

Ligand-Depended Adsorption Characteristics of Silver Nanoparticles on Activated Carbon

Hamza Simsir, Nurettin Eltugral, Selhan Karagoz

Abstract—Surface modification and functionalization has been an important tool for scientists in order to open new frontiers in nanoscience and nanotechnology. Desired surface characteristics for the intended applications can be achieved with surface functionalization.

In this work, the effect of water soluble ligands on the adsorption capabilities of silver nanoparticles onto AC which was synthesized from German beech wood was investigated. Sodium borohydride (NaBH_4) and polyvinyl alcohol (PVA) were used as the ligands. Silver nanoparticles with different surface coatings have average sizes range from 10 to 13 nm. They were synthesized in aqueous media by reducing Ag (I) ion in the presence of ligands. These particles displayed adsorption tendencies towards AC when they were mixed together and shaken in distilled water.

Silver nanoparticles (NaBH_4 -AgNPs) reduced and stabilized by NaBH_4 adsorbed onto AC with a homogenous dispersion of aggregates with sizes in the range of 100-400 nm. Beside, silver nanoparticles, which were prepared in the presence of both NaBH_4 and PVA (NaBH_4 /PVA-Ag NPs), demonstrated that NaBH_4 /PVA-Ag NPs adsorbed and dispersed homogeneously but, they aggregated with larger sizes on the AC surface (range from 300 to 600 nm). In addition, desorption resistance of Ag nanoparticles were investigated in distilled water. According to the results AgNPs were not desorbed on the AC surface in distilled water.

Keywords—Activated carbon, adsorption, ligand, silver nanoparticles.

I. INTRODUCTION

THE advancement of nanotechnology and nano materials lead to many scientific and technological advances [1]–[4]. When, nanoparticles compared to their bulk counterparts, they have tremendous surface area. Hence, nanoparticles can gain some different and significant properties from the bulk counterparts. For example, while Ag bulks do not have any antibacterial properties, antibacterial properties of AgNPs are well known [5]. And they were used as an antibacterial material for many times [5]–[7]. On the other hand, Due to the Ag bulks and AgNPs have conductive properties they were used in many applications as conductive materials [8], [9].

There are various synthetic methods in order to prepare silver nanoparticles (photochemical synthesis [10], laser ablation [11], wet chemical synthesis [12], etc.). Wet chemical

synthesis method is well known the most eco-friendly way for obtaining the AgNPs. With this method, AgNPs are synthesized from silver salts such as silver nitrate or silver chloride by reducing agent, coating ligands or protecting groups. Thus, metal nanoparticles can be prepared with controlled size and uniform dispersions [13], [14].

Activated carbons (AC) are obtained from natural products (sugars, cellulose, nutshells, mosses, etc.) with low production costs by pyrolysis method. In addition to their natural friendly synthesis process, they have substantial materials for industry [15], [16]. Since AC has a porous and an extensive surface area, it has been considered for many applications which could be categorized two main groups. First application group includes purifying pollutions on the earth. With this respect, ACs are used in some areas; water disinfection, air filtering technologies, removal of heavy metal ions from drinking water, etc. [15], [17]. Second main applications of ACs include surface modification and applications. Desired surface characteristics for the intended applications can be achieved with surface functionalization. Once functionalized with appropriate molecule(s)/ligand(s), metal nanoparticles can be adsorbed onto the surface of ACs that can be further utilized for specific purposes [18]. With these special properties ACs could be used as an electrode material especially in aqueous electrolytes and supporting material in different metal alloys [18], [19]. ACs supported with AgNPs have big potential material for many applications.

II. EXPERIMENTAL

A. Materials and Characterization

All reagents were analytical grade. Potassium carbonate (K_2CO_3), silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich. Polyvinyl Alcohol (PVA M.W. 16000) was purchased from Across Organics. Distilled water was used in all experiments. AgNPs were characterized by transmission electron microscopy (RTEM 200 kV) with electron diffraction. Samples of AgNPs were imaged and analysis was performed by using Jem Joel 2100F, acceleration voltage of 200 kV. AgNPs solutions were characterized by UV-vis absorbance spectroscopy (Perkin Elmer Lambda 35 UV-Vis). UV-vis absorbance spectra were measured in quartz cuvettes by using a double-beam spectrophotometer. The morphology of activated carbon and AgNPs loaded on activated carbon were performed by using a scanning electron microscope (Carl Zeiss Ultra Plus Gemini Fesem) at acceleration voltage of 500 V.

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B. Activated Carbon (AC)

The activated carbon used in the experiments was produced from German beech wood. 40 g precursor powder was mixed with K_2CO_3 (1:1 wt ratio) in 250 ml deionized water for 24 h prior to pyrolysis. Later, the resulting sample was dried in oven at $105^\circ C$. Pyrolysis was happen under nitrogen atmosphere at $800^\circ C$. The pyrolysis product was refluxed in 5M HCl for 2 h in order to eliminate impurities. The resulting sample was washed with hot and cold distilled water respectively until chloride ions were removed. Finally, produced activated carbon was dried at $105^\circ C$ for 4 h and it saved in closed glass bottles.

C. $NaBH_4$ Stabilized Silver Nanoparticle

Silver nanoparticles stabilized by $NaBH_4$ were prepared by chemical reduction method [20] Firstly, 0,00169 gr $AgNO_3$ were dissolved in 10 ml. distilled water (10^{-2} mmol.), (1 mM) at room temperature on magnetic stirrer for 15 minutes. 0,00226 gr solid $NaBH_4$ were dissolved in 30 ml distilled water ($6 \cdot 10^{-2}$ mmol), (2 mM) at room temperature on magnetic stirrer for 15 minutes. After that, $NaBH_4$ solution was cooled in an ice bath until its temperature was $0^\circ C$. Finally, 10 ml of $AgNO_3$ solution was poured on $NaBH_4$ solution drop by drop at 30 min in an ice bath at $0^\circ C$. When, 3 ml of $AgNO_3$ solution was poured on the $NaBH_4$ solution, which was started to seen yellowish. When, all of the $AgNO_3$ solution was poured, $NaBH_4$ solution was seen dark yellow and final solution was stirred in ice bath for 5 minutes more, and then reaction was ended up. Finally the solution ($[Ag]=0,25$ mM)] was kept waiting in a closed glass bottle.

D. $NaBH_4$ /PVA Stabilized Silver Nanoparticles

Firstly, 0,00169 gr $AgNO_3$ were dissolved in 10 ml. distilled water (10^{-2} mmol.), (1 mM) at room temperature on magnetic stirrer for 15 minutes. 0,00226 gr solid $NaBH_4$ were dissolved in 30 ml distilled water ($6 \cdot 10^{-2}$ mmol), (2 mM) at room temperature on magnetic stirrer for 15 minutes. After that, $NaBH_4$ solution was cooled in an ice bath until its temperature was $0^\circ C$. Finally, 10 ml of $AgNO_3$ solution was poured on $NaBH_4$ solution drop by drop at 30 min in an ice bath at $0^\circ C$. When, 3 ml of $AgNO_3$ solution was poured on the $NaBH_4$ solution, which was started to seen yellowish. When, all of the $AgNO_3$ solution was poured, $NaBH_4$ solution was seen dark yellow, in that time 0,7 gr PVA was added to reaction mixture and final solution was stirred in ice bath for 15 minutes more, and then reaction was ended up. Finally the solution ($[Ag]=0,25$ mM)] was kept waiting in a closed glass bottle.

E. Silver Nanoparticle Adsorption on Activated Carbon

Adsorption studies were performed at the same conditions of temperature, mixing time and silver concentration. For each set up of experiments, 0.05 gr AC was put into a 25 ml. reaction bottle. And then, 10 ml. of AgNP solution ($[Ag]=0,25$ mM)] which is prepared with the using of $NaBH_4$ and $NaBH_4$ -PVA as a ligand, was poured on activated carbon in a respective bottles at the room temperature on magnetic stirrer. 18 hours later reaction was ended up. After that, the solution

was filtrated and cooled at the room temperature for 1 day. Finally the solid was kept waiting in a closed glass bottle.

F. Silver Nanoparticle Desorption on Activated Carbon

Desorption process was performed at the same conditions of temperature, mixing time and silver concentration. For each set up of experiments, 0,04 gr $NaBH_4$ -AgNPs supported AC which was detected with the SEM images and 0,04 gr $NaBH_4$ -PVA-AgNPs supported AC which was detected with the SEM images also stirred in a 10 ml distilled water for 18 hours. After that, the solution was filtrated and cooled at the room temperature for 1 day. Finally the solid was kept waiting in a closed glass bottle.

III. RESULT AND DISCUSSION

A. Characterization of AgNPs

Colloidal solutions of AgNPs were prepared by chemical reduction of silver ions from $AgNO_3$ in the presence of $NaBH_4$ and $NaBH_4$ -PVA ligands in an aqueous media. Both solutions were seen dark yellow similarly. With the measuring the diameter of approximately hundred particles manually, AgNPs were calculated average sizes range from 10 to 13 nm (Table I).

TABLE I
PARTICLE COMPOSITIONS, SIZES AND SPECTRAL CHARACTERISTICS OF AG NANOPARTICLES

Nanoparticle	$AgNO_3$ (mM)	$NaBH_4$ (mM)	λ_{max} (nm)	Particle size (nm)
$NaBH_4$ -AgNPs	0.5	1.0	396	10(± 3)
$NaBH_4$ /PVA-AgNPs	0.5	1.0	396	10(± 3)

It means that AgNPs have been mono dispersed characteristic. Their absorbance peak was detected 396 nm and absorbance peak length was quite narrow. Absorbance band shape and position give us useful information about particle size and distribution. The narrower the bandwidth means that uniform the particles sizes (Fig. 1) [20], [21].

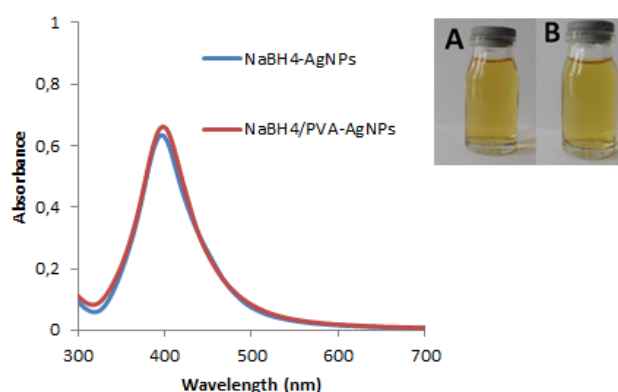


Fig. 1 Representative UV-visible spectra of Ag nanoparticles (A) $NaBH_4$ -AgNPs, (B) $NaBH_4$ /PVA-AgNPs

In the first impression, when their colors, AgNPs sizes and UV absorbance spectra were investigated, they seem quite similar. It is an expected result for us, since the same reduction

agent which is the most important effector to the size of AgNPs in aqueous media was used. In addition, according to the TEM images any size differences cannot be seen also (Fig. 2). Thus PVA was used in the second reaction in order to explain the characteristic of stabilizing agent. So, it is clearly seen that, NaBH_4 -AgNPs are more aggregated than NaBH_4 -PVA-AgNPs. It is an also expected result for us since, PVA is a strong stabilizing agent and it prevent the AgNPs from the aggregation (Fig. 2).

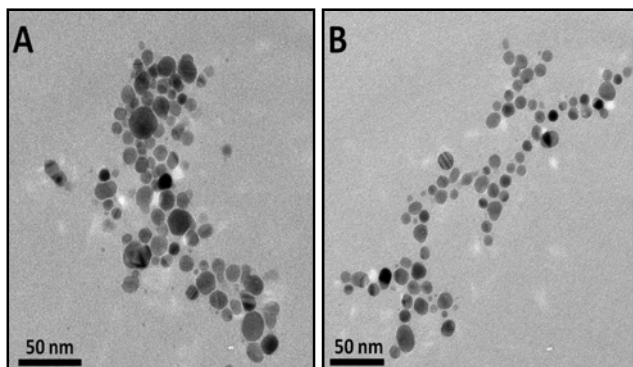


Fig. 2 Representative TEM images of Ag nanoparticles (A) NaBH_4 -AgNPs, (B) NaBH_4 /PVA-AgNPs

B. AgNPs Adsorbed-Desorbed on AC

Since AC has a porous and an extensive surface area, it gives us to opportunity of adsorbed AgNPs on their surface. In the presence of both ligands AgNPs had a uniform distribution on the surface of AC and their shapes were spherical (Fig. 3).

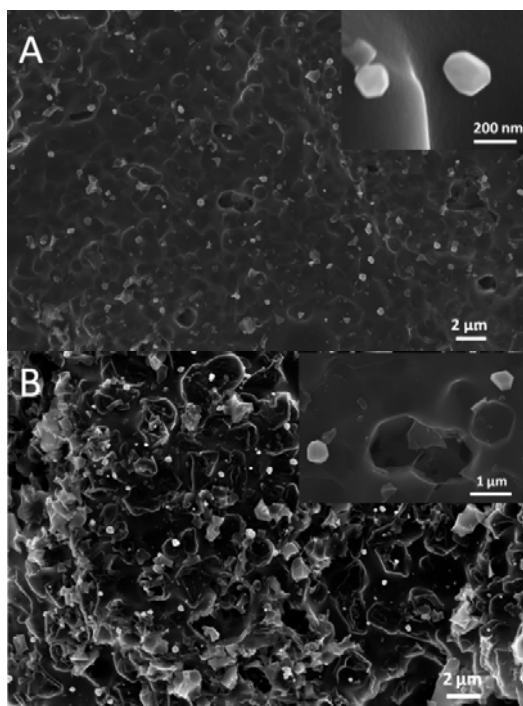


Fig. 3 Representative SEM photographs (A) NaBH_4 -AgNPs, (B) NaBH_4 /PVA-AgNPs. The insets show magnified images of nanoparticles on AC surface

When, nanoparticles were adsorbed on a material surface aggregation could be happen and it is well known result which could be seen former investigation [22]. According to the TEM images, AgNPs depicted better dispersion characteristics with the using NaBH_4 -PVA as ligand than only NaBH_4 was used as a ligand in the distilled water (Fig. 2). But according to the SEM images, AgNPs with the using of NaBH_4 -PVA as ligand was more aggregated than NaBH_4 using counterpart (Fig. 3). Particle size of NaBH_4 -AgNPs and NaBH_4 /PVA-AgNPs remained in the range of 100-400 nm and 300-600 nm respectively. The reason of this result could be explain that, AC surface effected to the stabilizing agent (PVA) more than reducing agent (NaBH_4), and it is caused to more aggregate to the AgNPs on AC surface.

After the desorption process AgNPs were still seen onto AC surface (Fig. 4). According to the desorption investigation of AgNPs with both ligands, AgNPs were adsorbed to AC surface strongly.

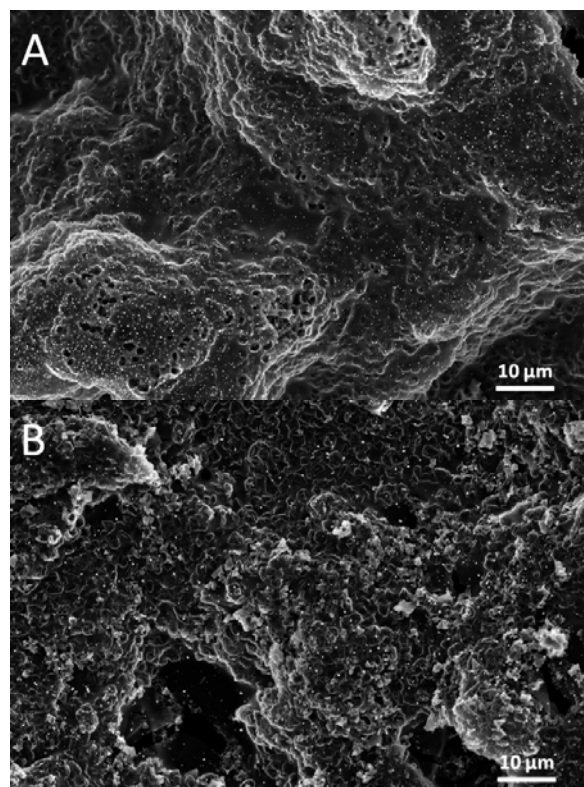


Fig. 4 SEM photographs of nanoparticle-loaded AC after desorption process with water. (A) NaBH_4 -AgNPs, (B) NaBH_4 /PVA-AgNPs

IV. CONCLUSION

This investigation depicted that, in the presence of NaBH_4 and NaBH_4 -PVA, silver nanoparticles could be synthesized nearly similar sizes, with the low production costs by chemical reduction method. When silver nanoparticles adsorbed onto activated carbon with the different ligand combinations, they adsorb onto AC with the different sizes. In addition to, AgNPs are not desorbed onto the AC in an aqueous media with the using of both ligands. It can be concluded that AC surface

moiety is suitable area for the adsorption of nanoparticles. AC materials having potentials in water treatment, air conditioning filters, antibacterial and electrolyte materials, etc.

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