Optical Characterization of Copper Doped Lead Oxide Nanoparticle Generated Through ECDM Process

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Abstract-An attempt has been made to synthesis copper doped lead monoxide by electrochemical spark process by using a strong electrolyte (KOH). L9 orthogonal array was used to design experiment at three levels by taking process parameters inter-electrode voltage, duty factor and electrolyte concentration. FESEM images revealed morphological structure of nanoparticles, while FTIR confirmed presence of PbO nanoparticles and in monolithic phase. With increase in applied voltage, rod-like shaped nanoparticles were produced while at low voltage sphere-like nanoparicles were produced. The size of nanoparticles crystal is directly proportional to pulse-on time. UV-Vis-NIS analysis was done to obtain optical properties of the nanoparticles. It was found that all the nanoparticles, synthesised under different conditions, possess similar optical properties and show same trend. EDX results show doping percentage which increases with increase in duty factor. As the duty factor increased from 30 to 35, doping percentage increased from 1.07% to 1.84% by weight.

Keyword: Electrochemical spark process, Nanoparticles, FESEM, UV-Vis spectroscopy.

I. INTRODUCTION

Nowadays nanomaterials and nanotechnology has attracted many of the researchers due to its certain properties and wide application in science and technology. Usually generation and characterisation of specific shape and size of nanoparticles with unique structural morphology is a challenge for understanding properties of material with respect to shape, size and dimensions of material (1). It can be produced by a number of methods such as chemical co-precipitation method, colloidal synthesis, laser ablation, sol-gel and ECDM process (2-5). Quasi spherical nanoparticles were produced when ZnO nanoparticles was synthesised by co-precipitation method. Furthermore doping of copper in ZnO nanoparticles has affected structural and electrical properties (6). Flower like structure of CuO nanoparticles can be generated by electrochemical discharge method and is mostly influenced by type of electrolyte and its rotational speed (7). The pH of electrolyte and the type of current used (direct current or pulsating direct current) also determines the shape and size of produced nanoparticles (8). Applied voltage, ion concentration and composition of solvent were are controlling parameters in tailoring the shape and size of ZnO nanoparticles produced by electrochemical procedure (9). Lead oxide (PbO) nanoparticles can be produced by sol-gel method of nearly 63 µm (10). Silver nanoparticles produced by arc discharge in aqueous solution of PVP are used for electronic packing. The size of the nanoparticles can be varied by heat input (11). Different oxides of lead can be produced by microwave irradiation technique and cellulose acetate-acetone method which is an easy, efficient and environment friendly technique (12). Above all the process, synthesis through ECDM process is the most elementary and economical technique for the production of nanoparticles (13). The process can be optimised by proper designing of experimental parameters. Taguchi Techniques is most common for designing array to set experimental parameters (14). These parameters help to separate different effect which helps in proper investigation of acquired results. A number of oxides of lead (Pb) are found such as PbO, PbO_2, and $Pb_2O_3$for which it is an important material from application point of view. It is used in storage batteries in form of lead acid, gas sensors, paints, luminescent glass materials, pigments and nano-scale electronic device (15). High storage capacity solar energy conversion requires use of copper doped zinc-oxide nanoparticles (16). PbO-ZnO nano-composites are used in making electrode of high performance super capacitor because of its high specific capacitance and larger surface area (17). The use of nanoparticles is not only restricted to industries and are being used in day to day life such as in cosmetics and healthcare (18). Very fine PbO nanoparticles are harmful when inhaled and can cause serious respiratory disease. Present study has shown that due to high permeability of PbO nanoparticles, it can be filtered by OF-90 - a protective filter (19). Now-a-days GO-Pb_3O_4 composites are used for shielding against X-ray because of their enhanced radiopacity (20). Recently it is discovered that addition of PbO nanoparticles changes the thermal behaviour of parent material like decomposition temperature and activation energy (21). Doping percentage and concentration changes crystal structure as it can be seen in case of PbO nanoparticles doped with zinc (22). Such has been the growth of nanotechnology and nanomaterials, tempting more and more researchers in this field.

II. EXPERIMENTAL

A. Materials and Experimental setup

A strong base electrolyte was prepared by using potassium hydroxide pellets of 99.9% purity manufactured by Merck and ethyl alcohol from Yangyuan Chemical, China. 100ml aqueous solution of KOH (1M, 2M and 3 M concentration each) was prepared with distilled water. Polished lead (Pb) plate of dimension (50mm x 30mm x 2mm) as anode and copper of (1mm diameter) as cathode were used for production of lead-oxide nanoparticles.
The ECDM setup consists of mainly a pulse generator of transistor type (capable of producing pulse up to 150V amplitude), stepper motor controlled cathode electrode, work-piece as anode clamped in an electrolyte bath and a tank. The output of the power source works within a range of 10 KHz-100 KHz frequencies which can be varied by using microcontroller. The motion of cathode was controlled by lab-view software to maintain the inter-electrode gap.

B. Experiment procedure.

Both lead work-piece and copper tool was cleaned with acetone to remove unwanted foreign materials from the surface. The copper tool was made negative while lead work piece as positive. The tank was filled with electrolyte. The setup was provided with a 150V pulsed DC power supply. The pulse can be varied by changing frequency or duty factor. The potential difference between electrodes, duty factor and concentration of electrolyte were major controlling parameters. The process parameter for experiment was designed by using Taguchi orthogonal array. Three factors i.e. duty factor, inter electrode voltage and electrolyte concentration were used in three levels for a total of nine observation. Material is removed by the basic principle of ECDM. The sample was given ultrasonic vibration to break the cluster of nanoparticles. Thereafter electrolyte containing nanoparticles was centrifuged at 10000 r.p.m until the nanoparticles settled at the base of test-tube. The obtained nanoparticles were cleaned with both distilled water and ethanol several times to nullify the effect of electrolyte. At last the collected nanoparticles were heated in an oven at 60ºC for 16 hours. The acquired samples of nanoparticles were characterized by different techniques on the basis of results obtained.

III. RESULTS AND DISCUSSION

A. Field emission scanning electron microscopy (FESEM).
FESEM analysis was done for morphological study of nanopowders. Synthesised nanopowder was stick to sample stub by using carbon tape and was placed in sample chamber. FESEM images of synthesised nanoparticles by using 1M KOH as electrolyte by varying process parameters is shown in fig-1. The size of nanoparticles increased with increase in applied voltage. At elevated voltage, more intense sparks are generated and hence more material is removed as bigger debris. Sphere-like nanoparticles were generated at lower voltage which transformed to rod like structure at elevated voltage.
When 2M KOH was used as electrolyte for synthesis of PbO nanoparticles, more number of rod-like nanoparticles was generated. FESEM images of produced nanoparticles are shown in fig-2 by varying process parameters with 2M KOH as electrolyte. It has also been observed that thickness of rod-like produced nanoparticles increased with increase in duty factor.

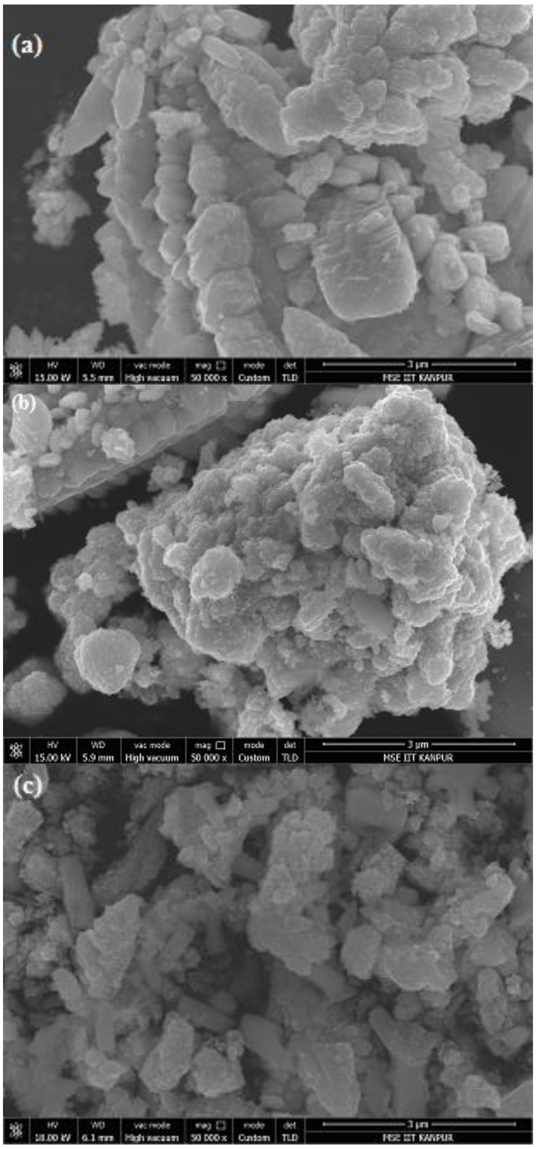

Fig 1: FESEM image of synthesised nanoparticles with 1M KOH as electrolyte at (a) 80V & 25DF, (b) 100V & 35 DF and (c) 120V & 30 DF.

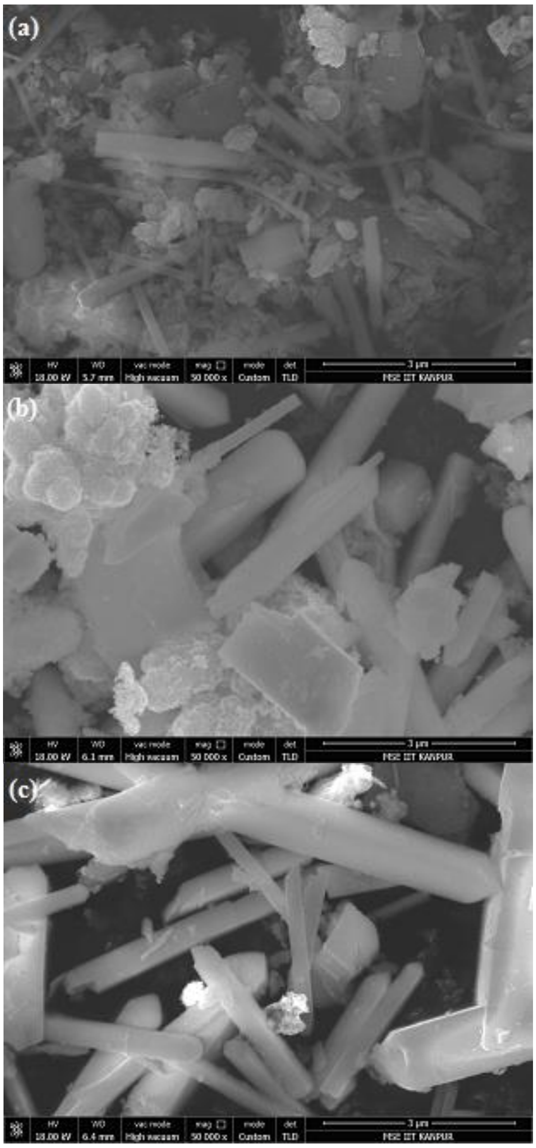

Fig 2: FESEM image of synthesised nanoparticles with 2M KOH as electrolyte at (a) 80V & 30DF, (b) 100V & 25 DF and (c) 120V & 35 DF.

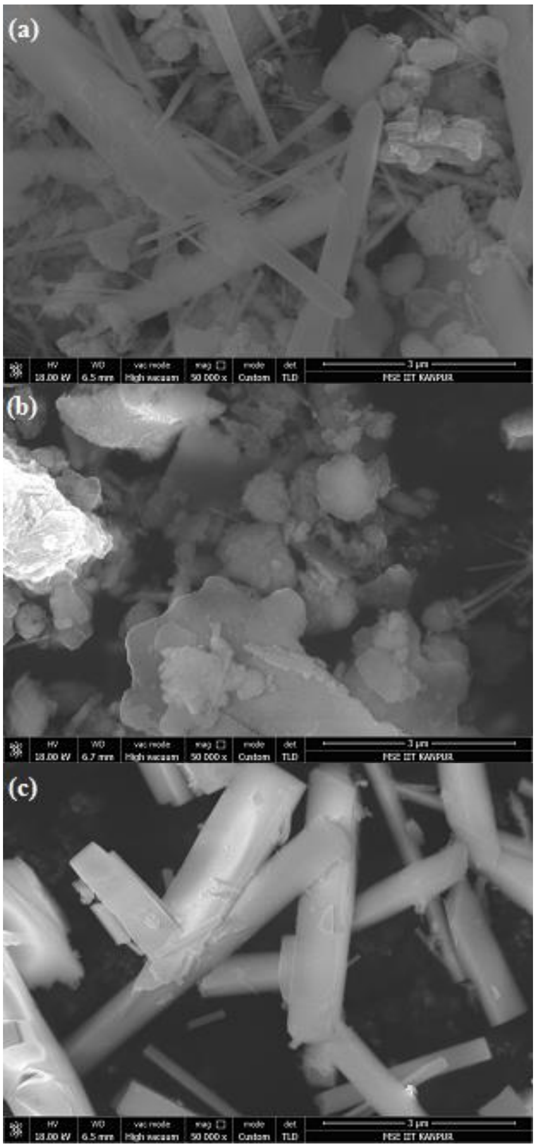

Fig 3: FESEM image of synthesised nanoparticles with 3M KOH as electrolyte at (a) 80V & 35DF, (b) 100V & 30 DF and (c) 120V & 25 DF.

On further increasing electrolyte concentration most of the nanoparticles produced were rod shaped. FESEM image of produced nanoparticles with 3M KOH electrolyte is shown in fig-3. With increase in duty factor size of nanoparticles increased. Duty factor is directly proportional to pulse-on time which is a direct function of input energy. Hence more material is melted and gets evaporated from both job and tool surface and pole like debris are produced which gets dissolved or suspended in electrolyte.

B. Energy-dispersive X-Ray spectroscopy (EDX).

Composition of produced PbO nanoparticles is identified by EDX analysis. The obtained plot for synthesised nanoparticles at 100V & 35DF is shown in fig-4. The obtained plot confirms presence of lead, oxygen, copper and carbon. With condition 100V, 35DF and 1M KOH as electrolyte the copper doping percent is nearly 1.84% by weight.

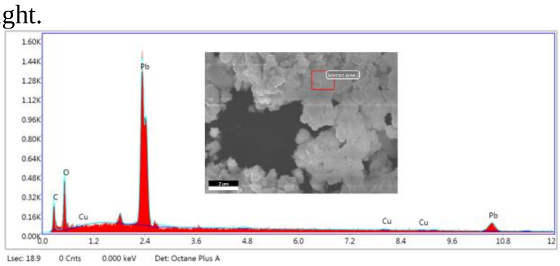

Fig4: EDX analysis of Cu doped PbO nanoparticles at 100V and 35DF.

With decrease in duty factor, doping percent of copper also decreased. With decrease in duty factor, pulse on time also decreases and hence input energy decrease. Thus less amount of copper is removed from tool which decreases doping percentage. With condition 120V, 30DF and 1M KOH as electrolyte the copper doping percent is nearly 1.07% by weight. The plot is shown in fig-5. Trace amount of carbon has appeared in the plot as the nanopowders were diffused on carbon tape during EDX analysis.

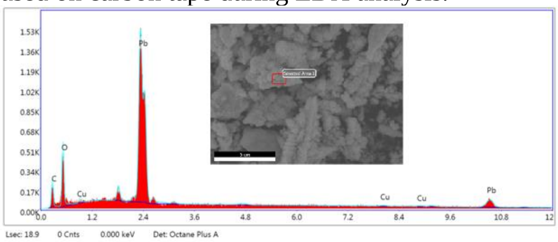

Figure 5: EDX analysis of Cu doped PbO nanoparticls at 120V and 30DF.

C. UV-Vis spectroscopy.

The variation in shape, size and mass defines optical properties of nanoparticls. With UV-Vis spectroscopy we can analyze the optical properties of nanoparticles. Due to low absorption coefficient of Barium sulfate, it was used as base correction. Fifteen milligram of PbO nanoparticles were put in a quartz cuvette of standard size. The cuvette was stationed in-between a photo detector and light source in a spectrometer. UV-Vis spectroscopy of PbO nanoparticles under different condition is shown in the fig-6.

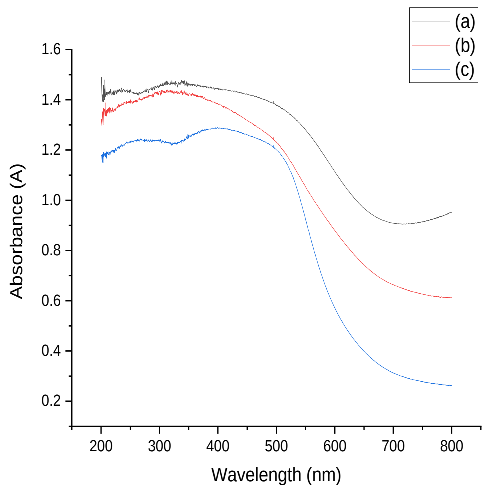

Fig6: UV-Vis absorbance spectra of PbO nanoparticles synthesis with condition: (a) 100 V, 35 DF & 1M, (b) 80 V, 30 DF & 2M and (c) 120 V, 25 DF & 3M of KOH solution.

The range of scanning distance is set from 200 to 800 nm. From the plot it can be seen that nanoparticles generated with different conditions shows similar trends of optical properties. Higher values of absorbance were found nearly 207 nm for condition 100V, 35DF & 1M, 323nm for condition 80V, 30DF & 2M and 399nm for condition 120V, 25DF & 1M of KOH solution. It can be seen that with decrease in duty factor and increase in electrolyte concentration, peak value of absorbance shifts towards higher values of wavelength.

D. FTIR analysis.

FTIR analysis is done to investigate the effect of copper doping in PbO bonding. The process was carried out by making pellets. Little amount of synthesised nanopowder were mixed with IR grade potassium bromide with 95% volume to form pellet. These pellets were put to diffuse reflectance accessory in a test specimen cup for scanning. FTIR spectra for PbO nanoparticles synthesised under different condition are shown in fig-7.The wave number of FTIR analysis lies in between 400cm^{-1} to 4000 cm^{-1}. The transmittance value increases rapidly to a higher value which is related to vibration of Pb-O bond and then decreases to a stabilized value. All these curves are similar in nature which represents synthesis of nanoparticles with different parameters. Nanoparticles generated with condition (a) shows a high transmittance value within range of 787cm^{-1} to 830cm^{-1}. Condition (b) and (c) shows high values of transmittance in the range of 765cm^{-1} to 939cm^{-1} and 626cm^{-1} to 710cm^{-1} respectively. Thus formation of PbO nanoparticles is validated by FTIR spectra.

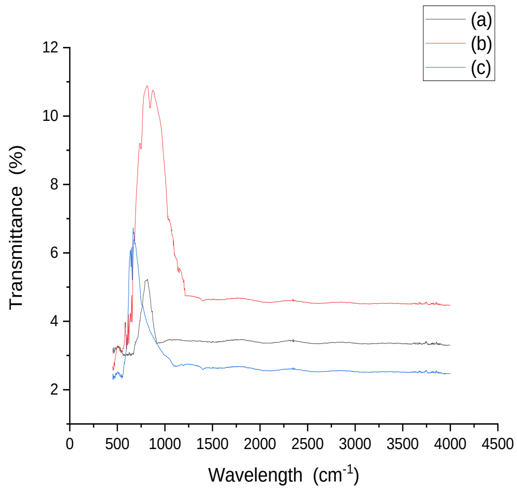

Fig 7: FTIR spectra of PbO nanoparticles synthesis with condition: (a) 80 V, 25 DF & 1M, (b) 100 V, 30 DF & 3M and (c) 120 V, 35 DF & 2M of KOH solution.

IV. CONCLUSION

Copper doped PbO nanoparticles were successfully prepared by electro chemical discharge machining. Process parameters like inter electrode voltage, duty factor and electrolyte concentration effected shape and size of nanoparticles as well as doping percentage. FESEM images confirm with increase in voltage and duty factor, size of nanoparticles increased as intense sparks were produced at elevated temperature and more materials get evaporated. It can also be seen with increase in electrolyte concentration more number of rod-like shaped nanoparticles were generated. EDX results revealed doping percentage of copper also increased with increase in voltage and duty factor for the same reason as material gets removed from both tool and work piece. UV-Vis analysis shows all the nanoparticles synthesised under different conditions have similar optical properties. Formation of PbO nanoparticles were confirmed by FTIR spectra. The synthesis process is an economical and green process as nanoparticles can be generated from scraps and waste material.

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