

VERTICAL GROWTH OF BIMETALLIC NANOSTRUCTURES AT AMBIENT CONDITIONS

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Certificate

This is to certify that this dissertation entitled "Vertical growth of bimetallic nanostructures at ambient conditions" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research Pune represents original research carried out by "M. K. Mahitha at IIT Madras" under the supervision of "T. Pradeep, Professor, Department of Chemistry, IIT Madras" during the academic year 2014-2015.



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Declaration

I hereby declare that the matter embodied in the report entitled "Vertical growth of bimetallic nanostructures at ambient conditions" are the results of the investigations carried out by me at the **Department of Chemistry, Indian Institute of Technology Madras (IIT Madras)**, under the supervision of **Prof. T. Pradeep** and the same has not been submitted elsewhere for any other degree.



(M. K. Mahitha)

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Abstract

Electrolytic spray is a very new technique to produce solvated metal ions from a metal wire by electrocorrosion. These solvated ions can be deposited on a substrate to form nanoparticles (NPs). We have developed methods to create different nanostructures and pattern them using suitable masks. Upon closer examination of the mask through microscopy, unusual structures were seen. These structures are formed because of the head on assembly of NPs. They are highly surface enhanced Raman spectroscopy (SERS) active with an enhancement factor of 10^7 which suggests that this class of materials can be an excellent platform for sensing and trapping of different molecules. Different metal salts have been used to create such unusual structures in high yield. Even, mixture of salts was electro sprayed to create bimetallic structures. Blending of two metals led to the emergence of some unpredictable structural morphologies. Morphological variations have been investigated using different combination of metals.

Introduction

Metallic nanostructures are of great interest in recent research due to their versatile electrical and electromagnetic properties, which are quite different from their bulk properties. The enhancement of electric field around these structures make them potential candidates for SERS, sensing of various biological and non-biological compounds, catalyzing various reactions, data storage, etc. Even though such nanostructures have potential implication in different areas still it is very difficult to synthesize in a control fashion, especially when it comes to well-defined structures. Usually these structures are made with a fine control in the reaction conditions. Several methods have been developed to create such nanostructures which include chemical vapor deposition (CVD),¹⁻⁷ physical vapor deposition,⁸⁻¹³ spray pyrolysis,¹⁴⁻²⁰ etc. They can also be synthesized using photolithography²¹⁻²⁴ or electron beam lithography²⁵⁻²⁷ as top down approaches. Template mediation^{28, 29} and self-assembly³⁰ are also used for making desired nanostructures.

Physical Vapor Deposition (PVD)

This includes a process of evaporating the source material and depositing it on a suitable substrate under vacuum. PVD contains heating of the desired material at high temperature or bombarding it with ions to form vapors. During heating a reactive gas is purged into the chamber. The vapors combine with this gas, condense and deposits as thin film coating on a substrate. No chemical reactions are involved in this process. The variants of PVD include cathode arc deposition, electron beam physical vapor deposition, evaporative deposition, pulse laser deposition and sputter deposition. The coating made by this method is usually very hard and wear resistant. This method is usually used to fabricate semiconductor device, metallic coatings. Fabrication of high quality single crystal ZnO wires were reported by this method.³¹

Chemical Vapor Deposition (CVD)

Chemical vapor deposition is a vacuum method used to deposit a wide range of conducting, semiconducting, and insulating materials. In this process, the precursor gas is passed through a chamber having a heated surface, where substrate is placed. The

precursor will react with this substrate to form products and gaseous by-products, which are removed in the gas flow. CVD has different branches according to the conditions used. CVD can work on atmospheric pressure, but most of the modern CVD technique, uses low pressure or ultra-high vacuum. The precursors can be injected as aerosol or directly as liquid. Organometallic CVD uses organic molecules as precursors. This process can be used to make quality uniform films. The material fabricated using CVD includes, silicon nitride,³²⁻³⁴ diamond,³⁵ etc. Majority of elements in the periodic table have been deposited to make thin films using CVD in pure form or as their compounds.

Spray Pyrolysis

It is a liquid phase method to deposit particles on suitable substrates. Spray pyrolysis is a low cost process to fabricate high quality thin films. The first step includes atomization of the precursors through a nozzle. The aerosol coming out undergoes various decomposition processes at different temperature conditions and solvent evaporates from the droplets to form structures on the substrate. One of the great advantages with this technique is that, this can be carried out at low temperature. The compounds that deposited using spray pyrolysis includes ITO (Indium tin oxide),³⁶ PbO,³⁷ ZnO,³⁸ ZrO₂,³⁹ etc.

All the above described processes are widely used to make quality thin films with accurate reproducibility. But all are done at high vacuum and temperature is a must condition to carry out them. If there is a process which is able to produce stable nanostructures at ambient condition, it will open up new possibilities in the field of sensing, trapping etc.^{40, 41} In the case of noble and transition metals, these structures will be excellent candidates in the field of catalysis and SERS. Synthesis of NPs and assembling them to form nanostructures is an active research area because of their excellent catalytic activity. Metal NPs are usually prepared by reducing metal precursors. Controlling particle size is the major challenge in this method. Since all these metals are very much reactive such that maintaining mono-dispersity is very difficult. During course of time aggregation also happens. Several capping agents are used to stabilize these particles. Even though they stabilize the particles to a great extent, sometimes they interfere with the properties and reduce the performance.

Electrochemical methods are found to be one of the simple method to synthesize metal NPs without any capping agent.⁴² Synthesized NPs are often stabilized by their counter ions. The particle size can be controlled by regulating the current density. Highly reactive ions produced during electrolysis.

Electrosprayionization (ESI)

This is used in mass spectrometry to ionize molecules using high voltage. ESI is a soft ionization technique, compared to others, since amount of fragmentation is very less. This is usually used to analyze large molecules such as peptides and proteins because in other techniques the amount of fragmentation is very high and these molecules will lose their features in the gas phase. John Fenn is considered as one of the pioneers in this field. He got Nobel Prize for chemistry in 2002 for his contributions in the area of electrospray ionization mass spectrometry (ESI MS).The simple apparatus of ESI includes two components in which one is a capillary needle held at very high voltage and contains the solution and the other is counter electrode, which can be a grounded plate or a mass spectrometer inlet. The main process includes ionizing the molecules in the solution, producing aerosol of charged droplets and solvent evaporation to produce gas phase ions.⁴³ The solution of the analyte is filled in this capillary, which is kept at high potential. As a result the molecules in the solution get ionized. Since there is potential difference between the electrodes, the ions are emitted as an aerosol of droplets. This is commonly mentioned as a Taylor cone of ions. The spray can be observed in naked eye by eliminating it with a laser pointer. The first formed droplets from the Taylor cone generally have size of 1 μm . During movement of these solvated ions, solvent evaporates from the droplets making them small in size. When the droplet size reaches the Rayleigh limit, the coulombic forces in the charged ions becomes excess and the droplets will undergo coulombic explosion to give smaller droplets. According to the previous reports, about 20 offsprings are produced from a droplet each having 15% charge and 2% mass of initial droplet. ⁴⁴ The ions coming out from these droplets can be neutralized in a grounded plate or can be detected using mass spectrometer.

When we deposit these ions on a grounded plate,⁴⁵ several parameters decides the particle size such as applied potential, solution flow rate, concentration of the solution, distance between the tip of the capillary and counter electrode, etc.⁴⁶ Even size of the capillary needle also determines the size of the droplets. Inside the capillary the charging of the solution happens to form ions. Sometimes capillaries made of conducting materials like steel are used or glass capillaries can also be used where a metallic wire act as electrode. Solution preparation and purity of solvent are very important in ESI. Sensitivity of detection and droplet nature depends on the solution conductivity, polarity, vapor pressure, etc. Since the process depends on the evaporation of the solvent, solvent plays an important role. Water-methanol, water-acetonitrile in different proportions is the commonly used solvents. The gradient in the potential between the emitter and the counter electrode plays a major role in the discharge of solution as a plume. If the electrode can take part in chemical reactions such as surface etching, it can be used in the synthesis of particles. This is the basis of electrolytic spray ionization.

The electrospray emitter i.e. the capillary tip determines the quality of the spray coming out and the propensity of electrochemical reactions. The inner and outer diameter of the capillary, tip diameter and flow rate of the solution determines the reaction which would happen inside the capillary. Usually the flow rate for typical ESI experiments is 3 $\mu\text{L}/\text{min}$ to 5 $\mu\text{L}/\text{min}$, for which the possibility of chemical reaction during the flow is limited. Electrochemical reactions occurring on the capillary can even change the pH of the solution.⁴⁷ These reactions happening inside the capillary can immensely affect the solution coming out. Thus the ions are so reactive such that the properties will be unpredictable. These ions can also reacting gas phase to form products which can be detected using mass spectrometer. In essence the ions in gas phase sometimes shows entirely different property compared to solution phase molecules due to the electrochemical reactions involved.⁴⁸ The molecules are sometimes ionized by oxidation or reduction. Molecules that have been ionized by electrochemical oxidation include metal organic complexes, aromatic and highly conjugated systems (polycyclic aromatic hydrocarbons [PAHs], carotenoids), ferrocene derivatives, and fullerenes.^{49, 50} Simple concept behind ESI is that playing with the parameters and constituents, it is possible to

maximize or minimize the electrolysis. In case of electrolytic spray process, a slow solvent flow rate, high conductivity of solution, and high voltage are the essential parameters. On the other side if want to reduce the electrolysis, sometimes high flow rate and low voltage are used. Electrospray ionization is simple electrochemical process in which, oxidation happens at the capillary and reduction occurs at the counter electrode. Electrochemistry is important in ESI. If the electrochemical process can make preferable changes in the gas phase ions, it can lead to unpredictable reactions. One of the most important drawback of the ESI-MS technique is that due to this high solution flow rate, it is very difficult to analyze several large molecules like oligosaccharides.⁵¹ Due to high flow rate, the surface activity of the molecules is suppressed.

A new variant called nanoESI is introduced to overcome this defect. The main feature makes this technique different from normal ESI is the low solution flow rate, otherwise these two are almost similar. Usually a glass capillary (5-30 μm) which is pulled mechanically using a puller instrument is used as spray emitter. A metal wire works as the electrode. The advantage about nanoESI is that it can work for low quantity of solution (about 5-10 μL) as the flow rate is very small in this case. For a tip of diameter below 2.5 μm it is difficult to see the spray. The diameter of the tip influence the liquid flow rate, which in turn affect the droplet size and current of deposition.⁵² Since the droplet size is reduced, the no of Coulombic explosions to release ions to the gas phase also reduces. During normal ESI due to extensive explosions and evaporation the desired molecule loses their surface activity and detecting this molecule is very difficult. This trend is seen in different oligosaccharides. Working with aqueous solution is a tedious process in ESI since the surface tension of water is very high and this problem can be solved in great extent using nanoESI, since the field around the tip varies with diameter. This technique has good sensitivity towards mixture of analytes, especially hydrophilic molecules with different chemical properties and shows tolerance against contaminants to considerable extent. Even it leads to solvent electrolysis such that the amount of ions in the gas phase will be excess compared to solution. Thus the efficiency of nanoESI in analyzing different mixture, electrochemical reaction, and producing stable charged droplets is very high compared to normal ESI.⁵³

Methods

Nanospray emitters were made using a micropipette puller instrument. This instrument was purchased from Sutter instrument, USA. A homemade nanospray emitting source was made and a high voltage power supply was connected to the electrode through a copper clip, and a potential in the range of 1-2 kV was applied. The electrode here was 0.5 mm diameter silver wire, purchased from Sigma Aldrich, India. Anhydrous ACN, from Mercks specialities private limited, Mumbai, India, was used as solvent in all electrolytic spray experiments. Anhydrous ACN is important; other solvents like methanol (MeOH), water (H₂O) or MeOH/H₂O mixture did not show the same result. To confirm presence of Ag ions, mass spectra were collected using an ion trap LTQ XL (Thermo Scientific, San Jose, California) mass spectrometer. ITO-coated glass slides were used as deposition substrate. ITO-coated slides were purchased from Toshniwal brothers (SR) private limited, India. Copper transmission electron microscopy (TEM) grids, purchased from Tedpella Inc. USA were used as mask and substrate for the growth. Locally available SS wire mesh was also used as the substrate. Parameters like distance of the spray emitter tip to substrate and deposition current were optimized by trial and error method. Approximately 5-10 mm was the distance and a deposition current of 40-50 nA was maintained during deposition. All the TEM measurements were done using a JEOL 3010 (JEOL Japan) transmission electron microscope. A scanning electron microscope by FEI was used to image these structures. Raman measurements were done using a Witec GmbH confocal Raman micro spectrometer, Germany with 532 nm and 633 nm laser excitation. For electro spray deposition, silver acetate and palladium acetate, Copper acetate, Cobalt acetate, Nickel acetate, Lead acetate from Sigma Aldrich, India, were used as precursors. Bimetallic structures were synthesized by electro spraying metal solutions mostly in 1:1 ratio. Different composition of metal salts, for example 1:3 Ag/Pd, 3:1 Ag/Pd, were also tried.

Results and Discussion

Synthesis of silver nanostructures was done by electrolytic spray deposition.⁵⁴ In this case silver wire was used as an anode. A capillary of outer diameter 1.5 mm and inner diameter 0.86 mm was pulled into two for using as nanospray emitters in all our experiments. Anhydrous acetonitrile (ACN) was used as solvent for electrolytic spray experiments. ITO coated glass slide was used as substrate to collect the solvated ions. The collector was grounded through a picoammeter to measure the deposition current. When a high potential of about 1-1.5 kV was applied to the silver wire, electro corrosion occur and solvated silver ions got ejected out of the capillary as plume. Solvent evaporation neutralization and aggregation of Ag ions occur to form particles. From the output current shown by the picoammeter, amount of ions deposited on the collector can be calculated. Figure 1A shows the schematic of the electrolytic process. The particles deposition on the ITO plate can be patterned using masks.⁵⁵ A close examination of the mask, in this case TEM grid, showed head on growth of Ag-NPs. Figure 1B shows a FE-SEM image of a TEM grid containing Ag brushes. A closer look on these structures shows that they are head on growth of Ag-NPs, like beads on a necklace. Figure 1C shows a schematic of the head on growth of Ag-NPs on a TEM grid.

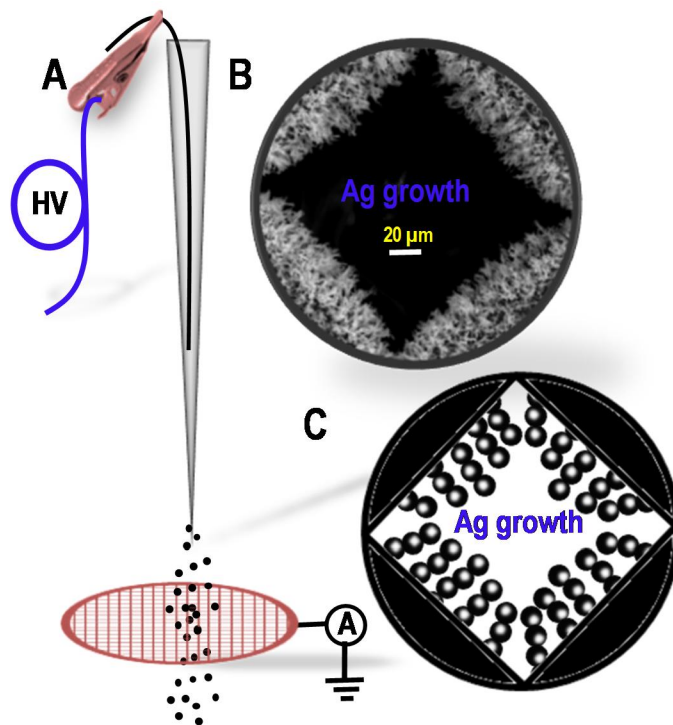


Figure 1. A) Schematic of the electrolytic spray process. B) FE-SEM image of the Ag nanostructures. C) Schematic of the head on growth of Ag NPs.

Since part of the plume was masked by the TEM grid, in one stretch we can form a NP pattern on the ITO as well as growth of brush like structures on the grid. The particles that synthesized using this process are free of counter ions. The advantage of this process is to make bare NPs, without using a capping agent, under ambient conditions. Figure 2A shows a TEM image of a TEM grid with silver brushes from the edge of the grid. From the image the growth of silver can be inferred as one dimensional, as they are not dendritic. The structures are uniformly distributed in the spot area of the grid over a diameter of 1.5-3 mm area (this can be varied changing the distance of the tip from the surface). As the time of electrolytic spray increases the length of brushes also increases. Figure 2B shows a higher magnification TEM image of the same brushes. From the image it is obvious that they are head on growth of particles. The typical ion flux during electrolytic spray process is 1.25×10^{11} per second. The solvent flow rate was 20 nL/min. So the concentration of silver ions is 10.37 μM . Since the ion flux during electrolytic spray is very less, it takes very long time to make bigger structure. But in the case of electrospray, where we use solution of a silver salt the concentration of Ag ions

is very high, hence less time is needed to make long structures. Figure 2 C, D show SEM image of a TEM grid after electro spray deposition of silver salt for 5 hours. The images show that the brushes are in the scale of 30-50 microns.

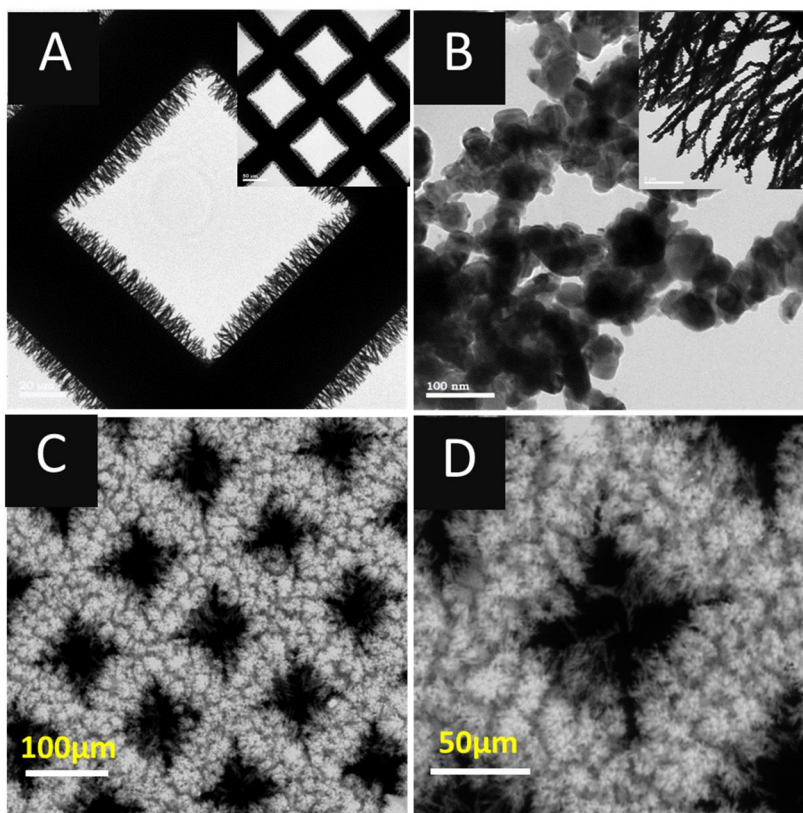


Figure 2. A) TEM image of a TEM grid containing silver brushes. Inset shows a large area TEM image of the same, B) a high magnification TEM image of the same showing pearl necklace like structure, C), and D) SEM image of a TEM grid after electro spray deposition of silver salt for 5 hours.

The SEM image in figure 2C shows that these structures are present all over the grid uniformly giving grassland like morphology. The possibility of making these structures was explored using other metal like palladium. In contrast Pd was not making similar kind of brushes, instead they were just depositing on the grid. Substrate such as

stainless steel wire mesh was also used for making silver brushes. The details mechanism has yet to be understood in detail.

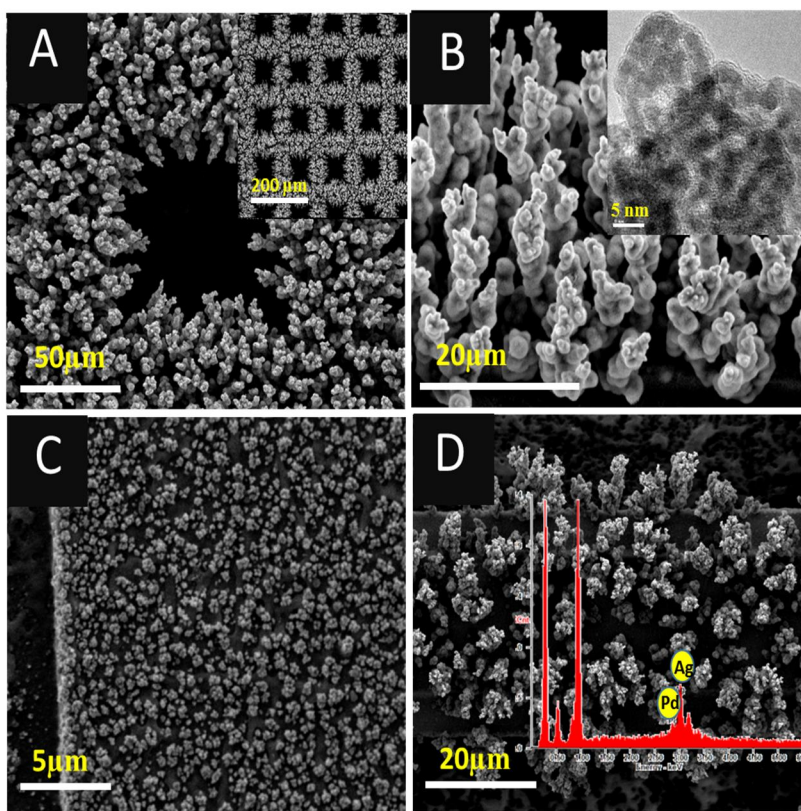


Figure 3. A) SEM image of growth of Ag-Pd NPs on a TEM grid. Inset shows the large area image B) SEM image of Ag-NPs growth at higher magnification. Inset shows the TEM image of the same, C) SEM image of the Ag-Pd bimetallic structures at the ratio 1:3 and D) SEM image of Ag-Pd bimetallic brush type structure at the ratio 3:1.

The blending of the properties of two metals can lead to interesting applications, which will be useful in catalysis. Figure 3A and B shows the SEM image of silver palladium bimetallic brush type structures on the TEM grid. Bimetallic NPs were synthesized by electrospaying 1 mM solutions of the acetate salts of Ag and Pd at a 1:1 ratio for 2 hrs at a current of 40 nA. Since Ag is forming brush type structures individually, same neutralization mechanisms can be inferred for the bimetallic structures also.

Experiments with different composition of Ag and Pd were done to see what happens with increase of Pd concentration. Result shows a significant change in structures with concentration of Pd. As we move from low to high concentration of Pd we see thickening of the brushes (Figure 3D), and at a very high concentration of Pd, for example 1:3 Ag: Pd, brush type structures did not form (Figure 3C). During electro spray, the ions are ejected as an aerosol and during the course of motion the solvent evaporates, and the ions come together and deposited as bimetallic structures on the copper grid. These structures are also made due to some weak interaction between the particles. In essence they are also not aggregates but made up of individual particles (Inset Figure 3B). The particle will neutralize in head on fashion to form vertical structures. The electric field present between the tip and the surface of the grid helps them to grow vertically. This is the reason why the brushes are mainly in upward direction. Compared to silver these bimetallic structures are thicker and they are branching out from the tip. The morphology and size of the structures are almost uniform throughout the spot.

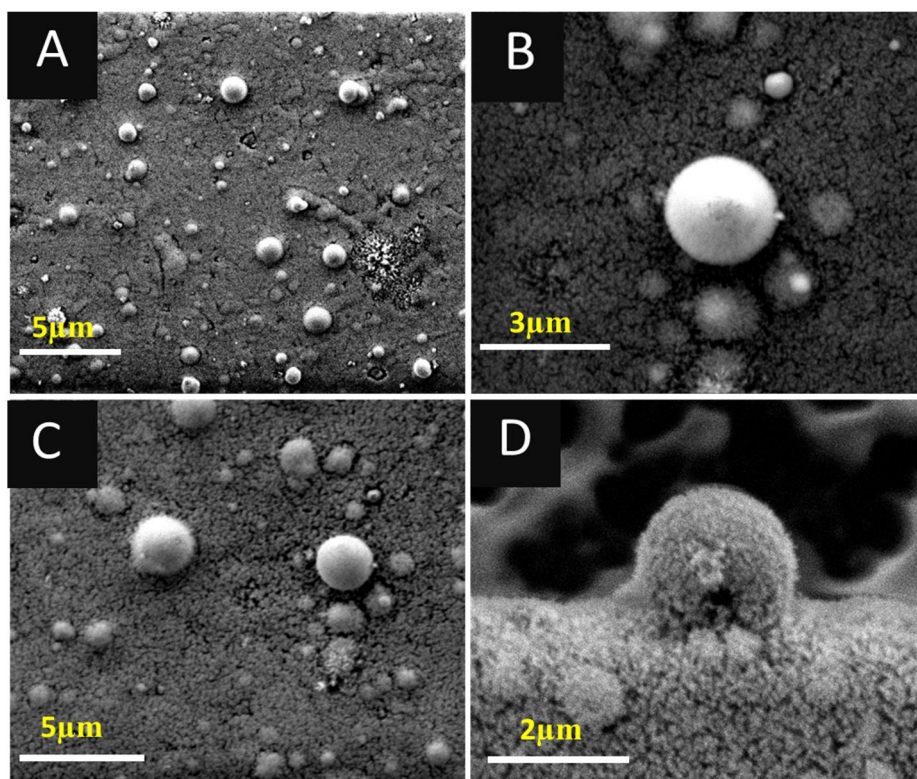


Figure 4. A, B, C and D) SEM image of Ni-Co bimetallic ball type structures.

In contrast Nickel (Ni) and cobalt (Co) are making ball type bimetallic structures. Figure 4 A, B, C, D shows SEM images of Ni-Co bimetallic balls at different magnifications. These structures were also made by electro spraying acetate salts of Nickel and Cobalt in 1:1 ratio. This variation in morphology may be due to different neutralization mechanism. These balls were of different size, found even on the ITO coated glass slide also. The amount of sample in the ITO was very high compared to the mask as the effective area was large. Long time of spraying was needed to get reasonable amount of samples on the mask. The NPs were moving down to the ITO.

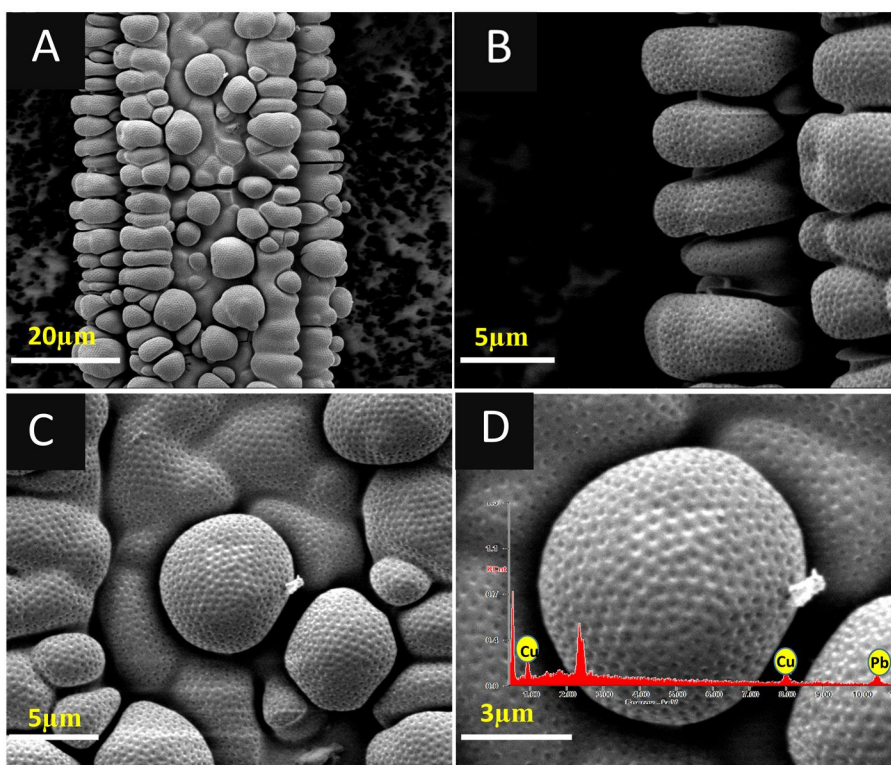


Figure 5. A, B, C, and D) SEM image of Cu-Pb bimetallic structures on a TEM grid.

Copper (Cu) and lead (Pb) bimetallic structures were prepared by spraying 1:1 solution of the acetate salts of Ni and Co. In contrast to all other structures they were making ball like structures on the copper grid. The average diameter of the balls is 6 μm. The balls were not uniform in size and a layer was seen below the ball which is uneven. The

particles may be first depositing to form a layer and from that the balls are forming. On the edges of the grid elongated structures were formed (Figure 5B). The interesting feature about this Cu-Pb bimetallic is that evenly distributed pits on them. It is seen on the balls and elongated structures. The mechanism of the formation of these pits has to be studied in detail, so as to find out the dimension of one hole which will lead to application such as functionalizing them and trapping desired molecules in this.

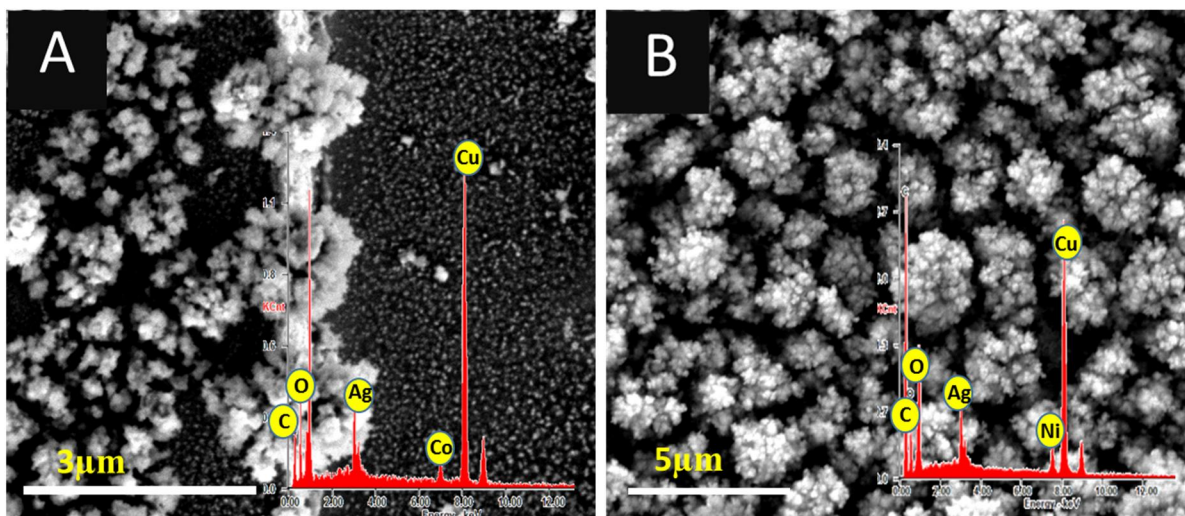


Figure 6. A), SEM image of Ag-Co bimetallic structures. Inset shows the SEM EDAX showing silver and cobalt B) SEM image of Ag-Ni bimetallic structures. Inset shows the SEM EDAX showing the same.

Figure 6 A, and B shows the Ag-Co, Ag-Ni bimetallic structures respectively. They are making flower kind of bimetallic structures. Ag-Ni flower type structures are spread uniformly all over the grid. But in the case of Ag-Co the size of each structure is different. The SEM EDAX spectrum shows the presence of both metals in bimetallic structures, even though it is not in 1:1 ratio.

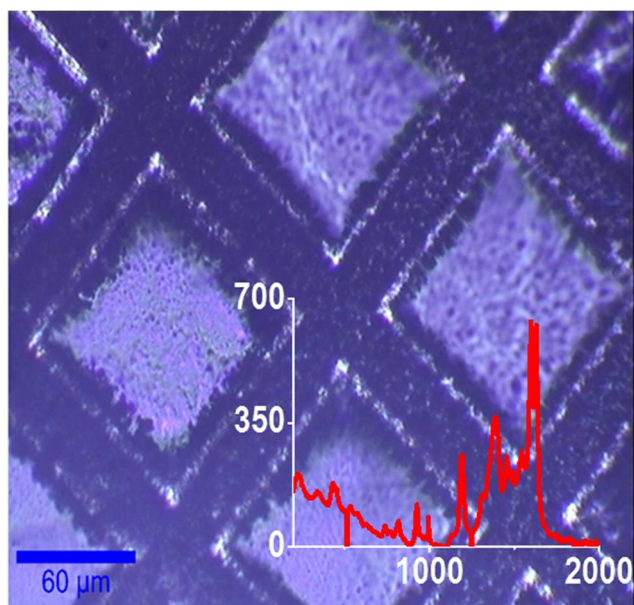


Figure 7. Optical image of an Ag bush containing TEM grid. Inset shows the Raman spectrum of the same, where 1×10^{-8} M crystal violet was used as the analyte.

As a part of application the SERS activity of these structures were analysed. Figure 7 shows an optical image of a TEM grid. Inset shows the Raman spectrum for crystal violet CV, where 1×10^{-8} M (CV) was used as the analyte. The characteristic peaks of CV range from 150-1700 cm^{-1} , where the signals around 1371 cm^{-1} , 1586 cm^{-1} and 1613 cm^{-1} are enhanced due to the SERS activity of Ag brushes with an enhancement factor of 7.3×10^5 . Since these structures are produced at ambient conditions and are quite stable with appreciable SERS activity they can be used for the sensing of molecules. These head-on growth mechanism of the particles gives surface roughness to these structures and can be an excellent trap for bacteria. The field nearby enhances the activity of these structures. Since the Ag NPs have antibacterial activity it not only captures bacteria, also kill them. They can be excellent candidates of trapping dust, volatile inorganic compounds and particulate matter. Altogether they are excellent sensing platforms.

Conclusion

Electrolytic spray ionization has been used to create diverse morphologies of alloy structures. This has been investigated with combination of metals. Such structures are formed over macroscopically large areas and have been used for applications such as SERS. Patterning these structures and using them for applications will be interesting aspects of future research.

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Visible Output

Paper

Sarkar, D.; M., K., Mahitha; Som, A.; Li, A.; Cooks, R., G.; Pradeep, T., Ambient growth of micrometer long metallic grasslands **Manuscript in preparation.**

Patent

Pradeep, T.; Sarkar, Depanjan; M. K., Mahitha; Som, Anirban; Cooks, R. Graham; Li, Anyin. Vertical growth of nanoparticles leading to micrometer long brushes by ambient electrolytic spray deposition. Patent Application No. IN 2014CH06669, submitted on January 9, 2015.