On the size control of nanoparticles synthesis without chemicals

Shyamal Mondal[1],* Arpan Maiti [2], and S. R. Bhattacharyya [3]
[1] *Physics, Maharaja Manindra Chandra College, 20 Ramkanto Bose Street, Kolkata-700003, India*
[2] *Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, IN, USA and*
[3] *Surface Physics & Materials Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhan Nagar, Kolkata-700064, India*

Nanoparticles and subnanometer size particles of metal or semiconductor have a very important role in preventing environmental degradation which is alarming now a days. Threat to environmental damage can be averted by resorting to clean energy sources instead of conventional fossil fuel such petroleum, coal, etc., and controlling the toxic materials from spreading as well as reducing their life time by catalysing their degradation. Catalyzing energy conversion and degrading toxic materials is possible by the use of metal nanoparticles of specific size ranges. In this article, a novel method of production of nanoparticle with precise control on their size without the use of chemical reagents is briefly described.

I. INTRODUCTION

Under the tremendous pressure of developing human civilization, nature is at risk where life once was found and kept flourishing. With the increase in human comfort demand of energy has increased gigantically. Until recently, the main power source has been the fossil fuels and burning of which emitting harmful gases which are main reasons behind the global warming. Not only that, the pressure of human civilization giving birth many toxic chemicals, toxic dye being one them, harming the environment. There are enormous efforts being put to save the environment by scientists from a wide variety of disciplines in recent days.

Replacing the conventional fossil fuels in energy generation is one of those efforts. The most pervasive source of clean energy is solar energy, which falls on the earths surface with a daily insolation that is more than sufficient to meet global energy demand [1]. The technology for the conversion of solar to electrical energy using photovoltaic devices, such as silicon solar cells or dye-sensitised solar cells, is well-established. However, the generated electrical energy is not easily stored in large amounts, while solar energy is both diurnal and intermittent, and is least available when it is most needed, i.e. at night in winter. One strategy to overcome these issues is to develop a technology that generates a readily utilised chemical fuel directly from the solar insolation. In this regard, the most clean and viable solution is water, which can be broken into hydrogen and oxygen in the presence of sun light with the help of metal-oxide photoanodes in a photoelectrochemical (PEC) cell using a Pt counter electrode. The main challenge in all these possibilities is the efficient use of solar insolation which is found to be solved by the use of metal nanoparticles as photocatalysts or co-catalysts [2]. Role played by these metals in photocatalysis can be generally divided into: activity enhancement, photosensitization of semiconductors, solely localised surface plasmon resonance catalyst, photo-thermal effects, light trapping effect, etc. [2]

These activities are highly sensitive or crucially dependent on the nanoparticle size because optical absorption or scattering is highly size dependent e.g., in metal nanoparticles below a certain size absorption is dominating where as in metal nanoparticle above a certain size scattering is dominant [3].

II. CHALLENGES

Synthesis of metal nanoparticles with controlled size needs to be easy and very clean i.e., without a trace of residual chemicals which might affect the light interaction with nanoparticle. Size control also require very rigorous chemistry. Nanoparticles of metal can also be obtained by physical methods such as dewetting of thin films upon high temperature annealing, atomic layer deposition, magnetron sputtering at room or elevated temperatures. But in these processes of nanoparticle synthesis it is impossible to control size and number density simultaneously and the control in size is not so straight forward.

III. BREAKTHROUGH

Above mentioned difficulties of controlling size and number density of nanoparticles can be overcome if a synthesis scheme in physical method of deposition where nanoparticles can be produced first and then they can be filtered according to their sizes and then can be deposited with controlled deposition kinetic energy on any substrate. The scheme has been described in the Fig. 1. Fortunately, cluster beam deposition method [4] is a physical deposition method which can be performed in high vacuum condition and follows exactly the above mentioned steps. In the following sections the mechanism of production of size controlled nanoparticles in gas phase, before size selection or filtration and deposition, will be described. This process can be categorized as

*e-mail : smondal.xray@gmail.com

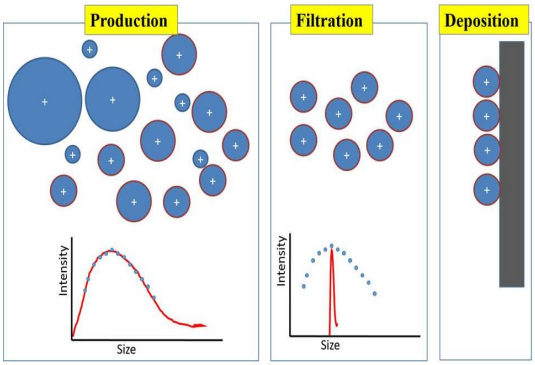

FIG. 1: A scheme for getting size selected deposition.

bottom up process where atoms are attached together to form clusters and then, through further growth, form nanoparticles. So the cluster production scheme is as follows: atom generation, nucleation and then aggregation or growth [5].

Atom generation Atom generation can be done in various ways e.g., thermal evaporation, ion sputtering, laser ablation, DC and RF magnetron sputtering, etc. In thermal evaporation heating of desired materials in crucible by resistive heating, electron beam induced heating are generally adopted. In ion beam sputtering highly energetic ions are used for striking out atoms from desired materials to get atoms. In laser ablation method high intensity laser is used to heat desired material to get desired atoms. For getting atomic vapour from wide range of materials from metals to insulators magnetron sputtering is best known so far.

Condensation In cluster production, the produced atomic vapour is condensed providing the desired condition to cool down the mixture of atomic vapour and the cooling gas. There are a few techniques to cool down the admixture e.g., low-pressure expansion through a nozzle called skimmer, collision by inert gas atoms. The area where this condensation takes place is known as the aggregation zone. In this zone, a supersaturated admixture is created in gas aggregation type source. Due to supersaturation of the atomic vapour small droplets are formed. These droplets are called nuclei. Through the growth of the nuclei in the aggregation zone clusters of different size are formed. The growth of clusters takes place through many possible mechanisms shown in Fig 2 and discussed below.

A. Atom attachment In this mechanism the nuclei collect more atoms on them to grow bigger forms clusters of different sizes. In this case atom attachment rate increases with size. Simply, this can be realized as $A_n + A \longrightarrow A_{n+1}$.

B. Coalescence Title and Author Details Two or more clusters when collide with each other in the gas

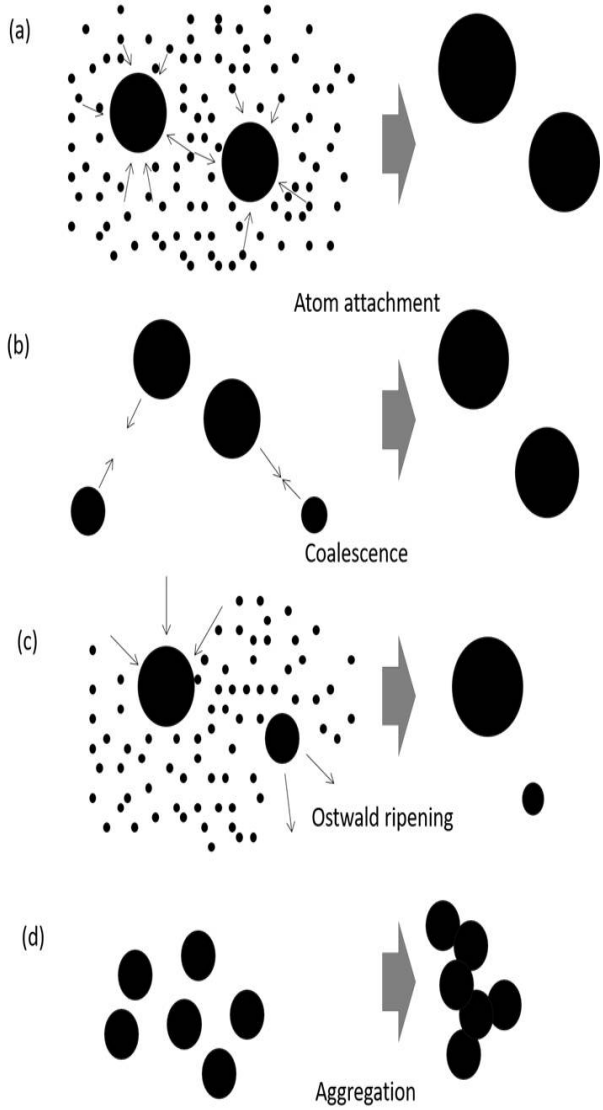

FIG. 2: Different schemes of cluster growth.

phase they stick and merges with each other to form larger cluster. This mechanism is called coalescence. This can expressed by the simple equation: $A_n + A_m \longrightarrow A_{n+m}$.

C. Ostwald ripening In this process formed clusters above a certain radius grows and at the cost of decay of some clusters less than that radius. This radius is called critical radius for cluster growth.

D. Aggregation In this process or mechanism clusters above a radius called critical radius for cluster coalescence do not merge completely when they come in contact with each other. In this mechanism of cluster-growth fractal type of structures are found to form.

IV. SIZE CONTROL

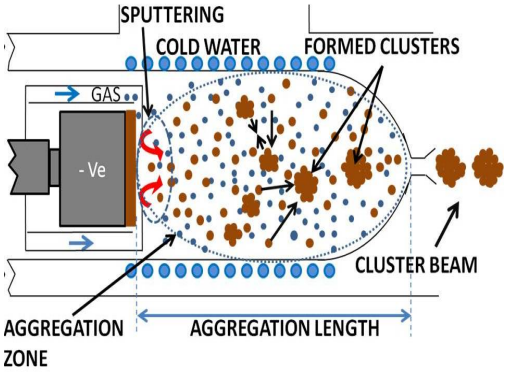

FIG. 3: Schematic diagram of magnetron based cluster source.

As cluster production consists of different stages, according to the discussions in the previous sections, it is obvious that different experimental parameters might affect the generation and growth of cluster eventually affecting the final size distribution of the produced clusters. Different types of cluster sources have different control parameters so the control of size will also differ. Here, the whole discussion will be devoted to the magnetron based gas aggregation type cluster source [5]. In this type of cluster sources which is described in the Fig. 3 atomic vapour is generated by magnetron sputtering. In magnetron sputtering, a negatively biased magnetron target head, made with the desired cluster material, gets sputtered out by Ar ions. That atomic vapour along with the Ar and He gas makes a supersaturated mixtures in the water cooled aggregation zone. Thus, the parameters which governs the size of clusters are i) Ar gas flow, ii) He gas flow, iii) aggregation zone length, iv) Magnetron power, etc. To see the variation of cluster size distribution in the produced clusters mass spectra are generally analysed. Mass spectrum is the plot of intensity or number of a particular size of clusters in y-axis against the size or mass in the x-axis. In the Fig. 4, variation of mean cluster sizes with the different source parameters, as mentioned above, are plotted. It can be observed that mean cluster size is increasing with Ar flow initially, saturate at some value and then decreases. The nature of variation is like this because with the increase of Ar flow more atoms from the target are sputtered which in turn increase the probability of growth of clusters both in number and size. But probability of growth is also dependant on the dwell time in the aggregation zone. If Ar flow increase, that can sweep the clusters faster away from the aggregation zone depriving the clusters of the possibility of growth. That is why after a certain flow cluster size decreases. Following the same reason, with increase in He flow the mean cluster size is found to decrease and with increase in aggregation length mean cluster size increases at a rate more than a linear dependent one, as shown in the Fig 4. Fig 4 also shows an initial increase in mean cluster size in the distribution with increase in magnetron power but after certain value the mean size decreases. Decrease in cluster size is associated with the increase in temperature in the aggregation zone due to increase in magnetron power. Thus mean cluster size and number of clusters produced can be controlled varying different suitable cluster source parameters. On the other hand it is clear that for any desired size we can choose the source parameters in such a way which can maximize the number of clusters or cluster-flux.

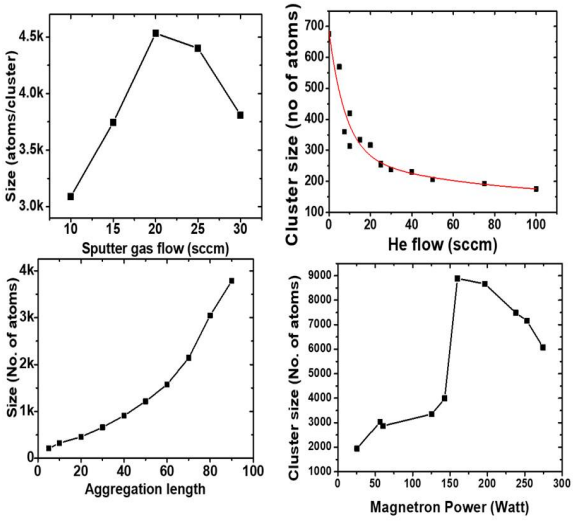

FIG. 4: Size variation with different source parameters indicated in the x-axes.

Peak Size (nm)	Magnetron power (watt)	Agg. Length (mm)	Ar flow (sccm)	He flow (sccm)
1.3	11	4.8	10	60
1.5	11	4.8	15	60
1.65	11	14.8	15	60
1.75	11	14.8	15	40
1.82	11	24.8	15	60
2.00	11	54.8	15	60
2.25	26.9	34.8	15	60
2.5	26.9	104.8	15	40
2.75	40	104.8	15	20
3.0	55.6	104.8	15	15
3.25	98.7	104.8	17	10

TABLE I: Mean cluster size and corresponding required parameters.

Highly precise control in size can be achieved by this technique. And by size selection mechanism using quadrupole mass filter (QMF) further finer size control is possible before required deposition. Degree of fineness in size control can be estimated from the Table 1 where fine variation of mean cluster sizes have been shown which have been obtained through the proper choice of experimental parameters [6]. The control of size is evindenced from microscopy data in the mentioned reference where

1.5 nm, 2nm and 3.0 nm size clusters were actually deposited and observed the contribution in charge retaining capacity in MOS devices.

V. CONCLUSION

From the above discussion it is evident that a very good size controlled production of nanoparticles is possible by cluster beam deposition method using magnetron based gas aggregation type source. One control parameter controls size with different precision than others. For example change of helium-flow-rate changes the position of size distribution peak in finer steps than argon flow rate. Change in aggregation length controls the peak position with bigger steps and so on. The process of size selected deposition is one step and do not require any rigorous knowledge of chemistry or use of chemicals. It should be noted that such a size control facilitate many applications which require stringent size control. There are enormous possibility in solar fuel generation where size controlled metal nanoclusters can be used as photocatalysts to efficiently convert solar energy as usable electrical and thermal energy. This technique, only, has the capability of controlling size and spatial density of deposited nanoparticles independently. The advantage is used in the work of Ref. [6].

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