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Synthesis of Copper Hydroxide Nitrate ($Cu_2(OH)_3NO_3$) micro-sheets by plasma electrolysis of $Cu(NO_3)_2$ aqueous solution in atmospheric air

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ABSTRACT

In this paper, interaction of the air plasma generated in an atmospheric pressure pin-to-solution electrical discharge with aqueous solution of copper nitrate is experimentally investigated in the cathode-plasma electrolysis configuration. An AC (50 Hz) high-voltage power supply (5 kV) with rectified current is used for the electrical discharge of air. Experiments show that, immediately after the discharging process, a pale green-blue powder is generated at the plasma-solution interface. The powder is found to be 'basic copper nitrate', $Cu_2(OH)_3NO_3$, through XRD characterization and EDS analysis. FESEM images of the powder reveal that it indeed consists of $Cu_2(OH)_3NO_3$ micro-plates with the thickness of 200 nm. It seems that generation of OH ions and radicals in the air plasma as well as dissociation of water molecules by energetic plasma ions is responsible for the powder synthesis.

1 Introduction

Electrical discharges and plasmas interacting with solutions offer new electrolysis configurations with plasma electrodes (rather than metal electrodes in conventional electrolysis) and have opened new and novel theoretical and experimental research fields [1, 2]. Interaction of plasmas with liquids and the resulted electrochemistry are more advantageous and versatile than the conventional electrolysis setups for a number of reasons [3, 4]: 1) the gas mixture of the plasma medium which has undeniable effects on the solution can easily be changed and controlled. 2) The discharge type (spark, corona, glow, arc, and etc.) and the polarity of the plasma electrode (i.e. cathode or anode) can both increase the diversity of experiments. 3) Species generated in the plasma (including ions, electrons, radicals and even neutrals) together with the amount of current passing through the plasma and entering the solution can trigger various plasma-chemical reactions each with different products. 4) The material and shape of the plasma-generating electrode can also have effects on the electrochemical processes. The plasma-liquid interaction as one of the critical research areas of the plasma community has many promising applications especially in nanotechnology which is being converted to an important branch of plasma science and technology [5].

The number of scientific studies in the literature on the synthesis of materials with electrical discharges

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contacting with solutions is growing rapidly. Many reports on the synthesis of metallic nanoparticles such as silver and gold particles as well as magnetic or none-magnetic iron oxides by plasma-solution interactions can easily be found in the literature [6-9]. In the present paper, the effect of a pin-to-solution electrical discharge in atmospheric air on copper nitrate aqueous solution is experimentally investigated in the cathode-plasma electrolysis. Results of this electrolysis show that a pale green-blue powder containing micro-plates of crystalline $Cu_2(OH)_3NO_3$ with nanometer thicknesses is synthesized. There are a number of reports in the literature regarding synthesis of similar $Cu_2(OH)_3NO_3$ micro-plates but with different methods such as plasma, chemical and sono-chemical reactions [10-14]. Synthesis of the powder by air-plasma interaction is, in fact, being reported for the first time (to the best of our knowledge) in this paper.

The paper is organized as follows: Experimental details are first considered. Then, the results are presented and discussed. Conclusions are drawn in the final section.

2 Experimental setup

A simple pin-to-solution electrical discharge apparatus as schematically depicted in Fig. 1 represents the setup. A peaked pin electrode made of copper wire with a diameter of 2 mm is placed 1 mm above the solution surface. The other electrode which is a metal (here silver) rod with a diameter equal to 3 mm is immersed into the solution. A high-voltage AC (50 Hz) source is used to supply the electrolysis circuit. In order to give a fixed polarization (cathode or anode) to the pin electrode, a high-voltage diode is used in the circuit to rectify the current. Direction of the diode which is indeed the same as the current direction points to the anode electrode. The gas above the solution is air at normal conditions. After pouring the desired solution in the vessel and adjusting the distance of the pin from the solution surface to below 1 mm by a micrometer, the power supply is turned on. The supply voltage is increased gradually until a stable electrical discharge between the pin and the solution is formed. This is before the voltage is fixed at nearly 5 kV with current of ~ 12 mA. The air plasma generated in this simple pin-to-solution setup is the so-called glow discharge plasma and, in fact, can play the role of an electrode in electrolysis process [15].

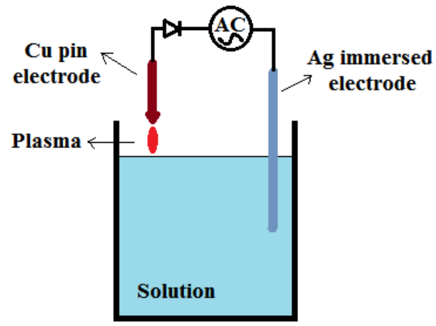

Figure 1. Schematics of the pin-to-solution glow discharge electrolysis supplied by a 50 Hz AC high voltage source with a copper pin electrode and immersed silver rod electrode. A diode is used to rectify the current and, hence, to give a fixed polarity (here cathode) to the pin electrode.

By this apparatus, any kind of solution can be plasma-interacted and studied. Here, aqueous solution of copper nitrate with different concentrations is considered. The desired solution is purred in a beaker and put under the plasma electrolysis experiment with cathode polarity of the pin. Experimental results are presented in the following section.

3 Results and discussion

An aqueous solution of copper nitrate, $Cu(NO_3)_2.3H_2O$, with arbitrary concentration of 0.3 M is put in the plasma-electrolysis setup of Fig. 1. It is observed that immediately after the start of the glow discharge between the cathode-pin and the solution, a green-blue powder is generated in the contact point and convectively spreads throughout the beaker. After two hours the powder is separated by a centrifuge and washed with distilled water. Its XRD pattern is seen in Fig 2.

By comparing the XRD pattern with standard ones it is noticed that the powder is 'basic copper nitrate' (BCN) with chemical formula $Cu_2(OH)_3NO_3$ with no impurities. In order to get more information about the synthesized BCN powder, it is analyzed by the Energy-Dispersive X-ray Spectroscopy (EDS) as shown in Fig 3. The spectrum shows that the obtained powder contains copper, oxygen and nitrogen.

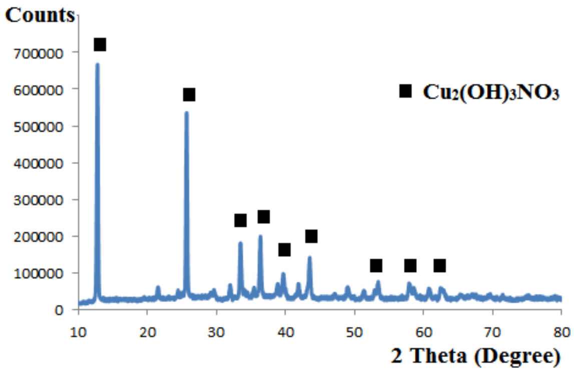

Figure 2. XRD pattern of the green-blue powder obtained from the cathode-pin plasma electrolysis of the $Cu(NO_3)_2$ aqueous solution. All diffraction peaks belong to the 'copper hydroxide nitrate' with chemical formula $Cu_2(OH)_3NO_3$.

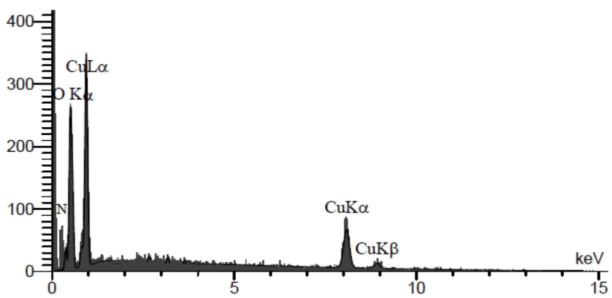

Figure 3. EDS spectrum of the synthesized BCN powder produced in the cathode-pin plasma electrolysis of the $Cu(NO_3)_2$ aqueous solution.

As the previous analysis, the synthesized BCN is investigated by the electron microscopy. FESEM images of the green-blue powder in different scales are shown in Fig 4.

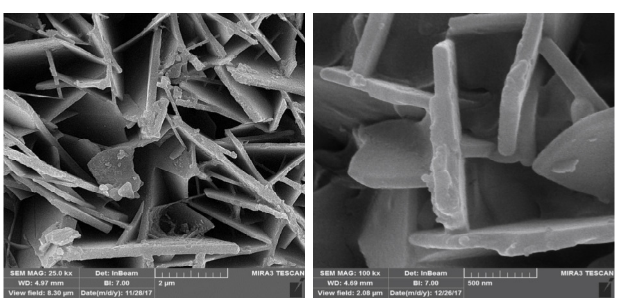

Figure 4. FESEM images of the synthesized BCN powder showing the micro-crystalline sheets of $Cu_2(OH)_3NO_3$.

The FESEM images clearly show that the synthesized powder contains micro-sheets of BCN with nanometer (100-300 nm) thicknesses.

From the above experimental results, the plasma electrochemistry of the solution can be explained as follows: The OH^- ions produced in the plasma-solution interface and also those produced by electrolysis of water molecule (or even $^*OH$ radical generated by dissociation of water molecules due to bombardment of the solution surface by plasma ions) can produce BCN through reactions [10]:

$$2e^-_{plasma} + 2H_2O \rightarrow 2OH^-_{(Air,aq)} + H_{2(g)},$$

$$2Cu^{2+}_{(aq)} + 3OH^-_{(plasma,aq)} + NO^-_{3(aq)} \rightarrow$$

$$Cu_2(OH)_3\ NO_{3(s)}, \qquad (1)$$

4 Conclusions

In the present paper, the electrolysis of aqueous solution of $Cu(NO_3)_2$ with the glow discharge plasma in the ambient air as the cathode electrode was studied. Based on the experimental results, it can be deduced that plasma electrolysis could produce micrometric plates of crystalline $Cu_2(OH)_3NO_3$. Experiments with different concentrations show the same results but with different amounts of the product. It seems that the production yield has a maximum in a special concentration of $Cu(NO_3)_2$. Determination of the optimum concentration is underway. Other solutions (rather than copper nitrate solution reported here) such as copper sulfate and copper chloride were also put in the plasma-electrolysis setup of Fig 1 by the authors of this study but the analysis of results are still in progress where exact details will be reported once correct conclusions are drawn. However, the first stage experiments show that plasma electrolysis of copper sulfate solution generates 'basic copper sulfate' and that of copper chloride produces 'basic copper chloride'. This shows that production of OH ions and radicals in the plasma and by the plasma through the reactions presented by Eq. (1) has a crucial role in the plasma-electrolyzed aqueous solutions in open-air conditions.

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