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Interesting nanoshapes by "nano artwork"

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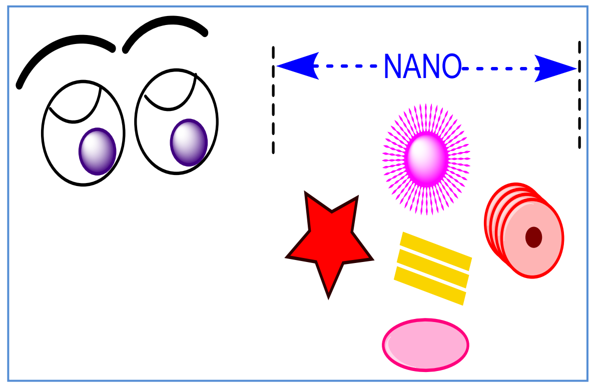
ABSTRACT

Nanomaterials of interesting shapes such as nanostars, nanodiscs, nanorods and nanoflowers are frequently synthesized by chemists, experimental physicists and material scientists nowadays. Large number of the bottom-up or top-down synthetic techniques are invented and reported for the synthesis of these materials with interesting shapes. Such shapes found to already exist in nature. The great nature has done this nano artwork with its power and unbeatable architectural skills at molecular level. The ultimate aim of the synthesis techniques invented may not be to mimic nature or challenge it but instead to explore the use of these variously shaped nanomaterials in technological and biomedical applications. These materials found to be applicable in their use as drug delivery systems, catalysis, and energy and as biosensors. In the present note some of the recent examples of such materials are discussed with their images taken with high resolution microscopes. Copyright © 2014 VBRI press.



Keywords: Nanostars; nanodiscs; nanorods; nanoflowers.

Sushilkumar A. Jadhav obtained his Master's degree in chemistry from Shivaji University, Kolhapur (MH), India and received his Ph.D. degree from University of Genoa, Italy in 2010. Presently he is working at Department of Chemistry of University of Turin, Italy. His research interest includes synthesis of organic and polymeric compounds for the surface modification of different nanostructures and synthesis of noble-metal, silica and iron oxide nanoparticles for the preparation of functional nanohybrids for various applications.

Introduction

The invention of *high resolution electron microscopes* such as scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), atomic force microscope (AFM) and scanning tunneling electron microscope (STM) enabled scientist to see the *nano* dimensions of the materials. It literally opened a third eye with a power to see beyond micro-dimensions. A variety of interesting shapes of different existing and newly synthesized materials are observed through these microscopes. The pictures of these nanomaterials are taken and reported in various research articles in different scientific journals with their potential applications. Nanostars, nanodiscs, nanorods and nanoflowers are some of the very interesting and commonly reported shapes of materials that appear in the literature. These shapes can be made of the same kind of material or in some cases they are made of hybrids complex materials. In case of a hybrid material the arrangement of the atoms in the *shape constituting crystals* is of great importance that is made in adjustment with the atoms of the other material which gives rise to a complicated shape with higher stability. All the nanomaterials in their different shapes have proven their potential applications in different fields such as construction of nanodevices **[1]**, sensing **[2]**, destroying pesticides **[3]**, water purification **[4]**, electronic and biomedical applications **[5, 6]**. The shape of the material synthesized and packing of the nanocrystals determines not only its intrinsic physical and chemical properties but also its relevance for optical, catalytic, electronic, and magnetic properties and applications. Most reported methods about the synthesis of complicated shapes are based upon controlling or manipulating growth process of the crystals and less information is available on their nucleation or seed formation mechanisms **[7]**. It is well known that there needs a precise control of the factors affecting size and shape of nanomaterials during their synthesis but suitable and careful modification of them may led to attractive shapes of the resulting nanomaterials. In the present short note latest reports and important observations about the special shapes of the nanomaterials are discussed in order to draw the attention of the readers both from scientific and general community to know the ability of nanoscience in fabricating geometrically complicated architectures at the nanoscale. Of course the great "nature" is master in this art as such kind of shapes are already found to exist in materials.

Nanostars

Stars have fascinated human being since their existence. Experience of observing stars in the sky with the help of high resolution telescopes has led to print the shape of star in our minds. Any two or three dimensional semicircular body having five pointed projections coming out the main shape reminds us the shape of the star. Gold, zinc oxide and vanadium pentaoxide are some of the materials of which nanostars are commonly prepared. The synthesis of vanadium pentaoxide nanostars of up to 6 micrometers by chemical vapor deposition (CVD) technique where complete retention of electronic structure in the obtained crystallites is observed which showed retention of properties upon formation of star shape by the material **[8]**. In an interesting work Lee et al. reported about the use of gold nanostars for SERS substrate based on high density gold nanostar assemblies as ultrasensitive SERS chemical sensors for nitro-aromatic explosives **[9]**. The use of stabilizers, reactant concentrations and their stoichiometric ration determines the shape of the resulting nanostructures. Kooij et al. **[10]** presented a seed mediated growth assisted method by surfactant to grow nanoparticles of gold (**Fig. 1**).

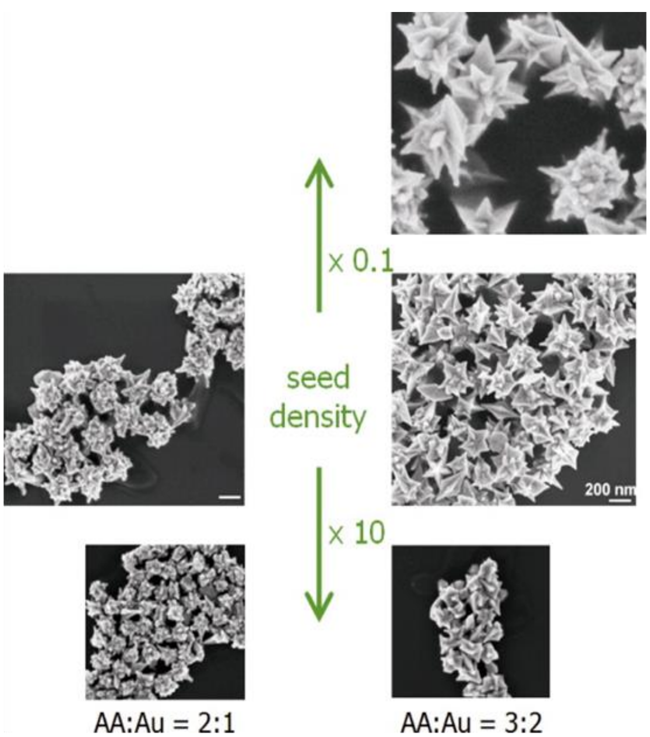


Fig. 1. Gold nanostars prepared by using gold nanoparticles as seed for their formation. Reproduced with permission from reference 10 Copyright © 2012, Elsevier.

The choice of seed particle, i.e. single crystal or multi-twinned, enables growth of nanorods and multi-branched nanoparticles which can be referred as nanostars. This is a classic example of how the shape and size of the nanoparticles can be tuned by varying the solution composition and relative reactant concentrations. Not only as such nanostars of gold **[11-12]** but also gold nanostars combined with other materials such as graphene **[13]** and nanostars of zinc oxide **[14]** are also reported.

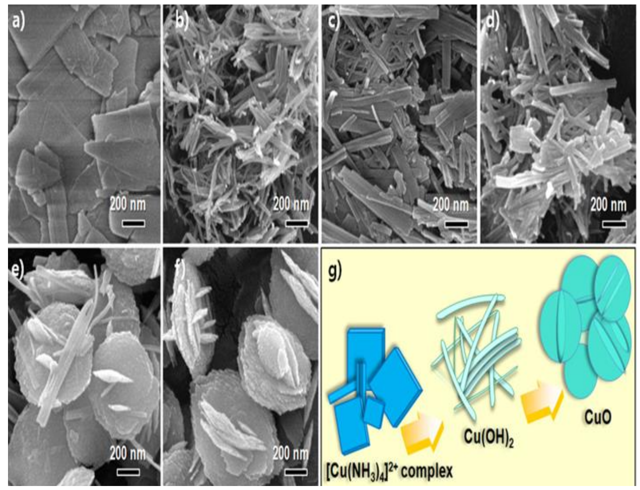


Fig. 2. FESEM images. (a) $[Cu(NH_3)_4]^{2+}$ complex, (b) $Cu(OH)_2$ nanowires at room temperature, (c-d) $Cu(OH)_2$ nanowires after reaching 40 and 50°C, respectively. (e-f) CuO-interlaced nanodiscs at 60°C after 0 and 3 h, respectively. (g) Schematic diagram of the morphology evolution steps for CuO nanostructures. Reproduced with permission from reference 19 Copyright © 2011, Springer.

Nanodiscs

Blood cells are also generally called globules may be because their resemblance to the disc shape. Disc's geometrical shape of not being a sphere helps them to occupy less volume and add them the ability to pack more compactly with each other with respect to other shapes. A catchy statement from a paper proves the importance of disc shaped nanomaterials in biomedical applications it says "*Size, surface charge, and material compositions are known to influence cell uptake of nanoparticles. However, the effect of particle geometry, i.e., the interplay between nanoscale shape and size, is less understood. Here we show that when shape is decoupled from volume, charge, and material composition, under typical in vitro conditions, mammalian epithelial and immune cells preferentially internalize disc-shaped, negatively charged hydrophilic nanoparticles of high aspect ratios compared with nanorods and lower aspect-ratio nanodiscs*" **[15]**. So it can be concluded that nanodiscs are up taken easily by cells with respect to other complicated nanostructures. Microemulsion based synthesis of Ag_2S nanodiscs is reported by Leidinger et al. these material found to have potential applications in solar cells and sensoristic devices based on their electron, ion and semiconducting properties of the discs shaped material obtained **[16]**. Other nanodisc materials reported are graphene nanodiscs with zigzag edges for constructions of spintronic devices **[17]**, Copper telluride Cu_2Te for photoluminescence applications **[18]**. **Fig. 2** shows copper oxide phase pure nanodiscs prepared by dehydrogenation of 1-D $Cu(OH)_2$ for improved electrochemical performance. It is interesting to note the change of morphology and shape of the same material from nanoflakes to nanowires to nanodiscs **[19]**.

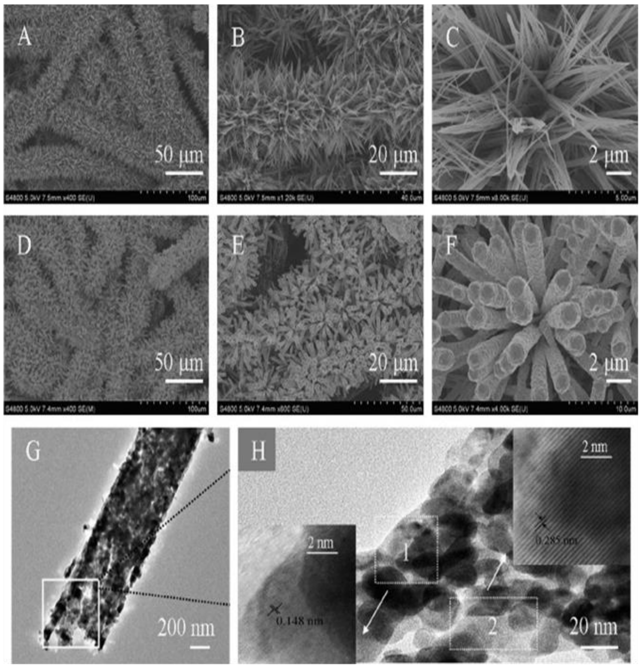


Fig. 3. Low (A, B) and high-magnitude (C) SEM images of the Co_3O_4 nanowire arrays; low (D,E) and high-magnitude (F) SEM images of the Co_3O_4/PbO_2 nanorod arrays. TEM image (G) and the high-resolution TEM images (H) of a single Co_3O_4/PbO_2 nanorod. Reproduced with permission from reference 25 Copyright © 2012, Elsevier

Nanorods

Nanorods represent another interesting three dimensional nanomaterial shape which has at least one dimension in the nanometers. Metallic and semiconductor nanorods are frequently prepared by researchers. Nanorods having width or diameter up to 2-20 nanometers and length more than 100 to 200 nanometers can be called as "nanosticks" and if the length is in micrometers they can be called as "nanowires". This length to width aspect ratio makes nanorods applicable in various fields. The semiconductor or magnetic nanorods can change their orientation upon application of external electric or magnetic fields this property is used for the design of electronic display devices by the use of fluorescent nanorods. Nanorods have shown their potential applications in the fields of biomedical fields gold-nanorod-silver hybrid nanorods were used for evaluating toxic effects of silver **[20]**. Porous titanium nanorods was found to be efficient catalysts in hydrogen production **[21]**, Titanium and zinc oxide nanorods were used for constructions of glucose sensors **[22, 23]** and bismuth sulfide (Bi_2S_3) nanorods shown potential applications in photochemical detection devices **[24]**. **Fig. 4A** to **E** shows high resolution SEM and TEM images of Co_3O_4 nanowires. **Fig. 3 F-H** shows the Co_3O_4/PbO_2 nanorods. The Co_3O_4/PbO_2 core-shell nanorod arrays supported on the carbon cloth were prepared and tested for their electrochemical ability for the detection of glucose towards construction of a glucose biosensor **[25]**. Shrestha et al. have reported the synthesis of CuO nanorods from easily available chemicals copper salt, lactic acid or its derivatives and sodium hydroxide as the base **[26]**. It is interesting to note that the obtained nanorods form 3-dimensional spherical assemblies which resemble like nanoflowers as shown in **Fig. 4A** and **4D**.

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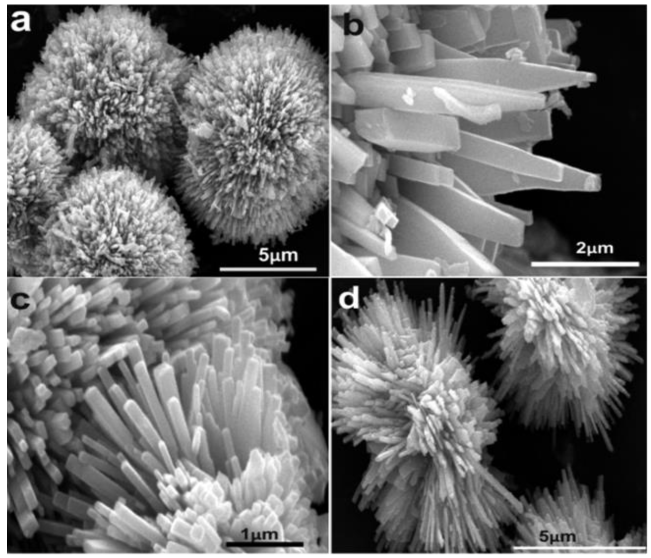

Fig. 4. Spherical assemblies of CuO nanorods synthesized using copper nitrate, lactic acid, and sodium hydroxide. Reproduced with permission from reference 26 Copyright © 2010, American Chemical Society.

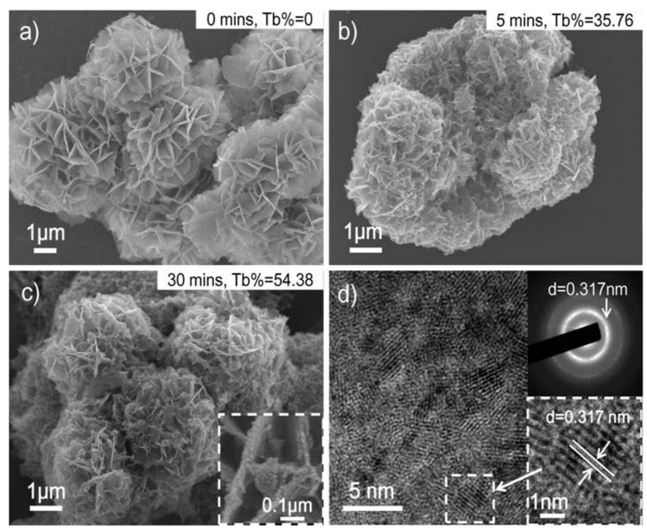

Fig. 5. Magnesium hydroxide nanoflower. Reproduced with permission from reference 34 Copyright © 2013, American Chemical Society.

Nanoflowers

The main natural or biological function of flowers is to attract insects which will help them in reproduction by transfer of pollen grains to continue their life. Flowers as we know may have complicated shape and artificially difficult to construct. Peculiar feature of this shape is the petals and their arrangement and orientation in an attractive way. Nanofolwers instead of merely attracting the attention of readers from scientific fields have proven their use in different applications. In a recent work by Zeng et al. **[27]** tin sulfide (SnS_2) nanoparticles resembling flower shape were synthesized by hydrothermal method. A composite material of these flowers with 1-butyl-3-methyl-imidazolium tetrafluoroborate an ionic liquid was prepared to modify carbon ionic liquid electrode to construct a biosensor for hemoglobin detection. Organic-inorganic nanoflower made up of glucose oxidase (GOx) and horseradish peroxidase (HRP) as the organic and enzyme components, and $Cu_3(PO_4)_2{\cdot}3H_2O$ as the inorganic component is reported **[28]**. These nanoflowers are used to develop a glucose biosensor. Growth of these nanoflowers from nanometer to micrometers is monitored by SEM and TEM. Iron oxide nanoflowers found their use in the purification of water as they can be employed for the selective removal of arsenic impurities from water **[29]**. Poly (diallyldimethylammonium chloride) functionalized graphene-MoS_2 nano-flower was synthesized by Feng at al. **[30]**. A composite material by combining the nanoflower obtained with gold nanoparticles is prepared and applied on electrodes and its electrochemical efficiency for the detection of eugenol is reported. Other recent observations include nanoflowers of gold-palladium alloy **[31]**, DNA **[32]** and Zinc stannate (Zn_2SnO_4) **[33]**. **Fig. 5** shows $Mg(OH)_2$ nanoflower prepared by chemical precipitation method. The nanoflower is employed for the treatment of wastewater containing low concentration rare earth elements (REEs). The paper also describes recovery of the elements separated from the water on the petals of the flower like shape of the magnesium hydroxide **[34]**.

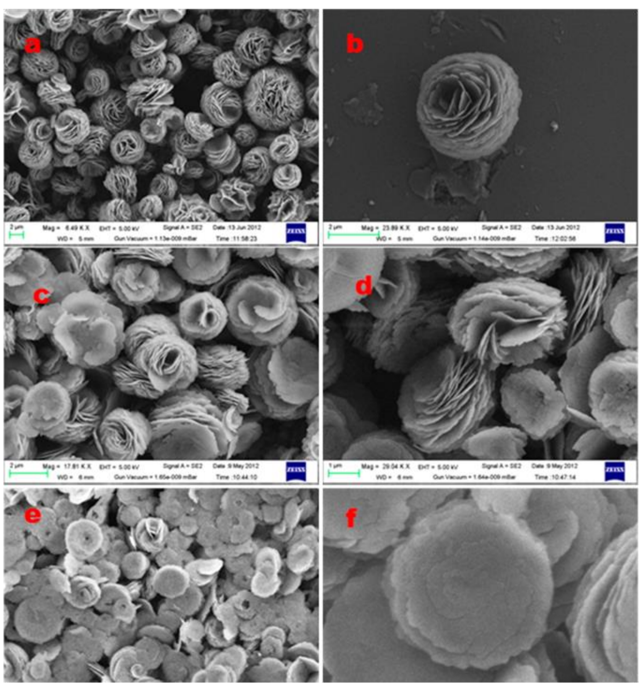

Fig. 6. Porous β-$Co(OH)_2$ nanoflower. Reproduced with permission from reference 35 Copyright © 2013, American Chemical Society.

The nanoflower-shaped porous β-$Co(OH)_2$ with a characteristic three-dimensional architecture resembling rose flower as shown in **Fig. 6** as a promising electrode material for supercapacitor application is reported **[35]**. Flowers are important on special occasions, religious ceremonies; they have also proved their importance in medicine and food instead nanoflowers are promising materials for several biomedical and diagnostic applications.

Conclusion

Representative examples of impressive "nano-artwork" with their images taken by electronic microscopes are presented in this short note review. Whatever be the "shape" these nanomaterials are coming up with lots of potential applications in all fields of technology and it will be of no surprise if the synthesis of these complex shapes will become routine laboratory tasks in future. The pace at which the scientific research is going nowadays the invention of more high resolution microscopes to see even beyond nano dimensions of matter is imminent at any point of time and if it happens it will be possible to discover and see more nature artwork at the molecular level in angstrom dimensions of the matter.

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