VECIMS 2009 - International Conference on Virtual Environments, Human-Computer Interfaces and Measurements Systems
Hong Kong, China
May 11-13, 2009

Biomolecule-Assisted Synthesis of 3D Structure Gold Nanocrystals

in the Presence of Cystamine Dihydrochloride or Cysteamine

Siyue Li[1], Xin Chen[1], Jian Weng[1], Qiqing Zhang[1]*

[1]Research Center of Biomedical Engineering, Department of Biomaterials, College of Materials, Xiamen Univerisity, Research Center of Biomedical Engineering of Xiamen City, The Key Laboratory of Biomedical Engineering of Fujian Province,

Xiamen 361005 P.R. China

Qiqing Zhang[2]*

[2]Institute of Biomedical Engineering, Chinese Academy of Medical Sciences & Peking Union Medical College, The Key Laboratory of Biomedical Material of Tianjin,

Tianjin 300192 P.R. China

zhangqiq@xmu.edu.cn

Abstract: **A facile cystamine-assisted route was designed for the selectively controlled synthesis of 1D and novel, interesting 3D gold litchi-like nanostructures. By controlling reaction conditions such as the molar ratio between $HAuCl_4$ and cystamine dihydrochloride and the reaction time, the synthesis of various 3D architectural structures and 1D structure in large quantities can be controlled. The formation mechanism for the gold litchi-like assemblies with well-arranged nanorods was also discussed. In addition, as the control test, featheriness gold structures were obtained through using cysteamine as the assisted agent. On the basis of the results from SEM studies and our analysis, we speculate that the different morphologies obtained by cystamine dihydrochloride and cysteamine due to the Au-S interaction. These differences in hydrogen storage capacity are likely due to the size and density of space/pores as well as the morphology of different nanostructures. This facile, environmentally benign, and solution-phase biomolecule-assisted method can be potentially extended to the preparation of other metal nanostructures.**

Keywords: cystamine • litchi-like gold nanostructures • Au-S interaction

I. INTRODUCTION

A growing interest is being shown in biomineralization and biomimetic synthesis[1] for the creation of nanoscale materials because environmentally benign, 'green' conditions can be used rather than the extreme conditions needed for conventional chemical synthesis.[2] Crystal morphology and size have often been biologically regulated by biomolecules[3,4] or organisms.[5,6] Some fundamental investigations have revealed that biomolecules and organisms can selectively recognize inorganic surfaces or serve as matrices for inorganic growth and nucleation.[7] Biomolecule-assisted synthesis methods have been a new and promising focus in the preparation of various nanomaterials where biomolecules have been exploited only as structure-directing agents.

Recently, biomolecule-assisted synthesis methods have been a new and promising focus in the preparation of various nanomaterials where biomolecules have been exploited only as structure-directing agents. Protein cages were adopted as the templates to synthesize nanocrystals.[8, 9] Virus, peptide, and lemongrass were utilized as templates to prepare transitional metal nanomaterials.[10-14] Nanoparticles and nanowires of metal sulfide semiconductors have successfully been fabricated and assembled using peptide, virus, bacteria, and fungus in the presence of Na_2S or H_2S.[14-20] These interesting works mainly focused on the preparation and assembly of semiconductor nanoparticles with the assistance of macro-biomolecules that only function as the structure-directing molecules rather than as the sulfur source. For example, it was confirmed that CdS nanoparticles could not form in the absence of sulfur-containing inorganic salts when fusarium oxysporum biomass was adopted.[20] More recently, Komarneni et al. used glutathione (GSH), a large polypeptide molecule, as both the assembling molecule and the sulfur source to synthesize the highly ordered snowflake structure of bismuth sulfide nanorods under microwave irradia- tion.[21] This thought-provoking work inspires us to explore a simpler and more economical method to prepare metal sulphides using small biomolecules. Thus, L-cysteamine ($HS\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$) has attracted researchers' attention because of its simple hydrosulfide-group-including structure. In a recent communication, Qian and co-workers synthesized antimony sulfide nanowires in the presence of cysteamine.[22] Cysteamine and glutathione have also been used to prepare biostabilized CdS nanoparticles,[23] where the band gap energies could be adjusted by varying the pH value, the biomolecules, and their corresponding concentrations. Very recently, we have also synthesized the porous spongelike Ni_3S_2 nanostructures on Ni foil substrate with high electrochemical activity in the presence of cysteamine.[24] Thus, it would be interesting to develop a simple L-cysteamine-assisted biological approach to prepare other sulfide nanomaterials, especially with a novel homogeneous self-assembly pattern of 1D semiconductor nanostructures. Herein we demonstrate the biological synthesis of large amounts of litchi-like gold nanoparticles by a single-step, room-temperature reduction of aqueous chloroaurate ions ($AuCl_4^-$) by the cystamine dihydrochloride and cysteamine.

978-1-4244-3809-9/09/$25.00 ©2009 IEEE

II. EXPERIMENTAL

A. Chemicals and Materials:

Hydrogen tetracholoroauric acid (HAuCl4•3H2O), sodium bisulfate were received from Shanghai chemical Co. Cystamine dihydrochloride and Cysteamine (99%) was received from Alfa Aesar. All solution were prepared using Millipore (Model Milli-Q) purified water.

B. Syntheses of Gold Nanocrstals:

Cystamine Dihydrochloride and Cysteamine was first added to de-ionised water (23 mL). The mixture was stirred with a magnetic blender for 10 min, then the aqueous solution of $HAuCl_4•3H_2O$ (2 mL, 0.01 M) was added dropwise. The solution turned yellow owing to the presence of $AuCl_4^-$ ions. The mixture solution was stirred for 30min at room temperature. In order to separate the Au nanoparticles from the solvent, the final solution was centrifuged at 3500 rpm for 30 min. The products were purified by repetitive dispersion/precipitation cycles with de-ionised water to ensure the complete removal of excess cystamine, and finally dispersed in de-ionised water with aid of sonication. Further experiments, which were similar to those presented above, were performed under desired conditions.

C. Characterization of Gold Nancystals:

Field-emission scanning electron microscopy (FESEM) images and corresponding energy-dispersive X-ray spectroscopy (EDX) patterns were obtained on LEO-1530 operated at 20 kV. Transmission electron microscope (TEM) images were obtained using JEM-2100 (HR) operated at 200kV. High-resolution transmission electron microscopy (HRTEM) images were obtained using Tecnai F30 operated at 300 kV. The selective area electron diffraction (SAED) patterns were taken on Tecnai F30 microscope. X-ray diffraction (XRD) patterns were measured on a Panalytical X'pert PRO. The samples were prepared by placing a few drops of the colloidal solutions either on copper grids coating with lacey carbon film for HRTEM, or on small pieces silicon wafer (P-100) for FESEM, and were allowed to dry at air. The UV-vis absorption data were collected on a Shimadzu UV2550 UV-vis spectrophotometer. The size distribution was obtained using Mavern Nano-ZS particle-size analyzer.

III. RESULT

The litchi-like gold nanoparticles were obtained by the simple mixing of an aqueous solution of cystamine dihydrochloride (0.1 mM) and $HAuCl_4$ (0.02 mM) at room temperature and stirring the solution for desired time. The solution suddenly turned to opaque after mixing, indicating the formation of Au nanoparticles. Fig. 1 shows the representative FESEM images obtained for the nanoparticles. Interestingly, the FESEM images show nanocrystals having peculiar shape and morphology, very similar to the litchi chinensis. The litchi-like gold nanoparticles have an average size of c.a.400 nm. In our case, the anisotropic particles have been obtained without such surfactants. Cystamine dihydrochloride not only functions as a reducing agent but also controls the growth of the particles as the surfactants. It should be mentioned here that the concentration of cystamine dihydrochloride controls the shape and surface morphology of the nanoparticles.

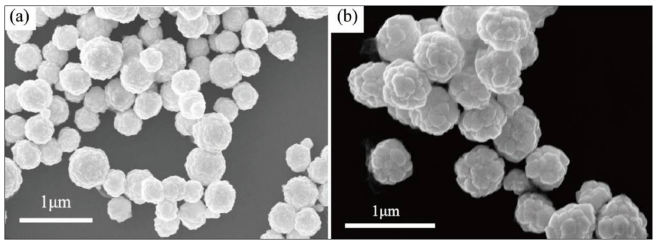

Fig. 1. FESEM images of the litchi-like gold nanoparticles synthesized in aqueous solution with cystamine dihydrochloride (0.1mM) and $HAuCl_4$(0.02mM) at room temperature for 30min.

The chemical composition of nanoparticles was determined by energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum (Fig. 2a) with only one peak corresponding to Au revealed that the nanoparticles were pure metallic Au. Fig. 2b presents an X-ray diffraction (XRD) pattern of the as-synthesized products on a glass substrate. It can be seen that the diffraction peak at ca. 38.2° assigned to the {111} lattice plane of face-centered cubic (fcc) Au crystal has an overwhelming intensity in the pattern. The ratio between the intensities of the {111} and {200} peaks is higher than the value reported for a conventional powder sample (Joint Committee on Powder Diffraction Standards (JCPDS) file number 04-0784, 2.54 versus 1.92), which indicates that the diffraction from {111} planes was enhanced.

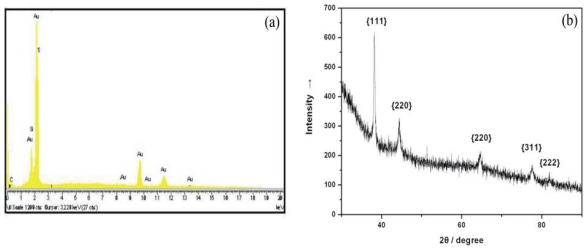

Fig. 2. XRD pattern of litchi-like gold nanoparticles synthesized in aqueous solution with cystamine dihydrochloride (0.1mM) and $HAuCl_4$(0.02 mM) at room temperature for 30min.

It is well-known that the surface morphology and shape of the nanoparticles strongly depends on the concentration of reducing/stabilizing agent and the metal precursor. Fig. 3 shows the morphology of the products synthesized at room temperature with different cystamine dihydrochloride concentrations fixing other parameters of the reaction. In this case, gold nanoparticles with different morphology and diameter were obtained. When the synthesis was conducted under increasing concentration of cystamine dihydrochloride

from 0.02M to 0.4M (the molar ratio of cystamine dihydrochloride to gold was changed from 1:1 to 20:1), the obtained gold products were dominated by particles with irregular form to litchi-like nanoparticles. We clearly observed that the shape of the nanoparticles becomes more and more regular with the concentration of cystamine dihydrochloride increase. During the synthesis of the litchi-like nanoparticles, the reaction was quenched at various time intervals to address the mechanism related to crystal growth and shape formation. The reaction could be easily followed through its distinctive color changes. The yellowish solution turned nearly colorless transparent at 1 min, then turned purplish-gray, and the final solution was turbidness deep yellow.

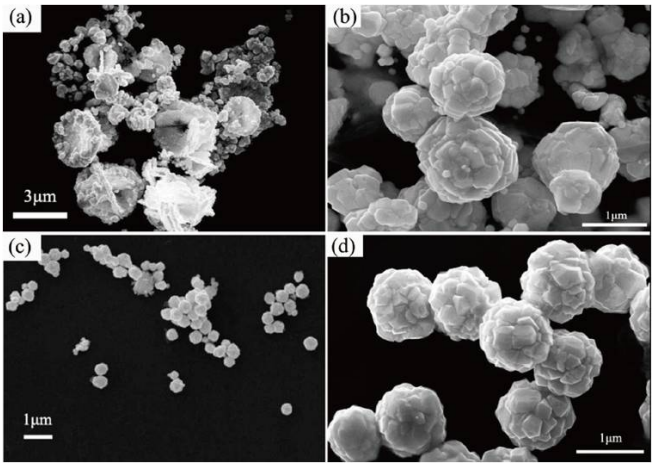

Fig. 3. FESEM images of the gold nanoparticles synthesized under different cystamine dihydrochloride concentrations (a) 0.02 mM, (b) 0.1 mM, (c) 0.2 mM, (d) 0.4 mM

With the primary reductant identified, it becomes possible to evaluate its role in generating nanostructures of specific shapes. As established, the shapes of final products are determined by the rate at which metal atoms add to metal clusters (fluxional assemblies) to form seeds (nonfluxional), the structures of these initial seeds (twinned vs. single crystal), the rate at which metal atoms add to seed faces, and the binding selectivity of capping agents.[25] As it known to all, the formation of anisotropic nanostructure in liquid media involves the utilization of a capping agent such as a surfactant to kinetically control the growth rate. In our case, the anisotropic particles have been obtained without such surfactants; cystamine dihydrochloride not only functions as a reducing agent but also controls the growth of the particles as the surfactants. It should be mentioned here that the concentration of cystamine dihydrochloride controls the shape and surface morphology of the nanoparticles. In order to investigate the role of cystamine dihydrochloride in the process of chemical synthesis, we chose cysteamine which has a similar functional group with cystamine dihydrochloride as the reductant. It is very interesting to note that the products obtained in that control experiment are very similar to the feather (Fig 4). Cysteamine, a very important biomolecule with several functional groups (SH, NH_2), has a strong tendency to coordinate with inorganic cations and metals, and has been exploited in the synthesis of quantum dots[26], nanotubes,[27] 3D spherical nanostructures from nanorods,[28] and flowerlike patterns with nanorods.[29] We clearly observed that the shape of the featheriness gold particles becomes more and more complicated with the concentration of cysteamine increase.

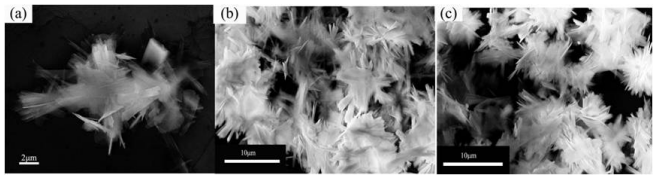

Fig. 4. SEM images of the samples with different cysteamine dihydrochloride concentrations (a) 0.1 mM, (b) 0.2 mM, (c) 0.4 mM

Cystamine, the dimer of cysteamine with a disulfide group, thus adsorbs on Au (111) due to the Au-S interaction much more slowly than cysteamine at the same concentration, and cystamine needs a higher concentration than cysteamine to approach adsorption saturation. [30] The thiol molecules (cysteamine and cystamine) contain a short carbon chain (only three carbons) but two strongly polar end groups (i.e. protonated amine and deprotonated carboxylic acid). Hydrogen bonds and electrostatic forces between carboxylic and amine groups must be strong and could have not only intermolecular but also intramolecular components. These strong forces undoubtedly play a crucial role in the molecular organization on the substrate and are likely to be the direct origin of the molecular hexamer (cysteamine) and trimer (cystamine) formation in their adlayers. The presence of increasing concentrations of cysteamine causes the CV peak at 0.25 V to gradually vanish and the double layer to inflate slightly (Figure 5A, curves b-d). The capacitance peak at 0.2-0.45 V is also strongly attenuated and the double-layer capacitance lowered (Figure 5B, curves b-d). This means that cysteamine molecules strongly adsorb in the whole potential range from -0.5 to 0.5 V and displace the adsorbed acetate. Similar patterns appear for cystamine, except that about 10-fold higher concentrations are needed to invoke similar attenuation as that of cysteamine. [30] This could be due to the fact that adsorption of thiol is strongly preferred to adsorption of disulfides. [31]

Dissociative adsorption of disulfides (with an S-S bond) is determined not only by equilibrium adsorption isotherms but also by the kinetics of the combined dissociation and adsorption process. Cystamine, the dimer of cysteamine with a disulfide group, thus adsorbs much more slowly on Au (111) than cysteamine at the same concentration, and cystamine needs a higher concentration than cysteamine to approach adsorption saturation. It can explain why the gold nanoparticles are litchi-like in the presence of cystamine but featheriness in the presence of cysteamine.

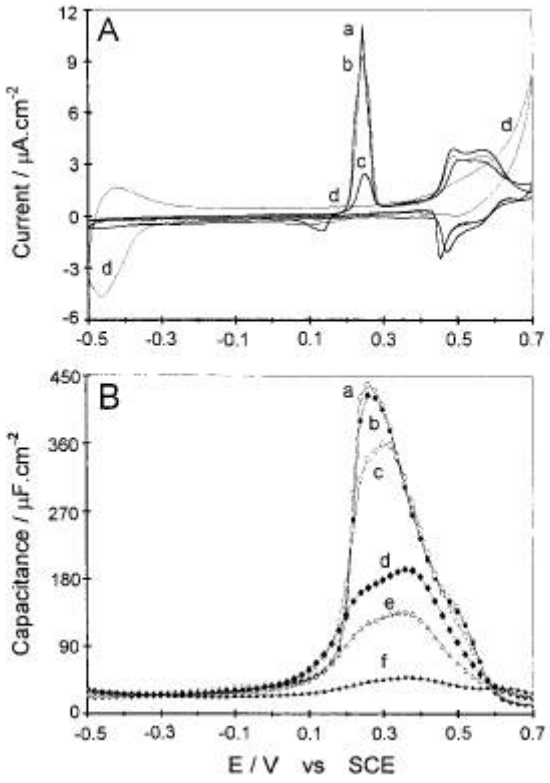

Fig. 5. Cyclic voltammograms (A) and capacitance versus potential curves (B) of Au(111) in 50 mM NH_4Ac (pH =4.6) containing cysteine (a) 0, (b) 1.0×10^{-7}, (c) 5×10^{-7}, (d) 1.0×10^{-6}, (e) 2.0×10^{-6}, (f) 5×10^{-6} M. Scan rate 50 $mV \cdot s^{-1}$ for the CVs.

Egon Matijevic et al illustrated that there are two main growth mechanisms, a. the growth mechanism involving only incorporation of additional metal atoms onto nuclei will favor the development of crystals of metal of regular shape (facets, edges) with few irregularities in their lattice, dense, and with very little internal grain boundary; b. metal particles formed through an aggregation mechanism will be mostly spherical and polycrystalline, having large internal grain boundaries and, consequently, a lower density.[32] In reality it is likely that mechanisms involving both growth and aggregation frequently take place in the same system. Depending on the prevailing process, the polycrystallinity, internal grain boundary, density and shape of the final particles will be between the extreme cases. On the basis of experimental results and discussions, a possible mechanism for the formation of the litchi-like gold nanostructures is proposed and displayed below. The proposed mechanism of growth of litch-like gold nanostructures consists of two steps. In the first step, the gold ions interact with small cystamine molecules through the mating reaction of $-NH_2$ and Au^{3+}; they are reduced to gold atoms. Small cystamine molecules can cap the surfaces of immediately formed Au nuclei, at the same time, they can also easily desorbs and leave from the surfaces of the Au nuclei because of the fast diffusion in solvent. In the second step, Small cystamine molecules could easily stick and connect with each other. When the Au nanoparticles meet together coincidently, the primary nanoparticles coalesce with other nearby primary nanoparticles or interact with cystamine through Au-S interaction to form large agglomeration, which are the final litchi-like nanostructures.

IV. CONCLUSION

We have successfully synthesized litchi-like gold nanoparticles through the one-step reduction of $HAuCl_4$ only using cystamine without any extra control, seed, and surfactant at room temperature. The existence of these small biomolecules is believed to be the origin of the Au particles as a functional reducing agent. Furthermore, we investigate the proper reduction mechanism of the whole process and detail compared two different morphologies of the products synthesized from cystamine and cysteamine. Cystamine, the dimer of cysteamine with a disulfide group, thus adsorbs much more slowly on Au than cysteamine at the same concentration, which result to a different morphology. The novel gold nanomaterials may find potential applications in biomedical fields. This facile, environmentally benign, and solution-phase biomolecule-assisted method can be potentially extended to the preparation of other metal nanostructures.

ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (2006CB933300).

REFERENCES

[1] E. Bauerlein, "Biomineralization of unicellular organisms: An unusual membrane biochemistry for the production of inorganic nano- and microstructures," Angew. Chem. Int. Ed, vol. 42, pp. 614-641, 2003

[2] P. Raveendran, J. Fu, and S.L. Wallen, "Completely "green" synthesis and stabilization of metal nanoparticles," Journal of the American Chemical Society, vol. 125, pp. 13940-13941, Nov 2003.M.

[3] M. Allen, D. Willits, J. Mosolf, M. Young, and T. Douglas, "Protein cage constrained synthesis of ferrimagnetic iron oxide nanoparticles," Advanced Materials, vol. 14, pp. 1562-1568, Nov 2002.

[4] S. Dieluweit, D. Pum, and U.B. Sleytr, "Formation of a gold superlattice on an S-layer with square lattice symmetry," Supramolecular Science, vol. 5, pp. 15-19, 1998.

[5] T. Douglas, E. Strable, D. Willits, A. Aitouchen, M. Libera, and M. Young, "Protein engineering of a viral cage for constrained nanomaterials synthesis," Advanced Materials, vol. 14, pp. 415-421, 2002.

[6] T. Douglas and M. Young, "Virus particles as templates for materials synthesis," Advanced Materials, vol. 11, pp. 679-688, Jun 1999.

[7] J.N. Cha, G.D. Stucky, D.E. Morse, and T.J. Deming, "Biomimetic synthesis of ordered silica structures mediated by block copolypeptides," Nature, vol. 403, pp. 289-292, Jan 2000.

[8] E. Gillitzer, D. Willits, M. Young, and T. Douglas, "Chemical modification of a viral cage for multivalent presentation," Chemical Communications, (no. 20), pp. 2390-2391, 2002.

[9] T. Douglas, D.P.E. Dickson, S. Betteridge, J. Charnock, C.D. Garner, and S. Mann, "Synthesis and structure of an iron(III) sulfide-ferritin

bioinorganic nanocomposite," Science (Washington D C), vol. 269, pp. 54-57, 1995

[10] W. Shenton, T. Douglas, M. Young, G. Stubbs, and S. Mann, "Inorganic-organic nanotube composites from template mineralization of tobacco mosaic virus," Advanced Materials, vol. 11, pp. 253-264, Feb 1999.

[11] S.S. Shankar, A. Rai, B. Ankamwar, A. Singh, A. Ahmad, and M. Sastry, "Biological synthesis of triangular gold nanoprisms," Nature Materials, vol. 3, pp. 482-488, Jul 2004.

[12] M. Knez, A.M. Bittner, F. Boes, C. Wege, H. Jeske, E. Maiss, and K. Kern, "Biotemplate synthesis of 3-nm nickel and cobalt nanowires," Nano Letters, vol. 3, pp. 1079-1082, Aug 2003.

[13] B.D. Reiss, C.B. Mao, D.J. Solis, K.S. Ryan, T. Thomson, and A.M. Belcher, "Biological routes to metal alloy ferromagnetic nanostructures," Nano Letters, vol. 4, pp. 1127-1132, Jun 2004.

[14] C.B. Mao, D.J. Solis, B.D. Reiss, S.T. Kottmann, R.Y. Sweeney, A. Hayhurst, G. Georgiou, B. Iverson, and A.M. Belcher, "Virus-based toolkit for the directed synthesis of magnetic and semiconducting nanowires," Science, vol. 303, pp. 213-217, Jan 2004.

[15] B. Gilbert, F. Huang, H.Z. Zhang, G.A. Waychunas, and J.F. Banfield, "Nanoparticles: Strained and stiff," Science, vol. 305, pp. 651-654, Jul 2004.

[16] C.T. Dameron and D.R. Winge, "Peptide-mediated formation of quantum semiconductors," Trends Biotechnol, vol. 8, pp. 3-6, 1990 1990.

[17] W. Shenton, T. Douglas, M. Young, G. Stubbs, and S. Mann, "Inorganic-organic nanotube composites from template mineralization of tobacco mosaic virus," Advanced Materials, vol. 11, (no. 3), pp. 253-262, Feb 1999.

[18] C.B. Mao, C.E. Flynn, A. Hayhurst, R. Sweeney, J.F. Qi, G. Georgiou, B. Iverson, and A.M. Belcher, "Viral assembly of oriented quantum dot nanowires," Proceedings of the National Academy of Sciences of the United States of America, vol. 100, pp. 6946-6951, Jun 2003.

[19] R.Y. Sweeney, C.B. Mao, X.X. Gao, J.L. Burt, A.M. Belcher, G. Georgiou, and B.L. Iverson, "Bacterial biosynthesis of cadmium sulfide nanocrystals," Chemistry & Biology, vol. 11, pp. 1553-1559, Nov 2004.

[20] A. Ahmad, P. Mukherjee, D. Mandal, S. Senapati, M.I. Khan, R. Kumar, and M. Sastry, "Enzyme mediated extracellular synthesis of CdS nanoparticles by the fungus, Fusarium oxysporum," Journal of the American Chemical Society, vol. 124, pp. 12108-12109, Oct 2002.

[21] Q.Y. Lu, F. Gao, and S. Komarneni, "Biomolecule-assisted synthesis of highly ordered snowflakelike structures of bismuth sulfide nanorods," Journal of the American Chemical Society, vol. 126, pp. 54-55, Jan 2004.

[22] X.Y. Chen, X.X. Li, Y. Jiang, C.W. Shi, and X.L. Li, "Rational synthesis of alpha-MnO_2 and gamma-Mn_2O_3 nanowires with the electrochemical characterization of alpha-MnO_2 nanowires for supercapacitor," Solid State Communications, vol. 136, pp. 94-96, Oct 2005.

[23] C. Barglik-Chory, C.R.H. Strohm, and G. Muller, "Adjustment of the band gap energies of biostabilized CdS nanoparticles by application of statistical design of experiments," Journal of Physical Chemistry B, vol. 108, pp. 7637-7640, Jun 2004.

[24] B. Zhang, X.C. Ye, W. Dai, W.Y. Hou, and Y. Xie, "Biomolecule-assisted synthesis and electrochemical hydrogen storage of porous spongelike Ni_3S_2 nanostructures grown directly on nickel foils," Chemistry-a European Journal, vol. 12, pp. 2337-2342, Mar 2006.

[25] Y.G. Sun, B. Mayers, and Y.N. Xia, "Transformation of silver nanospheres into nanobelts and triangular nanoplates through a thermal process," Nano Letters, vol. 3, pp. 675-679, May 2003.

[26] J.H. Gao, G.L. Liang, B. Zhang, Y. Kuang, X.X. Zhang, and B. Xu, "FePt@CoS_2 yolk-shell nanocrystals as a potent agent to kill HeLa cells," Journal of the American Chemical Society, vol. 129, pp. 1428-1433, Feb 2007.

[27] H. Tong, Y.J. Zhu, L.X. Yang, L. Li, and L. Zhang, "Lead chalcogenide nanotubes synthesized by biomolecule-assisted self-assembly of nanocrystals at room temperature," Angewandte Chemie-International Edition, vol. 45, pp. 7739-7742, 2006.

[28] S.L. Xiong, B.J. Xi, C.M. Wang, G.F. Zou, L.F. Fei, W.Z. Wang, and Y.T. Qian, "Shape-controlled synthesis of 3D and 1D structures of CdS in a binary solution with L-cysteine's assistance," Chemistry-a European Journal, vol. 13, pp. 3076-3081, 2007.

[29] B. Zhang, X.C. Ye, W.Y. Hou, Y. Zhao, and Y. Xie, "Biomolecule-assisted synthesis and electrochemical hydrogen storage of Bi_2S_3 flowerlike patterns with well-aligned nanorods," Journal of Physical Chemistry B, vol. 110, pp. 8978-8985, May 2006.

[30] Q.J. Chi, J.D. Zhang, E.P. Friis, J.E.T. Andersen, and J. Ulstrup, "Electrochemistry of self-assembled monolayers of the blue copper protein Pseudomonas aeruginosa azurin on Au(111)," Electrochemistry Communications, vol. 1, pp. 91-96, Mar-Apr 1999.

[31] Colin D. Bain, Hans A. Biebuyck, and George M. Whitesides, "Comparison of self-assembled monolayers on gold: coadsorption of thiols and disulfides", Langmuir, vol. 5, pp.723-727,1989.

[32] D.V. Goia and E. Matijevic, "Preparation of monodispersed metal particles," New Journal of Chemistry, vol. 22, pp. 1203-1215, Nov 1998.