

Preparation of Size Controlled Silver on Carbon from E-waste by Chemical and Electro-Kinetic Processes

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Abstract—Preparation of size controlled nano-particles of silver catalyst on carbon substrate from e-waste has been investigated. Chemical route was developed by extraction of the metals available in nitric acid followed by treatment with hydrofluoric acid. Silver metal particles deposited with an average size 4-10nm. A stabilizer concentration of 10-40g/l was used. The average size of the prepared silver decreased with increase of the anode current density. Size uniformity of the silver nano-particles was improved distinctly at higher current density no more than 20mA. Grain size increased with EK time whereby aggregation of particles was observed after 6h of reaction. The chemical method involves adsorption of silver nitrate on the carbon substrate. Adsorbed silver ions were directly reduced to metal particles using hydrazine hydrate. Another alternative method is by treatment with ammonia followed by heating the carbon loaded-silver hydroxide at 980°C. The product was characterized with the help of XRD, XRF, ICP, SEM and TEM techniques.

Keywords—e-waste, silver catalyst, metals recovery, electrokinetic process.

I. INTRODUCTION

NANO-SILVER (NS) magnetizes a significant awareness because of its wide range of applications in emerging areas of nano science and technology [1]. Size, shape, and surface morphology play pivotal roles in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials [2]. Three steps determine the preparation of nano-materials. They should be evaluated from a green chemistry perspective: the choice of the proper solvent medium used for the synthesis, the environmentally benign reducing agent, and the choice of a nontoxic material for stabilization of the nanoparticles. Shankar et al. [3] suggested that the reduction of aqueous AuCl_4^- and Ag^+ ions using extracts from geranium and lemongrass plants occurred due to the ketones / aldehydes groups present in the extract. This plays an important role in directing the shape evolution in these nanoparticles. However, the treatments are still relying on simple methods such as incinerator and landfill. Printed circuit board (PCB) consists of various metals including precious metals such as gold, silver and palladium [4]. Goosy and Kellner [5] reported the existence of 2% wt of silver in the e-waste. There have been several studies on the recycling of materials by mechanical [6], thermal [7] and chemical [8], [9]

processes, but most of them dealt with recovery of one or two specified materials of all PCB compositions. Recently, Pilone and Kelsall [10] reported on multi-metal electro-deposition with a mathematical model. Jun Park, J. and Fray D.J. claimed that Silver is relatively stable in aqua regia so about 98% wt. of the input metal was recovered without an additional treatment [11]. Silver nanoparticles of different shapes and size have been successfully obtained through various methods, the concentrations of nano-silver were extremely low or/and the reaction solution was always in micro-liter volumes in most of the procedures. It has been reported that organic compounds such as hydrazine hydrate reduces silver nitrate to silver metal in nano size [12]. Recently, concentrated dispersions of silver nanoparticles were prepared by reducing silver nitrate solutions with ascorbic acid in the presence of Daxad-19 as stabilizing agent [13]. However, the synthesis of well-dispersed silver nanoparticles in high yield is still a challenge. Synthesis of flake-like silver nanoparticles in high concentration can be obtained by aging an aqueous solution containing silver nitrate, urotropine, and poly-(vinylpyrrolidone) (PVP). Varying the aging time easily control the size and shape of the nano-silver under mild conditions [14]. Song et al. studied adsorption of Ag (I) ions from aqueous solutions, CNS (400–500nm in diameter). The surface of the nonporous CNS, after being activated by NaOH, was enriched with $-\text{OH}$ and $-\text{COO}^-$ functional groups. Despite the low surface area ($<15\text{m}^2/\text{g}$), the activated CNS exhibited a high adsorption capacity of 152mg silver/g. Under batch conditions, all Ag (I) ions can be completely absorbed in less than 6 min with the initial Ag (I) concentrations lower than 2ppm [15]. Cui J. and Zhang L. [16] reviewed recovery of metals from e-waste. They reported that precious metals can be recovered by pyrometallurgical, hydro-metallurgical leaching (cyanide, halide, thiourea and thiosulfate leaching), by cementation, solvent extraction, ion exchange, biosorption and bioleaching. Mulvaney [17] reported that the absorption spectrum of a metal sol in water is shown to be strongly affected by cathodic or anodic polarization, chemisorptions, metal adatom deposition, and alloying. Anion adsorption leads to strong damping of the free electron absorption. Cathodic polarization leads to anion desorption. Under potential deposition (upd) of electropositive metal layers results in dramatic blue-shifts of the surface plasmon band of the substrate. The deposition of just 0.1 monolayer can be readily detected by eye. In some cases alloying occurs spontaneously during upd. The underpotential deposition of silver adatoms

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onto palladium leads to the formation of a homogeneous silver shell, but the mean free path is less than predicted, due to lattice strain in the shell.

This paper approaches a method for preparation of nano-silver metal from e-waste on carbon substrate. Deposition of silver on carbon was matched by electro-kinetic or chemical adsorption route from dilute solution. The extent of recovery and quality of the end product was determined with the XRD, FTR and TEM techniques. Comparative technical and economic data of the two processes is given.

II. EXPERIMENTAL

A. Materials and Methods

1. The E-waste: Electronic waste weighing 10kg was collected from spent PCB (4kg), processors (2kg), mobile phone (2kg), and TV boards (2kg). These were crushed using a Joe crusher mill to pass 4mm size. It was further ground in a ball mill to a less size. The sample was sieved to 4 fractions; $<0.25\text{mm}$, $>0.25<0.5\text{mm}$, $>0.5<1\text{mm}$ and $>1\text{mm}<4\text{mm}$. These were designated F_1 through F_4 respectively.
2. Carbon Substrate: carbon sample (1) was obtained from graphite-doped polypropylene sheets having 0.35mm in thickness ready for silver deposition. Another type of carbon (sample 2) was prepared from synthetic graphite electrodes used for brine electrolysis. It was a product of carbon Loraine (France). The blocks were cut with the help of a rotating cutter disc to the desired dimensions. It was degreased by heating at 400°C in inert atmosphere. Both samples were cleaned with distilled water and dried before silver deposition.
3. Carbon Cathode for Electrokinetic Study: Cathode plate 30mm x 60mm height were prepared from carbon sample (1) was used as cathode for electrokinetic deposition of silver nanoparticles. Another set of experiments were carried out using thin block of the synthetic graphite electrode, 3mm in thickness cut out from mother synthetic graphite electrodes.
4. Chemicals Used: Nitric, HF, HCl, $\text{NH}_4(\text{OH})$ etc were of pure grade.
5. Water used throughout the work is doubly distilled.

B. Preparation of Silver Solution

The e-waste fractions were analyzed for silver content using XRF and ICP analyzer. The cuts were dissolved by stirring in nitric acid at 75°C for periods up to 24 hours. Dissolved metals were filtered. Hydrofluoric acid is then added to the filtrate whereby silver selectively went into solution whereby other metals precipitated. Adjustment of the pH value of the solution has been matched with the help of ammonia followed by filtration of the insoluble ammonium fluoride. Silver nitrate was obtained from the fluoride salt using equimolecular amount of potassium nitrate followed by filtration. Silver nitrate is used in for the deposition processes. Concentration

adjustment of silver ions (20 ppm) takes place with de-ionized water.

C. Electrokinetic Deposition of Silver Metal on Carbon Substrate

Deposition of silver metal on carbon substrate has been executed in an electrolyzing cell shown in Fig. 1. Titanium anode and carbon cathode (working area of 20cm^2) are fixed in a polystyrene container and separated by silk screen diaphragm. The cell is fitted with electrical heater thermostat (HS), mechanical stirrer (MS), separating funnel filled with silver stock solution SSS. A DC main is connected to a resistance R, a micro ammeter and micro voltmeter.

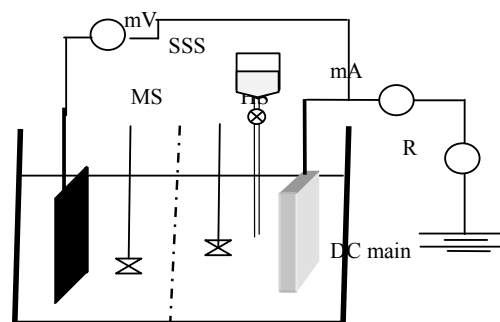


Fig. 1 Schematic diagram of the used electrokinetic cell

D. Deposition of Silver Nanoparticles on Carbon Substrate

1. By Electrokinetic Method

The studied parameters are time, cathode current density, temperature and stirring conditions. Silver diameter and morphology of the deposited particles were periodically determined with the help of X-ray diffraction, FTR spectrum and TEM measurements. The process of silver deposition can be matched for different periods to control the particle size.

2. Deposition by Chemical Process

An impregnating device has been developed. It is composed of a dissector containing a dish filled with silver solution. The dissector lid is connected to a vacuum pump fitted with a valve. Carbon cathode were heated at $100\text{--}120^\circ\text{C}$ outside the dissector and then carefully supported while hot on the edges of silver pot in the dissector. The dissector lid is placed and the vacuum valve is opened and the vacuum pump is switched on to 5mm Hg. The carbon sample was kept under vacuum for 30 minutes after which the vacuum valve is closed. The dissector was gently shaken to allow the carbon to fall in the silver pot. The vacuum tap is disconnected to maintain atmospheric pressure. After 1h, the carbon samples were taken out and dried in a drier. The loaded carbon was immersed in hydrazine hydrate to reduce silver nitrate to yield silver metal. The chemical process of silver deposition can be repeated several times to control the particle size.

E. E-Measurements of Physicochemical Properties

Identification and thickness of the deposited silver on the substrate was determined with XRF and SEM respectively.

Phase identification of the prepared silver is performed at room temperature using X-ray diffraction (XRD, Bruker axS D8, Germany) with Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation and secondary mono-chromator in the range 2θ -scale from 20 to 70 degree. The morphology information of the samples such as particle size and particle shape was investigated using transmission electron microscopy TEM with an acceleration voltage up to 120kV, a magnification power up to 600k, and a resolving power down to 0.2nm (TEM, JEOL-JEM-1230, Tokyo, Japan). Scanning electron microscope (SEM) JEOL instrument model JSM-5410 was used to determine the microstructure of the deposited silver. The Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FT-IR-3600 plus Japan.

III. RESULTS

Electrokinetic study was carried out at a potential range (+0.40) and (+0.80) with respect to standard hydrogen electrode. It was selected to be an intermediate redox potential of both hydrogen and oxygen gases [18]. Table I shows the metal content of the e-waste samples. It can be seen that silver content amounts to 0.2 % by weight of the e-waste material, Copper (15%), and base polymer (67.5%). Fig. 2 demonstrates a photograph of the e-waste sample.

TABLE I
THE METAL COMPOSITION OF A TYPICAL E-WASTE

Metal	Percent mass	
	Single side PCB	Double sided PCB
Cooper	15	25
Lead	2	3
Tin	2	3-3.2
silver	0.2-0.19	0.24-0.22
Gold	0.15-0.2	0.35-0.4
Base polymer	80.3	67.5

Chemical analysis of silver content in the obtained leaching solution revealed presence of 175 to 200mg/L of silver. The recovered solution was adjusted to 100-300ppm before silver deposition by dilution using bi-distilled water or by evaporation respectively.

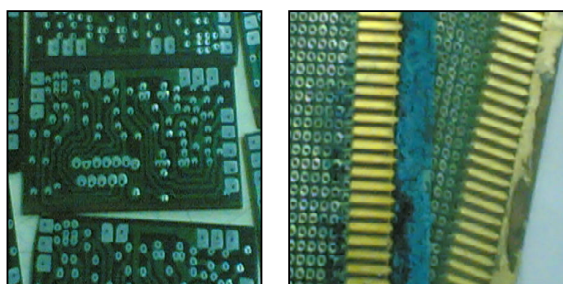


Fig. 2 A photograph of the e-waste (PC Boards)

Fig. 3 shows the extent of dissolution of silver as a function of nitric acid concentration at temperatures up to 100°C. It can be seen that the extent of metals dissolution increases with increasing temperature and time of dissolution. Complete recovery extent of silver takes place after 60min and at 100°C.

At room temperature and after 60 minutes, only about 50% recovery has been manifested

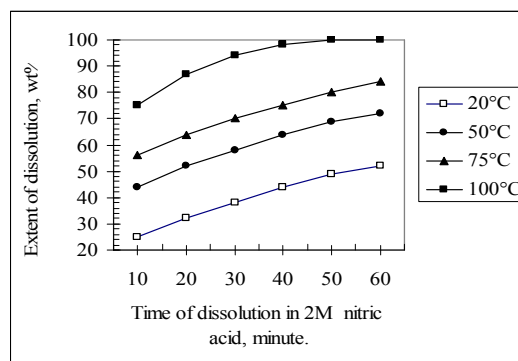


Fig. 3 Effect of nitric acid concentration and temperature on the extent of silver recovery from e-waste

Fig. 4 shows the weight of the electrodeposited silver nanoparticles on carbon samples (1). Experiments were conducted at room temperature using 20mg/L stabilizer. It can be seen that the weight of the electrodeposited silver nanoparticles increases linearly with time and current density up to 30 mA/cm². It is worthy to note that although the weight of the deposited silver particles obtained at 30mA/cm² overweighs that obtained with lower current density values, it was loose and not adhering to the substrate surface. The same results have been obtained with carbon sample (2). Table II shows the effect of concentration of the stabilizer on the weight of the deposited silver (25°C, 180min.). It is seen that the optimum weight of the deposited silver has been approached with 30mg/L.

TABLE II
EFFECT OF CONCENTRATION OF STABILIZER ON THE WEIGHT OF DEPOSITED SILVER

Concentration of stabilizer, mg/L	Weight of deposited silver, mg/cm ² (20mA/cm ² , 180 min)	
	25°C	50°C
10	95	105
20	190	205
30	200	215
40	202	215

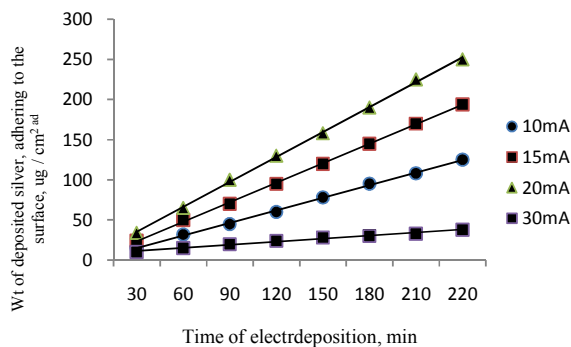


Fig. 4 The weight of the electrodeposited silver nanoparticles adhering to surface of carbon sample, room temperature and 20mg/L stabilizer

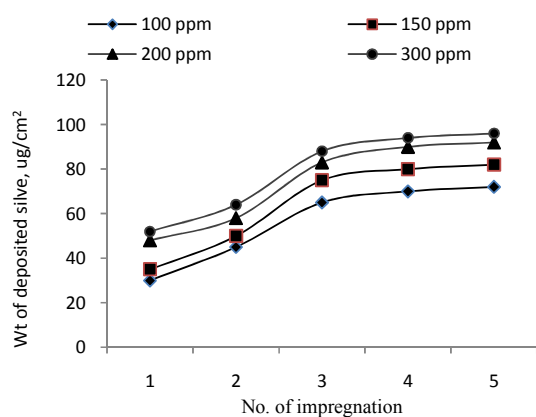


Fig. 5 (a) Wt of deposited silver nano particles on carbon sample (1) as affected by number of impregnation using silver solution of 100-300ppm

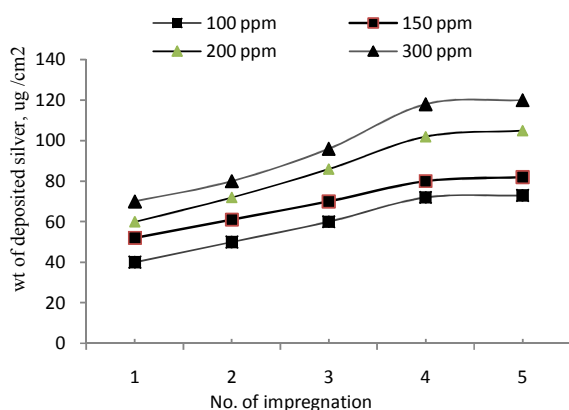


Fig. 5 (b) Weight of deposited silver nano-particles on carbon sample (2) as affected by number of impregnation using silver ion concentration of 100-300 ppm

Figs. 5 (a) and (b) show that the weight of silver deposited on the surface of carbon sample (2a, b) increases with increase of number of impregnation. It is also seen that a constant

weight of deposited silver particles is attained after the fourth impregnation.

Fig. 6 shows the XRD pattern of the deposited nanosilver particles. Diffraction peaks appeared at 37, 44 and 60 degrees of 2θ .

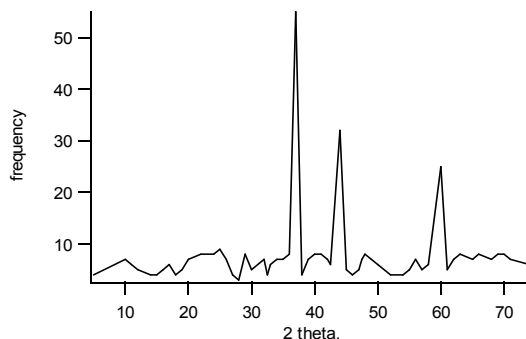
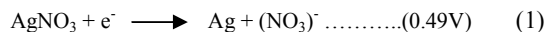


Fig. 6 The X-ray diffraction pattern of deposited nanosilver layer

IV. DISCUSSION

Nanosilver magnetizes a significant awareness on basis of its wide range of applications in emerging areas of nanoscience and technology. The formation of nanoparticles of silver is approached by electrokinetic process or by chemical adsorption technique. In the former method, silver solution of nitrate salt is electrolyzed between Titanium anode and carbon cathode. Silver can be deposited when under specific anodic current density and a cathode potential 0.49 V, for the reaction:



Increasing the cathode potential more than the reduction potential of silver is associated with the reduction of other metals present. The weight of deposited silver obtained with carbon sample (2) is slightly higher than that obtained with carbon sample (1). This is reasonable on basis of the fact that carbon sample (2) is more porous as compared to carbon sample (1). Porosity measurements of carbon sample (2) revealed that it contains a total porosity of $26.2\text{cm}^3/\text{g}$. Macro pores constitute 71%, mesopores 28.4% and micro pores 0.6% [19]. Total surface area of porous carbon exposed supporting silver deposition is higher compared to the less porous carbon sample (1). Electrokinetic process deposition produces more nanoparticles of silver to satisfy the available carbon surface sites accessible for adsorption compared to the chemical way. This is explained in the light of a model which assumes that ionic silver ions are regularly discharged on the cathode surface while chemical deposition involves silver molecules to be deposited via adsorption mechanism. In the electrokinetic method, more silver nanoparticles aggregated to form irregular shapes of silver particles. It is seen that electrokinetic process formed a mono layer of nanoparticles after short time of working

When the electrokinetic process takes place for long time aggregation of silver particles sets in. On the other hand, multi

impregnation takes place on accessible sites for adsorption and not aggregation of silver particles. It can be concluded that electrokinetic process is more capable to produce nanoparticles of silver under controlled time. With long time, more silver deposition per unit area of the substrate takes place with formation of silver particles having irregular shape and diameter. On the other hand, chemical route produces nanoparticles few layers in thickness. The deposition of metal silver was confirmed by the XRD pattern analysis. Fig. 5 shows a typical XRD pattern of as obtained silver nanoparticles. The broadening of the diffraction peaks attributes the nanosized formation of silver nanocrystals. The crystallite size was estimated by Debye-Scherrer's equation [20]. Size of the obtained silver sample ranges 4-10nm.

Fig. 7 is the FT-IR pattern that shows face-centered-cubic (fcc) lattice (JCPDS file no 04-0783) with strong diffraction peaks at 37, 44, 60 and 77 degrees of 2θ corresponds to (111), (200), (220) and (311) crystal planes

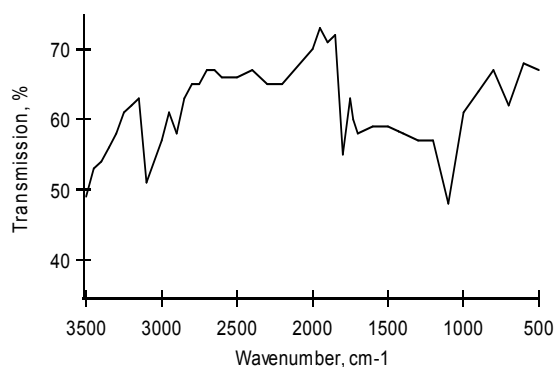


Fig. 7 FT-IR spectrum of nanosilver obtained by chemical process

Fig. 8 shows a typical transmission electron microscope (TEM) of the silver nanoparticles formed on carbon by EK or by chemical process. The particles are isotropic in shape. These results show successful preparation of silver nanoparticles by EK or by chemical process, involving reduction of silver nitrate using hydrazine hydrate at room temperature. Applying thermal decomposition of silver hydroxide by heating at 980°C revealed that this route produces particles with larger size. At that temperature, the reduced silver metal is in its molten state. Molten silver nanoparticles coalesce to larger size.

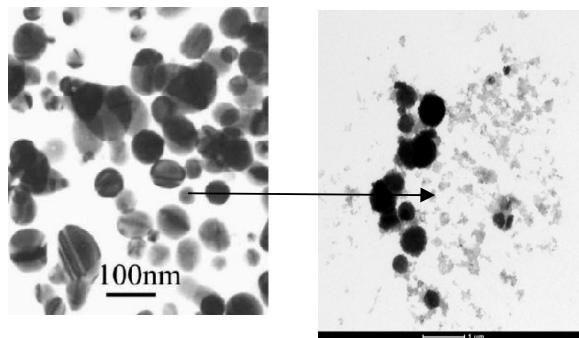


Fig. 8 TEM image of silver sample particle distribution

V. CONCLUSION

In conclusion, isotropic silver nanoparticles have been prepared from e-waste resources applying two routes. Silver metal present in the e-waste was recovered by leaching with nitric acid. The nitrate solution was adjusted with respect to concentration. It was electrokinetically deposited on carbon substrate. The size and shape of the obtained particles depend on the current density and time. The chemical way was found suitable by impregnating porous carbon with silver solution followed by reduction with hydrazine hydrate. Thermal decomposition of silver hydroxide impregnated in the porous system failed to produce nanoparticles due to coalesce to larger size.

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