RSC Advances RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Water-ethanol Solvent Mixtures: A Promising Liquid Environment for High Quality Positively-charged CdTe Nanocrystals Preparation

Yuan Jiang.[a,b] Shuhong Xu.[a] Zengxia Zhao.[a] Liang Zheng.[b] Zhuyuan Wang.[a]
Chunlei Wang[a*] and Yiping Cui[a*]

In this work, the record of photoluminescence (PL) quantum yield (QY) of positively-charged CdTenanocrystals (NCs) was brought up to 31%， by using water-ethanol mixture as a new media for NC synthesis. A series of water-ethanol feed ratios were investigated，with the maximal PL QY achieved in 50% ethanol solvent mixtures. Photoluminescence lifetime measurement and element analysis demonstrated an improved NC surface modification via the synthesis in the water-ethanol solvent mixtures.

INTRODUCTION

Semiconductor nanocrystals (NCs) have drawn great attention because of their unique size-dependent optical properties[1]. Aqueous synthesis of semiconductor NCs is more reproducible, cheaper and less toxic compared with the organometallic synthesis[2]. Moreover, the highly abundant free functional groups of water-soluble NCs facilitate the coupling with other molecules or matrix. Water soluble thiol ligands, especially negatively-charged thioglycolic acid (TGA) and mercaptoproponic acid (MPA)[3, 4], are usually used as capping or stabilizing reagents. Although positively-charged ligands, such as 2-mercaptoethylamine (MA) and 2-dimethylaminoethanethiol hydrochloride (DMAET), can also be used as stabilizer, such prepared positively-charged CdTe NCs have weak fluorescent[5] and broad size-distribution. The highest photoluminescence (PL) quantum yield (QY) for positively-charged CdTe NCs till now is 20%[6]. In comparison with the mature synthesis conditions of negatively-charged ligand capped NCs, more effort is still required for the synthesis of positively-charged NCs.

In the mean while, positively-charged NCs have particular value in applications especially in solar cells. By layer-by-layer (LBL) deposition[7-11] with the alternating layers of the positively and negatively charged NCs, NCs assemble with a high density of packing over a flat substrate. With different-sized NCs LBL deposition, efficient light absorption though transferred excitons can simply improve cell efficiency of NC-sensitized solar cells. Besides negatively-charged NCs, the MA-stabilized NCs and conjugated polymer precursor fabricated hybrid solar cells have illustrated improved photocurrent with reduced fill factor[3]. What's more, positively-charged NCs can be used for detection of small biomolecules via hydrogen bond[12] or ion exchange[13] and also detection of DNA hybridization[14]. Overall, the synthesis of high-quality positively-charged CdTe NCs is crucial for achieving a much higher detection sensitivity or solar cell performance.

Solvent mixtures are often used as reaction environment for chemical synthesis. Compared to individual solvent conditions, solvent mixtures have different solvent properties, such as dielectric constant, polarity, viscosity etc. These modified properties of solvent affect the reaction rate and mechanism of chemical reactions. For instance, organic solvents added to aqueous gold NPs can produce length-controllable 1D nanowires[15]; hydrazine in the growing system of aqueous NCs will promote their dynamic growth at room temperature[5, 16].

In this work, we showed that solvent mixtures can provide adjustable variables to control the NCs nucleation process, and thus benefitting the synthesis of NCs with better quality. Positively-charged CdTe NCs with enhanced PL QY and narrowed size-distribution can be synthesized in water-ethanol solvent mixtures. Compared to NCs directly synthesized in water solution, the maximal PL QY of MA-capped CdTe NCs in 50% ethanol proportion raises up to 31%, which is a new record for the PL QY of positively-charged CdTe NCs. We also monitored the nucleation and growth process of positively-charged CdTe NCs. The results indicate that water-ethanol solvent mixtures can weaken the electrostatic repulsion between NCs and free Cd-ligand complexes, and thus enable better ligand modification and higher PL QY of NCs.

EXPERIMENTAL

Materials

2-Mercaptoethylamine (MA) and Te powder were purchased from Aldrich. $CdCl_2$ was purchased from Beijing Chemical Factory. $NaBH_4$ was purchased from Guangdong Chemical Reagent Engineering Technological Research and Development Center. NaOH and ethanol were purchased from Shanghai Zhongshi Chemical Company. All materials used in this work were analytical reagents and used as received. NaHTe solution was prepared by using Te and $NaBH_4$ according to the methods described[17]. Deionized water was used in all preparations.

Synthesis of CdTe NCs in water-ethanol solvent mixtures.

MA-capped CdTe NCs were prepared by referring the synthesis of CdTe NCs in pure water[4]. In our work, ethanol-water solvent mixtures were used as NCs nucleation and NCs growth environment. Ethanol was mixed with water first, and then $CdCl_2$ and ligand was added into ethanol-water solvent mixtures keeping total volume in 100mL. The proportion of ethanol in total solution is 0%, 25% and 50%, respectively. 1.0mol/L NaOH solution was used to adjust pH value to 5.0, and then the mixture was aerated with N_2 for 30 min. After injection of freshly prepared NaHTe solution into the mixture, CdTe precursors were obtained. The initial molar ratio of $CdCl_2$/ligand/NaHTe was 1.0/4.0/0.1. The concentration was 5.0mmol/L referring to Cd[6]. Since the boiling points of ethanol-water solvent mixtures decreased from 100℃ to 78℃ with the increased proportion of ethanol, we selected 75℃ as NCs growth temperature to facilitate the comparison of NCs growth process.

Characterization

UV–vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Fluorescence experiments were carried out in Shimadzu RF-5301PC spectrofluorimeter. PL decay experiments were performed with an Edinburgh FLS 920 spectrofluorimeter. The excitation wavelength was 400nm. Room-temperature PL QY was determined by comparing the integrated emission of the NCs samples in water to Rhodamine 6G in ethanol with identical optical density. The absorbance at the first exciton peak is controlled to be 0.05 in the PL QY measurement[18]. Transmission electron microscopy (TEM) was recorded by a Tecnai F20 electron microscope with an acceleration voltage of 200kV. X-ray photoelectron spectroscopy (XPS) was investigated by using a PHI550 spectrometer with an Mg Kα excitation (1253.6eV). Binding energy calibration was based on SiO_2 at 103.0eV. For XPS measurements, purified CdTe NCs powder was used. To obtain the powder, freshly prepared NCs were precipitated from the solution by addition of NaCl[15] and then dried in vacuum.

RESULTS AND DISCUSSION

NCs Synthesized in Aqueous Solution VS Water-ethanol Solvent mixtures

The water and ethanol mixture was selected as a new media for synthesizing high-quality positively-charged CdTe NCs. In a typical synthesis, NCs nucleate in water-ethanol mixture and then grow under heating. The boiling points of ethanol-water solvent mixtures decreased from 100 ℃ to 78 ℃ with the increased ethanol proportion in the mixture. To exclude the influence of different growth temperature, 75℃ was selected as a standard NC growth temperature for all NC samples.

In a prototypical system of 50% ethanol proportion, MA-capped CdTe NCs nucleate in water-ethanol solvent mixtures and grew into NCs during heating at 75℃. And then NCs was re-dissolved in water after salt-based purification[19]. With different reflux time, the emission light ranges from green (504nm) to red (615nm) as shown in Figure 1(a). And NCs with strongest PL intensity emits about 576nm. Figure S1 shows the typical absorption and PL spectra of NCs with the strongest emission. CdTe NCs appeared as mono-dispersed quasi-spherical particles with regular crystalline structures as shown in TEM images in Figure 1(b). The average size of CdTe NCs is about 4.1nm in diameter. Figure 1(c) shows the XRD pattern of obtained CdTe NCs powders. The diffraction peaks at 24.0, 39.7 and 47.0 degrees assign to (111), (220), and (311) facet of cubic bulk CdTe, respectively. It indicates that the lattice parameters fit well to the zinc blende structure of bulk CdTe crystals. The TEM and XRD results indicated that water-ethanol solvent environment has not influence NCs structure and crystal lattice.

To compare different water-ethanol solvent environment, we choose 0%, 25% and 50% ethanol in volume as samples. After reflux the same time, NCs solution shows similar absorbance but different PL intensity (Figure S1). Under the irradiation of a UV lamp, NCs in 50% ethanol emits obviously brighter light than NCs in 0% and 25% ethanol when the PL peaks of three samples are all 578nm. We compared the PL QY of different-sized CdTe NCs in different water-ethanol solvent mixtures in Figure 2. Generally, PL QY of NCs greatly increases with the increase of ethanol proportion. The maximal PL QY locates between 570nm and 590nm in emission wavelength. In this range, CdTe NCs synthesized in 0% ethanol proportion exhibit PL QY of 20%, whereas CdTe NCs synthesized at 50% ethanol proportion possess the highest PL QY of 31%. In other words,

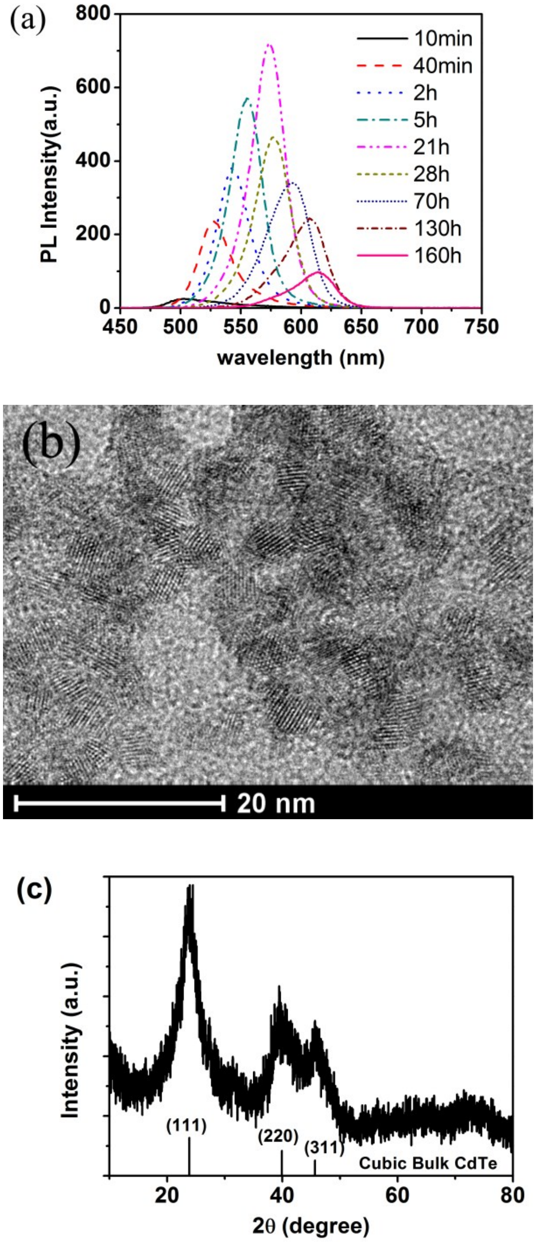


Fig. 1 (a) PL spectra evolution of MA-stabilized CdTe NCs in 50% ethanol; (b) TEM images of NCs in 50% ethanol. The excitation wavelength of PL spectra was 400 nm. The PL peak of NCs was 578nm; (c) XRD patterns of CdTe NCs after precipitation. The standard XRD patterns of bulk cubic zinc blende CdTe (bottom) were also indicated.

nearly a half enhancement of PL QY is achieved by just changing the synthesis media from water to water-ethanol solvent mixtures during NC synthesis. Besides, in the short wavelength range of 510-530nm, NCs in water-ethanol solvent mixtures also show strong luminescence, while NCs in water solution barely emit PL. Note that MA-capped CdTe NCs in 75% ethanol proportion will automatically precipitate from the mixture when NCs grow to a yellow emission (about 580nm). Large-sized NCs with orange or red light emission will not form in 75% ethanol proportion. Therefore, 50% ethanol proportion is selected as an optimal solvent mixture combining QY and stability.

We characterized NCs size distribution for the three ethanol proportion. NCs were synthesized in different ethanol proportion solution, and then three samples with PL peak in 578nm were chosen. TEM images associated with histograms in Figure S2 shows that the average sizes of NCs in 25% and 50% ethanol are similar(4.1±0.7), while NCs in water solution is slightly larger(4.5±0.7). As shown in Figure S3, the colloidal and optical stability of NCs was monitored by PL spectra. Samples with PL peak in 578nm were exposed in the air and in N$_2$-saturated condition at room-temperature with natural light illumination. After 5 days storage, three samples in the air all demonstrated blue shift in PL spectra. NCs in water solution blue shifted 33nm while those in 25% and 50% ethanol only about 15nm. According to reference, the blue-shifted PL peak and enhanced PL intensity are attributed to the formation of oxide layer (CdO or oxidized Te)[20]. In a contrast experiment, when NCs are kept in N$_2$ condition, no blue shift was observed.

We further measured the PL decay spectra of CdTe NCs synthesized in different solvent mixtures to characterize NCs surface ligand modification. As shown in Figure S4, the PL decay results were fitted by the bi-exponential equation, with goodness of fitting over 99.7%. As can be seen in Table 1, these samples reveal an obvious trend that NCs with increased ethanol proportion possess prolonged PL lifetime. For example, NCs of 50% ethanol possess PL lifetime of 11.2ns, much longer than that of the 0% ethanol proportion sample (9.5ns). As aqueous CdTe NCs with better surface thiol-ligand modification have longer PL lifetimes [21], the current results suggest a much better surface ligand modification for CdTe NCs synthesis in 50% ethanol proportion.

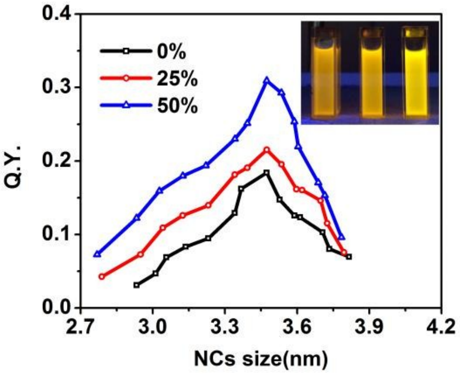


Fig.2 Evolution of PL QY of different-sized CdTe NCs with different ethanol proportions. Inset: the images of CdTe NCs synthesis in 0%, 25% and 50% ethanol (from left to right) under the irradiation of a UV lamp (365 nm).

XPS was employed to quantitatively measure the NC surface modification. CdTe NCs with size of 3.5nm (PL peak at 576nm) were used. Before XPS measurements, CdTe NCs were purified to get rid of unreacted molecules in solution to ensure the measured results reflect the real composition of NCs. As shown in Figure S5, the binding energy peak at 161.9eV assigns to 2p energy level of S^{2-}, whereas the binding energy peaks at 405.0eV and 411.7eV assign to 3d energy level of Cd^{2+}. Since S^{2-} can only come from thiol ligand, the atomic ratio of Cd/S reflects the modification of thiol ligand on NC surface. The quantitatively measured results of Cd/S atomic ratios are 1.0/1.1, 1.0/1.2, and 1.0/1.6 for NCs prepared in the condition of 0%, 25%, and 50% ethanol proportion (Table 2) respectively. Obviously, XPS results further suggest improved ligand modification by using water-ethanol mixture as NC synthesis media.

Table 1. Kinetic Parameters of the Emission Decay Analysis of MA-stabilized CdTe NCs with different ethanol proportions. The Equation Used to Simulated Luminescence Decay Curves: $Y = Y_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$. Average Lifetime$\tau = A_1\tau_1^2/(A_1\tau_1+A_2\tau_2)+(A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2)$

Ethanol Proportion	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\langle\tau\rangle$ (ns)
0%	3421.8	4.6	1396.3	13.6	9.5
25%	3525.3	5.5	1336.7	15.5	10.7
50%	3362.4	6.4	1485.6	15.7	11.2

Table 2. Element Ratios and Zeta potential of MA-stabilized CdTe NCs with different ethanol proportions.

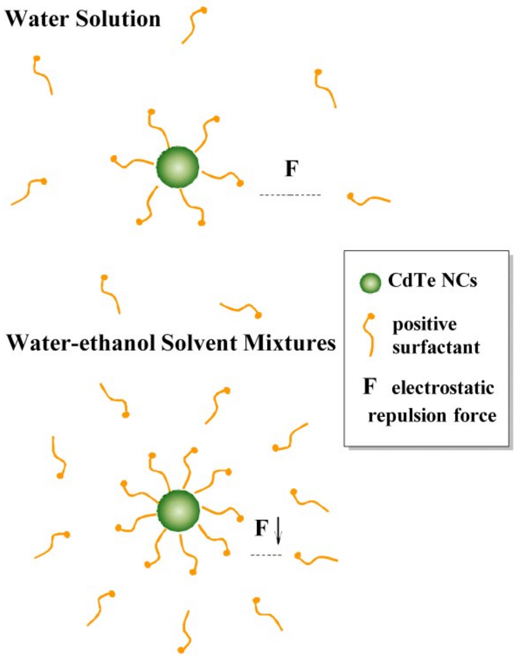
Ethanol Proportion	Cd/S Atomic Ratio	Zeta potential (mV)
0%	1.0:1.1	+23.6
25%	1.0:1.2	+15.7
50%	1.0:1.6	+6.6

Effect of Ethanol in the Mixture

On the basis of results above, it is proved that water-ethanol mixture improves the PL QY and ligand modification of NCs. A simple discussion about possible effects of ethanol during the growth process of positively-charged NCs is given below.

First of all, we would like to discuss the possible reason for the lower PL QYs of positively-charged CdTe NCs than negatively-charged CdTe NCs. The pH value of the negatively-charged NCs precursor solution is around 9.1~11.8[2], close to the logarithmic value of negative dissociation constant (pK_a) for thiol groups (pK_{pH}=10.53) [22], while the positively-charged NCs are commonly synthesized at low pH 5.0~5.9[2]. When the solution pH is higher than 10.0, thiol groups ionize from SH to S-, resulting in a much stronger coordination capacity of thiol with Cd on NC surface[17]. On the contrary, MA-capped CdTe NCs synthesized at pH 5.0~5.9 exhibit a rather low fluorescence quality due to the detachment of thiol groups from NC surface at reduced pH. The detailed influence of solution pH on the PL of aqueous CdTe NCs was investigated in our previous work[20]. Although pH may affect the PL of NCs in four different ways, only the discussed way above may lead to different PL QYs for negatively-charged and positively-charged NCs.

Ethanol we selected is a solvent with lower relative dielectric constants ($\varepsilon_{ethanol}$=24.6) than water (ε_{water}=80.1). After introducing ethanol into water, the relative dielectric constant of solvent mixture decreases from original ε_{water} to subsequent ε_{mix}[23]. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) model of colloidal stability theory[24,25], the electrostatic repulsion between particles decreases with the decrease of relative dielectric constant. Similarly, the decreased ε_{mix} will also induce a reduced electrostatic repulsion between positively-charged NCs and positively-charged free Cd-ligand complexes, and thus promotes the diffusion of free Cd-ligand complexes on NC surface (Scheme 1). That is, free Cd-ligand is easier to cover NCs surface in water-ethanol solvent mixtures than in water solution. As a result, improved ligand modification and PL QY of NCs can be realized. In zeta potential measurements summarized in Table 2, the surface potentials of NC precursor solution decrease from +21.6 to +8.3 mV as the ethanol increased from 0% to 50%. It confirms the decrease of electrostatic repulsion of positively-charged MA-stabilized NCs with the addition of ethanol. In a control experiment, we selected propanol ($\varepsilon_{propanol}$ =20.3) or isopropanol ($\varepsilon_{isopropanol}$ =19.9) as the co-solvent beside water, the results also show enhanced PL QY (about 30%) of CdTe NCs in propanol-water (or isopropanol-water) solution (Figure S6). These results indicate that the PL enhancement effect in the mixed solvent should attribute to the reduced dielectric constant. It should be mentioned that the polarity of solvent usually affects the emission position of NCs by the well-known solvent effect, but rarely affect the emission intensity of NCs.[26].



Scheme 1. Sketch of NCs growth mechanism in water solution and water-ethanol solvent mixtures.

CONCLUSIONS

In order to prepare positively-charged CdTe NCs with high PL QY, water-ethanol solvent mixtures are selected as the NCs nucleation and growth environment. NCs nucleate in water-ethanol mixture system without precipitation, and then grow into larger size after heating. With the proportion of ethanol increasing, NCs show stronger PL intensity. The QY of NCs in 50% ethanol increases up to 31%, which is a new record for positively-charged CdTe NCs. PL lifetime of NCs in different ethanol proportion demonstrates the improved surface modification in the water-ethanol solvent mixtures. Element analysis also confirms the increased ligands in NCs. In addition, we investigated the influence of water-ethanol solvent mixtures in NCs growth process, which is mainly contributed to the decreased relative dielectric constants ε_{mix}. The inter-particle electrostatic repulsion between NCs and free Cd-ligand complexes are also reduced and thus promotes the ligands diffusion in the solution.

Electronic Supplementary Information (ESI) available: absorption and PL spectra, colloidal and optical stability, lifetime, TEM and XPS results. See DOI: 10.1039/b000000x/

Acknowledgements

This work is supported by the National Key Basic Research Program of China (Grant No. 2015CB352002), National Natural Science Foundation of China (Grant Nos. 61475034, 21104009, 21403034, 61177033), the Fundamental Research Funds for the Central Universities (No. 2242014R30006), the natural science foundation of Jiangsu Province Youth Fund (No. BK20140650), Science and Technology Planning Project of Zhejiang Province (No. 2013C31064).

Notes and references

[a]*Advanced Photonics Center, School of Electronic Science and Engineering, Southeast University, Nanjing, 210096, China. E-mail: wangchl@seu.edu.cn, cyp@seu.edu.cn; Tel.: 86-25-83792470 ext. 208; Fax：86-25-83790201

[b]Lab for Nanoelectronics & Nanoelectronic Devices, Hangzhou Dianzi University, Hangzhou, China.

1. D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase and H. Weller, NanoLett, 2001, 1, 207-211.
2. N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller and H. Weller, J PhysChem B, 2002, 106, 7177-7185.
3. Z. Chen, H. Zhang, X. Du, X. Cheng, X. Chen, Y. Jiang and B. Yang, Energy & Environmental Science, 2013, 6, 1597-1603.
4. H. Zhang and B. Yang, Thin Solid Films, 2002, 418, 169-174.

5. D. Zhou, M. Lin, Z. Chen, H. Sun, H. Zhang, H. Sun and B. Yang, Chem Mater, 2011, 23, 4857-4862.
6. L. Zou, J. Wang, Z. Fang, Z. Gu and X. Zhong, J DisperSciTechnol, 2009, 30, 388-393.
7. H. Jin, S. Choi, R. Velu, S. Kim and H. J. Lee, Langmuir, 2012, 28, 5417-5426.
8. L. Sai and X. Kong, Appl Phys A, 2014, 114, 1153-1160.
9. S. Choi, H. Jin, J. Bang and S. Kim, J Phy Chem Lett, 2012, 3, 3442-3447.
10. H. Jin, S. Choi, H. J. Lee and S. Kim, J Phy Chem Lett, 2013, 4, 2461-2470.
11. J. Briscoe, D. E. Gallardo, S. Hatch, V. Lesnyak, N. Gaponik and S. Dunn, J Mater Chem, 2011, 21, 2517-2523.
12. T. Zhang, X. Sun and B. Liu, SpectrochimActa A, 2011, 79, 1566-1572.
13. J. Callan, R. Mulrooney and S. Kamila, J Fluoresc, 2008, 18, 1157-1161.
14. C. L. Feng, X. H. Zhong, M. Steinhart, A. M. Caminade, J. P. Majoral and W. Knoll, Advanced Materials, 2007, 19, 1933-1936.
15. H. Zhang and D. Wang, AngewandteChemie, 2008, 120, 4048-4051.
16. J. Han, X. Luo, D. Zhou, H. Sun, H. Zhang and B. Yang, J PhysChem C, 2010, 114, 6418-6425.
17. C. Wang, H. Zhang, J. Zhang, N. Lv, M. Li, H. Sun and B. Yang, J PhysChem C, 2008, 112, 6330-6336.
18. S. Xu, C. Wang, Q. Xu, R. Li, H. Shao, H. Zhang, M. Fang, W. Lei and Y. Cui, J PhysChem C, 2010, 114, 14319-14326.
19. C.-L. Wang, M. Fang, S.-H.Xu and Y.-P. Cui, Langmuir, 2009, 26, 633-638.
20. C. Wang, H. Zhang, J. Zhang, M. Li, K. Han and B. Yang, J. Colloid Interf. Sci. 2006, 294, 104-108.
21. X. Wang, L. Qu, J. Zhang, X. Peng and M. Xiao, NanoLett, 2003, 3, 1103-1106.
22. S. Xu, C. Wang, H. Zhang, Z. Wang, B. Yang and Y. Cui, Nanotechnology, 2011, 22.
23. C. Wang, M. Fang, J. Han, H. Zhang, Y. Cui and B. Yang, J PhysChem C, 2009, 113, 19445-19451.
24. H. Zhang, Y. Liu, C. Wang, J. Zhang, H. Sun, M. Li and B. Yang, Chemphyschem, 2008, 9, 1309-1316.
25. T. Kim, K. Lee, M.-s. Gong and S.-W.Joo, Langmuir, 2005, 21, 9524-9528.
26. S. Xu, C. Wang and Y. Cui, J MolStruct, 2012, 1010, 26-31.