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Electrophoretic deposition of nano-sized $BaTiO_3$

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Abstract In this study, a non-aqueous method in a simple one pot reaction process was employed to synthesize nano-sized $BaTiO_3$ particles and then electrophoretic deposition technique was employed for thin film coatings. In the first step of the preparation, metallic barium is directly dissolved in benzyl alcohol at slightly elevated temperatures. Then titanium isopropoxide was added following by a solvothermal treatment. At the end of the reaction, nearly spherical $BaTiO_3$ nanoparticles were obtained typically 5 nm in diameter. After establishing the stability of the $BaTiO_3$ suspension in ethanol, electrophoretic deposition process was performed without any additional operation. Alumina with platinum plating was used as substrate. To achieve the optimal process parameters, various voltages were applied by altering the cathode to anode distance as well as deposition time. High voltages application was possible without causing hydrolysis, because of the non-aqueous ethanol medium with higher surface charge of the nanoparticles. The deposited surface coatings were dried in air and sintered at various temperatures. SEM, EDX and XRD analysis were employed for the investigation of the coating.

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Introduction

$BaTiO_3$ is a well-known dielectric material for electronic applications like multilayer capacitor, transducer, thermistor and electrooptic device applications. Even though some metal oxides such as SnO_2, ZnO, In_2O_3, TiO_2, α-Fe_2O_3, HfO_2 and $BaSnO_3$ have been widely investigated for gas sensing applications [1], it is a relatively new research area for $BaTiO_3$. Various fabrication techniques have been employed for $BaTiO_3$ manufacturing, e.g., spin coating, sol-gel, screen printing, tape casting, CVD, PVD, thick film deposition, injection molding, cold pressing, slip casting, extrusion/callendering, plasma spray, electrophoretic coating etc. [2–4]. Among them, electrophoretic deposition (EPD) is a relatively new and versatile technique. EPD has great application potential in electronics–magnetics, electrolytic and superconducting thick films, structural and high-temperature ceramics [4]. Desired sensors with high sensitivity, stability can be tailored with this method by altering the substrates morphology, surface area (particle size), structure, porosity as well as dopants [5]. The aim of this study is to deposit nanocrystalline porous $BaTiO_3$ film layer on alumina substrate plated with platinum by electrophoretic deposition for sensor applications.

The $BaTiO_3$ nanoparticles were prepared by a non-aqueous process involving the solvothermal reaction of metallic barium dissolved in benzyl alcohol with titanium isopropoxide [6,7]. Non-aqueous processes have become a valuable alternative to aqueous processes, because they enable the synthesis of highly crystalline metal oxide nanoparticles at relatively moderate temperatures over a wide range of compositions

[8], including binary (HfO_2, SnO_2, In_2O_3 [9, 10]) as well as ternary oxides ($PbTiO_3$, $LiNbO_3$, $BaZrO_3$ [6, 11]).

Experimental

For a good sensor application it is necessary to have nano-sized particles with good homogenity and good morphology. Based on this scientific reality, it is aimed to have high purity $BaTiO_3$ in the first step of this study. Nanocrystalline $BaTiO_3$ was synthesized as reported before [6,7]. In this method, high purity titanium (IV) isopropoxide (99.999% of Aldrich), metallic barium (99.999% of Aldrich) and anhydrous benzyl alcohol (99.8%) have been used. Solvothermal treatment was performed in Parr acid digestion bombs with 45 ml Teflon cups. In the first step of the synthesis, 2 mmol of barium (274.7 mg) was stirred in a vial with 25 ml benzyl alcohol until complete dissolution at slightly elevated temperature. Then, 1 mole equivalent of titanium isopropoxide was added drop wise while stirring the solution and transferred to autoclave. The autoclave was heated to 200 °C for about 48 h to perform the synthesis. The product was centrifuged, and the precipitate was washed with ethanol and diethyl ether. The washed nano powder was dried in air at 60 °C overnight. Size and morphology of the synthesized nanoparticles were investigated by CM200 FEG (Philips) TEM at 200 kV. BET surface area of the powder is analyzed by Quantachrome Autosorb-1C.

In the second step of this study, the stable solution of $BaTiO_3$ was prepared for the EPD process. The $BaTiO_3$ nanocrystalline particles were dispersed in ethanol and directly used without any additional process. Zeta potential and particle size distribution of the $BaTiO_3$ suspension dispersed in ethanol were measured with a Malvern Nano ZS. The pH of the solution was measured by Orion 555A with pentrode probe. Vertical EPD set up were established for the coating process (Fig. 1). Electric field applied to the electrodes to minimize the effect of the gravitational forces. Pt plated alumina substrates (1.1 × 1.1 cm) were used as cathode.

Gold–Palladium alloy in metal sheet form (1.1 × 1.1 cm) was used as anode. The surface smoothness of the electroded surface of the substrate affects the final coating surface roughness. Platinum plating on Al_2O_3 substrates were processed in two steps to achieve a smooth surface and consequently smooth coating. Firstly, Pt applied to the surface by a thin brush followed by Pt screen printed for full coverage of the surface. Keithley 2410C source meter was used for obtaining constant DC voltage or constant DC current. Various voltages (1.0, 1.5, 2.0, 10, 15, and 20 V) and currents (0.5, 0.75, and 1 A) were applied by altering the cathode to anode distance (1.0, 1.5, and 2.0 cm) as well as deposition time (30, 60, 90, and 120 s) for optimal process control. The EPD coated surfaces were dried in air for 12 h and sintered at various temperatures (800, 900, 1,000, and 1,100 °C) and times (15, 30, 60, 90, and 120 min.). Microstructural analyses were performed by scanning electron microscope (SEM, ZEISS Supra VP 50) and elemental analyses were performed with Oxford EDX detector. Bruker D8 diffractometer equipped with a scintillation counter were used for XRD analyses.

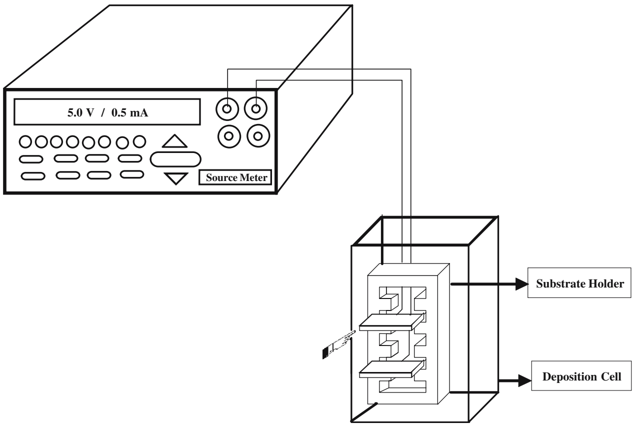


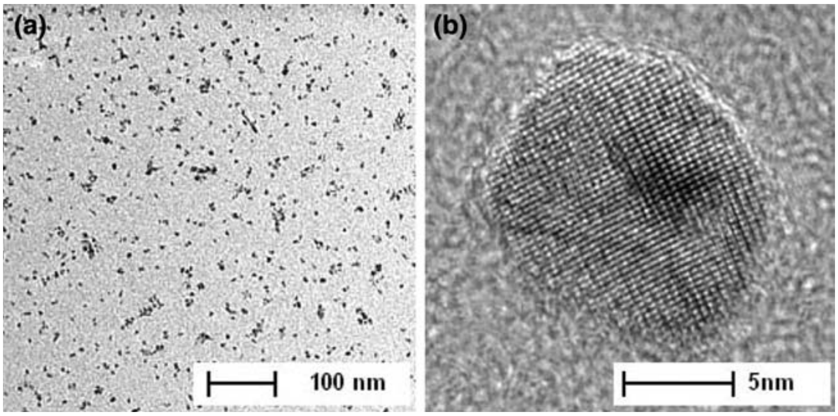
Fig. 1 Schematic diagram of electrophoretic deposition cell

Results and discussion

Synthesis of nanoparticles and its stability:

The low temperature solvothermal synthesis results in high purity $BaTiO_3$ powder with high crystallinity. TEM analysis of the powder revealed that the sample was composed of nearly monodispersed, nano-sized particles (Fig. 2a). Many of the particles were isolated and their size ranges from 4–8 nm. Figure 2b displays a high resolution TEM micrograph of an exceptionally large particle of about 10 nm. The presence of well-developed lattice fringes underlines the high crystallinity of the nanoparticles. The crystallite size of the particles was also calculated by XRD as ~6 nm. It is interesting to note that high-energy X-ray diffraction gave evidence for a complex three-dimensional atomic ordering in this nanocrystalline $BaTiO_3$ [12]. On average, it is cubic-like, however shows locally slight distortions of a tetragonal-type. BET analysis revealed that the surface area of the $BaTiO_3$ powder was

Fig. 2 TEM images of as-synthesized $BaTiO_3$ nanoparticles. (**a**) TEM overview image, (**b**) HRTEM image of one single particle



$100\ m^2/g$. Those results also confirmed isolated and nanosized characteristics of the particles when they were precipitated in benzyl alcohol medium.

EPD on alumina substrates:

Electroding the alumina substrate with platinum paste

It is possible to obtain continues and network like electrode pattern on the alumina substrate depending on the application method. Top view of the coated surfaces with continues pattern and network like pattern are shown in Figs. 3 and 4 respectively. Depending on the application area both of the pattern can be applicable. Successful EPD coating was achieved for both electrode type. However, for sensor application we preferred to use continues electrode pattern. Continuity of the inter-digital electrode is important for the repeatable read outs. Platinum paste were applied with combination of initial surface treatment to achieve continues film. Thickness of the film was ~5 μm, and the surface of the coating was slightly rough. Average size of the platinum grain on the film was around 4.5 μm.

Preparation of the stable suspension for the EPD

The most important first step of the EPD coating is the preparation of a stable solution with appropriate zeta potential. The synthesized powder was dried and re-dispersed in ethanol for the EPD process. The particle size distribution was analyzed again to verify whether powder characteristics changed during drying and subsequent re-dispersion. It was found out that although the particle size distribution stayed monodisperse, the mean particle size distribution shifted to ~50 nm (Fig. 5). This result indicates formation of agglomerates during drying and re-dispersion in ethanol. However, 50 nm ranges is still a good particle size distribution for sensor applications. Although the mean particle size was observed as 50 nm, a few larger agglomerates have also been observed on SEM studies.

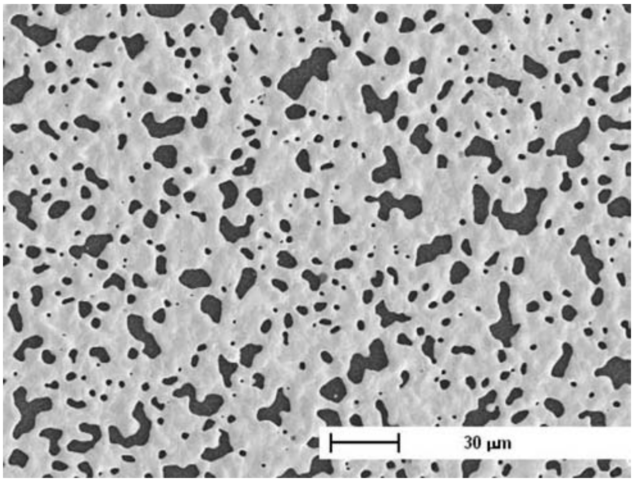


Fig. 3 Platinum plated surface with perforated structure

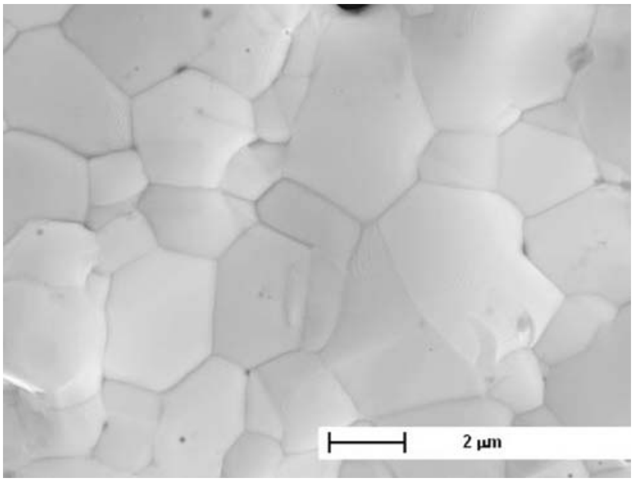


Fig. 4 Platinum plated surface with continues structure

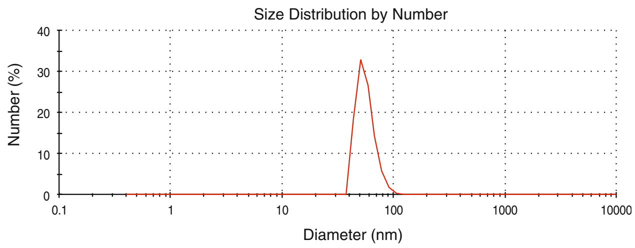


Fig. 5 Particle size distribution of $BaTiO_3$ dispersed in ethanol medium

Zeta potential which has critical importance on the surface charge of particles for electrophoretic deposition process of the $BaTiO_3$ was measured as +37 mV in ethanol. This zeta potential was high enough for accelerating particles toward cathode under an electric field during EPD coating. In addition, pH and conductivity of the suspension were 8.7 and 18.1 μS/cm, respectively.

EPD coating the metal plated surface with $BaTiO_3$ nanoparticles

After achieving the stable suspension EPD process were started. Its is important to state here again that the goal of this investigation was not obtain fully dense surfaces, which is necessary for capacitor application, but create controlled porous network structure, which is essential for sensor applications. All the EPD process was performed on room temperature. For an optimal coating there are four important parameters on the EPD process; anode to cathode distance, energizing time, voltage, and current. At the initial stage of the investigation anode to cathode distance were determined by altering the distance and observing the coating surface and measuring the quantity of the deposited amount. As a result 2 cm was chosen as the anode to cathode distance. Then keeping the distance constant, EPD coating was performed by using various voltages, currents and time. Various voltages of 5, 10, and 15 V were applied to the suspension for 30, 60, 90, and 120 s, to determine the optimum voltage-time variation. The best deposition with a thickness of 1 μm was achieved when 5 V–120 s combinations was applied to the suspension. Figure 6 shows the top view SEM micrograph of the coating. Although thickness of coating increased as time increased at 5 V, utilization of higher voltages such as 10 and 15, did not give better results because of inhomogeneous deposition surface. Under constant voltage operation condition, it has been observed that resistance increases with increasing time during the EPD process. As a result of this, electric field reduces and longer deposition times become necessary for the same film thicknesses. On the other hand, if a constant current is utilized during the process, electric field remains constant and this makes the deposition rate constant [13]. Referring to this fact, further experiments were performed with constant currents (i.e., 0.5, 0.75, and 1 A) for various times such as 30, 60, 90, and 120 s. Deposition weight vs. time experiment has been realized at 0.5 A constant current (Fig. 7). As expected, deposition weight increases with increasing deposition time. Deposited amount increases almost linearly with increasing time for 0.5 A. When longer duration under applying 0.5 A or higher currents e.g., 0.75 A and 1 A were applied to the systems cracks were seen after drying (Fig. 8). These results show that optimum coating thickness and quality can be achieved in the current system for 0.5 A and 120 s (i.e., nanocrystalline $BaTiO_3$ in ethanol).

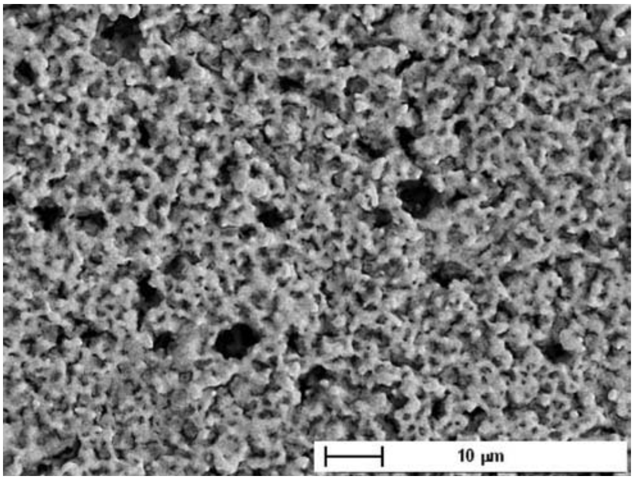


Fig. 6 Microstructure of deposited surface by EPD at 5 V 120 s (unsintered)

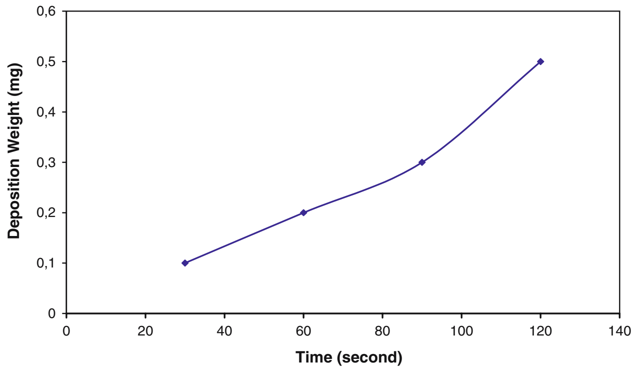


Fig. 7 Deposition weight change with time at 0.5 A current

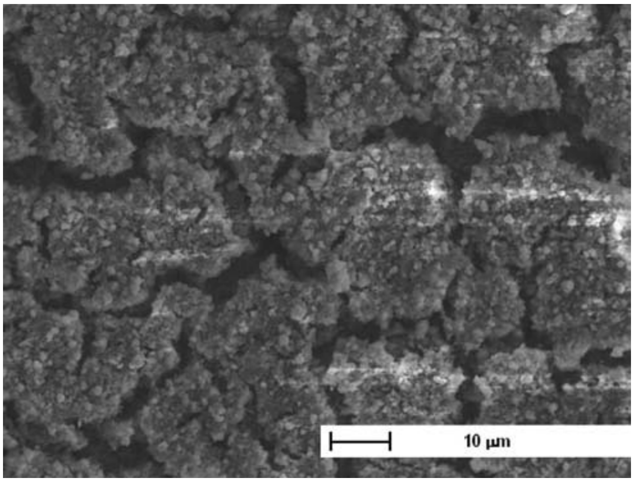


Fig. 8 Crack formation for longer deposition time. Dried but unsintered sample

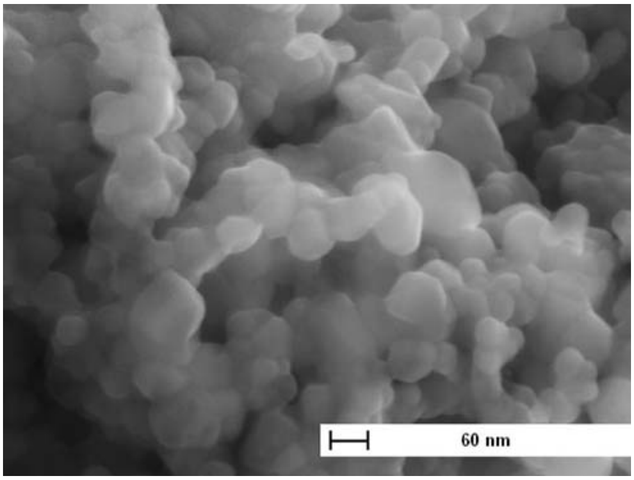


Fig. 10 SEM image of deposited $BaTiO_3$ after sintering at 900 °C for 15 min

Sintering of the $BaTiO_3$ nanoparticles

The aim of the sintering for the senor application is not to get fully dense structure. Opposite to that, high surface area, which means very fine grain size, and fine porosity are essential for sensing applications. Therefore, sintering should be utilized for only achieving neck formation among particles to improve mechanical integrity of the coating. Other important parameter is the connectivity of oxide $BaTiO_3$ to metal platinum. It is necessary to have good contact between this to different phases to get good signals read outs. EPD coated surface of the samples processed at 0.5 A and 5 V for 30 s and sintered at 900 °C were extensively searched to investigate the interfacial properties between $BaTiO_3$ and platinum. Figure 9 shows the ceramic interface between $BaTiO_3$ and platinum. As it is seen there is very good contact between ceramic and metal.

At the first stage of the study, sintering of the well EPD coated samples were performed at 900, 1,000, and 1,100 °C for 2 h. It has been observed that at 900 °C the particles sintered well which is good connectivity and neck formation. Sintering at high temperature (1,000 and 1,100 °C) causes high densification and closure of the porosity which is an undesired case for sensor application. So systematic sintering studies were performed at 900 °C for various time internal (15, 30, 60, and 90 min) to obtain good enough mechanical integrity with neck formation and controlled porosity for sensor application.

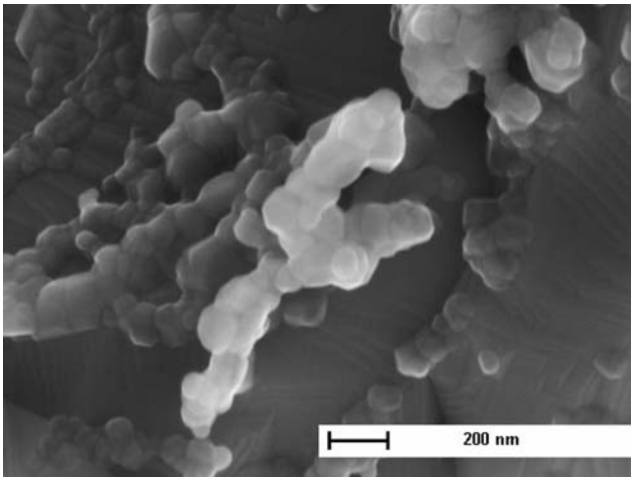


Fig. 9 Nanoparticle $BaTiO_3$ attachment interface with platinum electrode

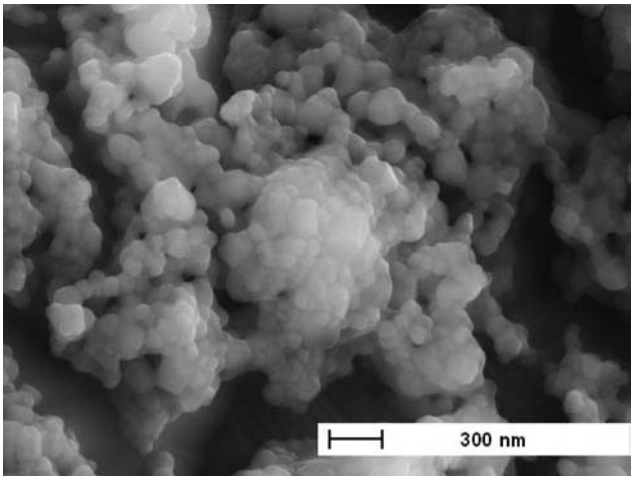


Fig. 11 SEM image of deposited $BaTiO_3$ after sintering at 900 °C for 60 min

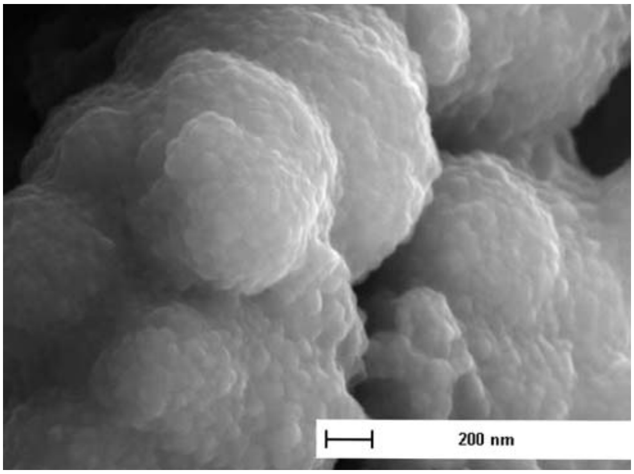


Fig. 12 SEM image of deposited $BaTiO_3$ after sintering 900 °C for 2 h

Sintering at 900 °C for 15 min creates good neck formation and integrity between $BaTiO_3$ crystallites of 20–50 nm, as it is seen on the Fig. 10. However, increasing sintering time causes sinter-agglomeration of the samples. Figure 11 shows the SEM photograph of the sintered sample of 60 min at 900 °C. Even further sintering at high temperature creates cauliflower shaped growth high densification (Fig. 12).

Conclusion

In conclusion, $BaTiO_3$ nanocrystalline powder produced by chemical low temperature synthesis is used in electrophoretic coating process without any treatment. Porous deposition layer is obtained by sintering Pt plated alumina. By using the powder suspended in ethanol, $BaTiO_3$ porous film layer is deposited on the Pt plated alumina substrate. 5 V–120 s and 0.5 A–120 s give promising results for the coating. Sintering temperature was chosen according to the SEM images. It has been determined that sufficient sintering can be achieved after heating at 900 °C for 15 min. The resultant porous surface with nanometer sized particles may be appropriate for high surface area processes like gas sensing.

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