

# Solvothermal synthesis of CdO and CuO nanocrystals

Moumita Ghosh <sup>a,b</sup>, C.N.R. Rao <sup>a,b,\*</sup>

<sup>a</sup> Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

<sup>b</sup> Chemistry and Physics of Materials Unit and CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India

Received 26 March 2004

## Abstract

Nanocrystals of CdO have been obtained by the decomposition of the cupferron complex in the presence of tri-*n*-octylphosphine oxide (TOPO) under solvothermal conditions. The precursor:TOPO ratio plays an important role in determining the size of the nanocrystals. The nanocrystals have been characterized by electron microscopy, absorption spectroscopy and fluorescence spectroscopy, besides X-ray diffraction. The CdO nanocrystals are single crystalline and show evidence for quantum confinement. CuO nanocrystals could also be prepared by the decomposition of the cupferronate under solvothermal conditions, the particle size being controlled by the initial precursor concentration.

© 2004 Elsevier B.V. All rights reserved.

## 1. Introduction

CdO is a direct band gap (2.3 eV) semiconductor, with an indirect band gap of 1.36 eV. Due to its large linear refractive index ( $n_0=2.49$ ), it is a promising candidate for optoelectronics applications and other applications, including solar cells [1,2], phototransistors [3], photodiodes [4], transparent electrodes [5] and gas sensors [6]. Reduction in the dimensionality of such materials from the three dimensional bulk phase to the zero-dimensional nanoparticles can lead to enhanced non-linearity, determined by the quantum size effects and other mesoscopic effects. Because of these interesting possibilities, there has been some effort to prepare nanoparticles of CdO. Wu et al. [7] prepared a nanometer-sized CdO organosol from an aqueous solution of  $\text{Cd}(\text{NO}_3)_2$ , a surfactant and toluene, while Liu et al. [8] synthesized CdO nanoneedles by chemical vapour deposition. CdO nanowires have been synthesized by decomposing  $\text{CdCO}_3$  in a  $\text{KNO}_3$  salt flux [9]. Zou et al. [10] have prepared CdO

nanoparticles by the micro-emulsion method employing AOT reverse micelles. There is also a report of stearate-coated CdO nanoparticles of 5–10 nm size range, obtained by the micro-emulsion method starting from an aqueous solution of a cadmium salt and stearic acid in xylene [11]. We have developed a new method to prepare CdO nanoparticles, wherein a cadmium precursor compound, is decomposed under solvothermal [12,13] conditions in presence of a capping agent. For this purpose, we have employed cadmium cupferronate,  $\text{Cd}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_2$  as the precursor, and obtained CdO nanoparticles of different sizes by using tri-*n*-octylphosphine oxide (TOPO) as the capping agent [14]. We have characterized the nanoparticles by X-ray diffraction (XRD), electron microscopy and electronic absorption and emission spectroscopies. We have also synthesized CuO nanocrystals by the decomposition of the cupferronate [15] under solvothermal conditions.

## 2. Experimental

The cupferron complex of Cd(II),  $\text{Cd}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_2$ , was prepared by the reaction of cadmium acetate with

\* Corresponding author. Fax: +91-80-846-2766/23622760.

E-mail address: [cnrrao@jncasr.ac.in](mailto:cnrrao@jncasr.ac.in) (C.N.R. Rao).

cupferron (*N*-nitroso-*N*-phenylhydroxylamine, ammonium salt). In a typical reaction, 1.27 g of AR grade  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 25 cm<sup>3</sup> of water in a beaker. In another beaker, 1.5 g of cupferron was solubilised in 60 cm<sup>3</sup> of water. The two solutions were cooled at 0 °C and the cupferron solution slowly added to the solution of  $\text{Cd}(\text{CH}_3\text{COO})_2$  under vigorous stirring. The white precipitate obtained was collected, washed with 2.5%  $\text{NH}_3$  solution followed by milli-q water, to remove the excess cupferron. The complex was characterized by chemical analysis was as follows: C, 35.77% found (calculated 37.27%); H, 2.665% (2.59%); N, 14.09% (14.49%). Thermogravimetric analysis of the as-prepared  $\text{Cd}(\text{cup})_2$  in a nitrogen atmosphere, showed that there was sharp weight loss due to decomposition around 250 °C.

In a typical reaction, 0.1 g (0.0258 mmol) of  $\text{Cd}(\text{cup})_2$  and 0.1 g (0.254 mmol) of TOPO were taken in 48 cm<sup>3</sup> toluene and sealed in a Teflon-lined autoclave of 80 cm<sup>3</sup> capacity. The mixture was heated at 240 °C for 150 min. A dark reddish brown solid, insoluble in toluene was obtained as the product. It was washed with toluene for several times, followed by methanol, and dried at 40 °C for 2 h. This preparation with a  $\text{Cd}(\text{cup})_2$ :TOPO ratio of 1:1 yielded one-dimensional structures of CdO. Different  $\text{Cd}(\text{cup})_2$ :TOPO ratios were employed to obtain nanocrystals of different sizes. When the ratio was 1:2 and 1:5, insoluble orange-colored solids were obtained, and the latter ratio also yielded yellow dispersions in toluene. The orange solid contained relatively bigger nanocrystals (18–30 nm diameter), which was washed thoroughly with toluene for further characterization. Nanoparticles were precipitated out from the yellow organosol by the addition of methanol. The precipitated nanocrystals which could be redispersed in toluene had diameters in the 3–12 nm range. The size of the nanocrystals could be changed by varying the relative concentrations of the reactants. With a 1:5 ratio of  $\text{Cd}(\text{cup})_2$ :TOPO, we were able to synthesize toluene-soluble CdO nanocrystals, without any insoluble fraction.

In addition to CdO nanocrystals, we have been able to prepare CuO nanocrystals by decomposing  $\text{Cu}(\text{cup})_2$  in toluene under solvothermal conditions. We have carried out the reactions in the absence of any capping agent and obtained different sizes of nanocrystals by varying the  $\text{Cu}(\text{cup})_2$  concentration. The reactions yielded a dark brown organosol which was stable in toluene and hexane. By the addition of *n*-octylamine to the organosol in toluene, the CuO nanocrystals could be solubilized completely, giving rise to transparent solutions. In a typical reaction to obtain 10.5 nm nanocrystals, 0.2 g (0.58 mmol) of  $\text{Cu}(\text{cup})_2$  was taken in 48 cm<sup>3</sup> toluene (75% filling fraction) and sealed in a Teflon-lined autoclave of 80 cm<sup>3</sup> capacity. The autoclave was heated at 180 °C for 300 min.

XRD patterns of the samples were recorded in the  $\theta$ – $2\theta$  Bragg–Brentano geometry with a Siemens D5005 diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 0.151418$  nm) radiation. For transmission electron microscope (TEM) studies, a solution or a dispersion of the sample in a suitable solvent was allowed to evaporate on a carbon-coated Cu grid. A JEOL (JEM3010) microscope with an accelerating voltage of 300 kV was used to obtain TEM images. UV–vis absorption spectra of nanocrystals in toluene were recorded using a Hitachi U3400 spectrometer. The reference used was toluene solution of TOPO. Photoluminescence spectra were recorded with a Perkin–Elmer model LS50B luminescence spectrometer.

### 3. Results and discussion

In Fig. 1, we show the XRD patterns of the CdO nanocrystals prepared in the presence of TOPO. Pattern (a) is that of the insoluble orange coloured solid product obtained with a  $\text{Cd}(\text{cup})_2$ :TOPO ratio of 1:2. The pattern is characteristic of the rock-salt structure with  $a = 4.695$  Å (JCPDS card no 05-0640), as established by Rietveld profile analysis [16]. We show the goodness of fit as well as the difference profile in Fig. 1a. Based on the X-ray line broadening, the particle diameter was estimated to be 18 nm. In Fig. 1b, we show the XRD pattern of nanocrystals, which are smaller than 18 nm. The X-ray line widths show them to be around 12 nm in diameter. In Fig. 2a, we show the TEM image of the nanocrystals corresponding to the XRD pattern in Fig. 1b. The particle size distribution is shown as an inset. The

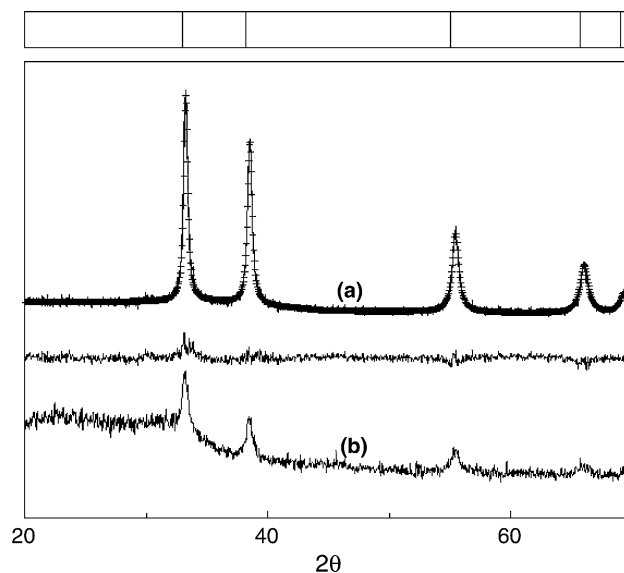


Fig. 1. Powder XRD patterns of TOPO-capped CdO nanocrystals of (a) 18 nm (b) 12 nm diameter. Rietveld fit is shown in (a) along with the difference profile. The vertical lines at the top of the figure are the expected peak positions.

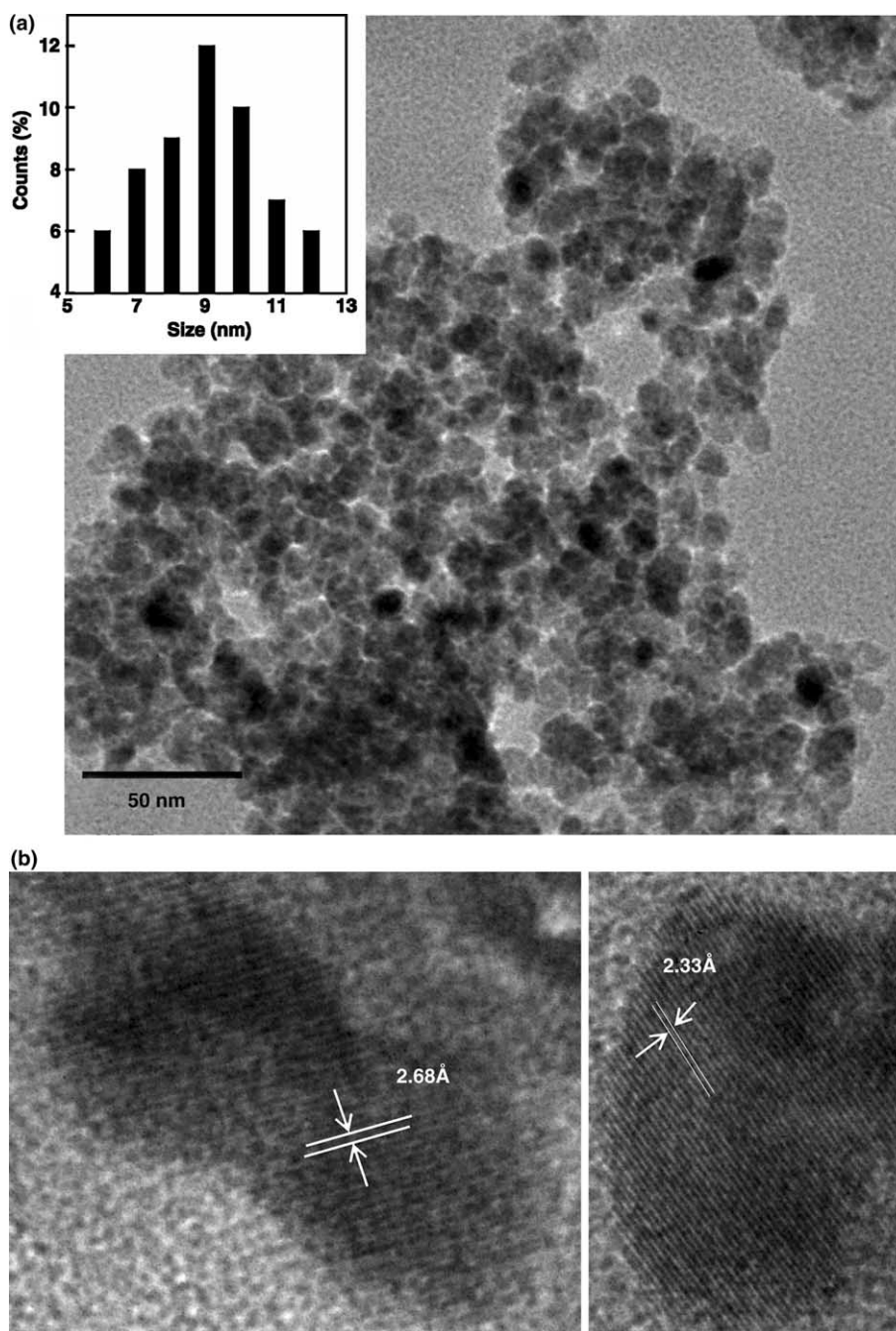


Fig. 2. (a) TEM image of TOPO-capped CdO nanocrystals of an average diameter of 9.5 nm. The XRD pattern of these particles is shown in Fig. 1b. Inset shows the size distribution of the nanocrystals. (b) HREM images of CdO nanocrystals.

average particle size from TEM appears to be around 9.5 nm. These particles are single crystalline as revealed by the high resolution electron microscope image in Fig. 2b. The particles are spherical or elliptical in shape, not unlike those reported by Dong et al. [11]. The fringe spacing of 2.68 Å observed in the high-resolution electron microscope image (HREM) corresponds to the separation between the {111} lattice planes, whereas the 2.336 Å spacing corresponds to the separation between the {200} planes.

In Fig. 3a, we compare the electronic absorption spectra of the TOPO-capped CdO nanocrystals with diameters of (a) ~18 nm, (b)  $9.5 \pm 2$  nm and (c)  $4.5 \pm 1.5$  nm. The 18 nm nanocrystals show an absorption edge around 2.5 eV (curve (a) in Fig. 3a). Recall that the bulk sample with an absorption edge of 2.3 eV, show a broad maxima around 500 nm. The 9.5 nm nanocrystals show an absorption edge of ~2.8 eV while the 4.5 nm nanocrystals show an absorption edge of ~3.27 eV, as revealed by spectra (b) and (c) respectively in Fig. 3a.

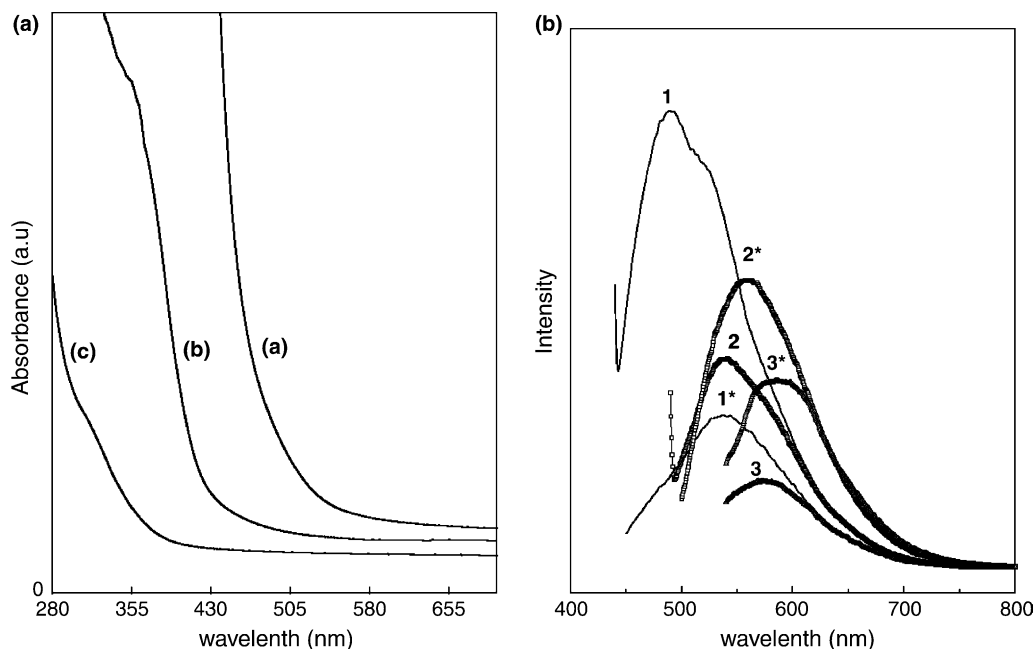


Fig. 3. (a) Electronic absorption spectra of TOPO-capped CdO nanoparticles with an average diameters of (a) 18 nm (b) 9.5 nm and (c) 4.5 nm. (b) Photoluminescence spectra of 18 and 4.5 nm CdO nanocrystals at different excitation wavelengths. Curves 1–3 are the photoluminescence spectra of the 4.5 nm nanocrystals at excitation wavelengths of 430, 480 and 520 nm respectively, 1\*, 2\* and 3\* correspond to the 18 nm particles.

The large blue-shift relative to the bulk CdO observed with the 4.5 nm nanocrystals is attributed to quantum confinement. The bulk exciton Bohr radius of CdO is not available in the literature and it is therefore difficult to conclude as to which confinement regime the CdO nanocrystals belong.

Photoluminescence spectra of CdO have been reported by Wu et al. [7] who suggest that the band at 480 nm arises from the transition between the conduction and valence bands. They also report a band at 530 nm due to near band-gap radiative combination. In Fig. 3b, we show the photoluminescence spectra of the 18 and 4.5 nm nanocrystals recorded at the excitation wavelengths of 430, 480 and 520 nm. The 18 nm nanocrystals exhibit bands around 540, 560 and 590 nm respectively at excitation wavelengths of 430, 480 and 520 nm. The corresponding bands of the 4.5 nm nanocrystals occur at 495, 540 and 570 nm. We observe the maximum blue-shift in the case of the lowest wavelength emission band, which is considered due to transition between valence and the conduction bands.

In Fig. 4 we show the typical XRD patterns of CuO nanocrystals, obtained by varying the concentration of Cu(cup)<sub>2</sub> in toluene. The patterns (a), (b) and (c) correspond to particle sizes of 10.5, 6 and 4 nm respectively, as obtained from the X-ray line broadenings. These XRD patterns give the monoclinic structure of CuO in agreement with the literature (JCPDS card no 45-0937). TEM image of CuO nanocrystals with an average diameter of 10 nm is shown in Fig. 5a. The inset in this frame shows the particle size distribution. The particles are

highly crystalline in nature, as revealed by the HREM image, shown in Fig. 5b. The line spacing of 2.35 Å corresponds to the separation between {111} planes.

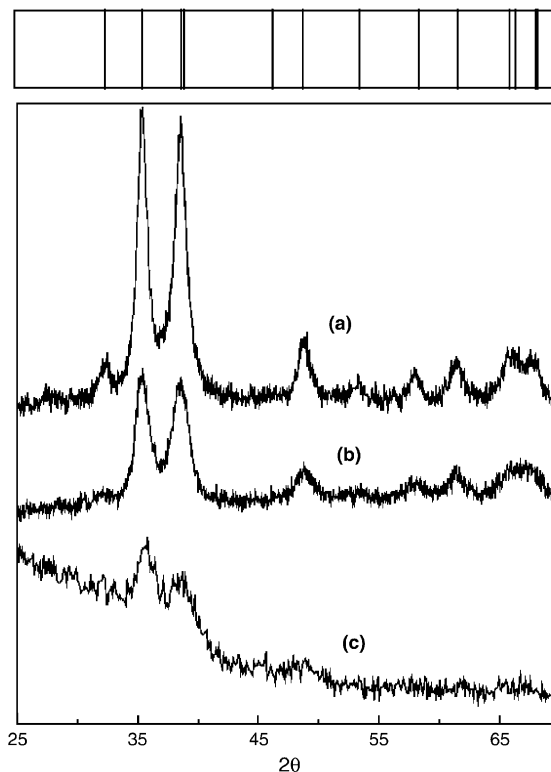


Fig. 4. XRD patterns of CuO nanocrystals of (a) 10.5 nm, (b) 6 nm and (c) 4 nm diameter. The vertical lines at the top are the expected peak positions.

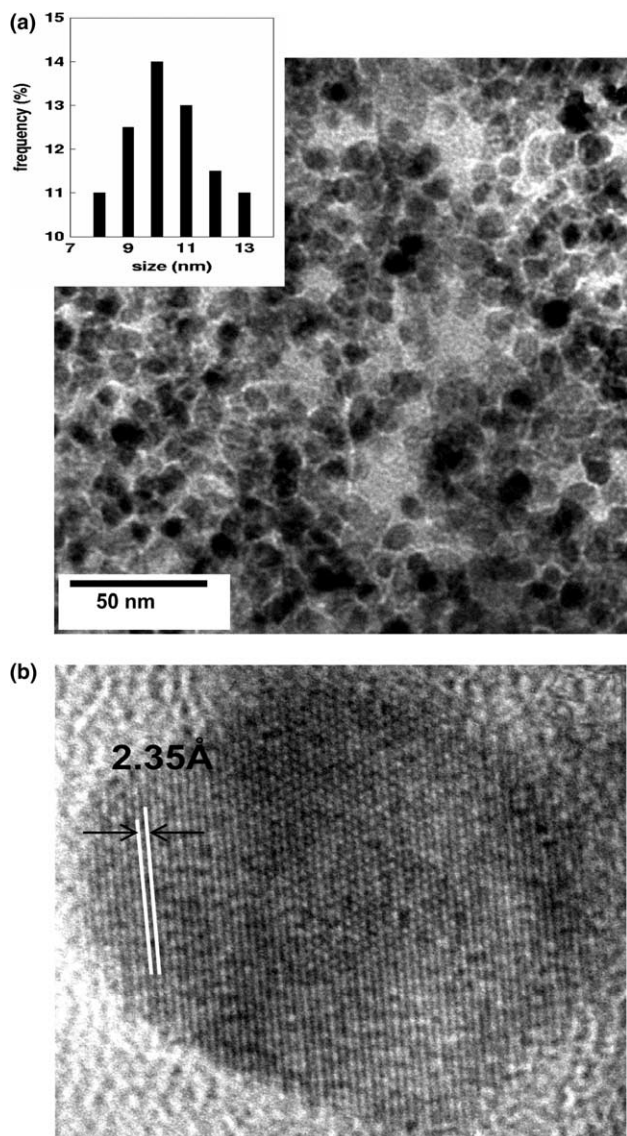


Fig. 5. (a) TEM image of CuO nanocrystals. Inset shows the size distribution of the nanocrystals. (b) HREM image of a single CuO nanocrystal.

#### 4. Conclusions

CdO and CuO nanocrystals have been prepared successfully by a solvothermal route involving the decomposition of the metal cupferronate in toluene medium. As most of the transitional metals and some non-transition metals form complexes with cupferron, this route can be readily employed to prepare nanocrystals of various metal oxides soluble in organic solvents. The CdO and CuO nanocrystals obtained by us are single crystalline in nature as revealed by electron microscopy. The CdO nanocrystals of 4.5 nm diameter show evidence for quantum confinement.

#### References

- [1] C. Sravani, K.T.R. Reddy, O.Md. Hussain, P.J. Reddy, J. Solar. Energy. Soc. India 1 (1996) 6.
- [2] L.M. Su, N. Grote, F. Schmitt, Electron. Lett. 20 (1984) 716.
- [3] R. Kondo, H. Okimura, Y. Sakai, Jpn. J. Appl. Phys. 10 (1971) 1547.
- [4] F.A. Benko, F.P. Koffyberg, Solid State Commun. 57 (1986) 901.
- [5] A. Shiori Jpn. Patent No. 7 (1997) 909.
- [6] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 77th edn., CRC Press, Boca Raton, 1996/1997, 3/278, p. 12/97.
- [7] X. Wu, R. Wang, B. Zou, L. Wang, S. Liu, J. Xu, J. Mater. Res. 13 (1998) 604.
- [8] X. Liu, C. Li, S. Han, J. Han, C. Zhou, Appl. Phys. Lett. 82 (2003) 1950.
- [9] Y. Liu, C. Yin, W. Wang, Y. Zhan, G. Wang, J. Mater. Sci. Lett. 21 (2001) 137.
- [10] B.S. Zou, V.V. Volkov, Z.L. Wang, Chem. Mater. 11 (1999) 3037.
- [11] W. Dong, C. Zhu, Opt. Mater. 22 (2003) 227.
- [12] M. Rajamathi, R. Seshadri, Curr. Opin. Solid State Mater. Sci. 6 (2002) 337.
- [13] S. Thimmaiah, M. Rajamathi, N. Singh, P. Bera, F.C. Meldrum, N. Chandrasekhar, R. Seshadri, J. Mater. Chem. 11 (2001) 186.
- [14] C.B. Murray, D.J. Norris, M.G. Bawendi, J. Am. Chem. Soc. 115 (1993) 8706.
- [15] J. Rockenberger, E.C. Scher, A.P. Alivisatos, J. Am. Chem. Soc. 121 (1999) 11595.
- [16] J.-F. Béar, P. Garnier, NIST Spec. Publ. 846 (1992) 212.