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Predictor packing in developing unprecedented shaped colloidal particles

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Abstract –Developing particles of different 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. Gold atoms of certain transition state develop monolayer assembly at solution surface around the light glow (known in argon plasma) being generated at bottom of copper capillary (known in cathode). The rate of uplifting gold atoms to solution surface is being controlled by forcing energy (travelling photons) pursuing electrons and high energy photons (in high density) entering to solution. Gold atoms dissociated from the precursor under dissipating heat energy into the solution supplied under propagating photons characteristic current through immersed graphite rod (known in anode). Placing packets of nano shape energy of tuned pulse protocol over compact monolayer assembly comprising transition state atoms develop tiny-sized particles of formed shape. On separation of joint tiny particles into two equilateral triangular-shaped tiny particles, exerting forces of surface format elongate atoms of one-dimensional arrays converting them into structures of smooth elements. Due to immersing level of force, such tiny-shaped particles pack from

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different zones at centre of light glow where they assembled structures of smooth elements for developing mono-layers of different shapes of particles. Developing one-dimensional particles deal assembling of structures of smooth elements of packing tiny-shaped particles from nearly rearward zones of reflection of north-south poles, whereas, developing multi-dimensional particles deal assembling of structures of smooth elements of packing tiny-shaped particles from the east-west poles and near regions. Depending on the number of assembled structures of smooth elements at point of nucleation, packing of tiny-shaped particles from different zones develop different shapes of the anisotropic particles. At fixed precursor concentration, increasing the process time results into develop particles of low aspect ratio. Under tuned parameters, developing mechanisms of particles exhibiting unprecedented features are discussed.

Keywords: Fundamental Forces; Transition state gold atoms; Packing and assembling; Process parameters; One-dimensional particles; Multi-dimensional particles.

1. Introduction

To design a different sort of material, it is remained crucial since the birth of materials science. Among the categories of materials, the synthesis of materials in particles shape and size remained dominant in the past few decades as well as in the current ages and they hold a promising future too. 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. The required size and shape of particles of diversified materials may be directly or indirectly the origin of certain cutting-edge applications.

But, undoubtedly, when the nanoparticles and particles showing the same morphology-structure (features of shapes) under their microscopic images, they raise a combined 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 of same shape and structure 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 their electronic structure under unchanged dynamics is to be remained the same because of the same nature since existence.

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]. The catalytic activity of metallic nanostructures is 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 supperlattices 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 and potentially 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 development 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

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and size of metallic structures have remained under the 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 a 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 beauty and evolution of science behind technological advanced materials.

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 [26-29]. While synthesizing spherical-shaped nanoparticles, electron flux at a 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 which was the cause of anisotropic growth [34]. The influence of Brownian motion along with the 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 developing various tiny-sized particles under different process conditions is discussed [38]. The development of gold nanoparticles and particles under varying precursor concentration is studied [39]. Tapping opportunity of tiny-shaped particles and role of precursor in developing shaped particles under the same setup is presented in a separate study [40]. Different shaped tiny particles along with their extended shapes developed under varying the ratio of bipolar pulse and pulse polarity modes [41]. Development of tiny-sized particles and extended shaped particles under increasing process duration along with origin of physics and chemistry of

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materials is disclosed where role of van der Waals interactions and surface plasmons phenomenon are disregarded [42]. A detailed study is presented discussing development mechanism of a tiny-shaped particle dealing localized gravity and when developing mono-layer of certain shape developing particle [43]. Atoms of electron transitions elongate or deform but do not ionize where forcing energy (photons) propagating through inter-state electron gaps is related to photonic current instead of electronic (electric) current [44]. Atoms of those electron transitions where conservative forces are involved to engage binding energies for evolving their different dimension and format structures is discussed elsewhere [45]. The phenomena of heat and photon energy are revealed while dealing the matter at atomic level [46]. Atomic behaviors along with the behavior of field forces are quite diligent in showing their performance for nanoparticles and when using them for nanomedicine [47]. A study on switching dynamics of morphology-structure under varying process parameters in carbon-deposited films is reported elsewhere [48].

To synthesize tiny-sized particles and large-sized particles for different suitable materials, it is an easy task, but it is difficult to understand and pinpoint their underpinning mechanisms of development. This work describes fundamental process of developing triangular-shaped tiny particles and in relation to their predictor packings for developing different geometric anisotropic particles where certain force-energy behaviors originated under the set process conditions. Under set parameters, gold atoms dissociated from the precursor as per dissipated heat energy into the medium which transferred through immersed graphite rod where uplifting to solution surface against the reaction of entrance of electron streams (carrying forced energy of travelling photons) and high energy photons (in high density) where packets of nano shape energy (generated under tuned pulse protocol) bind them in own (formed) shape dealing the predictor packings to develop various particles of one-dimensional shapes and multi-dimensional shapes, in large number.

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 to conduct experiment under the optimized conditions as shown in Figure 1. Copper tube internal diameter 3 mm along with flowing argon gas was utilized as a source of forced energy electron streams and forcing energies (travelling photons) where 100 sccm flow rate of argon gas was maintained through digital 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 where distance (gap) between the bottom of copper capillary and solution surface was maintained ~ 0.4 mm. The length (distance) between the copper capillary and 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 ±1°C accuracy. An optimized precursor concentration for developing geometric anisotropic particles in high number was chosen 0.3 mM (after the conduction of many experiments results of which are presented in different studies [38-42]). Total quantity of solution prepared was 100 ml. The processing time of the solution was set 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), which has almost stabilized in the duration of the afterward process. Step-up transformer increased voltage 40 times. Bipolar pulse ON/OFF time was set 10 µsec.

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 (in Figure S1). Zones related to the placing packets of nano shape energy under controlled tuned pulse protocol, impinging electron streams and traveling photons of different wavelengths at the surface of monolayer gold atoms are pointed out by (7), (8) and (9), respectively in Figure 1. Further details of these are 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

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drop of solution from prepared concentration was poured on copper grid and was kept in Photoplate degasser (JEOL EM-DSC30) for the elimination of moisture.

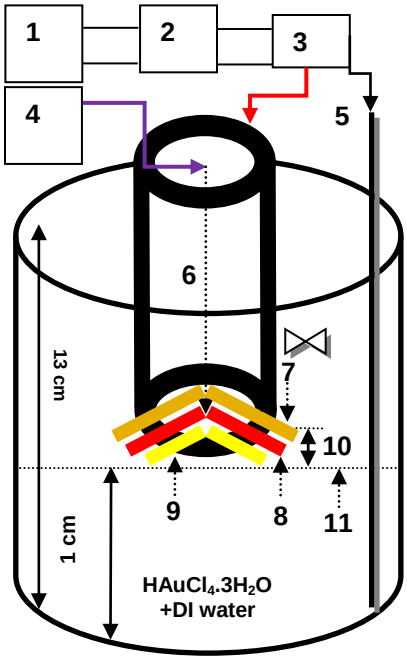

Figure 1: Layout of pulse-based electronphoton-solution interface process; (1) power supply, (2) pulse power controller, (3) step-up transformer, (4) argon gas, (5) graphite rod, (6) inner (hollow) region of copper capillary, (7) placing of nano shape energy in a double-packet (outer region of light glow), (8) electron-solution interface (middle region of light glow), (9) photon-solution interface (inner region of light glow), (10) distance between copper capillary and solution surface ~0.4 mm and (11) air-solution interface

3. Results and discussion

Surplus photonic current under set power propagates through the graphite rod, which is working for the positive terminal as known conventionally in the flow of current through wire while it is known as anode in the case of electrochemistry. Mainly, the photonic current propagates through the wire known in negative terminal which is connected to copper capillary handling flow of argon gas also. The flowing argon gas splitted into the electron streams at the bottom of copper capillary. Because of no availability of unfilled states in the argon gas atoms and due to excess given field of propagating photons characteristic current through their inter-state electron gap resulting into split them where light glow is observed [44], which is known in plasma and that glow is just ignited at the bottom of the copper capillary, which is known in cathode. Gold atoms dissociated from the precursor by dissipated heat energy where the source of that heat

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energy was the dismantling of entered photons to the solution. Those photons propagated in the graphite rod, which worked as positive terminal, in the form of photons characteristic current. That heat energy is resulted from the interacted photons characteristic current to solution as they propagated through inter-state electron gaps of graphitic state atoms of the immersed graphite rod. A separate study discussed conversion of photon energy to heat energy while interacting to certain medium [46]. The uplifting of metallic atoms to solution surface while dealing the transition is under the reaction of entering forced energy of electrons and high energy photons (in high density). The high energy photons entering to solution are resulted because of the splitting of flowing argon atoms where they didn't work for splitted electrons. The splitted electrons carry their own photons (force-energy) to pursue inside the solution.

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 the normal manner to their points of generation entered to solution instead of traveling along the air-matter interface because they carried their direction of travelling given at the point of their generation [41]. Argon gas was used to activate the process of generating electron streams and high energy photons, hence, developing gold particles in different sizes and shapes. Splitting of inert gas atoms not only delivered electrons to impinge underlying gold atoms but also enabled the propagation of photons characteristic current to inter-state electron gaps, prior to split, resulting into allow them to travel in their increasing wavelength under the ease of 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 a place utilizing forcing energy to align underlying electronic structure of elongated triangular-shaped tiny particle in the case of perturbed electron states of atoms, thus, modify further the structure of elongated atoms of tiny-shaped particle into structure of flatten smooth elements [43]. The inert gas atoms split under the application of excess propagation of photons characteristic current through their inter-state electron gaps for which further detail is given elsewhere [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 where tuned pulse protocol was controlled during each pulse ON/OFF time cycle. Underneath copper

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capillary where monolayer assembly of gold atoms is developed, packets of nano shape energy are placed horizontally over them resulting into bind atoms of monolayer assembly into tiny particles of own shape nearly all around the region of light glow at solution surface. 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 sized particles of monolayer in their own shape. The gold atoms when bound into monolayer tiny-sized particle at solution surface under the energy of triangular-shaped packet, they were under the re-crystallization state [43]. A double-packet of nano shape energy placed over the compact monolayer assembly results into bind gold atoms (of transition state) into the formed shape where the orientation of electrons was more along the adjacent as exerting naturally available opposite pole forces of surface format. Placing of nano shape energy in a double-packet is resulted under the bipolar pulse ON/OFF time (10 µsec). Placing of nano shape energy in a single packet is resulted under the unipolar pulse ON/OFF time (10 µsec) as for the case in reference 41 (in Figure 1). As graphite rod is immersed into the solution from bottom level to top level of solution, surplus propagation of photons related to current (wavelength lower than hard X-rays and in the gap of inter-state electron gaps) occurs into it, on leaving the propagation of inter-state electron gaps, it enters in the solution while converting into heat energy under the interaction of medium 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 their force of reaction results into develop the monolayer assembly of atoms. Due to the feature of bipolar pulse having unity ratio of pulse OFF to ON time, each tiny-sized particle is first developed in shape of two joint triangles. The detail of their separation into two equal equilateral triangular-shaped tiny particles is given elsewhere [41-43].

Figure 2 shows dissociation of gold atoms under the supply of heat energy *via* immersed graphite rod and their uplifting to solution surface under the entering forced energy streams of splitted electrons and photons of high energy (in high density). These both constitute the light glow (plasma), thus, hereafter, where a light glow is referred it is related to both electrons carrying photons and standalone photons.

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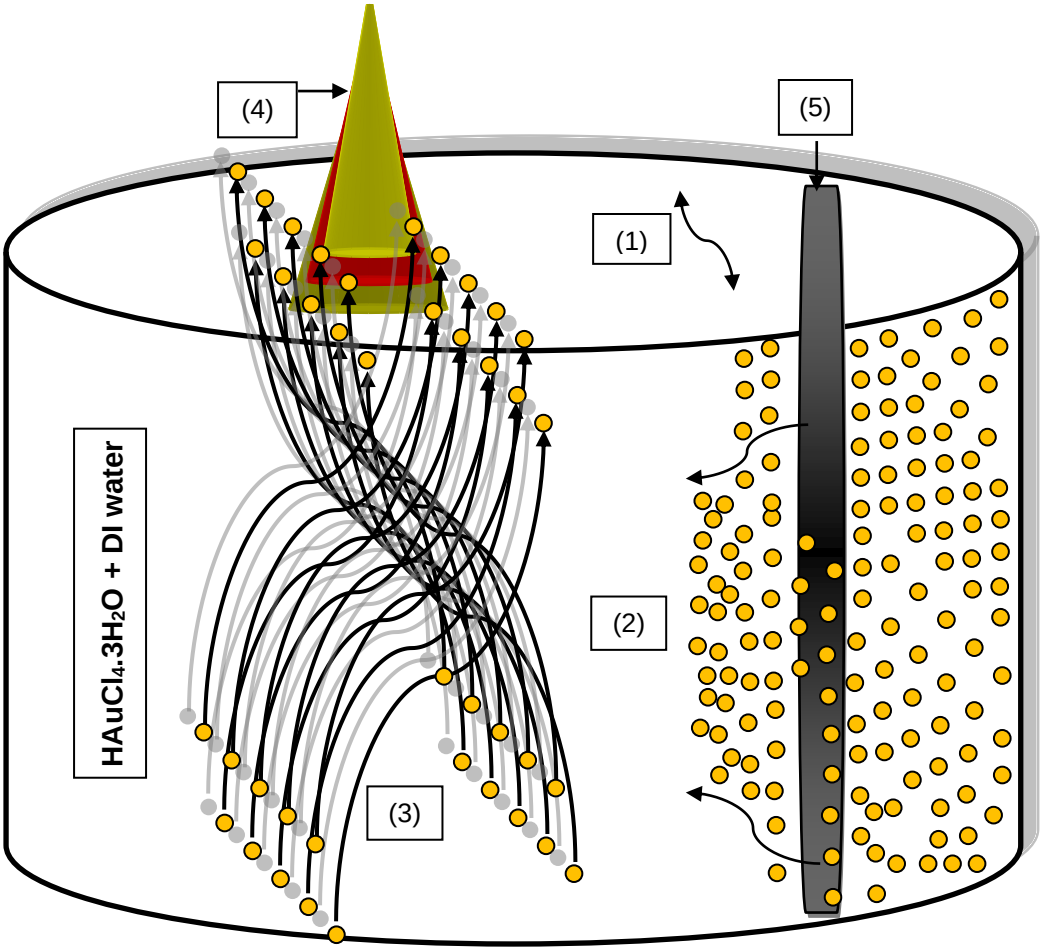

Figure 2: Gold atoms dissociating from the gold precursor for uplifting to solution surface under their certain transition state; (1) solution surface, (2) dissociating gold atoms from the precursor on dissipating the heat energy resulted on dismantling of photons (propagated in characteristic current through inter-state electron gaps of atoms of graphite rod) under the interaction inside the solution, (3) uplifting of gold atoms under the reaction of entering force-energy of splitted electrons and standalone photons of high density, (4) light glow known as plasma generating at bottom points of copper capillary known as cathode and (5) graphite rod handling excess propagation of photons (characteristic current) known as anode

Signatures of nano shape energy, electron streams and high energy photons (in high density) covering 3D space while interacting circular plane surface of solution are shown in Figure S2; accelerated electron streams under gained instantaneous velocities by means of pursuing photons and high energy photons (in high density) form the light glow, which is known in their plasma. Therefore, interactions of nano shape energy (outer circular cone-shape), electron streams (middle circular cone-shape) and high energy photons (inner circular cone-shape) to compact monolayer assembly of transition state gold atoms at solution surface are labelled respectively in Figure S2; the

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points of generating packets of nano shape energy, electron streams and high energy photons (in high density) at the bottom of copper capillary are also shown in (6).

At solution surface, gold atoms under transition state construct monolayer assembly nearly in the circular shape but by exempting the regions of zero-force axes as shown in Figure 3. Placed packets of nano shape energy bound transition state atoms of monolayer assembly into tiny-sized particle of own (formed) shape where having the monolayer three-dimensional structure in surface format, which is known in hcp structure or two-dimensional structure. However, our recently published work further elaborates the origin of developing three-dimensional structure of gold atoms where atoms of one-dimensional arrays remained non-elongated [40]. But, the evolution of structure in gold atoms and in atoms of other closely-related family of elements, they do not evolve three-dimensional structure under the natural span of their electron-dynamics as only maximum three sorts of forces can exert for dedicated state electron in those atoms because they deal the grounded format [45]. During processing $AgNO_3$ solution, there was no developing of triangular-shaped tiny particles although nearly the same process conditions were employed indicating that silver atoms deal transition state (re-crystallization state) to elongate at different level of ground surface as compared to the case of gold atoms [40]. In the case of gold solution, it was not like silver and entire solution in the beaker changed in a certain color under steady-state behavior; color of the solution changed at fast rate in the initial few seconds utilizing atoms for developing tiny-sized particles, nanoparticles and particles since start of process.

In view of above-said, our setup to process gold solution under optimized concentration of gold precursors along with pulse time, duration of processing solution along with positions of the copper capillary and graphite rod in glass beaker remained vital to process the solution for developing various shapes of anisotropic particles. But, the setup was not remained successful when the solutions of silver precursor and binary composition were processed. Placed double-packets of nano shape energy bind atoms of monolayer assembly into joint triangular-shaped tiny particles, in each case, where binding transition state gold atoms of monolayer assembly in their own (formed) shape as shown in Figure 3. 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

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the arrow signs where it sinks one step down under dealing the localized gravity. Binding of such mono-layers in developing particle of certain shape is through the lateral-orientation of electrons of elongated atoms of structures of smooth elements [43]. Tiny-shaped particles worked and directed as a one-unit from the regions of their developing to pack at already allocated unfilled regions to develop a certain shape particle under the immersing force exerting at the tips of their structures of smooth elements. Structures of smooth elements of triangular-shaped tiny particles while passing the regions of impinging electron streams may further elongate and prior to pack at centre of light glow for developing a certain shape particle. An electron imagines to underlying matter under the carrying force-energy of a photon is discussed elsewhere [46]. On assembling for certain particle, structures of smooth elements acquire further smoothness by travelling photons of interface.

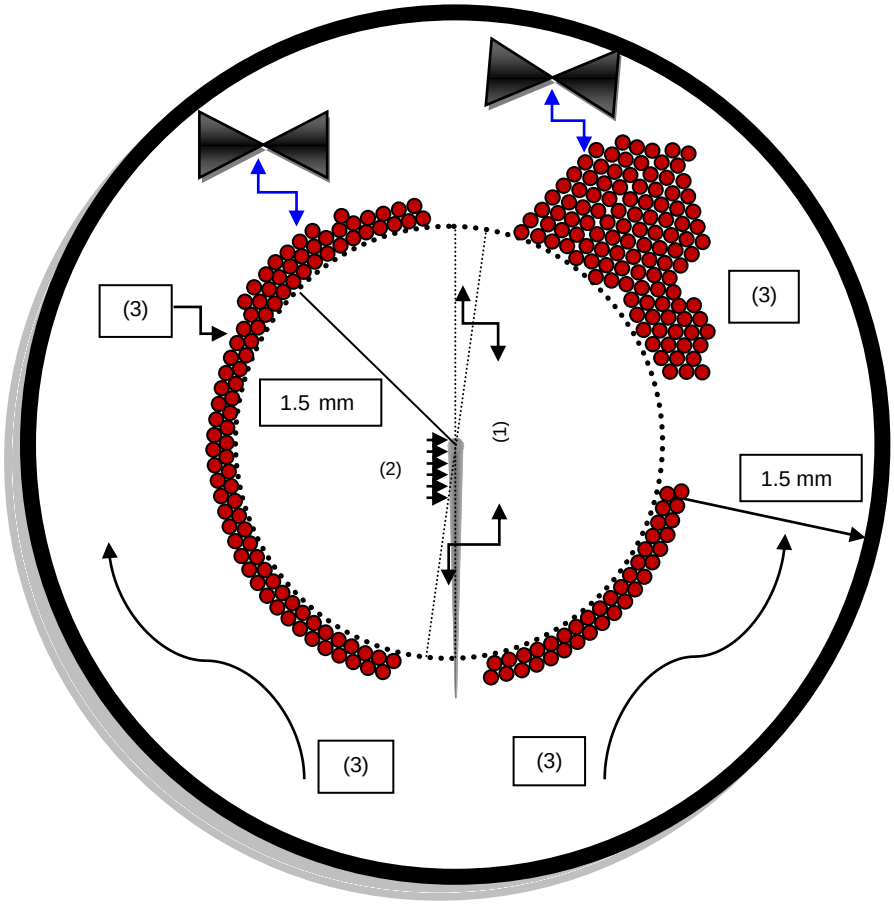

Figure 3: Gold atoms at solution surface in suitable circular zone width i.e. 1.5 mm where double-packets of nano shape energy placed over the compact monolayer assembly to bind transition state atoms in formed (own) shape and size where amalgamations of the atoms along the zero-force axis (rear-

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sides of the north and south poles) do not occur; (1) zero-force axes, (2) developing mono-layer and developed mono-layers of a certain shape developing particle, (3) monolayer assembly of transition state gold atoms around the favorable regions of the light glow dealing packets of nano shape energy

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 µsec) along with other set parameters described in the experimental details, the each developed tiny particle contained the two connecting triangular-shaped tiny particles. Joint triangular-shaped tiny particle separated into two equal triangular-shaped tiny particles under the difference of force exerted along their slightly perturbed opposite poles (at point of connection of their single atoms). It can be observed in the illustration given in Figure 3 where tiny particles of joint triangular-shape are developing on placing double-packets nano shape energy over the compact monolayer assembly of gold atoms.

The disconnected tiny-shaped particle is in queue to go for packing while following the packing of the earlier one in each case of separating a tiny particle of joint triangular shape into two equilateral triangular-shaped tiny particles. One triangular-shaped tiny particle directed tips of structures of smooth elements toward the regions of packing under exerting force of surface format in immersing manner till their reaching to those regions. In the similar manner, the other triangular-shaped tiny particles are arriving with their structures of smooth elements to pack at pre-allocated regions as a one-unit in each case to develop each mono-layer of developing certain shape particle. The termination of their packing at any point results into sinking of particle where each mono-layer binds under the mechanism of lateral-orientation of electrons [43]. In the case of rod- and bar-shaped particles, tiny-shaped particles were developed at oppositely-sided regions available at the sides of rear north-south poles on the solution surface as illustrated in Figure S3. Such shaped particles are said to be particles of one-dimensional shape but the packing of tiny-shaped particles in developing them remained from the two sides (opposite to each other from the centre point). In the case of plate-like particles in multi-dimensions, packed tiny-shaped particles also developed in triangular-shaped tiny particles but in the regions of east-west poles and near regions of east-west poles. To develop an ideal triangular-shaped particle, at one time, the tempo of packing remains the same from all three sides and for each tiny-shaped

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particle, it is at 120° angle. To develop hexagonal-shaped particle, at one time, the momentum of packing remains the same from all six sides where packing of each tiny-shaped particle remains at orientation of 60° angle and from the six different zones of solution surface.

Figure 4 shows developing of connected triangular-shaped tiny particles where the size is decreasing with prolonging the process duration. As discussed above, such tiny particles separated into equal triangular-shaped tiny particles under exerting force along their slightly perturbed axis. Decreasing the size of triangular-shaped tiny particles resulted into decrease the aspect ratio of their particles also because they are being developed by the packing of decreasing-sized tiny-shaped tiny particles as per reducing time of processing the solution. At start of the process, large-sized tiny-shaped particles are developed and their packings into certain shape particle also give the high aspect ratio of that particle. As the size of the tiny-shaped particle decreases on reducing the number of atoms per unit area at solution surface, particles of decreasing aspect ratio develop with time despite of the fact that they maintain the same shape of their tiny-sized particles (triangular-shaped tiny particles). Under the fixed concentration of precursor, the number of amalgamating atoms into monolayer assembly reduced significantly resulting into lower 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 developing tiny particle was varied depending on the ratio of pulse OFF to ON time also.

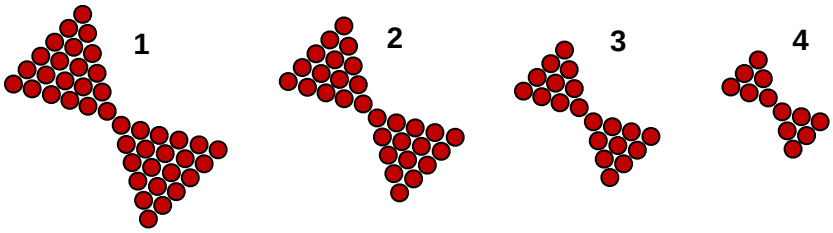

Figure 4: Size of connected triangular-shaped tiny particles (through point of connection of their single atoms) decreases with respect to process time under fixed precursor concentration of gold precursor

Each developing layer of the geometric anisotropic particle self-deal the packing as left vacant places provide the force of exertion to structures of smooth elements for each packing triangular-shaped tiny particle from the relevant zone. Therefore, the predictor packing is related to self-filling of unpacked regions of a developing particle in

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certain shape. May be, a complete mono-layer of developing geometric anisotropic particle developed for each step of pulse ON time (10 µsec). That developed mono-layer went down to solution surface while dealing the localized gravity and followed by developing a new mono-layer starting exactly at the centre of the one previously developed, in the same size and shape, as the developing of triangular-shaped tiny particles along with predictor packing remained the same for that period, the shape of developing particle is being maintained under the synchronization of the process. While developing upper layer, downward layer descends level upto ~0.3 nm (an approx. diameter of gold atom; lateral width), however, under the break of developing layers for next set period of pulse ON time (10 µsec), the particle sinked by leaving the solution surface completely resulting into leave the centre of light glow, thus, allowing to develop a new particle. Once, the process of developing a new mono-layer to develop certain shape 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-shaped particles around centre, the newly developed tiny-shaped particles started utilizing themselves under 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 sized tiny-shaped particles packed simultaneously at 120° angle placed side by side, it will result into develop a particle of triangular-shape and when six equal sized tiny-shaped particles simultaneously packed at 60° angle placed side by side, it will result into develop a particle of hexagonal-shape.

Figure 5 shows particles of various anisotropic shapes which were developed under predictor packing of triangular-shaped tiny particles arriving from the relevant regions of solution surface. The different shapes of particles in Figure 5 clearly figure out the degree of orientation at which predictor packing is taken place and in each plane of the particle by taking the centre of particle as a reference point. Therefore, photons working at the place help in constructing perfect smooth elements having approx. equal inter-spacing distance of each developed mono-layer of developing multi-dimensional shaped particle and one-dimensional shaped particle as illustrated in Figure S4.

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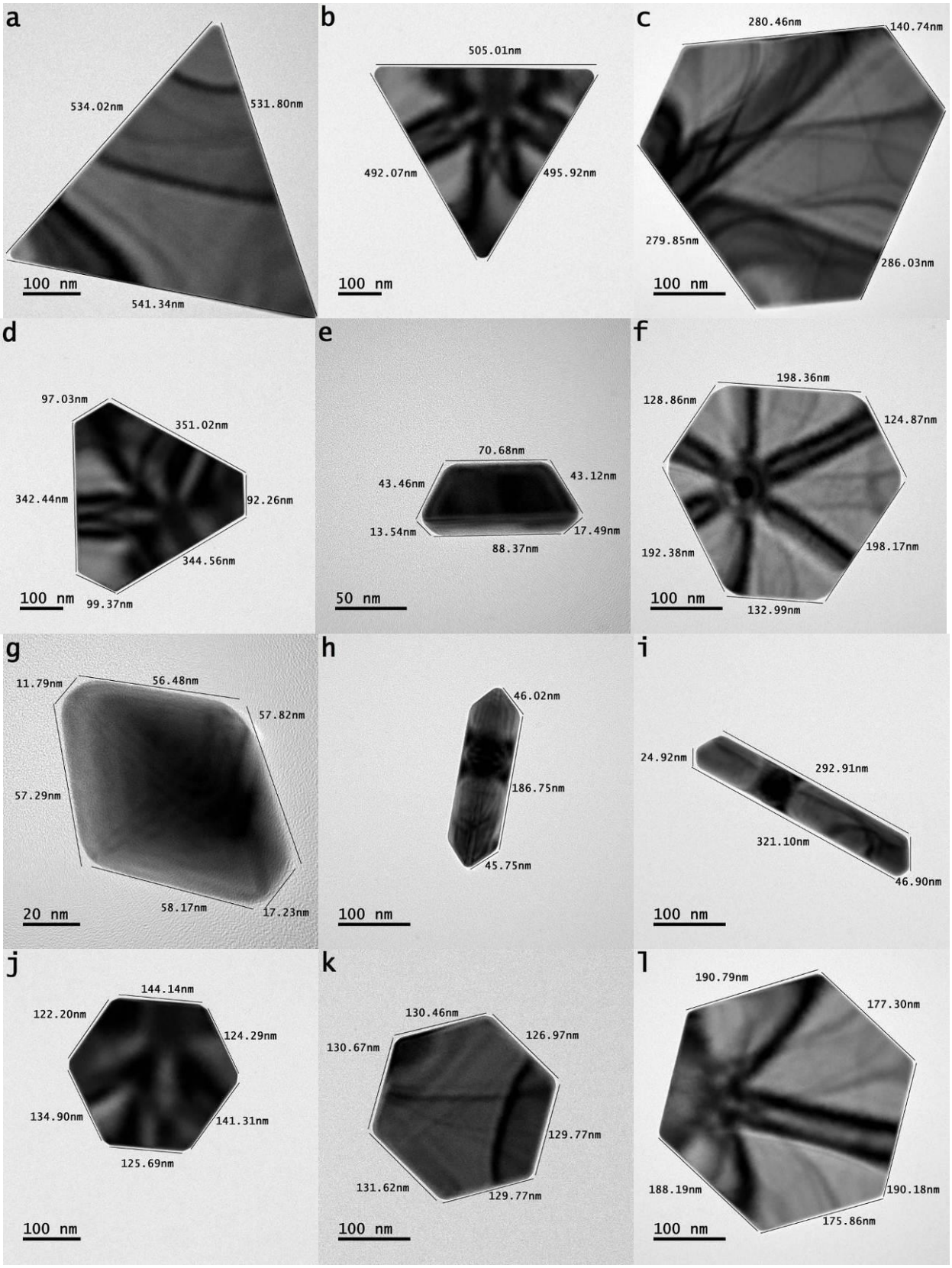

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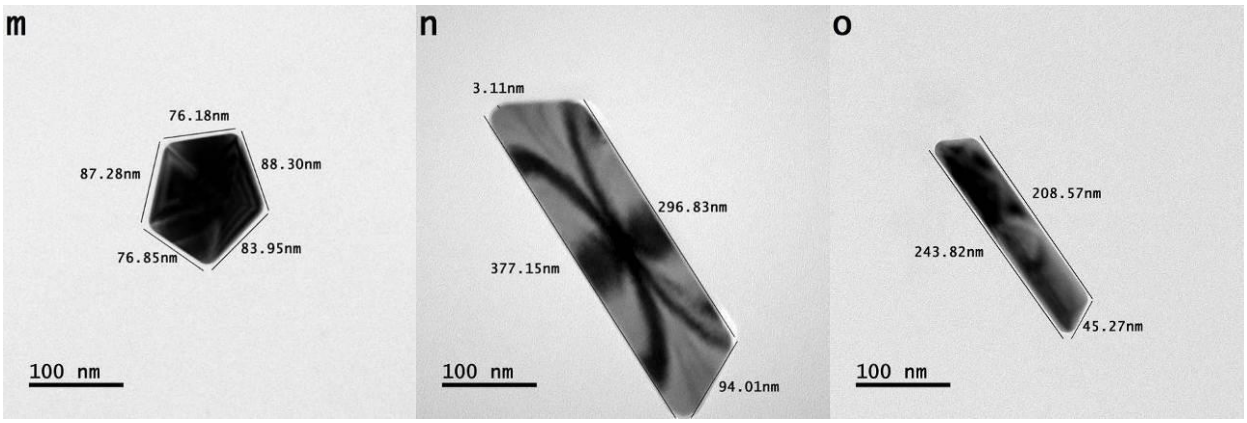
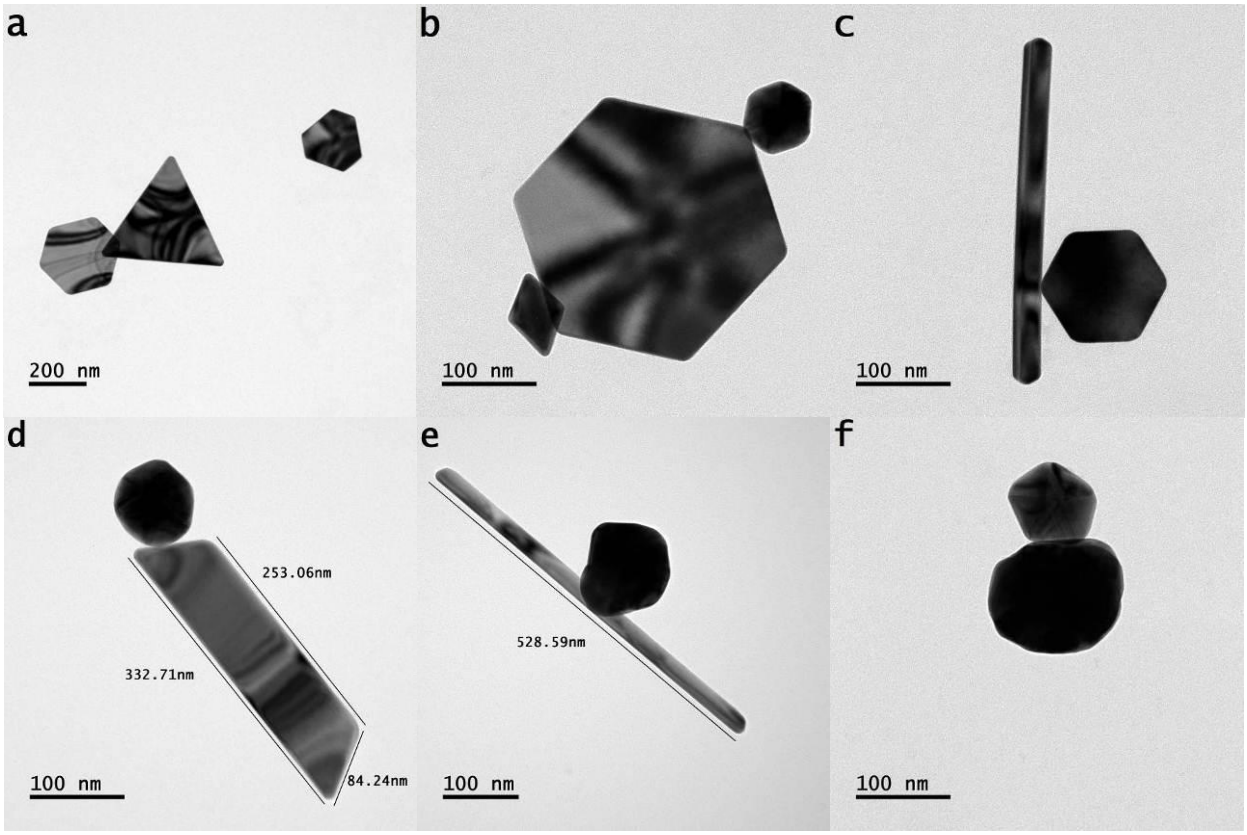


Figure 5: (a-o) bright field transmission microscope images of standalone triangle-, hexagon-, isosceles trapezoid-, rhombus-, rod-, pentagon-, tape- and skating-like particles

In addition to several shown geometric anisotropic particles in Figure 5, such particles adhere to each other or approach to each other and to distorted (amorphous structure) particles as well under prevailing forces as per their shape and their overall situation in the solution as 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.



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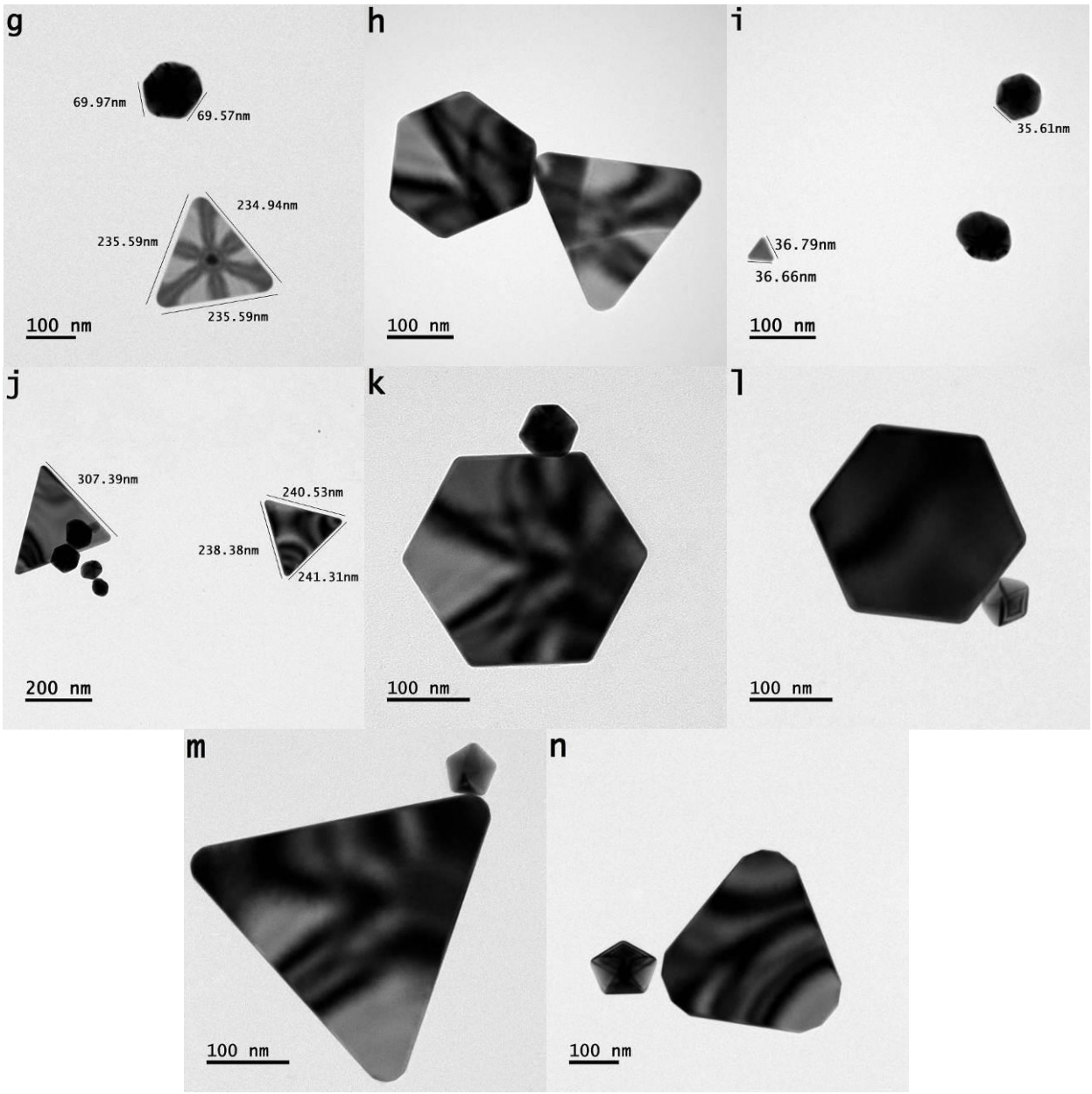

Figure 6: (a-n) bright field transmission microscope images of various geometric anisotropic particles; in some cases, they are coupling to each other, in some cases, they keep the distance, and, in some cases, they adhere to the distorted (amorphous structure) particles

In this work, an optimized pulse sequence (pulse ON/OFF time: 10 µsec) along with optimized parameters of developing geometric anisotropic particles (precursor concentration: 0.30 mM, distance between copper capillary and solution surface: 0.4 mm, input power, quantity of solution and shape of beaker, etc.) were employed. Unoptimized pulse sequence was studied as well [41] where developing particles start to develop in amorphous structure (distorted shape). Therefore, in the certain regions of

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solution and under the certain scheme of monolayer assembly, tiny-sized particles of shape other than equilateral triangle developed where their packing under mixed-dimension of exerting forces resulted into develop amorphous structure particle. They do not possess a specific shape, hence, possess anisotropy. Such particles are neither in their one-dimensional shape nor in their multi-dimensional shapes. They are related to distorted shapes. Particles of amorphous structure developed under the packing of those tiny-sized particles (or tiny-shaped particles) where they assemble structures of smooth elements under non-uniform (in mixed-dimension) exertion of forces. Further details of developing amorphous structure (distorted) particles is given elsewhere [39, 41].

Atoms of monolayer assembly at solution surface remained in their compact scheme. Gold atoms when at solution surface, they are in their certain transition state as they are not at their original level. But, a grounded level is below to the ground level surface. So, at solution surface, they deal the exerting forces of surface format at electron levels. But, prior to uplifting of gold atoms, they were in their different state. Therefore, just at the surface of solution, their atoms of one-dimensional arrays of triangular-shaped tiny particles elongate under the exertion of those forces. Elongated atoms of each one-dimensional array developed a structure of smooth element [43]. Therefore, while packing a triangular-shaped tiny particle for developing a certain shape particle, all structures of smooth elements belonging to it work as a one-unit prior to their assembling but, on reaching in the required regions of assembling, they adjust them as per the previously assembled ones where controlled force handling their inter-spacing distance, was available. On terminating the packing of developing large-sized particles, they sink under free fall. The developing of various geometric anisotropic particles and their sinking enables the arriving of new stock of gold atoms at air-solution interface, thus, developing a new monolayer assembly at air-solution interface. The binding of mono-layer developed in certain shape of developing particle bind to another mono-layer placing over it under the lateral-orientation of electrons of elongated atoms where expansion and contraction of energy knots contribute. Expansion and contraction of clamped energy knots to electrons for different nature atoms under varying orientating gravitational force and levitational force when they are in liquid transition

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states discussed [50]. A separate study discussed the precise structures of particles of one-dimensional shapes and multi-dimensional shapes developed under the assembling of structures of smooth elements, which resulted from the packing of tiny-shaped particles arriving from different zones of the solution surface [51].

Photons propagated through graphite rod, they provided energy to dissociate gold atoms from the precursor at solution surface, thus, developing monolayer assembly around the pulse-based electronphoton-solution interface is under the reaction of forced energy provided by the electron streams along with high energy photons (in high density) entering to solution. Therefore, entering photons of different wavelengths along with the electrons (under the carrying force-energy of photons) to solution from the region of light glow don't appear to dissociate metallic atoms from precursor in such a large number. As the energy is associated with them as well but they can't dissociate the gold atoms in such a large quantity. Therefore, dissociation of the gold atoms from the precursor is mainly through the immersed graphite rod. However, the systematic placement of gold atoms at solution surface while uplifting in each cycle of bipolar pulse ON time is under the reaction of entering electrons carrying force-energy of photons and high energy photons (in high density). Therefore, uplifting of atoms to solution surface is because of the light glow while their dissociation from the precursor is under the immersed graphite rod. 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 and propagating photons through graphite rod also.

Here, the word 'monolayer' refers to compact assembly of gold atoms in a single layer at solution surface but the word 'mono-layer' refers when tiny-shaped particles are packed to develop a single layer of the certain shape developing particle under the assembling of structures of smooth elements.

4. Conclusions

Under the optimized process parameters, different geometric anisotropic shapes of gold particles developed in pulse-based electronphoton-solution interface process. For the controlled excess input power, photons characteristic current propagated through

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immersed graphite rod which transformed into heat energy on entering to solution resulting into dissociate gold atoms from their precursor. Under tuned pulse protocol, flowing argon atoms splitted into electrons where their carrying force-energy (photons), pursuing to them, enter them to solution, as a reaction, dissociated gold atoms are uplifted. Forced energy streams of electrons impinge to underneath passing tiny-sized particles arriving to pack. When impinging electron streams transporting the forced energies do not block by the passing tiny particles, they enter to the solution. In addition to entering electrons carrying force-energy (photons), high energy photons (in high density) also enter to solution. They both enable the uplifting of gold atoms to develop monolayer assembly at solution surface while their entrance. They both are generated at the bottom of copper capillary constituting the argon plasma.

Monolayer assembly developed around the light glow, on utilizing, renovated because of uplifting the gold atoms. The placing packets of nano shape energy resulted under the tuned bipolar pulse protocol enable the developing of joint triangular-shaped tiny particles where gold atoms (of transition state) are isolated from monolayer assembly. A tiny particle of joint triangular-shape separated into two equilateral triangular-shape tiny particles on exerting the force along a bit perturbed axis at point of their connection. Atoms of such tiny-shaped particle elongate under the existed exerting force at electron levels where converting each of their one-dimensional array into structure of smooth element. But, such tiny-shaped particles work as a one-unit to pack at centre of light glow where their structures of smooth elements deal immersing force at uniform rate. A tiny-shaped particle doesn't go for pre-allocated region of packing to develop particle unless it has geometry of equilateral triangular-shape. Triangular-shaped tiny particles undertake packing at pre-allocated regions first at the centre of light glow following by unfilled regions of developing mono-layers of a certain shape developing particle. The developed feature of tiny particles self-ensured regions of their packings. Their packings develop particles of unprecedented features not possible through other means.

On separation into two equal triangular-shaped tiny particles, a tiny-shaped particle directed towards already reserved region of developing particle and same is the case for the companion tiny-shaped particle, but packs aside to the earlier packed one. But,

prior to assemble as a one-unit, a tiny-shaped particle has been developed into the structure of smooth elements. The numbers of initially packed tiny-shaped particles, at one time, from different zones of solution surface nucleate a particle where initial number of simultaneously packing tiny-shaped particles flowing by continuity in the packing for each developing mono-layer determine the shape and aspect ratio of that particle. The synchronization of the setup resulted into develop several unprecedented featured particles having their different sizes and shapes. Our investigations lead into present new trends of researching means not only in the field of materials science and physics but in the field of nanoscience and nanotechnology also.

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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.

Last and final version

[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.

Last and final version

[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.

Last and final version

[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 $HAuCl_4$ 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 (last version)

[39] M. Ali, I –N. Lin, Development of gold particles at varying precursor concentration. http://arXiv.org/abs/1604.07508 (last version)

[40] M. Ali, I –N. Lin, Tapping Opportunity of Tiny-Shaped Particles and Role of Precursor in Developing Shaped Particles. *NANO* **13** (7), (2018) 1850073 (16 pages). https://doi.org/10.1142/S179329201850073X

Last and final version

[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 (last version)

[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 (last version)

[43] M. Ali, The study of tiny-shaped particles developing mono-layer dealing localized gravity at solution surface. http://arxiv.org/abs/1609.08047 (last version)

[44] M. Ali, Atoms of electron transition deform or elongate but do not ionize while inert gas atoms split. http://arxiv.org/abs/1611.05392 (last version)

[45] M. Ali, Structure evolution in atoms of solid state dealing electron transitions. http://arxiv.org/abs/1611.01255 (last version)

[46] M. Ali, Revealing the Phenomena of Heat and Photon Energy on Dealing Matter at Atomic level. https://www.preprints.org/manuscript/201701.0028/v10

[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 –N. Lin, Phase transitions and critical phenomena of tiny grains carbon films synthesized in microwave-based vapor deposition system. http://arXiv.org/abs/1604.07152 (last version)

[50] M. Ali, Why Atoms of Some Elements are in Gas State and Some in Solid State, but Carbon Works on Either Side (2018). https://www.researchgate.net/profile/Mubarak_Ali5 (https://www.preprints.org/manuscript/201803.0092.v1)

[51] M. Ali, I –N. Lin, Precise Structural Identification of Different Shapes of High Aspect Ratio Gold Particles. (submitted for consideration)

Last and final version

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