Research Article Adv. Mat. Lett. 2013, **4**(4), 252-260 ADVANCED MATERIALS Letters

www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2012.8405

Transition metal ion-induced anisotropic architectures using 4,4’-dicarboxy-2,2’-bipyridyl-silver nanopetals

Narayanasamy Vilvamani, Sasanka Deka, Tarkeshwar Gupta[*]

Department of Chemistry, University of Delhi, Delhi 110 007, India

[*]Corresponding author. Tel: (+91) 11 27662642; Fax: (+91) 11 27662642; Email: tgupta@chemistry.du.ac.in

Received: 08 August 2012, Revised: 24 August 2012 and Accepted: 26 August 2012

ABSTRACT

Designing anisotropic nano- and micro-structures are imperative in many technology oriented fields. Here we have reported a self templating method, where flower like microstructure of silver particles were used as template to generate several anisotropic structures such as rectangular cum dumbbell, cubes, hexagonal whiskers, and rectangular bars etc. under controlled catalytic activity of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} respectively. The initial flower like microstructure (template) of silver particles have been prepared from silver salt using disodium salt of 4,4’-dicarboxy-2,2’-bipyridyl(Na_2dcbpy) as the reducing as well as capping agent. Then this architecture was used as the initial template to generate several anisotropic structures. The straightforward anisotropic microstructure preparation procedure does not require any other external template, which avoids the subsequent complicated workup. The nucleation processes and optical properties were studied using optical absorption spectroscopy. The anisotropic structure of the as-synthesized Ag particles and the formations of various shaped microstructures have been confirmed by Scanning Electron Microscopy (SEM). A possible mechanism has been proposed explaining the role of dcbpy in the growth of silver particles and the transition metal ion induced anisotropic structures. Copyright © 2013 VBRI press.

Keywords: Silver particles; nucleation and growth; nanomaterials; anisotropic structure.

Narayanasamy Vilvamani is a Ph. D. student at Department of Chemistry, University of Delhi, Delhi, India. He received his M.Sc., Chemistry from Gandhigram Rural University, Tamil Nadu. His major research area is functionalization of nanoparticles with metal complexes.

Sasanka Deka is Assistant Professor at University of Delhi. He received his doctorate degree from National Chemical Laboratory and worked at NNL, CNR-INFM, Lecce, Italy and IIT, Genova, Italy for postdoctoral research. His research interest deals with synthetic nanochemistry.

Tarkeshwar Gupta is Associate Professor at University of Delhi. He worked at DDU Gorakhpur, IISc Bangalore, WIS Israel, UC Berkeley and University of Heidelberg, Germany. His research interests include nanoscale assembly of molecular-derived materials.

Introduction

Inorganic micro- and nano-structures are of great importance because of their unique physical and chemical properties which vary with nano- to micron sized metal structures **[1-3]**. The fashion to prepare novel materials with multidimensional morphologies at micro- to nano-scales craft an innovative cultural impact on the scientific environment for potential applications such as in catalysis, electronics, photography, photonics, sensing, imaging process, and medicine **[4a-g]**. Numerous methodologies have been developed to syntheses size, shape and structure selective formation of nanostructures using various capping reagents such as sodium citrate, polyvinylpyrolidone

(PVP), n-cetyltrimethylammonium bromide (CTAB), amines, phosphines, thiols, micelles, dendrimers, polymers, and biomolecules **[5a-f]**. In this regards, interface chemistry in combination with self-assembly process play important role for miniaturization of desirable nanostructures **[5g-h]**. This can be done through template-mediated decoration of nanoparticles on the preformed nanotemplates, but this process require further physical or chemical treatment, which may modify surface morphology and properties of the assembled materials **[6-8]**. Various anisotropic structures such as Ag plates **[9]**, Ag wires **[10, 11]**, Pd cubes **[12]** have been prepared by adopting diverse methods. Apart from the conventional shapes as above, some complex anisotropic shaped particles have been synthesized recently, such as jelly-fish type gold biomimetic fiber **[13]**, star shaped gold **[14]**, nanodendrites (Pd, Pt, Au) **[15]**. The flower like structures of Ag particles with sharp edges can be useful for Surface-Enhanced Raman Scattering (SERS) study, which are capable of focusing electromagnetic field of excitation light at their ends to realize extremely large field enhancement for SERS **[16, 17]**. The surface roughness and possible high index planes of star-shaped structures may have special applications in catalysis due to much higher active sites **[18]**. Despite such fascinating applications, synthesis of noble metal nano and micro-structures with a high degree of structural anisotropy is still a great challenge. Recently, Tang et al. prepared silver micro particles constructed of mutually intersecting 2D nanoflakes using electrochemical approach **[19]**. L. Hong et al. prepared silver microstructure composed of nanopetals using ascorbic acid and citric acid **[20]**. Further, recently A. Tiwari and his group have reported several biomedical related applications of these nano/micro-particles and nanocomposites [**21**]. Apart from these fascinating reports, there are few other reports where novel synthesis procedures for Ag particles using biological methods and application thereof have been described [**22**].

Mostly, template free nanostructure constructions utilize carboxylate containing reagents due to its dual role, strong reducing as well as surface stabilizing property **[23-25]**. As an example, shapes of the silver nanoparticles are fully influenced by the configuration of surface capping agent on its surface in order to stabilize its specific facets **[26]**.

A unique structural evolution process is fully based on the relative rates of nucleation and the crystal growth process. In such a process, control over size can be achievable by changing parameters such as concentration of metal precursor, the nature of stabilizing agent, temperature, and solvent of the reaction medium **[27]**. Attempts to understand structural transformation at nanoscale level through nucleation and growth process are still under exploration **[28]**.

2,2'-bipyridine-4,4'-dicarboxylic acid (H_2dcbpy) is a well-known potential candidate for rich coordinating ability with series of metals in different modes of bonding through primary and exodentate sites **[29]**. In this study, we have considered this dual coordinating ability of H_2dcbpy as an advantage to make desirable and novel shaped materials.

Therefore, a novel synthesis procedure for the formation of flower like morphology of silver particle without using any structure directing agent is very important. Moreover, use of this morphology to produce various anisotropic shaped silver particles in presence of transition metal ions would be interesting. Here, we have reported a novel synthesis method to prepare flower like morphology of Ag particles and change of the parent morphology to other anisotropic shape, such as rectangular dumbbells, cubes, hexagonal whiskers, and rectangular bar etc. We have synthesized dcbpy-Ag particles *via* a simple one pot synthesis in aqueous media (reducing silver precursor in aqueous media) and the resulting dcbpy-Ag microstructure used as a template for the formation of various anisotropic shaped microstructures, including rectangular dumbbells, cubes, hexagonal whiskers, and rectangular bar with dendrites, in presence of series of transition metal nitrates (Co, Ni, Cu and Zn) at room temperature. The selective introduction of transition metal ions to the resulting dcbpy-Ag colloid resulted in the formation of renewed structures. To the best of our knowledge, this is the first report of synthesis of anisotropic flower like Ag microstructure formation using 4,4'-dicarboxy-2,2'-bipyridine and its various anisotropic structures in the presence of series transition metal nitrates. The novelty of present work is that, by utilizing flower like silver particles as starting material, various anisotropic structures such as rectangular cum dumbbell, cubes, hexagonal whiskers, and rectangular bars with dendrites formed by reacting with transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) in room temperature.

The formation of selective various anisotropic architectures achieved through ionic interaction between silver microparticle and transition metal ions introduced at room temperature without external structure directing agent was the core objective of this work. These silver anisotropic structures with features are expected to find applications in catalysis and SERS studies.

Experimental

Materials and methods

$AgNO_3$ (99+%, Alfa Aesar), 4,4'-dimethyl-2,2'-bipyridyl (Sigma Aldrich, 99%), ($Co(NO_3)_2.6H_2O$, 97.0%), ($Ni(NO_3)_2.6H_2O$, 98.0%), ($Zn(NO_3)_2.6H_2O$, 98.0%) are purchased from Thomas Baker, ($Cu(NO_3)_2.3H_2O$, 95-103%) from Fischer scientific, India. All the chemicals were used as received without further purification. Solvents such as hexane (AR grade) from spectrochem, acetone from Merck, ethanol was distilled and stored on molecular sieves. All the aqueous solutions were prepared with double distilled water unless mentioned otherwise. Microscopic cover glass (2 × 2 cm^2) was used as a substrate for the sample surface image studies. Microscopic slides were treated with aqua regia (1:3 mixture of HNO_3/HCl) to remove any adsorbed organic impurities and washed with ample amount of double distilled water followed by sonication in ethanol for 5 min and dried at 85^{0}C. All glass wares were thoroughly cleaned with aqua regia (1:3 HNO_3/HCl) and rinsed extensively with double distilled water before use.

Safety caution

Aqua regia is an aggressive oxidizing agent; it should be handled with care.

Synthesis of 4,4'-dicarboxy-2,2'-bipyridine (DcbpyH$_2$)

This compound has been prepared following literature procedure **[30]** and purity has been checked by ^{1}HNMR. [^{1}H-NMR, 400MHz, DMSO-d$_6$, δ]: 7.90 (dd, J=4.8 Hz and 2H, 1.6Hz, H5, H5'), 8.83(s, 2H, H3, H3') 8.90(m, 2H, H6, H6').

Synthesis of disodium-4,4'-dicarboxy-2,2'-bipyridyl (DcbpyNa$_2$)

A solution of NaOH (25% w/v in water, 2 mL) was added to dcbpyH$_2$ (0.104g, 4.25mmol) until the solid was dissolved completely, at this **condition** the solution pH was adjusted from 3 to 9. Acetone (70 ml) was added to precipitate out the title compound as white crystalline solid (0.129g, 99%).

Synthesis of Dcbpy-stabilized flower like silver particles - (Dcbpy-Ag particles)

Aqueous solution of AgNO$_3$ (1 mM, 25 ml) was ultrasonically pretreated for 5 minutes to ensure the complete solubility, and heated over an oil bath at 80 ^{0}C with constant vigorous stirring. At this temperature disodium salt of dcbpy (0.5% w/v, 5ml water) was added dropwise quickly with vigorous stirring. A pale yellow color appeared after 5 minutes, the solution was allowed to stir for another 10 min. which resulted in the intense yellow colour Ag microsized particle formation. The solution were cooled down to room temperature naturally and stored under dark for further analysis at room temperature.

Transition metal ion-induced anisotropic architectures of Ag-nanoparticles

For silver anisotropic structures, about 1 ml (0.01 M) of metal nitrate solutions, M(NO$_3$)$_2$·6H$_2$O (M = Co, Ni, Zn) or Cu(NO$_3$)$_2$·3H$_2$O were added into 2 ml of dcbpy-Ag particles solution at room temperature and allowing for 24 hr. During this time, dark brown, brown, yellow, and yellowish brown precipitate were observed for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} respectively.

Characterization

Scanning electron microscopy: The samples for SEM analysis were first centrifuged and washed with ethanol thrice and then redispersed in ethanol. 20 µl of sample solution was deposited on the cleaned microscopic glass slide under dark by drop casting method and the substrates were allowed to get dry at room temperature. The samples surface morphologies and size were characterized by scanning electron microscopy (Oxford Instrument, EVO/ MA 15 ZEISS SEM) operated at accelerated electron beam energy 20.0 kV under vacuum (10^{-5} torr) and secondary electron images were recorded.

UV-visible spectroscopy: Each samples after washed with ethanol, redispersed in 3 ml of ethanol and utilised to record UV-visible spectroscopy. This procedure is followed for all nanostructures to obtain respective UV-Vis spectra of anisotropic silver particles.

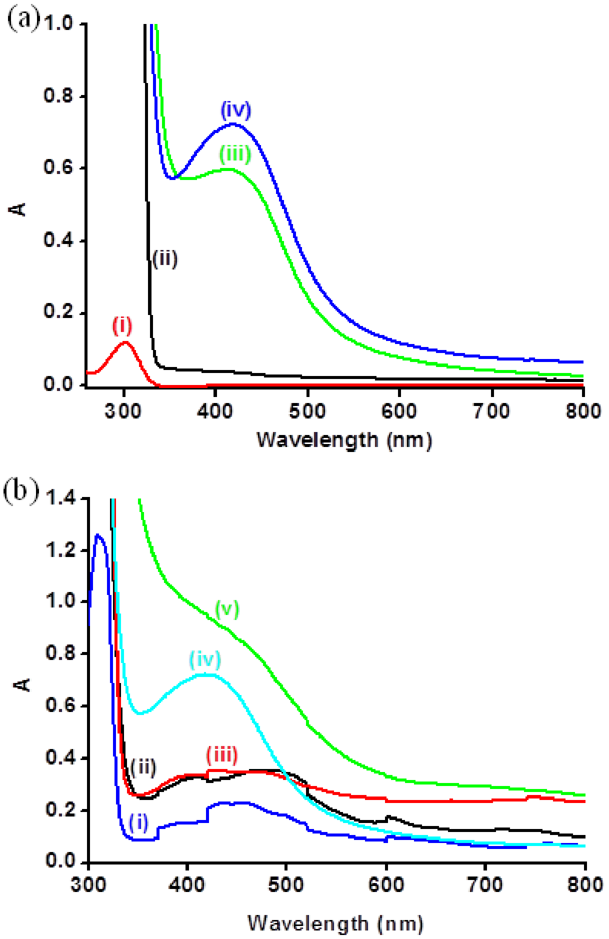
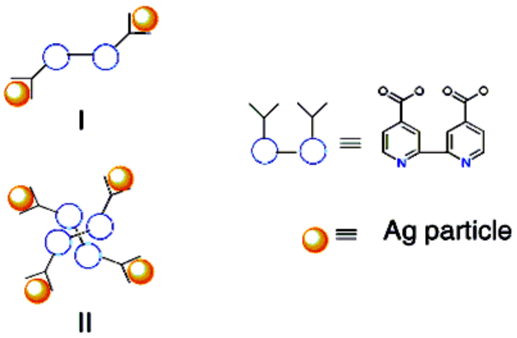


Fig. 1.(a) UV-Vis spectra of silver nitrate solution (i), 4,4'-dicarboxy -2,2'-bipyridine solution (ii), 4,4'-dicarboxy-2,2'-bipyridine-silver particles (Dcbpy-Ag particles) (iii), after washing with hexane (iv), and (b) UV-Vis spectra of silver particles after reaction with Zn^{2+}(i), Co^{2+}(ii), Ni^{2+}(iii), Cu^{2+}(iv), and blank dcbpy-Ag particles (v) respectively.

Results and discussion

Dcbpy-capped Ag Particles formation was followed by recording UV-Visible spectra of the resulting colloidal solution, which showed surface plasmon band at 415 nm **(Fig. 1a)**. This value is well corroborated with literature value for surface plasmon of silver particle **[11]**. It could be noted that, there are different kind of binding modes are available for dcbpy **[31]**. Out of all modes, the possible mode of chemisorption of dcbpy on Ag particle surface is shown in **Scheme 1**.



Scheme 1. Representation of various possible binding sites and orientation of 4,4'-dicarboxy-2,2'-bipyridine over Ag particles surface.

The dcbpy-Ag particles were washed with hexane, which resulted in the enhancement of absorbance without changing the stability (i.e. no aggregation, no red or blue shift in the UV-Vis region) of dcbpy-Ag particles **(Fig. 1a)**. During this process, about 1 ml of dcbpy-Ag particles was taken and kept along with hexane. The slow distribution of dcbpy-Ag particles into nonpolar hexane was noticed after long waiting time at room temperature. This confirms the possible orientation of dcbpy on Ag surface would be as in **Scheme** (I, II), but these configurations must be less populated.

After purification, dcbpy-Ag particles (2 ml) were reacted with 0.01 M aqueous solution (1 ml) of a series of representative transition metal nitrate salt of Co, Ni, Cu and Zn. The changes in homogeneous dcbpy-Ag particles were noticed visually after addition of metal nitrates and chemical changes (shape transformation) were monitored through recording UV-Vis spectra **(Fig. 1b)**. These changes were analyzed based on the nature of metal ions, and dcbpy ligand orientation on Ag particles surface.

The anisotropic morphology growth mechanisms were studied to understand the crystal formations through shape transformation in nanocrystal synthesis **[32]**. The attachment of ions/molecules to a primary dcbpy-Ag particle forming an anisotropic crystal, such crystallization can proceeds along nanoparticle based reaction channels **[33]**. For Ag, the final shapes of anisotropic crystals were determined primarily by the internal structure of the corresponding seed and the facets exposed on it **[34]**.

Nucleation and growth of microarchitectures

We hypothesized the possible nucleation and growth for the formation of flower like silver morphology. In this reaction, initially, the univalent Ag^+ ions start to nucleate by the reduction over carboxylate group on dcbpy molecules. Thus formed Ag^0 nuclei act as nucleation center for the further growth via seed formation and further reduction of unreduced Ag^+ in the solution resulted in the formation of anisotropic flower like Ag structure.

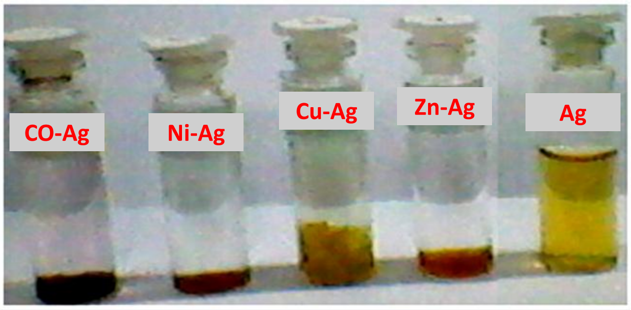


Fig. 2. Optical image of shape transformations of dcbpy-Ag particles in the presence of metal nitrates (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in aqueous medium and dcbpy-Ag particles. The flower like Ag structure has the size of 20 µm with petal in nanometer scale which was surrounded by fibrous networks at the bottom. Thus formed structures are expected to from an intermolecular interaction between dcbpy ring N-atom and Ag particles protected by other dcbpy molecules forming a network which are connected to the bottom of the flower like structures (Fig. 3).

While adding dcbpy solution in silver nitrate solution drop wise, initially lower concentration of dcbpy and higher Ag^+ ions present in reaction (**Fig. 2)**. So, carboxylate group may be engaged on both sides of the dcbpy in the beginning. But after continuous addition of dcbpy provides enough carboxylate to reduce remaining Ag^+, makes them water miscible. In growth stage, the interaction between N-atom of dcbpy ring with Ag particles would make fibrous network around flower like morphology (**Fig. 3)**. Unless mentioned interaction, the flower like Ag morphology formation was in question. The interaction between N-atom and Ag particles were predominant, because during synthesis enough amount of dcbpy was used.

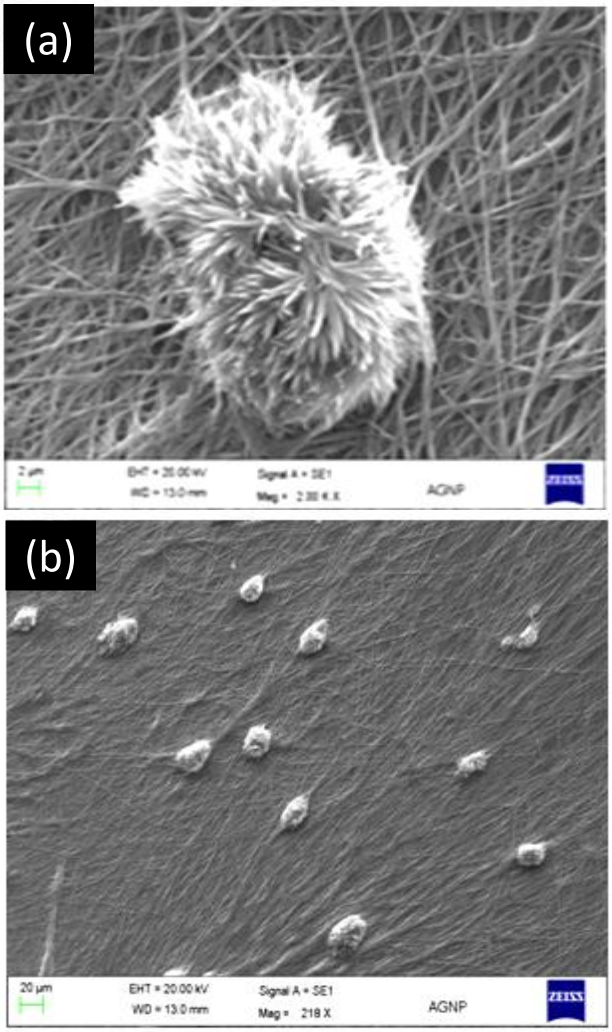


Fig. 3. SEM images of dcbpy-capped Ag particles structure at higher magnification (single dcbpy-Ag particle) and collection of dcbpy-Ag flower like particles. Higher magnification clearly showed the presence of fibrous network at the bottom of every flower like structure.

Ag particle morphologies in the presence of metal nitrates

The chemical growth of micro- or nanometer-sized materials inevitably involves the process of precipitation of a solid phase from solution **[35]**. The addition of an excess of metal nitrates (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in stable colloidal dispersion of dcbpy-Ag particles would result in precipitation and formation of an anisotropic structures. Thus, in the case of various anisotropic structure formations, to induce precipitation, the solution was made supersaturated by adding 10 times more concentrated metal nitrate solutions (0.01M) to homogeneous dcbpy-Ag particles. This precipitation process consist of particle growth through selective metal ion induced self-assembly process **[36]**. The addition of aqueous solution of Co^{2+} to dcbpy-Ag particles lead to the formation of rectangular cum dumbbell structures. Many changes were noticed after addition of Co^{2+}, complete dismantles of the former structure of Ag particles (flower like structure), the formation of renewed structure followed by disappearance of nest fibrous networks around flower like morphology were noticed **(Fig. 3)**.This shape/morphology transfer process informs that the flower like morphology composed completely with ionic interactions and these interactions were get disturbed by the addition of Co^{2+} ions. This shape transformation process was observed not only with Co^{2+} but commonly noticed with all three metal nitrates (Ni^{2+}, Cu^{2+}, Zn^{2+}) in dcbpy-Ag particles.

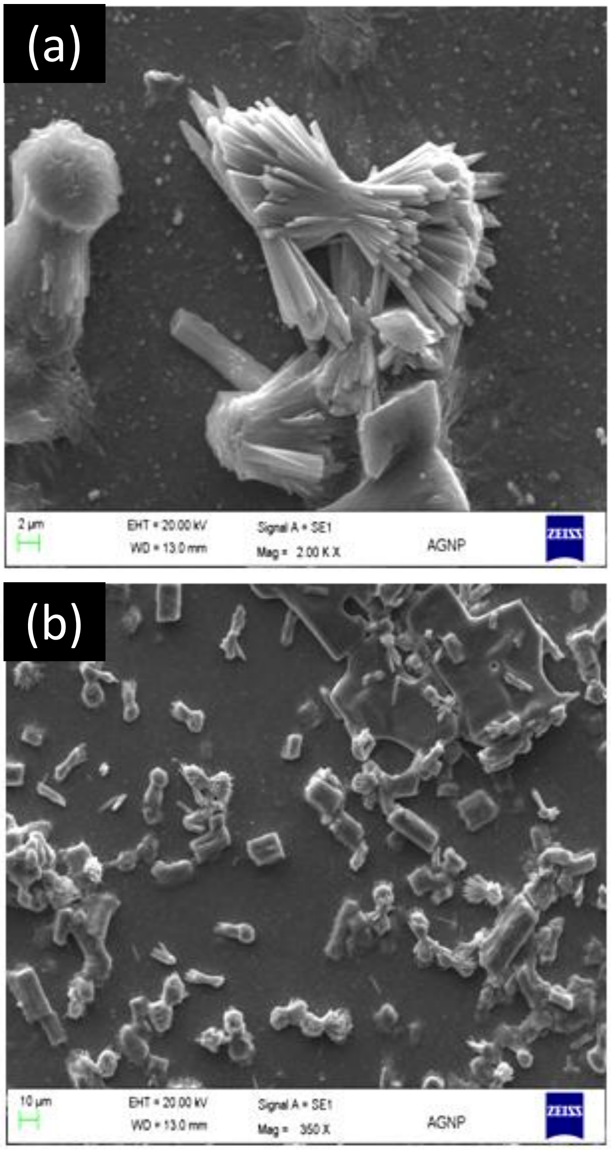


Fig. 4. SEM images of Co^{2+} added dcbpy-Ag particles, at different magnifications.

Addition of Co^{2+} solution to the as-prepared Ag-particle solution brought a great change to the morphology of the parent particles. Images in **Fig.4** show the absence of fibrous network and formation of rectangular cum dumbbell structures due to the addition of Co^{2+} ions. By the addition of Ni^{2+} solution, symmetric flower like structure of dcbpy-Ag particles were sliced into cubic shape with rough surface, approximately 2-3 µm in size (**Fig. 5)**. The most common shape formation by nickel was cubic **[37]**.

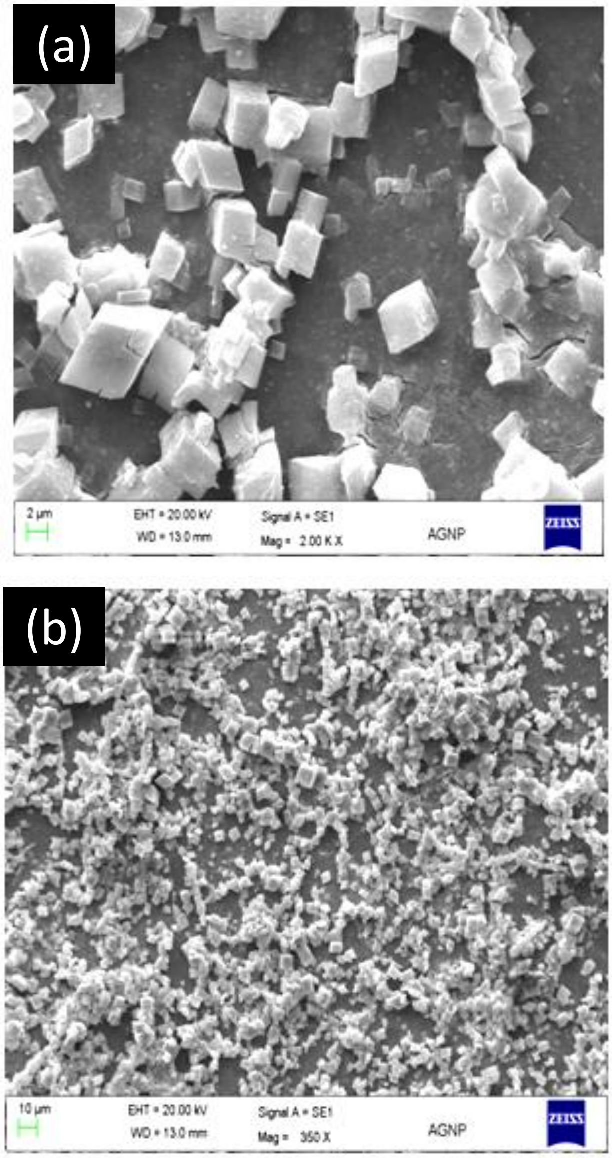


Fig. 5. SEM images of nickel nitrate added dcbpy-Ag particles, at two different magnifications. Closer look of Ni^{2+}-dcbpy-Ag particles showed cubic structures and its shape uniformity showed in lower magnification image.

The addition of Cu^{2+} in dcbpy-Ag particles creates hexagonal whisker like structures and having average diameter about 1.5 µm, and this showed enhanced optical property out of all remaining structures (UV-Vis spectra, (**Fig. 1b)**). The hexagonal whisker like morphology formation through replacement of nitrate in an octahedral coordination site of Cu^{2+} in an aqueous medium with nitrate counterpart in axial and remaining position through carboxylate group was possible **[38, 39]**. Such crystals include twin defects and stacking faults, which provide a break to cubic symmetry naturally **[40]**.

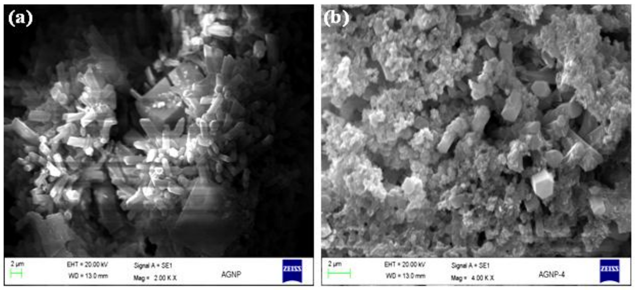


Fig. 6. SEM images of hexagonal whisker morphology observed with Cu^{2+}-dcbpy-Ag particles at different magnifications.

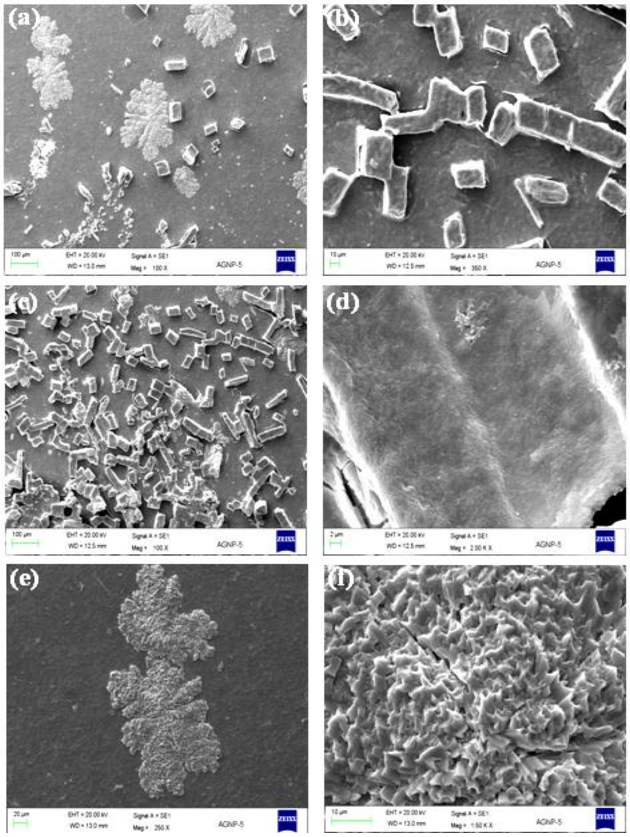
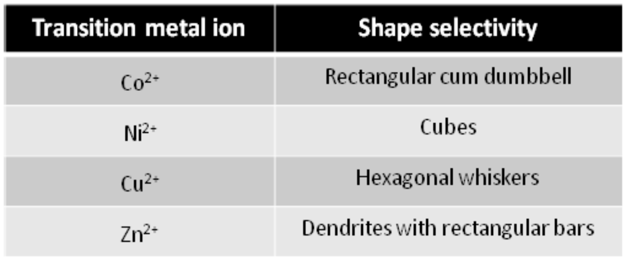


Fig. 7. SEM images of dcbpy-Ag particles, with Zn^{2+} at different magnifications, rectangular bars (a, b, c and d) with dendrite morphologies (e and f). Both anisotropic structures were found to be rough morphology which may act as platform for surface catalysis.

Among the fcc metals, Ag have the lowest energy barriers for incorporating stacking faults and planar defects introduced self-propagating ledges which can act as active sites for crystal growth **[41]**. When a simple planar defect was involved, hexagonal plates can form in an initial stage of growth due to six-fold symmetry of an *fcc* lattice **[42]**. The interaction of Zn^{2+} with dcbpy-Ag particles forms dendrites morphology along with rectangular bar structures. The SEM images of the Zn^{2+} ion added dcbpy-Ag particles are shown in **Fig. 6.** Introduction of Zn^{2+} induces dendrite structure formation in dcbpy-Ag particles **[43]**.

The overall length of dendrite was about 200 µm and the bars were distributed in two size ranges about 45 µm and 80 µm, respectively. The morphology of bar structure was found to be rough **[Fig. 7d]**. Two distinct structures were created by Zn^{2+} system, and behave analogous with dcbpy-Ag-Ni^{2+} optically (UV-Vis spectra, **Fig. 1b**). The fusion of cubic structure was observed, which produce rectangular bars. This unique rectangular bar morphology correlated with the process of sharing of common facets to minimize surface energy favors cubes to rod morphology **[Fig. 7]**. Even though the exact mechanism of formation of dendrites by divalent zinc along with Ag is not understood clearly **[43]**.

Table 1. The added transition metal ions and corresponding morphologies. [Reaction conditions: 1 ml of M(NO$_3$)$_2$·6H$_2$O (M = Co, Ni, Zn) addition into 2 ml of dcbpy-Ag particles solution at room temperature and standing for 24 h].



Transition metal ion	Shape selectivity
Co^{2+}	Rectangular cum dumbbell
Ni^{2+}	Cubes
Cu^{2+}	Hexagonal whiskers
Zn^{2+}	Dendrites with rectangular bars

In all cases, the larger anisotropic structures were formed at the expense of Ag flower like anisotropic structure. Thus, the dcbpy-Ag particles (petal width about 0.3 µm) act as a precursor/template for different structure formations in the presence of metal ions. Dcbpy-Ag particles symmetry was entirely vanished in each case and produced different unique metal selective morphologies (see **Table 1.**). Hence, the use of a capping agent directs the shape of a crystal in thermodynamic point with respect to the metal system. It makes some facets thermodynamically more favorable by reducing their interfacial free energies through chemisorptions on the exposed facets of the metal surface **[40]**. Apart from, a number of spectroscopic techniques (XPS, EDXS, FTIR) used to confirm the presence of a capping layer, the exact orientation of the surface capping agent on the surface of crystals is not clear **[44]**.

The structural transformations were analyzed by anisotropic structure growth mechanisms which are more applicable for crystalline materials growth in aqueous media viz., Ostwald Ripening (OR) and Oriented Attachment (OA) growth mechanism. In both OR and OA, the crystal growth were involved at the expense of small sized particles through diffusion-controlled process. These mechanisms were suitable for aqueous media based anisotropic structure growth where particles can move freely **[45]**. Moreover, the role of the oriented attachment in the formation of natural twins, although more likely to occur in environments where crystals were free of moving and interacting, which was not explainable by a nucleation stage also possible **[46]**.

In general conditions, both [OR + OA] mechanisms favorable along with phase and structure transformations **[47]**. The charge distribution on dcbpy after binding on Ag surface and charge induced selective metal ion binding matters in each anisotropic structure formation. The selective surface adsorption of metal ions at enough metal concentration slower OR growth rate **[48]**. This eliminates the possibility of OR mechanism in this study. This makes unclear boundaries to study the crystal growth process. By considering all processes, the metal ion induced anisotropic structure formation followed OA mechanism with defects. If crystal growth follows only OA, it should produce defect-free single crystals with uniform distribution **[49]**, but not found without any defect. Nickel system alone gave cubic structure without any other morphology (**Fig. 5**).

The emerging oriented attachment process observed under near natural crystallization conditions and spontaneous self-organization of nanoparticles could shed new light on understanding of the detailed interaction mechanism between inorganic nanoparticles and their subsequent higher order self-assembly mechanism **[50]**.To make clear the mechanism for this type of anisotropic structure growth studies, more extensive work have to be done with advancement of theories with clear boundaries, which can give distinguishable key factors for their growth out of OA and OR theories.

This method has salient features as follows: a) Template free synthesis of silver flower like structure through simple reduction process in water, b) Usage of aqueous medium instead of organic solvents for anisotropic morphologies formation, c) Instead of using Polyvinylpyrolidone (PVP), n-Cetyltrimethylammonium bromide (CTAB), etc., a coordinating rich moiety, 4,4'-dicarboxy-2,2'-bipyridyl utilized for first time for silver flower like anisotropic structure synthesis, d) The flower petals of silver structure was tuned into various anisotropic structures with unique structural features with respect to each transition metal ion, e) Transition metal ion induced self-assembly of different anisotropic structures were observed, f) Environmentally benign approach, no toxic chemicals involved throughout anisotropic structure formation. These selective morphologies are expected to find applications in SERS and shape selective metal sensor, catalysis, magnetism studies and minerals formation in nature with specific metal selective binding studies.

Conclusion

We have synthesized dcbpy-Ag particles using a coordination rich 4,4'-dicarboxy-2,2'-bipyridyl as a surface capping agent. Its optical and structural behaviors were analyzed and discussed. Dcbpy-Ag particles unique symmetrical flower like morphology formation was proved via nucleation and growth mechanism. The change in optical properties in dcbpy-Ag particles, after addition of metal nitrates were discussed and morphological changes were monitored via SEM. Dcbpy-Ag particles showed better optical property in the presence of Cu^{2+} is key factor to design novel material for electronics. The SEM images clearly showed that the formation of various anisotropic structures induced by the transition metal ions. The metal ions induced self-assembly of anisotropic structures of dcbpy-Ag particles were studied by compiling crystal growth mechanisms (OR and OA mechanism). Each theory has its certain limits on morphology formation discussions. By comparing these theories, we believe that the presence of defects and high surface energy minimization factors may play the main role in the anisotropic structures growth. For complete understanding of such growth in solution phase, detailed theories with experimental advancements are yet to explore.

Acknowledgements

Authors gratefully acknowledge DST Nanomission, University of Delhi for financial support, and Dr. N. C. Mehra, Department of Geology for providing SEM facility.

Reference

1. a) Halperin, W. P. *Rev. Mod. Phys*. **1986**, *58*, 533.
   DOI: 10.1103/RevModPhys.58.533
   b) Mann, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 3392.
   DOI: 10.1002/1521-3773(20001002)39.
2. Templeton, A. C.; Wuelfing, W. P.; Murray, R. W.; *Acc. Chem. Res.* **2000**, *33*, 27.
   DOI: 10.1021/ar9602664.
3. El-Sayed, M. A. *Acc. Chem. Res.* **2000**, *34*, 257.
   DOI: 10.1021/ar960016n.
4. a) Lewis, L. N. *Chem. Rev*. **1993**, *93*, 2693;
   b) Shankar, S.S. ; Deka, S. *Sci. Adv. Mater*. **2011**, *3*, 169.
   DOI: 10.1166/sam.2011.1150.
   c) Hamilton, J. F. *Adv. Phys.* **1988**, *37*, 359;
   d) Sanders, A.W.; Routenberg, D. A.; Wiley, B. J.; Xia, Y.; Dufresne, E. R.; Reed, M. A. *Nano Lett.* **2006**, *6*, 1822.
   DOI:10. 1021/nl052471v.
   e) Taton, T. A.; Mirkin, C. A.; Letsinger, R. L. *Science* **2000**, *289*,1757.
   DOI:10.1126/science.289.5485.1757.
   f) Wang, H.; Brandl, D. W.; Nordlander, P.; Halas, N. J. *Acc. Chem. Res.* **2007**, *40*, 53.
   DOI: 10.1021/ar0401045.
   g) Chen, J.; Saeki, F.; Wiley, B. J.; Cang, H.; Cobb, M. J.; Li, Z.-Y.; Au, L.; Zhang, H.; Kimmey, M. B.; Li, X.; Xia, Y. *Nano Lett*. **2005**, *5*, 473.
   DOI: 10.1021/nl047950t.
   h) Cang, H.; Sun, T.; Li, Z.-Y.; Chen, J.; Wiley, B. J.; Xia, Y.; Li, X. *Opt. Lett.* **2005**, *30*, 3048.
   DOI: 10.1364/OL.30.003048.
   i) West, J. L.; Halas, N. J. *Annu. Rev. Biomed. Eng.* **2003**,*5*,285.
   DOI:10.1146/annurev.bioeng.5.011303.120723.
   j) Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A. *NanoToday* **2007**, *2*, 18.
5. a)Xia, H.; Bai, S.; Hartmann, J.; Wang, D. *Langmuir* **2010**, *26*, 3585.
   DOI: 10.1021/la902987w.
   b) Yin, B.; Ma, H.; Wang, S.; Chen, S. *J. Phys. Chem. B* **2003**,*107*, 8898.
   DOI: 10.1021/jp0349031.
   c) Jana, L. R.; Gearheart, L.; Murphy, C. J. *Chem Comm.* **2001**, *7*, 617.
   DOI: 10.1039/b100521i.
   d) Sotiropoulou, S.; Sierra-Sastre, Y.; Mark, S. S.; Batt, C. A. *Chem. Mater*. **2008**, *20*, 821.
   DOI: 10.1021/cm702152a.
   e) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev*. **2002**, *102*, 3757.
   DOI: 10.1021/cr010350j.
   f) Niemeyer, C. M. *Angew. Chem. Int. Ed.* **2001**, *40*, 4128.
   DOI: 10. 1002/1521-3773(20011119)40.
   g) Tanoue, R.; Higuchi, R.; Enoki, N.; Miyasato, Y.; Uemura, S.; Kimizuka, N.; Stieg, A. Z.; Gimzewski, J. K.; Kunitake, M. *ACS Nano* **2011**, *5*, 3923.
   DOI: 10.1021/nn200393q.
   h) Ciszek, J. W.; Huang, L.; Tsonchev, S.; Wang, Y.; Shull, K. R.; Ratner, M. A.; Schatz, G. C.; Mirkin, C. A. *ACS Nano* **2010**, *4*, 259.
   DOI: 10.1021/nn901383d.
6. Förster, S.; Antonietti, M. *Adv. Mater.*, **1998**, *10*, 195.
   DOI:10.1002/(sici)1521-4095(199802)10.
7. Han, Y-J.; Kim, J. M.; Stucky, G. D. *Chem. Mater*. **2000**, *12*, 2068.
   DOI: 10.1021/cm0010553.
8. Teranishi, T.; Sugawara, A.; Shimizu, T.; Miyake, M. *J. Am. Chem. Soc.* **2002**, *124*, 4210.
   DOI: 10.1021/ja017536k.
9. Chen, S. H.; Carroll, D. L. *J. Phys. Chem. B.* **2004**, *108*, 5500.

DOI: 10.1021/jp031077n.

10. Viau, G.; Piquemal, J-Y.; Esparrica, M.; Ung, D.; Chakroune, N.; Warmont, F.; Fievet, F. *Chem. Commun.* **2003**, *17*, 2216.
DOI: 10.1039/B304021F.
11. Dong, X.Y.; Ji, X. H.; Wu, H.L.; Zhao, L. L.; Li, J.; Yang, W. S. *J. Phys. Chem. C.* **2009**, *113*, 6573.
DOI: 10.1021/jp900775b.
12. Niu, W.X.; Li, Z. Y.; Shi, L. H.; Liu, X. Q.; Li, H. J.; Han, S.; Chen, J.; Xu, G. B.*Cryst. Growth Des*. **2008**, *8*, 4440.
DOI: 10.1021/cg8002433.
13. Qiu, P.; Mao, C. *ACS Nano* **2010**, *4*, 1573.
DOI: 10.1021/nn9009196.
14. Kumar, P. S.; Pastoriza- Santos, I.; Rodriguez-Gonzalez, B.; Garcia de Abajo, F. J.; Liz-Marzan, L. M. *Nanotechnology* **2008**, *19*, 15606.
DOI: 10.1088/0957-4484/19/01/015606.
15. Mohanty, A.; Garg, N.; Jin, R. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 4962.
DOI: 10.1002/anie.201000902.
16. Rodriguez-Lorenzo, L.; Alvarez-puebla, R. A.; Garcia de Abajo, F. J.; Liz-Marzan, L. M. *J. Phys. Chem.C* **2010**, *114*, 7336.
DOI: 10.1021/jp909253w.
17. Raju, J. R.; Kumar, K. J. *J. Raman spectrosc.* **2011**, *42*, 1505.
DOI: 10.1002/jrs.2895.
18. Bratlie, K. M.; Lee, H.; Komvopoulos, K.; Yang, P. D.; Samorjai, G. A. *Nano Lett.* **2007**, *7*, 3097.
DOI: 10.1021/nl0716000.
19. Tang, S. C.; Meng, X. K.; Wang, C. C.; Cao, Z. H. *Mater. Chem. Phys.* **2009**, *114*, 842.
DOI: 10.1016/j.matchemphuys.20088.10.048.
20. Hong, L.; Li, Q.; Lin, H.; Li, Y. *Mater. Res. Bull.*, **2009**, *44*, 1201.
DOI: 10. 1016/J.materresbull.2009.01.017.
21. (a) Recent Developments in Bio- Nanocomposites for Biomedical Applications, Ed. Ashutosh Tiwari, Nova Science Publishers, Inc., New York, USA, ISBN: 978-1-61761-008-0, 2010; b) Intelligent Nanomaterials, Eds. Ashutosh Tiwari, Ajay K. Mishra, Hisatoshi Kobayashi, Anthony PF Turner, Wiley-Scrivener Publishing LLC, USA, ISBN 978-04-709387-99, 2012; c) Biomedical Materials and Diagnostic Devices, Eds. Ashutosh Tiwari, Hisatoshi Kobayashi, Anthony PF Turner, Wiley-Scrivener Publishing LLC, USA, 20112; d) Integrated Biomaterials for Biomedical Technology, Eds. Murugan Ramalingam, Ashutosh Tiwari, Seeram Ramakrishna, Hisatoshi Kobayashi, Wiley-Scrivener Publishing LLC, USA, 20112.
22. (a) Singh, C.; Baboota, R. K.; Naik, P. K.; Singh, H. *Adv. Mat. Lett.* **2012**, *3(4)*, 279-285.
DOI: 10.5185/amlett.2011.10312.
b)Varshney, R.; Bhadauriaa, S.; Gaur, M. S. *Adv. Mat. Lett.* **2010**, *1(3)*, 232-237.
DOI: 10.5185/amlett.2010.9155.
c) Zhang, Y.; Wang, Y.; Yang, P. *Adv. Mat. Lett.* **2011**, *2(3)*, 217-221.
DOI: 10.5185/amlett.2011.2223.
d) Ashutosh Tiwari, *Adv. Mat. Lett.* **2012**, *3(1)*, 1-1.
DOI: 10.5185/amlett.2012.13001.
e) Hussain, J. I.; Sunil Kumar, Hashmi, A. A.; Zaheer Khan. *Adv. Mat. Lett.* **2011**, *2(3)*, 188-194.
DOI:10.5185/amlett.2011.1206.
f) Christensen, L.; Vivekanandhan, S.; Misra, M.; Mohanty, A. K. *Adv. Mat. Lett.* **2011**, *2(6)*, 429-434.
DOI: 10.5185/amlett.2011.4256.
23. Bradley, J.S.; Tesche, B.; Busser, W.; Maase, M.; Reetz, M.T. *J. Am. Chem. Soc.*, **2000**, *122*, 4631.
DOI: 10. 1021/ja99409y.
24. Jin, R. C.; Cao,Y. W.; Mirkin, C. A.; Kelly, K. L.; Schatz, G.C.; Zheng, J.G. *Science* **2001**, *294*, 1901.
DOI: 10.1126/science.1066541.
25. Jacobs, B. W.; Houk, R. J. T.; Anstey, M. R.; House, S. D.; Robertson, I. M.; Talin, A. A.; Allendorf, M. D. *Chem. Sci.* **2011**, *2*, 411.
DOI: 10.1039/c0sc00377h.
26. a) Yu, S.; Chow, G. M. *J. Mater. Chem.***2004**, *14*, 2781.
DOI: 10.1039/b404964k. b) Yu, D.; Yam, V. W.-W. *J. Am. Chem. Soc*. **2004**, *126*, 13200. c) Yu, D.; Yam, V.W.-W. *J. Phys. Chem. B* **2005**, *109*, 5497.
27. a) Bradley, J. S.; Schmid, G. *In Clusters and Colloids: From Theory to Applications* (Eds.); VCH: Weinheim, **1994**, 459; b) Turkevich, J.; Stevenson, P. C.; Hillier, J. *J. Discuss. Faraday Soc.*, **1951**, 55.
28. Oxtoby, D.W. *Nature* **2000**, *406*, 464.
DOI: 10.1038/35020163.
29. Tynan, E.; Jensen, P.; Kruger, P.E.; Lees, A. C.; Nieuwenhuyzen, M. *Dalton Trans.* **2003**, *7*, 1223.
DOI: 10.1039/b212318e.
30. Fuldner, S.; Mild, R.; Siegmund, H. I.; Schroeder, J. A.; Gruber, M.; Konig, B. *Green Chem.* **2010**, *12*, 400.
DOI: 10.1039/b918140g.
31. Liu, Y. H.; Lu, Y-L.; Wu, H-C.; Wang, J-C.; Lu, K-L. *Inorg. Chem.* **2002**, *41*, 2597.
DOI: 10.1021/ic011192h.
32. Ribeiro, C.; Vila, C.; Elias, J.M.; Bettini, J.; Longo, E.; Leite, E. R. *Chem. Eur. J.* **2007**, *13*, 5798.
DOI: 10.1002/chem.200700034.
33. Cölfen, H.; Mann, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 2350.
DOI: 10.1002/anie.200200562.
34. a) Wiley, B.; Sun, Y.; Mayers, B.; Xia, Y. *Chem. Eur. J.* **2005**, *11*,454;
DOI: 10.1002/chem.200400927.
b) Wiley, B.; Sun, Y.; Chen, J.; Cang, H.; Li, Z.-Y.; Li, X.; Xia, Y. *MRS Bull*. **2005**, *30*, 356.
DOI: 10.1557/mrs2005.98.
c) Wiley, B.; Sun, Y.; Xia, Y. *Acc. Chem. Res.*, **2007**, *40*, 1067;
DOI: 10. 1021/ar7000974.
d) Tao, A. R.; Habas, S.; Yang, P. *Small*, **2008**, *4*, 310.
DOI: 10.1002/smll.200701295.
35. Niederberger, M.; Cölfen, H. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3271.
DOI: 10.1039/b604589h.
36. Si, S.; Raula, M.; Paira, T. K.; Mandal, T. K. *ChemPhysChem*, **2008**, *9*, 1578.
DOI: 10.1002/cphc.200800121.
37. Vaidya, S.; Rastogi, P.; Agarwal, S.; Gupta, S. K.; Ahmad, T.; Antonelli, A.M.; Ramanujachary, Jr. K. V.; Lofland, S. E.; Ganguli, A. K. *J. Phys. Chem. C* **2008**, *112*, 12610.
DOI: 10.1021/jp803575h.
38. a) Tang, A.; Qu, S.; Li, L.; Hou, Y.; Teng, F.; Cao, J.; Wang, Y.; Wang, Z. *Nanotechnology*, **2010**, *21*, 85602.
b) Wang, S.; Ning, J.; Zhao, L.; Liu, B.; Zou, B. *J. Cryst. Growth*, **2010**, *312*, 2060.
39. Park, S-H.; Kim, H. J. *J. Am. Chem. Soc.* **2004**, *126*, 14368.
DOI: 10.1021/ja047425w.
40. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. *Angew. Chem. Int. Ed.* **2009**, *48*, 60.
DOI: 10.1002/anie.200802248.
41. Ming, N.; Sunagawa, I. *J. Cryst. Growth*. **1988**, *87*, 13.
42. Lofton, C.; Sigmund, W. *Adv. Funct. Mater.* **2005**, *15*, 1197.
DOI: 10.1002/adfm.200400091.
43. Wen, X.; Xie, Y. T.;. Mak, M. W. C.; Cheung, K. Y.; Li, X. Y.; Renneberg, R.;Yang, S. *Langmuir* **2006**, *22*, 4836.
DOI: 10.1021/la060267x.
44. a) Huang, H. H.; Ni, X. P.; Loy, G. L.; Chew, C.H.; Tan, K. L.; Loh, F. C.; Deng, J. F.; Xu, G. Q. *Langmuir* **1996**, *12*, 909.
DOI: 10.1021/la950435d.
b) Zhang, Z.; Zhao, B.; Hu, L. *J. Solid State Chem.* **1996**, *121*, 105.
c) Bonet, F.; Tekaia-Elhsissen, K.; Sarathy, K. V. *Bull. Mater. Sci.* **2000**, *23*,165. d) Gao, Y.; Jiang, P.; Liu, D. F.; Yuan, H. J.; Yan, X. Q.; Zhou, Z. P.; Wang, J. X.; Song, L.; Liu, L. F.; Zhou, W. Y.; Wang, G.; Wang, C. Y.; Xie, S. S.; Zhang, J. M.; Shen, D. Y. *J. Phys. Chem. B* **2004**, *108*, 12877.
DOI: 10.1021/jp037116c.
45. Banfield, J. F.; Hamers, R. J. "*Geomicrobiology: Interaction Between Microbes and Minerals vol.35 of Reviews in Mineralogy* Banfield", J. F.; K. H. Nealson, (Eds.) (Mineralogical Society of America, Washington, DC, 1997), 86.
46. Nespolo, M.; Ferraris, G. *Eur. J. Mineral.* **2004**, *16*, 401.
DOI: 10.1127/0935-1221/2004/0016-0401.
47. Zhang, H.; Banfield, J. F. *Chem.Mater.* **2002**, *14*, 4145.
DOI: 10.1021/cm020072k.
48. a) Hu, Z.; Oskam, G.; Penn, R. L.; Pesika, N.; Searson, P. C. *J. Phys. Chem. B* **2003**, *107*, 3124.
DOI: 10.1021/jp020580h.
b) Oskam, G.; Hu, Z.; Penn, R. L.; Pesika, N.; Searson, P. C. *Phys. Rev. E.*, **2002**, *66*, 114039.
DOI: 10.1103/PhysRevE.66.011403.

49. Zhang, J.; Huang, F.; Lin, Z. *Nanoscale.*, **2010**, *2*, 18.
DOI: 10.1039/B9NR00047J.

50. a) Yu, S. H.; Ceolfen, H. *Nature-inspired Nanoparticle Superstructures;* Kotov, N.N.; Taylor & Francis Group, FL, (Eds.); CRC Press: **2005**, Chapter 11, 269; b) Zhang, Q.; Liu, S-J.; Yu, S-H. *J. Mater. Chem.* **2009**, *19*, 191.
DOI: 10.1039/B807760F.