticles and investigate the parameters that affect the size of these nanoparticles. We have used formaldehyde and PVP as reductant and protective agents, respectively.

EXPRIMENTAL

Poly(N-vinyl-2-pyrolidone) (PVP) was dissolved in water and silver nitrate (1×10^{-2} mole), formaldehyde (2.2×10^{-2} mole), and $H_3PW_{12}O_{40}$ (1.07×10^{-5} mole) were added, respectively. Then, the mixture solution was irradiated by UV light (125W high voltage mercury vapor lamp) under continuous stirring.

After 30 min, the color of the mixture changed to black, indicating the formation of silver nanoparticles. The nanoparticles were separated by high speed centrifugation, washed twice with acetone/water and dried in a vacuum oven.

RESULTS AND DISCUSSION

Silver nanoparticles were synthesized by the reduction of Ag^+ using water as an environmentally safe solvent and Keggin acid as a green reaction promoter. In our process, all reagents were organic materials except the $AgNO_3$ precursor. The final product was only pure silver nanoparticles without any other metal ion impurities. The x-ray diffraction (XRD) pattern is shown in Figure 1. The reflection peaks indicate that silver is well crystallized.

Products of silver colloids were characterized mainly with particle size distribution. The transmission electron microscopy (TEM) images for these nanoparticles showed that the nano silver particles are spherical with diameter of about 2-20 nm.

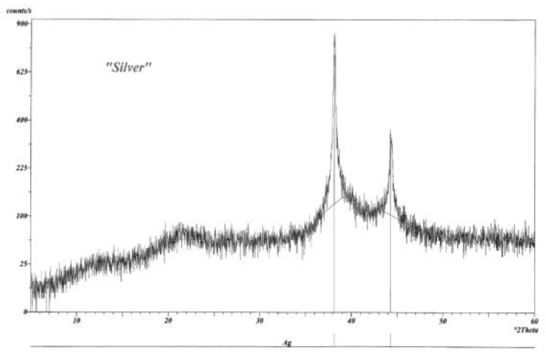

Fig. 1. XRD pattern of Ag nanoparticles.

According to the results, controlling sizes of these particles can be achieved via POM concentration. By increasing Keggin concentration, size of synthesized nanoparticles was reduced to about 5 nm. This is due to the reduction rate of silver ion which affects the initial nucleation of particles. One way for achieving smaller size of NPs could be by increasing the concentration of reducing reagents (reduced POM). This causes the reaction to be faster and nanoparticles becomes smaller (around 2- 10 nm).

To prevent agglomeration of synthesized silver nanoparticles due to the van der Waals or Coulomb forces, we have added PVP to the suspension as stabilizer. The PVP can form a protective layer on the particle's surface. The repulsive forces between polymer molecules stabilize the nanoparticles. Amount of stabilizer affects the size of silver NPs. Our results shows that particle size is increased with increasing stabilizer concentration. The reason is that at low stabilizer concentration, the stabilizer layer is not effectively built-up around the Ag^0 atoms and they grow to become larger. At the same time, new nuclei are formed during the growth process, resulting in a wide size distribution.

Besides these, irradiation time also have a very important role in the synthesis of nanoparticles. Increase in the irradiation time could make the morphology of NPs uniform and shorten the formation time of the nanoparticles. The results suggested that prolonging irradiation time will promote generation of reduced Keggin, which results in a certain amount of silver nanoparticle formation. With overextended irradiation times, the silver nanoparticles become too large to be stable and cause aggregation and precipitation easily.

CONCLUSIONS

In this research, synthesis of silver nanoparticles has been carried out using Keggin acid as a green and solid superacid using photochemical reduction method. of POM and PVP amounts and irradiation time as effective parameters on silver nanoparticles were investigated. It is shown that increasing amount of $H_3PW_{12}O_{40}$ and irradiation time, and decreasing PVP as stabilizer increase the size of synthesized nanoparticles.

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