

Predictor packing in developing unprecedented shaped colloidal particles

Mubarak Ali ^{a,*}, I –Nan Lin ^b and C. –J. Yeh ^c

^a Department of Physics, COMSATS Institute of Information Technology, Islamabad 45550, Pakistan, * Email: mubarak74@comsats.edu.pk, mubarak74@mail.com

^b Department of Physics, Tamkang University, Tamsui Dist., New Taipei City 25137, Taiwan (R.O.C.). e-mail: inanlin@mail.tku.edu.tw

^c Department of Engineering and system Science, National Tsing-Hua University, Hsinchu 30013, Taiwan (R.O.C.). e-mail: arayray220@gmail.com

Abstract –Developing particles of various geometric anisotropic shapes are the hot topic since decades as they guarantee some special features of properties not possible through other means. Again, controlling atoms to develop certain size and shape particle is a quite challenging job. In this study, gold particles of different shapes are developed *via* pulse-based electronphoton-solution interface process. Here, it is discussed that gold atoms while transition of cold state to re-crystallization state amalgamate at solution surface around the light glow to develop monolayer assembly. The rate of uplifting gold atoms to solution surface is as per the reaction of entering force of electron streams and photons of varying wavelength achieved under optimized process conditions. Prior to uplifting of gold atoms, they dissociated from the precursor through absorption of heat energy given to solution by the immersed graphite rod. On the other hand, packets of nano shape energy developing tiny particles of own shape on binding their energy to energy knots clamping to electron states of atoms of monolayer assembly under the achieved transition state. Simultaneously, atoms of developed monolayer tiny particles start elongating to both sides from their centers under the influence of working surface format force at level of solution surface where electrons deal adjacent placement under orientational-based stretching of clamping energy knots

resulting into transform one-dimensional arrays of atoms into structure of smooth elements where tip of each one faces the centre of light glow under their immersing force resulting into pack as one unit. Due to the feature of bipolar pulse having unity ratio of pulse OFF to ON time, each tiny particle is first developed in shape like two joint triangles. As adjacent connection between their two atoms dealing force of opposite pole at perturbed axis, they first separated into two equal triangular-shaped tiny particles under the application of surface format force. They directed as one unit from the regions of formation to pack at already allocated unfilled regions to develop certain shape particle under the force as per their rate of development in different zones of solution surface. Structures of smooth elements of triangular-shaped tiny particles in the reach of packing at centre of light glow further elongate while impinging electron streams at fixed angle. Structures of smooth elements further shape and acquire smoothness under the forcing energy of high density travelling photons at the instant of (on) packing. Depending on the zone of development of tiny particles along with their number of together packing develop various geometric anisotropic shaped particles. At fixed precursor concentration, increasing the process time results into develop particles of low aspect ratio. Under tuned parameters, developing mechanisms of particles of high aspect ratio exhibiting unprecedented features are located.

Keywords: Fundamental and applied physics; Process parameters; Force-energy; Anisotropic particles; One-dimensional particles; Three-dimensional particles

1. Introduction

To design different sort of material, it is remained crucial since the birth of materials science. Intellectuals' and scientific leaders' fields of materials and interdisciplinary areas remained engaged to design specific materials in all ages as per need and demand of on-going era. Among the categories of materials, the synthesis of materials in particles shape remained dominant in the past few decades as well as in the current ages and they hold promising future too. To describe the scope and significance of tiny particles, nanoparticles, and particles, it is easy to say that several scientific leaders as well as emerging scientific leaders are working to reach out required size and shape of particles in diversified class of materials along with their anisotropy and aspect ratio as

such materials may be directly (indirectly) the origin of certain cutting-edge application that may not only bring scientific and technological impact but also social impact. In this context, various scientific journals covering all class of materials are publishing syntheses of particles under different means along with various targeted aspects of their applications. The explanations which are put forth on the development mechanisms of tiny particles, nanoparticles and particles are spanned over different class of opinions and scientific arguments.

But, undoubtedly, when the nanoparticles and particles showing the same morphology-structure (features of shapes) under their different microscopic images, they raise a combine question i.e., “Why they contain a lot of diversified ranges of explanation and viewpoints”. Obviously, it is to be; the scientific explanations vary process to process and within the same process also. The particles are almost delivering similar sort of result along with their practical demonstration at forefronts of cutting-edge applications. In the synthesis process of nanoparticles and particles, facilitator of their atoms can be varied, but the product is to be remained the same as comprised the same material of their shape and structure.

Overall, to design material at nanoscale for getting unique benefits has always been the prime objective of scientific community and investigating structure under the least wavelength available at light-spectrum has great challenges. To manipulate and probe matter at nanoscale for development of new tools is critical for nanoscience and nanotechnology [1]. One-dimensional nanowires [2] and two-dimensional free-floating sheets have been developed by strong dipole-dipole interaction [3]. To structure matter on the scale of length comparable or smaller to the wavelength of light can deliver phenomenal optical properties [4, 5] and catalytic activity of metallic nanostructures, enhanced significantly on controlling phase [6, 7].

Formation of tiny clusters and their coalescence into extended shape of particles is one of the long and continuously over-looked phenomena [8-18]. Nanometer-sized gold clusters behave like simple chemical compounds and may find a wide range of applications in catalysis, sensors and molecular electronics [8]. The discrete nature and stability of nanocrystals along with their tendency to form extended superlattices suggest ways and means for the design and fabrication of advanced materials having

controlled characteristics [9]. Development of single crystal by the aggregation of nanocrystals appears as a realistic goal [10]. The development of new, ultimately small, electronic devices is one of the most prominent potential long-term applications of nanoparticles technology [11]. Self-assembly offers a very promising route to construct complex shapes at nano-/micro-meters level and engages many of the classical disciplines of science and engineering [12]. A grand challenge is to assemble and position the nanoparticles at preferred sites which will enable the construction of complex and higher-order functional structures [13]. To organize nanometer-sized building blocks into specific shapes is one of the current challenges [14]. On successful assembling of colloidal particles into useful structures the 'atoms' and 'molecules' will become tomorrow's materials [15]. Understanding the electronic absorption and dynamics of individual nanoparticles is pre-requisite for their transformation into an ordered array instead of their agglomeration [16]. Possibility to coalesce nanocrystals allows one to develop materials with abundant selections, which leads to the opening of entirely new field [17]. On controlling precisely, the surface properties of nanoparticles will lead to direct their assemblies into higher order structures [18]. Tiny particles are molecular-like structures and certain numbers of atoms form hcp structure [19]. Shape and size of metallic structures has remained under extensive debate and generated significant interest in several newly emerging areas of nanoscience and nanotechnology [20-22]. It has been shown that shape entropy drives the phase behavior of systems of anisotropic shapes through directional entropic forces [23]. Geometry and entropy of colloidal particles not only explain the structure but dynamics also [24]. In known protocol, in addition to the disordered jammed configuration, there are ordered metrics capable to characterize the order of packing [25]. Those studies are the growth and beauty of science behind materials of technological advance.

Efforts have also been made to synthesize tiny clusters and anisotropic shapes of gold by employing various plasma solution methodologies. Mainly, four approaches remained under operation: (1) DC plasma discharge in contact to liquid [26-29], (2) DC glow discharge plasma in contact to liquid [30], (3) pulse plasma discharge inside the liquid [31-36], and (4) gas-liquid interface discharge [37]. Hydrogen peroxide was the most probable reaction mechanism to synthesize gold nanoparticles and aqueous

electrons to drive the process [26-29]. While synthesizing spherical-shaped nanoparticles, electron flux at given current remains constant on the surface of solution [32] and plasma electrons act as cathode [33]. Hydrogen radicals generated in the discharge where their rate increased consistently with the external field and due to dissolution of nanoparticles, reduction rate lowered and was the cause of anisotropic growth [34]. The influence of Brownian motion along with surface charge of nanoparticles explained their stability [35] and negatively charged surface of nanoparticles kept them away from agglomeration [36]. Gold nano-plates and nano-rods developed at the surface of solution and spherical-shaped particles in the solution [37].

The fundamental process of formation of various tiny-sized particles at different process conditions is discussed elsewhere [38]. The development of gold nanoparticles and particles under varying precursor concentration has been discussed elsewhere [39]. Tapping opportunity of tiny shaped particles and role of precursor in developing shaped particles under the same setup are given elsewhere [40]. Different shaped tiny particles along with their extended shapes developed under varying the ratio of bipolar pulse and different pulse polarity [41]. Development of extended shaped particles at increasing process duration along with the adjacent and lateral placement of electrons in atoms of tiny particles while developing structure of smooth elements are shown elsewhere [42]. A detailed study presented about the development mechanism of tiny shaped particles dealing localized gravity of their mono layer at solution surface while developing certain shape particle where modified one-dimensional arrays of atoms into structure of smooth elements [43]. Atoms of electronic transitions deform or elongate but don't ionize where forcing energy is related to photonic current instead of electronic current [44] and those atoms are eligible to evolve different structure of one-dimension, two-dimension and three-dimension depending on the dealing force of certain format [45]. The phenomena of heat and photon energy are discussed elsewhere [46] where silicon atom was taken model system. Atomic behaviors Along with field force behaviors are quite diligent in showing the performance of nanoparticles while using them as nanomedicine [47]. Recently, switching dynamics of morphology-structure in carbon deposited films are reported elsewhere [48] where slight variation in the process conditions resulting into alters morphology-structure of evolving grains and crystallites.

To synthesize particles of different materials is easy but it is difficult to understand the underpinning mechanism of their development. The present work describes the fundamental process of formation of triangular-shaped tiny particles at solution surface in relation to their predictor packing and developing the particles of various geometric anisotropic shapes under the working force in pulse-based electronphoton-solution interface process. Under set parameters, gold atoms dissociated from the precursor while absorbing energy which is being transferred through immersed graphite rod mainly where they uplifted to solution surface against the reaction of entering force for developing monolayer assembly where dealt certain transition state to binding as per shape of placed packets of nano shape energy.

2. Experimental details

Hydrogen tetrachloroaurate (III) trihydrate was purchased from Alfa Aesar and different concentrations of solution were prepared after mixing with DI water. A layout of pulse-based electronphoton-solution interface process was designed in the case of present experiments is shown in Figure 1. Copper tube internal diameter 3 mm was utilized as a cathode and 100 sccm argon flow rate was maintained through it *via* mass flow controller. Graphite rod (width: 1 cm) was immersed in the solution which is also known as anode. The bottom of the copper capillary was adjusted just above the surface of solution (~ 0.4 mm) and distance from the graphite rod was kept 4 cm. Symmetric-bipolar modes of pulses were employed which were generated by the pulse DC power controller (SPIK2000A-20, MELEC GmbH Germany). Temperature of the solution was recorded from the distance of one meter by LASER-guided meter (CENTER, 350 Series); 21°C at the start and 47°C at the end of 20 minutes with $\pm 1^\circ\text{C}$ accuracy. The precursor concentration was 0.3 mM. Total quantity of solution was 100 ml. The processing time of the solution was 20 minutes. In each experiment, the average input DC power was measured to be 36 (watts) where running voltage was ~30 (volts) and current was ~1.2 (amp) and light glow sustained after few seconds under the slight variation of input power; power fluctuation was more at the start of the process (initial few seconds) and became nearly constant (very less fluctuated) during the entire

process. Step-up transformer increased voltage 40 times. Bipolar pulse ON/OFF duration in each experiment was set 10 μ sec.

Thickness of the copper capillary wall was 1.5 mm, whereas, the diameter of inner hollow space through which argon gas flows was 3 mm as shown in Figure S1. Zones related to placing packets of nano shape energy, impinging electron streams and traveling photons of different wavelengths at surface of monolayer gold atoms are pointed out by (7), (8) and (9), respectively in Figure 1 along with further detail given in Figure S2. To characterize features of various particles both bright field and high-resolution microscope images of particles were captured (TEM, JEOL JEM2100F; operated at 200 kV). Prior to those investigations, a drop of solution from each prepared concentration was poured on copper grid and was kept in Photoplate degasser (JEOL EM-DSC30) for the elimination of moisture.

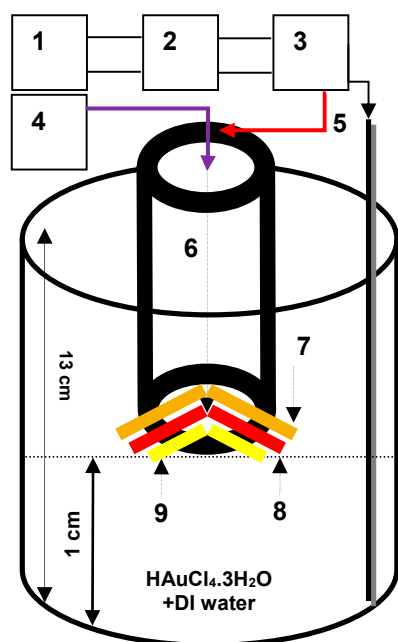


Figure 1: Layout of pulse-based electron-photon-solution interface process; (1) power supply, (2) pulse power controller, (3) step-up transformer, (4) argon gas, (5) graphite rod, (6) inner (hollow) region of copper capillary, (7) region of placing nano shape energy (outer region of light glow), (8) electron-solution interface (middle region of light glow) and (9) photon-solution interface (inner region of light glow)

3. Results and discussion

Photonic current propagating through the graphite rod provided the heat energy to precursor for dissociating gold atoms. Heat energy is resulted during the interaction of

traveling of photons into the liquid medium on leaving the graphite rod. The uplifting of metallic atoms to solution surface is under the reaction of entering force. The entering force is being resulted through the entering of electron streams along with releasing photons of increasing wavelength on splitting the flowing inert gas atoms. It is discussed elsewhere [38] that both electron streams and photons result on splitting of flowing inert gas atoms. Photons of high energy travelling more in normal to their points of release entered in the solution instead of traveling along the air-matter interface as discussed elsewhere [41]. Argon gas was used to activate the process of developing gold particles. Splitting of inert gas atoms not only delivered electrons to impinge underlying gold atoms but also enabled the propagation of photons characteristic current into inter-state electron gap prior to split resulting into allow them to travel in increasing wavelength in the open medium. Therefore, a certain amount of flowing inert gas atoms split just over the solution surface where photons increasing in their wavelengths work at place utilizing their forcing energy to align underlying electronic structure of elongated triangular-shaped tiny particle in the case of perturbed electron states of atoms, thus, modify the structure of tiny particle to structure of smooth elements by compensating any left discrepancy [43]. The inert gas atoms split under the application of excess propagation of photons characteristic current through their inter-state electron gaps [44].

Auto-controlled current for set pulse duration propagating through copper tube gave packets of nano shape energy under the application of step-up transformer. Underneath copper capillary where monolayer assembly of gold atoms is developed, packets of nano shape energy are being placed horizontally resulting into crop atoms of monolayer assembly into tiny particles in their own shape at solution surface of round shape around the region of light glow. The round surface width i.e. 1.5 mm, which is approximately equal to the thickness of wall of copper capillary, is shown in Figure S1. Therefore, packets of nano energy shape like connected triangles developed tiny particles of their own shape, which were resulted under the application of bipolar pulse having tailored ON/OFF time controlled by the auto setup as discussed in the experimental details. The placed horizontally double-packets of nano shape energy over the surface of solution dealt gold atoms of transition state where the placement of many of their electrons is more along the surface format poles (east-west poles) resulting into

bind. The developing such tiny particles while considering gold atoms as the model system is discussed elsewhere [43]. As graphite rod is immersed into the solution from bottom level to top level surface, surplus propagation of current occurs into it, on leaving the propagation of inter-state electron gap enter in the solution to dissociate the gold atoms from the precursor. On the other hand, entering forcing energy of photons along with splitted electron streams uplifting those dissociated gold atoms under the force of reaction resulting into develop monolayer assembly of gold atoms. Figure 2 shows dissociation of gold atoms under the supply of heat energy through immersed graphite rod and their uplifting to solution surface under the entering force of light glow, which constituted both electron streams and high energy photons.

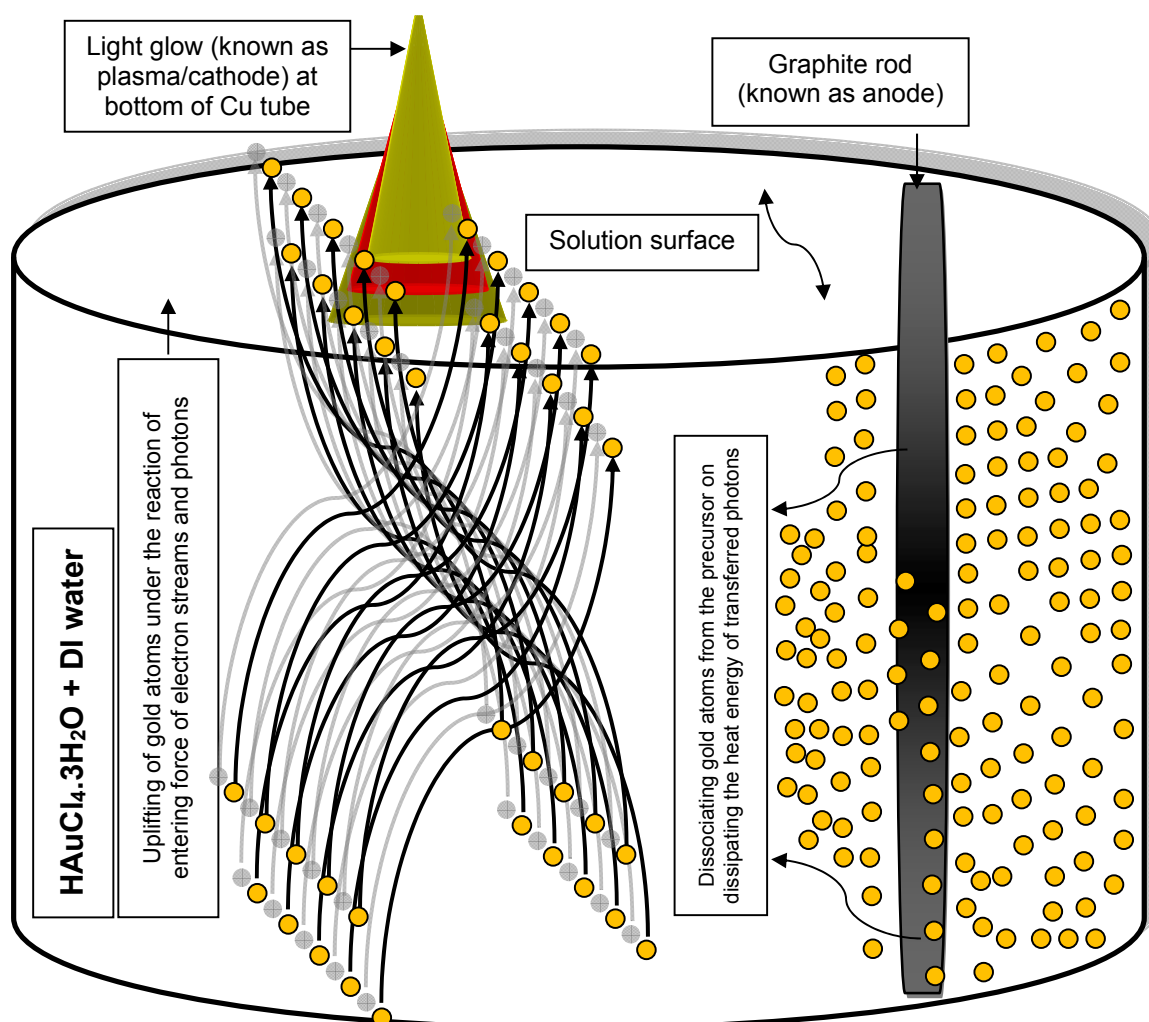


Figure 2: Gold atoms dissociating from the precursor and uplifting to solution surface

Signatures of nano shape energy, electron streams and light glow dealing 3D space while interacting circular solution surface are shown in Figure S2. Therefore, interactions of nano shape energy, electron streams and photons are consecutively (one at one time) in three cones like shapes; outer cone shape is belonged to placing packets of nano shape energy, middle impinging electron streams and inner one is belonged to photons travelling along the interface and entering in the solution. High energy photons enter in the solution under strong interaction while low energy photons dissipate heat energy just over the surface of solution under poor interaction.

At solution surface, gold atoms under transition state construct monolayer assembly in circle but by leaving the regions of zero-force axis as shown in Figure 3. Placed nano shape energy cropped transition state atoms of monolayer assembly into tiny particles having three-dimensional structure of surface format, which is being known in hcp structure. A detail study on structural evolution in different formats is given elsewhere along with the distribution of surface format force in different poles [45]. During processing AgNO_3 solution, there was no formation of triangular-shaped tiny particles even though same process conditions were employed indicating that silver atoms deal transition state (re-crystallization state) to elongate is at different level of ground surface instead of the gold atoms as they are elongating at solution surface set for the same height as for the case of processing silver solution. In the case of gold solution, it was not like silver and entire solution in the beaker changed into a color rapidly and uniformly. In the case of gold solution, color of solution was changing at fast rate in the initial few seconds due to utilization of atoms into formation of their tiny particles, nanoparticles and particles. Placed double-packets of nano shape energy for binding atoms of monolayer assembly into two connecting triangular-shaped tiny particles, in each case, binding them in their own shape are shown in Figure 3; zones related to photons at work (and light glow), impinging electron streams and placing horizontally packets of nano shape energy are in the central region, in the middle region and in the outer region, respectively, as roughly sketched in the figure. At centre of light glow, a developing mono layer of certain shape particle is also shown along with several earlier developed mono layers as indicated by the arrow signs where sinking one step down while dealing the localized gravity. Binding of such mono layers in developing particle of

certain shape is through the lateral placement of electrons in their partially elongated atoms. Further detail of binding mono layers in developing certain shape particle while dealing the localized gravity at solution surface is discussed elsewhere [43].

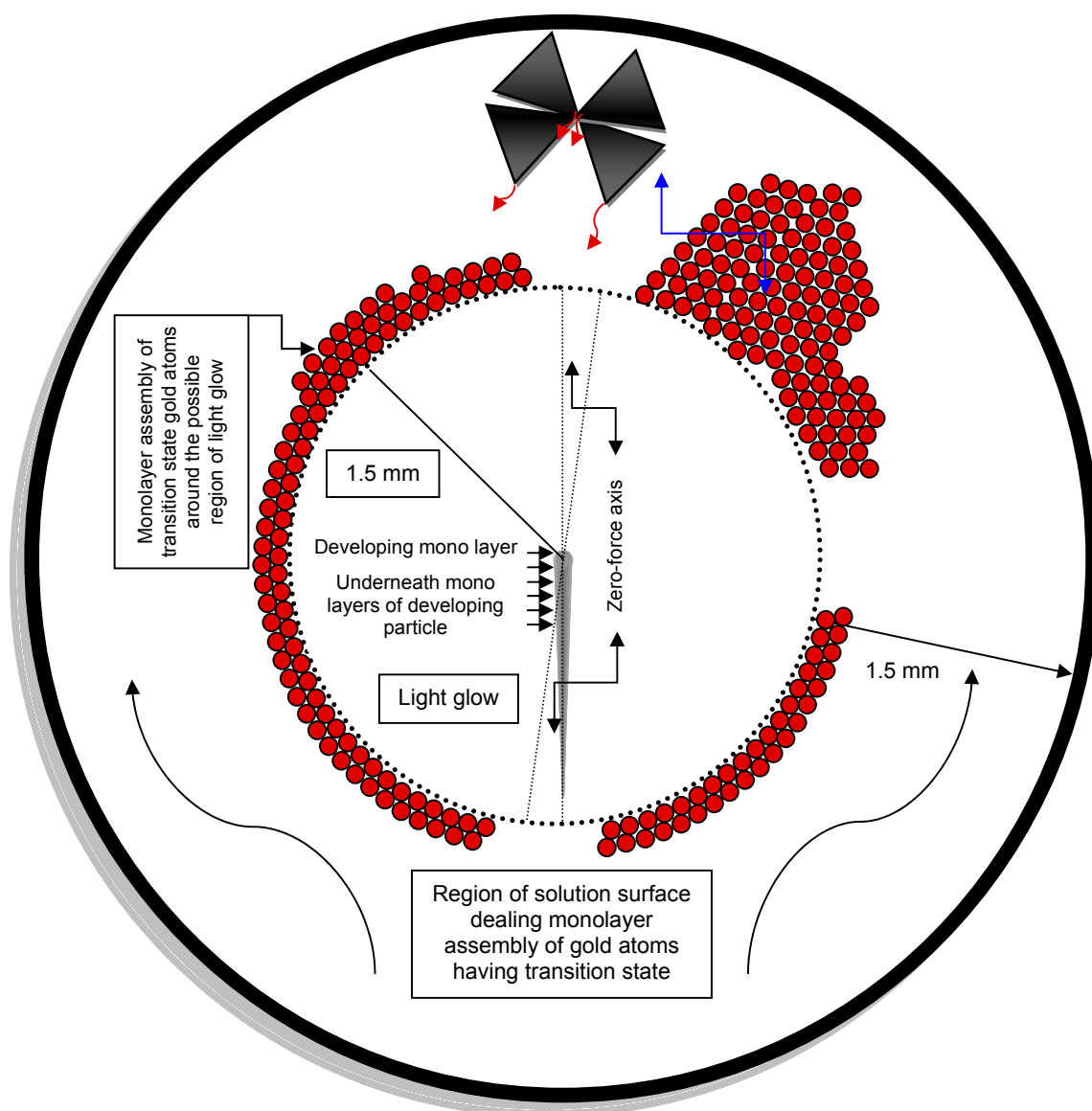


Figure 3: Gold atoms at solution surface in suitable circular zone width i.e. 1.5 mm where double-packets of nano shape energy placed over monolayer assembly to bind transition state atoms in own shape and size where no amalgamation of the atoms along the zero-force axis occurs

The predictor packing of triangular-shaped tiny particles is from the same region where they were developed. At tuned bipolar pulse mode (pulse ON/OFF time: 10 μ sec) along with other set parameters as described in the experimental details, the each developed tiny particle contained the two connecting triangular-shaped tiny particles.

Two joint triangular-shaped tiny particles separated into two equal size triangular-shaped tiny particles under the difference of force influencing at opposite pole between their connected atoms. However, triangular-shaped tiny particles developed directly under the application of unipolar pulse [41]. It can be observed in the illustration given in Figure 3 where tiny particle of two connecting triangles developed under the application of double-packet nano shape energy and further details is given elsewhere [39-43].

The left one (companion) tiny particle is waiting to follow the packing of earlier one in each case is indicated in Figure 3; the left one triangular-shaped tiny particle turned and directed tip towards the region of packing dealing the force of surface format, a bit in tilted manner, till reaching at centre of light glow. In the similar manner, elongated triangular-shaped tiny particles are arriving to pack at pre-allocated regions of developing monolayers of developing certain shape particle where the packing at any point results into sinking of particle on termination under the force of gravity where each layer binds under the mechanism of lateral placement of electrons as discussed elsewhere [43]. In the case of rod-/bar-shaped particles, tiny particles were developed at oppositely-sided regions available at the sides of rear north-south axes as illustrated in Figure S3. Such shaped particles are said to be particles of one-dimensional shape but binding (packing) of tiny particles in developing their structure remained two-sided (opposite to each other from the centre point) and they possess more width of their developed structure of smooth element as compared to particles of three-dimensional shapes where binding (packing) of tiny particles in developing their structure remained three-sided.

In the case of plate-like particles, monolayer assembly cropped into triangular-shaped tiny particles as well due to the availability of atoms at solution surface along east west poles around pulse-based electronphoton-solution interface. To develop triangular-shaped particle, at one time, the momentum of packing remains the same from all three sides where each tiny particle packing secures orientation at 120° angle and from three different zones under the force toward their respective regions of packing. To develop hexagonal-shaped particle, at one time, the momentum of packing remains the same from all six sides where each tiny particle packing secures orientation

at 60° angle and from six different zones under the force toward their respective regions of packing and so on.

Figure 4 shows formation of connecting triangular-shaped tiny particles where the size is decreasing under the prolonged process duration. As discussed above, such tiny particles separated into equal triangular-shaped tiny particles while dealing the force of opposite pole between the points of their joint atoms. Decreasing the size of triangular-shaped tiny particles resulted into decrease the aspect ratio of their particles as they are being developed in the presence of reduced amount of gold atoms and at later stage of the process. At start of the process, mainly large-sized tiny particles were developed and their packing into particles possesses large aspect ratio too. As the size of the tiny particle decreases on reducing the number of atoms per unit area at solution surface, particles of decreasing aspect ratio develop with time even though they possess the same shapes as for those developed at initial stage of the process. Under fixed concentration of precursor, the number of amalgamating atoms into monolayer assembly reduced significantly resulting into lowering the aspect ratio of particles developed with the passage of prolonging the process time. It is estimated that in the beginning of the process, the size of tiny particle was varied depending on the ratio of pulse OFF to ON time.

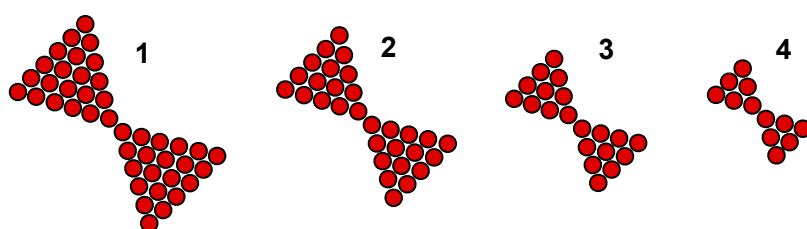
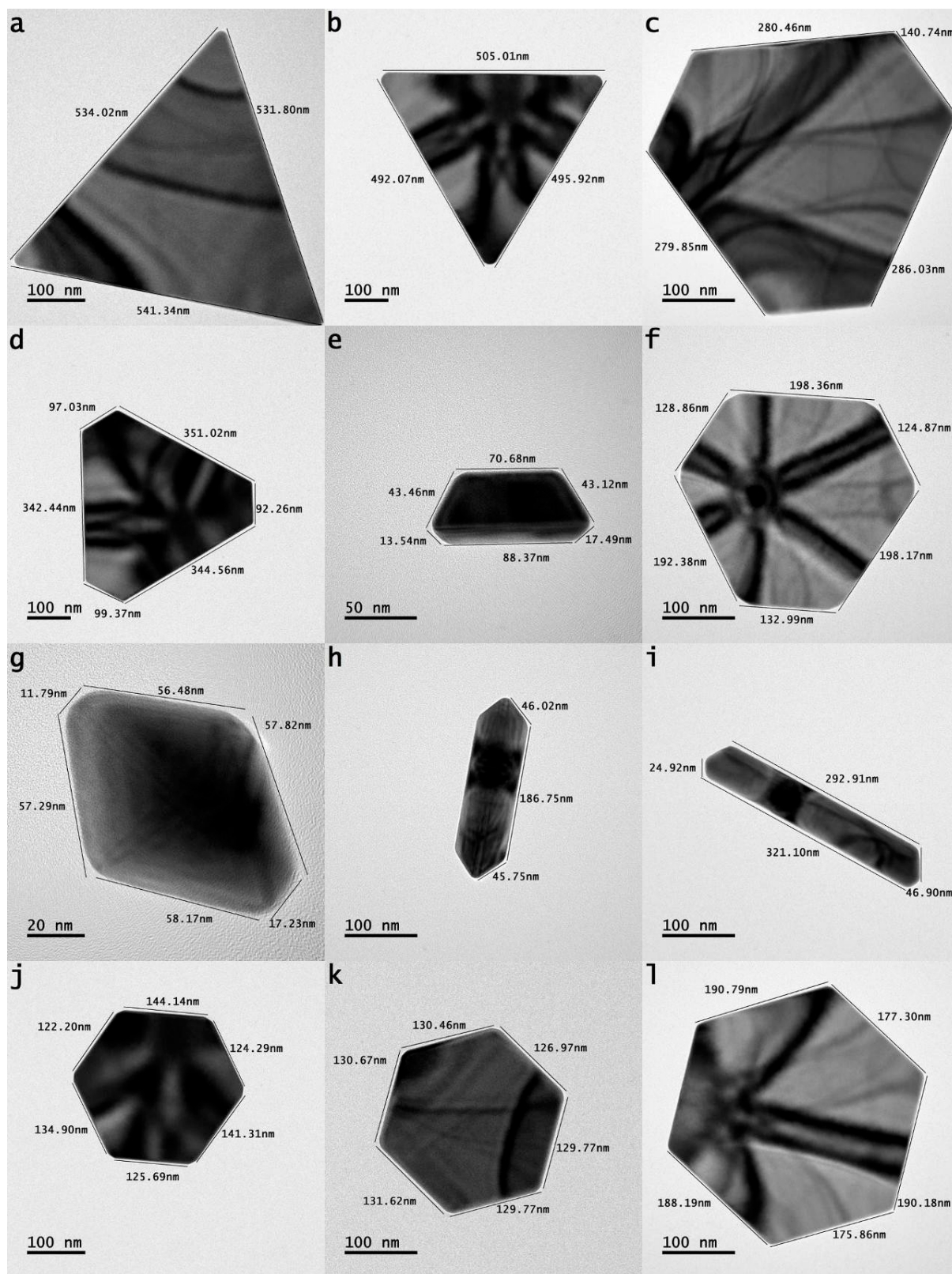


Figure 4: Connected triangular-shaped tiny particles decreasing size with respect to process time while dealing the fixed precursor concentration of the process

Each developing layer of the geometric anisotropic shaped particle self-deal the packing as vacant left place which provides the force to triangular-shaped tiny particle in the relevant zone of developing particle where those places pack for fit size at exact time and fill that vacant allocated place, therefore, it is also subjected to self-filling of unpacked regions besides the predictor packing as referred. A complete layer of developing geometric anisotropic shaped particle developed in each step of pulse ON

time (10 μ sec) where they possess structure of smooth elements. That developed monolayer structure of smooth elements went down to solution surface while dealing the localized gravity and followed by developing new layer starting exactly at the centre of the one prior developed, in the same size and shape, as the formation of triangular-shaped tiny particles along with predictor packing remained the same for the period of formation of that particle. While developing upper layer, downward layer descends level upto ~ 0.3 nm (\sim diameter of gold atom), however, under the break of developing layers for next set period of pulse ON time (10 μ sec), the particle sinked by leaving the solution surface completely resulting into leave the centre of light glow at solution surface, thus, allowing to develop a new particle. Once, the process of formation of new layer in developing certain particle is timed out; the particle is no more under growth. This leads into start the developing process of the new particle. On utilizing the developed tiny particles around centre, the newly developed tiny particles started utilizing their predictor packings, thus, developing new particles of geometric anisotropic shapes. Lower the number of binding mono layers, then, higher is the aspect ratio of resulted particle. The particle's shape varies depending on the region of initially packed triangular-shaped tiny particles, at one time, along with their quantity; when three equal size tiny shaped particles packed simultaneously at 120° angle placed side by side, it will result into develop triangular-shaped particle and when six equal size tiny shaped particles simultaneously packed at 60° angle placed side by side, it will result into develop hexagonal-shape particle.

Figure 5 shows particles of various anisotropic shapes which developed under predictor packing of triangular-shaped tiny particles. The differently shape shown particles in Figure 5 clearly figure out the degree of orientation at which predictor packing takes place and in each face of the particle by taking the centre of particle as a reference point. Therefore, photons worked at the place help in constructing perfect smooth elements having their equal inter-spacing distance in each forming layer of developing particle as illustrated in Figure S4.



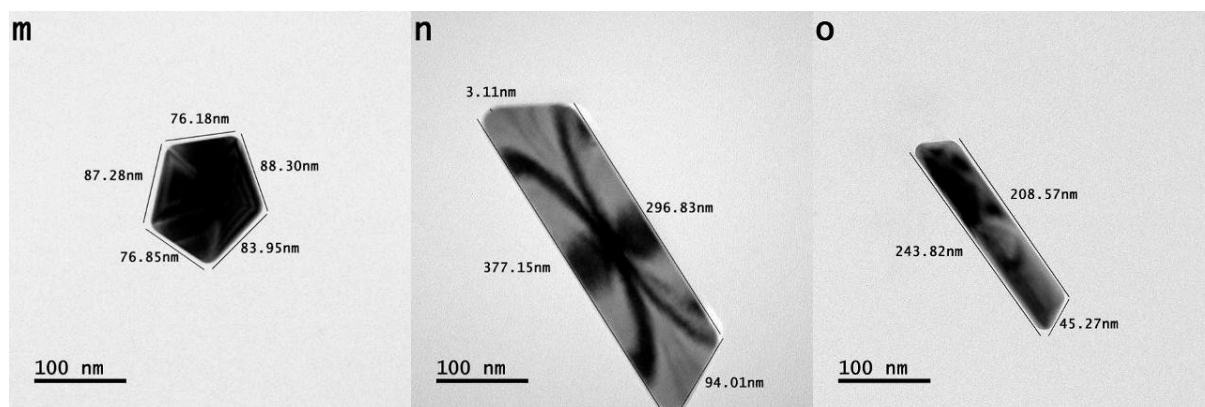
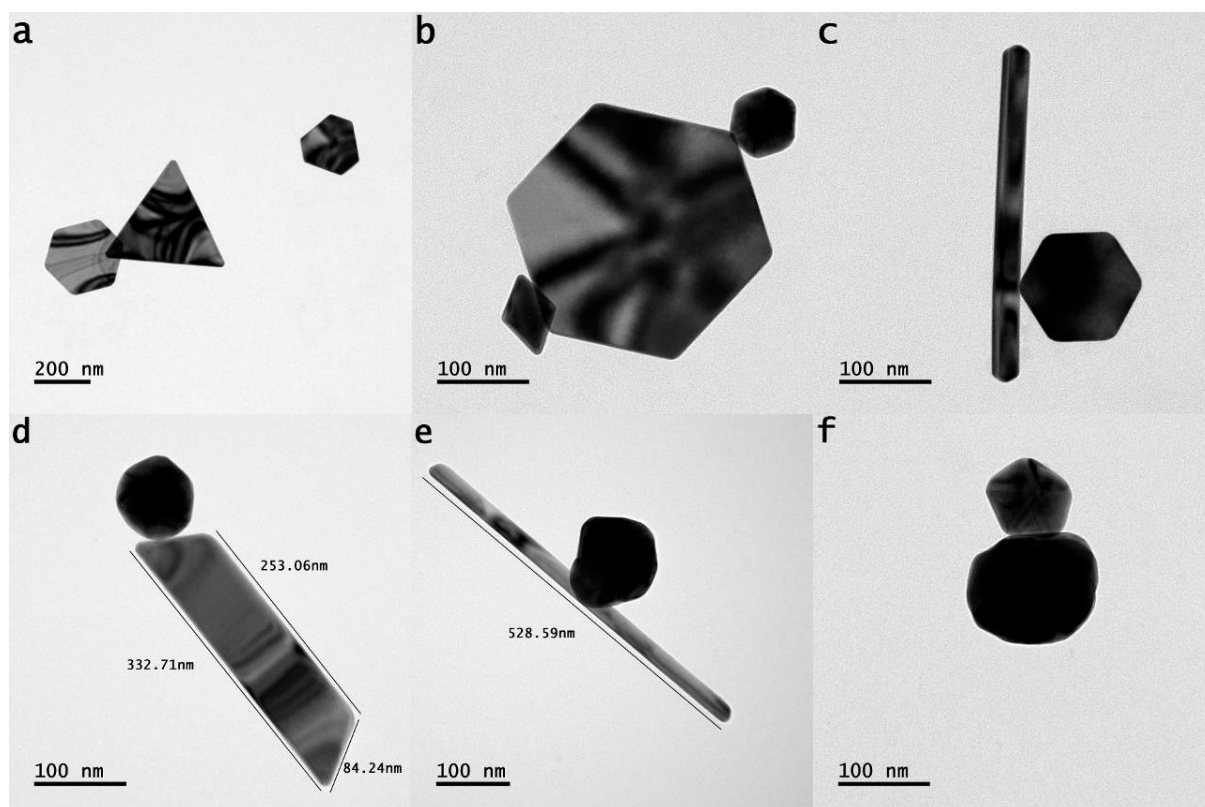


Figure 5: (a-o) bright field transmission microscope images of standalone triangle-, hexagon-, isosceles trapezoid-, rhombus-, rod-, pentagon-, tape- and skating-like particles

In addition to several geometric anisotropic shaped particles shown in Figure 5, particles of various geometric anisotropic shapes together with distorted ones developed as well, which are shown in Figure 6 where they possess different size and shape. In those particles, some of them possess very small size while others possess very large size despite of that they have the same shape in some cases.



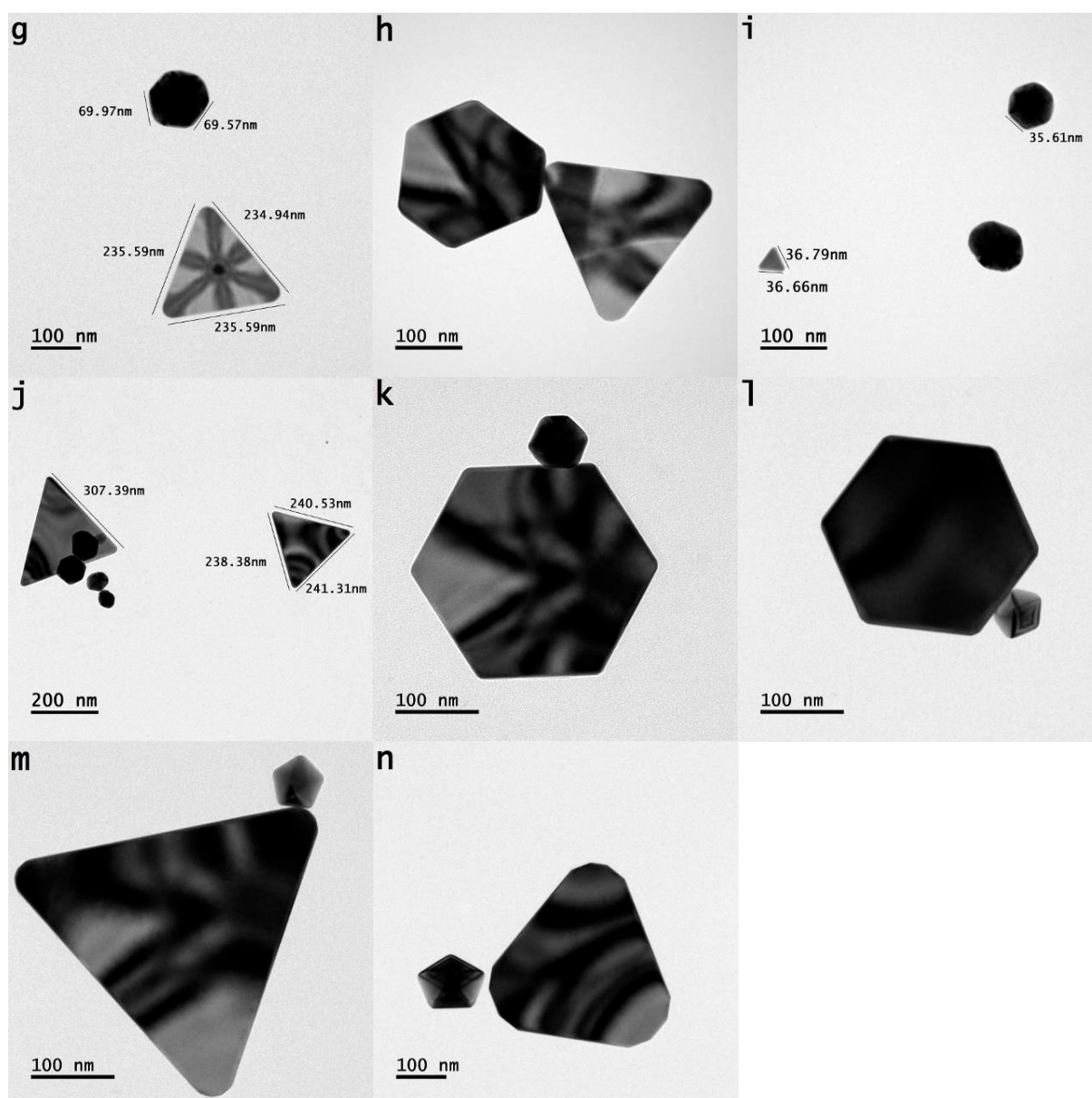


Figure 6: (a-n) bright field transmission microscope images of various geometric anisotropic shaped particles; in some cases, they are coupling to each other, in some cases, they keep the distance, and, in some cases, they adhere to distorted particles

Atoms of monolayer assembly at solution surface remained bound under the difference of force of oppositely faced poles. Once a gold atom (and atoms of other elements belonging to same family) comes at ground level (state), it deals (focuses) only single force, which is at dominating end. But prior to uplift gold atoms, they were at their solid state. So, just at the surface of solution triangular-shaped tiny particles, they deal localized force applicable in their regions for packing into particles of various

shapes. On terminating the packing of developing large-sized particles, they sink under free fall. The developing of various geometric anisotropic shaped particles and their sinking enables arriving new stock of gold atoms at air-solution interface, thus, forming new monolayer assembly at air-solution interface. The binding of mono layer developed in certain shape of developing particle bind to another layer placing over it under the lateral placement of electrons in their atoms where expansion and contraction of their clamping energy knots contribute. Expansion and contraction in the case of atomic behavior where its certain electron deal different states under varying gravitation and levitation behaviors is discussed elsewhere [50]. Atoms of one-dimensional arrays while in tiny particle or in large size particle maintain inter-spacing distance in addition to show only elongation of atoms. In the case of impinging electron streams from the external source, elongated atoms of tiny particles under opposite poles forces are further elongated. Thus, each tiny particle works as one unit while packing where new set of atoms arrive at solution surface under the reaction of force of entering splitted electron streams of argon atoms and photons of different wavelength just under the bottom copper tube. Force is being entered to solution through high density penetration of splitted electron streams of argon atoms along with photons of exceeding wavelengths normal to the solution surface. The photonic current propagated through elongated atoms of tiny grains of carbon film under the accelerated density resulting into enhanced field emission as discussed elsewhere [49]. Different states of electron clamping energy knot, both in terms of solid atom and gas atom, is discussed elsewhere [50].

Photons propagated through graphite rod, they provided energy to dissociate gold atoms from the precursor at solution surface, thus, forming monolayer assembly around the pulse-based electronphoton-solution interface is under the reaction of force provided by the electron streams along with the increasing wavelength of photons in the light glow developing centre of gravity at solution surface as well. Therefore, entering photons of different wavelengths along with penetration of electron streams in solution in the region forming the light glow don't appear to dissociate metallic atoms from precursor and their systematic placement at solution surface while uplifting in each cycle of bipolar pulse ON time is under the reaction of that entering force. Therefore,

uplifting of atoms to solution surface is because of providing force through light glow while dissociation of metallic atoms from their precursor is under immersed graphite rod known as anode. Thus, developing monolayer assembly at solution surface under the uplifting of metallic atoms to solution surface is not only because of the one component but involving both light glow known in plasma generating at point of copper bottom known in cathode and propagating photons characteristic current through graphite rod known in anode also.

4. Conclusions

In this study, under optimized process parameters, various high aspect ratio geometric anisotropic shaped particles of gold developed in pulse-based electron-photon-solution interface process. Under the tuned input power, high density of photons characteristic current propagated through graphite rod transformed into energy on entering to solution resulting into dissociates gold atoms from the precursor. When force behind electron streams enters in the solution, as a reaction, dissociated gold atoms are uplifted. The forcing energy of photons under set pulse ON time generating at the bottom of copper capillary entering in solution under high density contribute as well to uplift atoms to solution surface under the reaction of their entrance.

A monolayer assembly developed around the light glow in each pulse cycle where placing horizontally packets of nano shape energy, they result into develop loosely joint triangular-shaped tiny particles of monolayer following by separation into equal two same shape tiny particles under the force of opposite poles between their two connected atoms because of perturbed axes. Atoms of each tiny particle of triangular shape elongate under the force of surface format working along opposite poles from their centers where each one-dimensional array of atoms transforms into structure of smooth element, thus, working as one unit to pack at centre of light glow under immersing force because of the design of process. A tiny particle doesn't go for pre-allocated region of packing of developing particle unless it has geometry of equilateral triangle shape. Triangular-shaped tiny particles structure of smooth elements initiate packing at pre-allocated regions first at centre of light glow following by unfilled regions of developing mono layers in developing various particles of high anisotropy. The

developed feature of tiny particles self-ensured the points (regions) of their packings, thus, their packing results into develop certain shape particle which possesses unprecedented features not possible to attain through other means.

Prior to pack elongated tiny particles, they elongated further while impinging electron streams at electron-solution interface. On separation into two equal triangular-shaped tiny particles, a tiny particle turned and directed towards already reserved region of developing particle and same is the case for the companion tiny particle, but packs aside to the earlier packed one. The numbers of initially packed tiny particles, at one time, from different zones of solution surface nucleate certain shape particle. Initial number of packed tiny particles, at one time and their continuity in the packing along with size of developed tiny particle determine the shape and size of particle. The synchronization of the setup resulted into develop several unprecedented featured particles in different sizes and shapes. Present study sets new trends in the field of materials science, physics, nanoscience and nanotechnology.

Acknowledgements

Mubarak Ali thanks National Science Council (now MOST) Taiwan (R.O.C.) for awarding postdoctorship: NSC-102-2811-M-032-008 (August 2013-July 2014). Although, Dr. Yeh is co-author of this paper yet first author appreciates giving his time and arriving from Hsinchu to conduct TEM operation under the given directions.

References

- [1] P. Kim, C. M. Lieber, Nanotube Nanotweezers, *Science* **286**, (1999) 2148-2150.
- [2] Z. Tang, N. A. Kotov, M. Giersig, Spontaneous Organization of Single CdTe Nanoparticles into Luminescent Nanowires, *Science* **297**, (2002) 237-240.
- [3] Z. Tang, Z. Zhang, Y. Wang, S. C. Glotzer, N. A. Kotov, Self-Assembly of CdTe Nanocrystals into Free-Floating Sheets, *Science* **314**, (2006) 274-278.
- [4] Y. Liu, X. Zhang, Metamaterials: a new frontier of science and technology, *Chem. Soc. Rev.* **40**, (2011) 2494-2507.
- [5] A. Kuzyk, *et al.* DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response, *Nature* **483**, (2012) 311-314.

- [6] J. Kim, Y. Lee, S. Sun, Structurally ordered FePt nanoparticles and their enhanced catalysis for oxygen reduction reaction, *J. Am. Chem. Soc.* **132**, (2010) 4996-4997.
- [7] K. Kusada, *et al.* Discovery of face-centered-cubic ruthenium nanoparticles: facile size-controlled synthesis using the chemical reduction method, *J. Am. Chem. Soc.* **135**, (2013) 5493-5496.
- [8] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, Synthesis of Thiol-derivatised Gold Nanoparticles in a Two-phase Liquid-Liquid System, *J. Chem. Soc., Chem. Commun.* (1994) 801-802.
- [9] R. L. Whetten, *et al.* Nanocrystal Gold Molecules, *Adv. Mater.* **8**, (1996) 428-433.
- [10] L. O. Brown, J. E. Hutchison, Formation and Electron Diffraction Studies of Ordered 2-D and 3-D Superlattices of Amine-Stabilized Gold Nanocrystals, *J. Phys. Chem. B* **105**, (2001) 8911-8916.
- [11] M. Brust, C. J. Kiely, Some recent advances in nanostructure preparation from gold and silver particles: a short topical review, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **202**, (2002) 175-186.
- [12] G. M. Whitesides, M. Boncheva, Beyond molecules: Self-assembly of mesoscopic and macroscopic components, *Proc. Natl. Acad. Sci. USA* **99**, (2002) 4769-4774.
- [13] J. Huang, F. Kim, A. R. Tao, S. Connor, P. Yang, Spontaneous formation of nanoparticle stripe patterns through dewetting, *Nature Mater.* **4**, (2005) 896-900.
- [14] S. C. Glotzer, *et al.* Self-assembly of anisotropic tethered nanoparticle shape amphiphiles, *Curr. Opin. Colloid Interface Sci.* **10**, (2005) 287-295.
- [15] S. C. Glotzer, M. J. Solomon, Anisotropy of building blocks and their assembly into complex structures, *Nature Mater.* **6**, (2007) 557-562.
- [16] S. Link, M. A. El-Sayed, Shape and size dependence of radiative, nonradiative and photothermal properties of gold nanocrystals, *Int. Rev. Phys. Chem.* **19**, (2000) 409-453.
- [17] D. Vanmaekelbergh, Self-assembly of colloidal nanocrystals as route to novel classes of nanostructured materials, *Nano Today* **6**, (2011) 419-437.

- [18] C. P. Shaw, D. G. Fernig, R. Lévy, Gold nanoparticles as advanced building blocks for nanoscale self-assembled systems, *J. Mater. Chem.* **21**, (2011) 12181-12187.
- [19] Y. Negishi, *et al.* A Critical Size for Emergence of Nonbulk Electronic and Geometric Structures in Dodecanethiolate-Protected Au Clusters, *J. Am. Chem. Soc.* **137**, (2015) 1206-1212.
- [20] N. Liu, M. L. Tang, M. Hentschel, H. Giessen, A. P. Alivisatos, Nanoantenna-enhanced gas sensing in a single tailored nanofocus, *Nat. Mater.* **10**, (2011) 631-637.
- [21] N. Li, P. Zhao, D. Astruc, Anisotropic Gold Nanoparticles: Synthesis, Properties, Applications, and Toxicity, *Angew. Chem. Int. Ed.* **53**, (2014) 1756-1789.
- [22] M. L. Brongersma, N. J. Halas, P. Nordlander, Plasmon-induced hot carrier science and technology, *Nature Nanotechnol.* **10**, (2015) 25-34.
- [23] G. van Anders, D. Klotsa, N. K. Ahmed, M. Engel, S. C. Glotzer, Understanding shape entropy through local dense packing, *Proc. Natl. Acad. Sci. U.S.A.* **111**, (2014) E4812–E4821.
- [24] V. N. Manoharan, Colloidal matter: Packing, geometry, and entropy, *Science* **349**, (2015).
- [25] S. Atkinson, F. H. Stillinger, S. Torquato, Existence of isostatic, maximally random jammed monodisperse hard-disk packings, *Proc. Natl. Acad. Sci. U.S.A.* **111**, (2015) 18436-18441.
- [26] W. -H. Chiang, C. Richmonds, R. M. Sankaran, Continuous-flow, atmospheric-pressure microplasmas: a versatile source for metal nanoparticle synthesis in the gas or liquid phase, *Plasma Sources Sci. Technol.* **19**, (2010) 034011-18.
- [27] D. Mariotti, J. Patel, V. Švrček, P. Maguire, Plasma –Liquid Interactions at Atmospheric Pressure for Nanomaterials Synthesis and Surface Engineering, *Plasma Process. Polym.* **9**, (2012) 1074-1085.
- [28] J. Patel, L. Němcová, P. Maguire, W. G. Graham, D. Mariotti, Synthesis of surfactant-free electrostatically stabilized gold nanoparticles by plasma –induced liquid Chemistry, *Nanotechnology* **24**, (2013) 245604-14.

- [29] X. Huang, Y. Li, X. Zhong, Effect of experimental conditions on size control of Au nanoparticles synthesized by atmospheric microplasma electrochemistry, *Nanoscale Research Lett.* **9**, (2014) 572-578.
- [30] N. Shirai, S. Uchida, F. Tochikubo, Synthesis of metal nanoparticles by dual plasma electrolysis using atmospheric dc glow discharge in contact with liquid, *Jpn. J. Appl. Phys.* **53**, (2014) 046202-046207.
- [31] C. Richmonds, *et al.* Electron-transfer reactions at the plasma-liquid interface, *J. Am. Chem. Soc.* **133**, (2011) 17582-17585.
- [32] M. Witzke, P. Rumbach, D. B. Go, R. M. Sankaran, Evidence for the electrolysis of water by atmospheric-pressure plasmas formed at the surface of aqueous solutions, *J. Phys. D: Appl. Phys.* **45**, (2012) 442001-05.
- [33] J. Hieda, N. Saito, O. Takai, Exotic shapes of gold nanoparticles synthesized using plasma in aqueous solution, *J. Vac. Sci. Technol. A* **26**, (2008) 854-856.
- [34] N. Saito, J. Hieda, O. Takai, Synthesis process of gold nanoparticles in solution plasma. *Thin Solid Films* **518**, (2009) 912-917.
- [35] M. A. Bratescu, S. -P. Cho, O. Takai, N. Saito, Size-Controlled Gold Nanoparticles Synthesized in Solution Plasma, *J. Phys. Chem. C* **115**, (2011) 24569-24576.
- [36] Y. K. Heo, M. A. Bratescu, D. Aburaya, N. A. Saito, phonon thermodynamics approach of gold nanofluids synthesized in solution Plasma, *Appl. Phys. Lett.* **104**, (2014) 111902-05.
- [37] K. Furuya, Y. Hirowatari, T. Ishioka, A. Harata, Protective Agent-free Preparation of Gold Nanoplates and Nanorods in Aqueous H₂AuCl₄ Solutions Using Gas-Liquid Interface Discharge, *Chem. Lett.* **36**, (2007) 1088-1089.
- [38] M. Ali, I -N. Lin, The effect of the Electronic Structure, Phase Transition, and Localized Dynamics of Atoms in the formation of Tiny Particles of Gold. <http://arxiv.org/abs/1604.07144>.
- [39] M. Ali, I -N. Lin, Development of gold particles at varying precursor concentration. <http://arXiv.org/abs/1604.07508>.
- [40] M. Ali, I -N. Lin, Tapping opportunity of tiny shaped particles and role of precursor in developing shaped particles. <http://arxiv.org/abs/1605.02296>.

- [41] M. Ali, I –N. Lin, Controlling morphology-structure of particles at different pulse rate, polarity and effect of photons on structure. <http://arxiv.org/abs/1605.04408>.
- [42] M. Ali, I –N. Lin, Formation of tiny particles and their extended shapes -Origin of physics and chemistry of materials. <http://arxiv.org/abs/1605.09123>.
- [43] M. Ali, The study of tiny shaped particle dealing localized gravity at solution surface. <http://arxiv.org/abs/1609.08047>.
- [44] M. Ali, Atoms of electronic transition deform or elongate but do not ionize while inert gas atoms split. <http://arxiv.org/abs/1611.05392>.
- [45] M. Ali, Structure evolution in atoms of solid state dealing electron transitions. <http://arxiv.org/abs/1611.01255>.
- [46] M. Ali, Revealing the Phenomena of Heat and Photon Energy on Dealing Matter at Atomic level. <https://www.preprints.org/manuscript/201701.0028/v11>.
- [47] M. Ali, Nanoparticles-Photons: Effective or Defective Nanomedicine. *J. Nanomed. Res.* **5** (2017) 00139.
- [48] M. Ali, M. Ürgen, Switching dynamics of morphology-structure in chemically deposited carbon films –A new insight, *Carbon* **122** (2017) 653-663.
- [49] M. Ali, I –Nan. Lin, Phase transitions and critical phenomena of tiny grains thin films synthesized in microwave plasma chemical vapor deposition and origin of v1 peak. <http://arXiv.org/abs/1604.07152>.
- [50] M. Ali, Why atoms of some elements are in gas state and some in solid state, but carbon works on either side (2018). (in submission).

Authors' biography:



Mubarak Ali graduated from University of the Punjab with B.Sc. (Phys& Maths) in 1996 and M.Sc. Materials Science with distinction at Bahauddin Zakariya University, Multan, Pakistan (1998); thesis work completed at Quaid-i-Azam University Islamabad. He gained Ph.D. in Mechanical Engineering from Universiti Teknologi Malaysia under the award of Malaysian Technical Cooperation Programme (MTCP;2004-07) and postdoc in advanced surface technologies at Istanbul Technical University under the foreign fellowship of The Scientific and Technological Research Council of Turkey (TÜBİTAK; 2010). He completed another postdoc in the field of nanotechnology at Tamkang University Taipei (2013-2014) sponsored by National Science Council now M/o Science and Technology, Taiwan (R.O.C.). Presently, he is working as Assistant Professor on tenure track at COMSATS Institute of Information Technology, Islamabad campus, Pakistan (since May 2008) and prior to that worked as assistant director/deputy director at M/o Science & Technology (Pakistan Council of Renewable Energy Technologies, Islamabad; 2000-2008). He was invited by Institute for Materials Research (IMR), Tohoku University, Japan to deliver scientific talk on growth of synthetic diamond without seeding treatment and synthesis of tantalum carbide. He gave several scientific talks in various countries. His core area of research includes materials science, physics & nanotechnology. He was also offered the merit scholarship (for PhD study) by the Government of Pakistan but he couldn't avail. He is author of several articles published in various periodicals (<https://scholar.google.com.pk/citations?hl=en&user=UYjvhDwAAAAJ>).



I-Nan Lin is a senior professor at Tamkang University, Taiwan. He received the Bachelor degree in physics from National Taiwan Normal University, Taiwan, M.S. from National Tsing-Hua University, Taiwan, and the Ph.D. degree in Materials Science from U. C. Berkeley in 1979, U.S.A. He worked as senior researcher in Materials Science Centre in Tsing-Hua University for several years and now is faculty in Department of Physics, Tamkang University. Professor Lin has more than 200 referred journal publications and holds top position in his university in terms of research productivity. Professor I-Nan Lin supervised several PhD and Postdoc candidates around the world. He is involved in research on the development of high conductivity diamond films and on the transmission microscopy of materials.