



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Applied Surface Science 205 (2003) 256–261

applied
surface science

www.elsevier.com/locate/apsusc

Influence of surface-capping molecule exchange on the hyper-Rayleigh scattering of CdS nanoparticles

Yu Zhang^{a,b,*}, Xin Wang^b, Ming Ma^b, Degang Fu^b, Ning Gu^b,
Juzheng Liu^b, Zuhong Lu^b, Yi Ma^a, Ling Xu^a, Kunji Chen^a

^aNational Laboratory of Solid State Microstructures and Department of Physics,
Nanjing University, Nanjing 210093, PR China

^bNational Laboratory of Molecular and Biomolecular Electronics,
Southeast University, Nanjing 210096, PR China

Received 1 May 2002; received in revised form 27 August 2002; accepted 21 September 2002

Abstract

Hyper-Rayleigh scattering (HRS) or incoherent second harmonic generation (SHG) technique has been used to investigate the second-order optical nonlinearities of nanoparticles and seems sensitive to nanoparticle surfaces. Here, more direct evidence that shows the importance of surfaces for HRS response of nanoparticles was experimentally obtained. Two CdS nanoparticles of 3 nm average diameter with different surface-capping molecules, CdS/AOT-SO₃⁻ (AOT-SO₃⁻ is anion of bis (2-ethylhexyl) sulfosuccinate, disodium salt) and CdS/Py/AOT-SO₃⁻ (Py represents pyridine molecule), were studied by HRS technique. The “per particle” first-order hyperpolarizability β values were evaluated to be 3.98×10^{-27} esu for the CdS/AOT-SO₃⁻ and 2.63×10^{-27} esu for the CdS/Py/AOT-SO₃⁻ nanoparticles. A reduction in β value is found when AOT-SO₃⁻ on CdS nanoparticle surface is replaced by pyridine. Similarly, the reduction of HRS signal intensity of a solution containing the CdS/AOT-SO₃⁻ nanoparticles was observed when increasing pyridine concentration in the solution. Furthermore, the dynamic process of the surface-capping molecule exchange was studied by detecting both HRS signal intensity and electroconductivity variations with time. Possible effect mechanism is discussed in terms of a two-level model approximation derived from molecular chromophores, when considering the influence of different surface-capping molecules on the polarity of Cd-S bonds at nanoparticle surfaces.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: CdS nanoparticles; Surface modification; Hyper-Rayleigh scattering

1. Introduction

Surface and interfacial phenomena are of practical and fundamental interest. A lot of attention has been devoted to the development of experimental character-

ization methods of these regions, defined as a few atomic and molecular layers near the surface or interface. Based on the second-order nonlinear optical phenomena, surface specific techniques such as second harmonic generation (SHG) and sum frequency generation (SFG) have proven extremely useful for studying the chemical and physical properties of surfaces and interfaces [1–3]. These techniques have been mainly employed in studying macroscopic planar surfaces.

* Corresponding author. Tel.: +86-25-3594836;
fax: +86-25-3595535.
E-mail address: zhangyu@netra.nju.edu.cn (Y. Zhang).

Recently, Eisenthal and co-workers have demonstrated the expansion of this capability to probe the surfaces of particles of down to micro and submicro dimensions [4,5]. For particles of nanometer size much less than the coherence length of the nonlinear process, however, these techniques become not competent due to their inherent coherent length restriction. In contrast, hyper-Rayleigh scattering (HRS) technique, an incoherent second-order light scattering methodology, is not restricted by the size of systems studied. Generally, this technique, though developed at beginning of the 1990s, has been mainly used to study the second-order optical nonlinearities of molecule chromophores in solution. Very recently, the second-order optical nonlinearities of inorganic nanoscale particles of SiO₂, TiO₂, CdSe, CdS, and Au in solution have been experimentally studied by HRS technique, and their first-order hyperpolarizability β values are large (10^{-27} – 10^{-24} esu per particle) [6–13]. It has been preliminarily shown that the second-order nonlinear optical response of these nanoparticles originates from their noncentrosymmetric nature and seems to have a surface-localized signal generation source. However, there have only been few studies for this surface contribution mechanism of the HRS response of nanoparticles. An important feature of nanoparticles is to have very large ratio of surface atoms to volume atoms. The existence of this vast surface can have a profound effect on the physical and chemical properties of nanoparticles, and these properties are also intensely affected by surrounding medium. From this viewpoint, in this paper, we study the influence of different surface-capping molecules on the HRS response of CdS nanoparticles, in order to provide more direct evidence for the surface contribution mechanism.

2. Experimental

CdS colloid capped with AOT-SO₃⁻ in heptane was prepared by reverse micelle method with $[Cd^{2+}]/[S^{2-}] = 1.5$, similar to that described in the literature [14]. The yellow floccule occurs by adding a proper volume of DMF to the CdS colloid. The surfactant (AOT-SO₃⁻) stabilized CdS nanoparticles (named as CdS/AOT-SO₃⁻), finally obtained by centrifugation, washing, and drying, can be redissolved in heptane, chloroform, and pyridine but not in DMF.

Pyridine-capped CdS nanoparticles (named as CdS/Py/AOT-SO₃⁻) were made by the redispersion of the CdS/AOT-SO₃⁻ nanoparticles into pyridine, where a so-called surface-capping molecule exchange reaction takes place on CdS nanoparticle surfaces, shown as follows (Fig. 1):

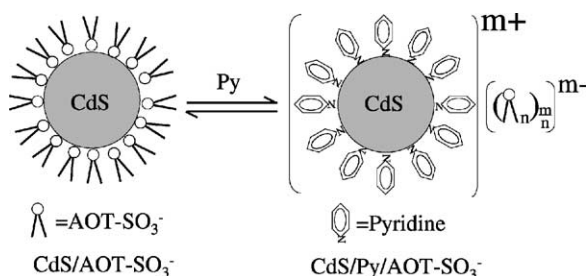


Fig. 1. Process of surface-capping molecule exchange reaction on CdS nanoparticle surface.

The occurrence of this reaction may be attributed to stronger coordinating bonds between Cd²⁺ and pyridine than the electrostatic interaction of Cd²⁺ and AOT-SO₃⁻ on CdS nanoparticle surfaces. Considering charge balance, the replaced AOT-SO₃⁻ remains present as counterions. The CdS/Py/AOT-SO₃⁻ nanoparticle powder was precipitated by addition of heptane to the pyridine sol containing CdS/Py/AOT-SO₃⁻ nanoparticles. The powder can be redissolved in pyridine but not in heptane and chloroform.

For HRS experiments, the CdS/AOT-SO₃⁻ nanoparticles were redispersed in heptane or chloroform, and the CdS/Py/AOT-SO₃⁻ nanoparticles in pyridine. HRS setup used is similar to the literature [15]. The Q-switched Nd-YAG laser pulse (10 Hz, 8–10 ns pulse width) at 1064 nm was focused into an 8 cm length glass cell with the pulse energy lower than 1 mJ. HRS signal was measured by the photomultiplier tube (PMT) at harmonic frequency using a 532 nm interference filter with 3 nm bandwidth. The signal from the PMT was analyzed with a microprocessor-based boxcar integrator (EG & G 4400, 4402) which is triggered by the Q-switch of the laser. To calibrate our experimental setup, para-nitroaniline (*p*-NA) dissolved in chloroform was utilized as a standard sample. The obtained β value of *p*-NA was 36.6×10^{-30} esu in satisfactory agreement with the literature value (34.5×10^{-30} esu) [16].

3. Results and discussion

UV-Vis absorption spectra measurements showed same absorption spectra for the two CdS nanoparticles, implying their same size distribution. From absorption edges (405 nm), the size of the two CdS nanoparticles was determined to be 3 nm in diameter according to the particle-in-a-box calculation with finite barrier height [17]. This result was in good agreement with transmission electron microscopy (TEM) observation. Electronic diffraction (ED) experiments showed the cubic zinc blend structure for the two CdS nanoparticles studied. From absorption spectra, it can also be seen that the two CdS nanoparticles have negligible absorption at the frequency-doubled light of 532 nm.

In HRS experiments, good quadratic dependences of the HRS signal intensity on the incident intensity were observed for the two CdS nanoparticles, as expected for a second-order scattering process. Fig. 2(a) and (b) shows the concentration dependences

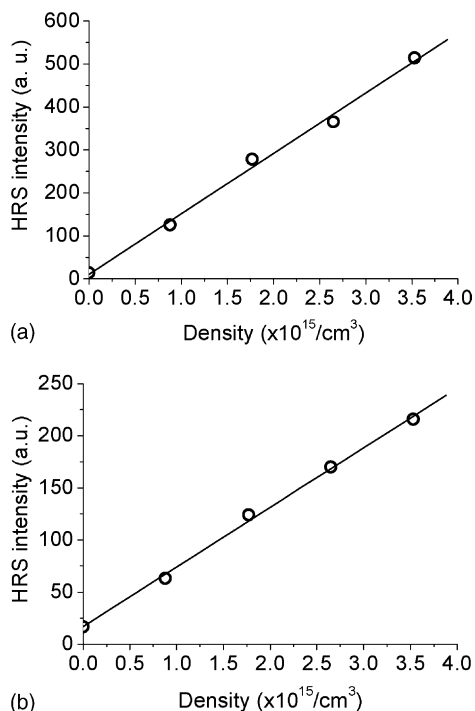


Fig. 2. Concentration dependence of HRS signal intensity for CdS/AOT-SO₃⁻ nanoparticles in heptane (a) and CdS/Py/AOT-SO₃⁻ nanoparticles in pyridine (b).

of HRS signal intensity for the CdS/AOT-SO₃⁻ nanoparticles in heptane and the CdS/Py/AOT-SO₃⁻ nanoparticles in pyridine. Good linear relationships conform to following equation [9]:

$$I_{2\omega} = G(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle)(I_\omega)^2 \quad (1)$$

where I_ω is the incident intensity, $I_{2\omega}$ the HRS intensity, β the first-order hyperpolarizability, N the number density of each component, and G is a constant parameter relating to collection efficiencies and local field corrections. Subscripts 1 and 2 refer to solvent and solute, respectively. N_1 is constant for low solute concentration and β_1 has been previously established. The CdS particle number density N_2 was estimated in terms of the CdS formula unit concentration in solution divided by the mean agglomeration number of CdS particles depending on their mean size. We adopted the internal reference method (IRM) to determine the β_2 value of CdS nanoparticles. The plot of N_2 versus $I_{2\omega}/(I_\omega)^2$ yields a straight line with the slope of $G\langle\beta_2^2\rangle$ and the intercept of $GN_1\langle\beta_1^2\rangle$, so β_2 could be obtained from the slope divided by the intercept. Here using heptane ($\beta = 0.61 \times 10^{-30}$ esu) and pyridine ($\beta = 0.48 \times 10^{-30}$ esu) as internal reference, the “per CdS particle” β values are estimated to be 3.98×10^{-27} esu for the CdS/AOT-SO₃⁻ nanoparticles and 2.63×10^{-27} esu for the CdS/Py/AOT-SO₃⁻ nanoparticles. In contrast, the β value decreases when AOT-SO₃⁻ on CdS nanoparticle surface is replaced by pyridine.

Furthermore, the change in HRS signal intensity of the CdS/AOT-SO₃⁻ nanoparticles in chloroform was observed when gradual addition of pyridine to the solution, as shown in Fig. 3. Systematic reduction is presented in agreement with the previous results of β values. Similarly, this is also attributed to the occurrence of the surface-capping molecule exchange shown in Fig. 1.

The hyper-Rayleigh scattering originates from the orientational and density fluctuations of the molecules or particles in the bulk solution. There is second-order optical nonlinear response in the electric dipole approximation only for the noncentrosymmetric scatterers in solution. An important feature of nanoparticles is very large surface-to-volume atomic ratio. For nanoparticle scatterers, surface termination of the crystalline lattice creates a condition of noncentrosymmetry observable by HRS [18], where surface

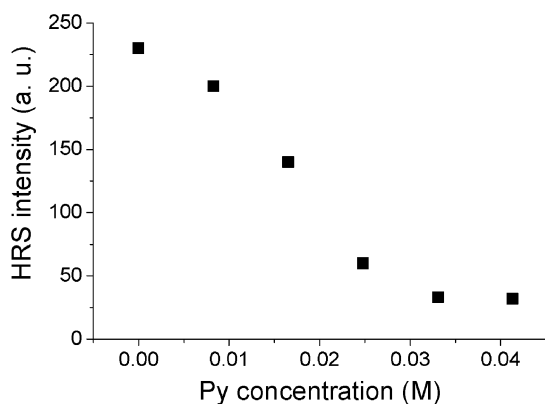


Fig. 3. Change in the HRS signal intensity of CdS/AOT-SO₃⁻ nanoparticles in chloroform with increasing pyridine concentration.

dangling bonds, surface lattice constriction, surface defects (dislocations, vacancies and so on), and absence of long-range order etc. are some main contributions. These lead to that surface or defect-localized “molecule-like” scatterers, for example, Cd–S polar bonds at surface of CdS nanoparticles, are highly noncentrosymmetric and highly polarizable [9,11], and these may contribute substantially to the second-order optical nonlinear signal. It should also be pointed out that cancellation effects of HRS signals on opposite sites of nanoparticle surface can be excluded due to the noncentrosymmetric characters of nanoparticle surface described earlier and the previous reports [8,19]. Based on the importance of nanoparticle surface contribution to HRS process, we emphasize the role of surface-capping molecules for modifying the polarity of Cd–S bonds. In fact, many experimental studies have suggested that the surface of nanoparticles plays a crucial role in determining their chemical and physical properties, such as emission behavior and third-order optical nonlinearities, and these properties are intensely affected by surrounding medium [20,21].

For the CdS/Py/AOT-SO₃⁻ nanoparticles, the nitrogen σ donation of pyridine to Cd²⁺-rich surface of CdS has been elucidated by XPS (X-ray photoelectron spectroscopy) and Fourier transform infrared (FT-IR) spectra [22,23]. As shown in Fig. 4, the formation of the σ donation results in a large charge-transfer from N atom to Cd atom, which was previously indicated by XPS spectra where the electron binding energy of N atom in the CdS/Py/AOT-SO₃⁻ nanopar-

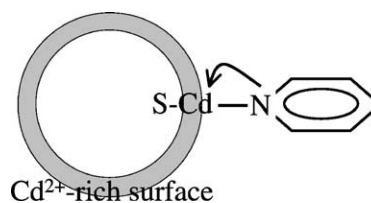


Fig. 4. Scheme of interaction between pyridine and Cd–S polar bonds on CdS/Py/AOT-SO₃⁻ nanoparticle surface. Arrow shows electron transfer from N to Cd.

ticles (403.6 eV) increases compared to pure pyridine molecule (398 eV). Considering Cd–S polar bonds as the “molecule-like” scatterers of HRS signal, a two-level model can be adopted to explain the influence of the σ donation formation on HRS response. The two-level model is derived from molecular chromophores [24] and has already been utilized to successfully interpret the influence of surface protonation on the HRS signal intensity of SiO₂ nanoparticles where surface or defect-localized oxo-to-silicon charge-transfer transitions with high energy were considered [6]. This two-level model is expressed as follows:

$$\beta = \frac{3\mu_{12}^2 \Delta\mu_{12} E_{op}^2}{2(E_{op}^2 - E_{inc}^2)(E_{op}^2 - 4E_{inc}^2)} \quad (2)$$

where β is the first-order hyperpolarizability, E_{op} the surface or defect localized sulfur-to-cadmium charge-transfer transition energy, E_{inc} the energy of incident radiation, $\Delta\mu_{12}$ the change in dipole moment, μ_{12} the transition dipole moment. From Eq. (2), the contribution of the charge-transfer transition to β can scale roughly as $1/E_{op}^2$. It is believed that at nanoparticle surface the sulfur-to-cadmium charge-transfer transition arising from the polarization of the Cd–S bonds is affected by surface-modifying molecules. As a result, E_{op} increases when AOT-SO₃⁻ on CdS nanoparticle surface is replaced by pyridine, due to the large charge-transfer from nitrogen to cadmium, while oxygen in AOT-SO₃⁻ possesses larger electronegativity and the interactions between CdS and AOT-SO₃⁻ are weaker. Therefore, β decreases with increasing E_{op} and HRS signal intensity of $I_{2\omega}$ reduces known from Eq. (1).

Note that, on applying the two-level model, one should consider both the bulk and surface contributions to the nonlinear response. The previous discussion only considers surface contribution but not bulk

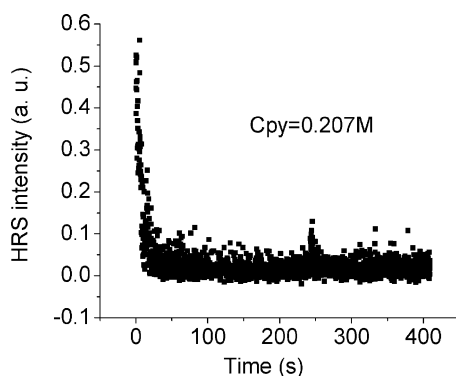


Fig. 5. HRS signal intensity variation after addition of 0.207 M pyridine to the sol of CdS/AOT-SO₃⁻ nanoparticles in chloroform.

effect. If we consider bulk contribution, in the previous two-level model E_{op} should represent the electronic transition energy of CdS nanoparticles, i.e. optical bulk band-gap. It has been demonstrated that, however, both the optical band-gap and dipole moment of CdS nanoparticles are not affected by surface-capping molecule exchange [25]. Our experimental observations also showed that the absorption spectra of the CdS/AOT-SO₃⁻ nanoparticles in heptane and CdS/Py/AOT-SO₃⁻ nanoparticles in pyridine are the same. Therefore, we may not consider bulk contribution when adopting the two-level model to explain the influence of surface-capping molecule exchange on β .

To further study the dynamic process of the surface exchange reaction, the variation of HRS signal intensity with time was measured after addition of pyridine of 0.207 M to the CdS/AOT-SO₃⁻ chloroform sol, as shown in Fig. 5. It can be seen that the HRS signal intensity rapidly reduces at the initial stage of the reaction and fast reaches a constant intensity value. This indicates that, on the CdS nanoparticle surface, the process of AOT-SO₃⁻ replaced by pyridine is a reaction to rapidly reach equilibration. This process was also demonstrated by electroconductivity measurements during redissolving the CdS/AOT-SO₃⁻ nanoparticle powder into pyridine (Fig. 6). Note that the electroconductivity of the CdS/AOT-SO₃⁻ nanoparticles in heptane or chloroform is nearly zero, attributed to charge balance and no separation between Cd²⁺-rich surface and AOT-SO₃⁻ [23]. Once the CdS/AOT-SO₃⁻ nanoparticle powder was redissolved into pyridine, the electroconductivity of

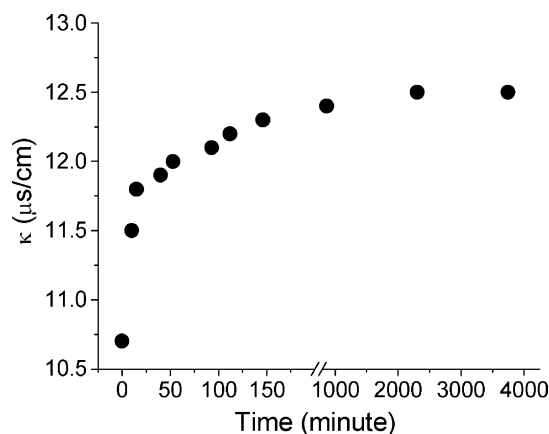


Fig. 6. Electroconductivity variation after redissolving CdS/AOT-SO₃⁻ nanoparticle powder into pyridine.

the obtained sol enhanced immediately to 10.7 $\mu\text{S}/\text{cm}$, and then slowly increased and reached a saturation value. The enhancement of the electroconductivity is due to the occurrence of the surface exchange reaction, where anions of AOT-SO₃⁻ are replaced by pyridine and remain present as counterions. As shown in Fig. 1, the CdS/Py/AOT-SO₃⁻ is a salt-like structured nanoparticle which contributes to the electroconductivity of the sol. In the previous work [22], we also studied the concentration dependence of the electroconductivity of the CdS/Py/AOT-SO₃⁻ nanoparticles in pyridine, and a good agreement with Kohlrausch's empirical rule was obtained.

To eliminate the possible influence of the presence of counterions in the salt-like structured CdS/Py/AOT-SO₃⁻ nanoparticles on the HRS signal intensity, we also measured the HRS signal intensity of CdS/Py/BPh₄⁻ nanoparticles in pyridine, which were synthesized by counterion exchange method [23] reported previously. Results exhibited the nearly same intensity value of HRS signals for both the CdS/Py/AOT-SO₃⁻ and CdS/Py/BPh₄⁻ nanoparticles in pyridine at same concentration, implying that the influence of the counterions of AOT-SO₃⁻ and BPh₄⁻ on the HRS signal intensity is negligible. In addition, effects from third-order optical nonlinear process, based on nanoparticle surface static electric field and solvent field with low frequency instantaneous fluctuations, on HRS response have been experimentally excluded [6,7]. Therefore, we here may not consider the contributions of these two fields for charged nanoparticles studied here.

4. Conclusions

The direct surface-capping molecular exchange and its influence on the second-order optical nonlinearity of CdS nanoparticles have been studied by the incoherent HRS technique. The β value or HRS signal intensity reduces when AOT-SO₃⁻ on CdS nanoparticle surface is replaced by pyridine. For the HRS response of CdS nanoparticles, although, a bulk-like contribution resulting from the noncentrosymmetric zinc blend structure should be considered, our experimental observations still directly demonstrate the importance of surface contribution which arises from the special surface structure of nanoparticles. In fact, the bulk-like contribution has been shown to be trivial for nanoscale CdS [10], CdSe [8], and TiO₂ [7]. A two-level model approximation derived from molecular chromophores is also adopted to explain the influence of surface-capping molecules on HRS response, based on that the polarity of the surface molecule-like scatterers (Cd-S polar bonds) can be affected by coordinating atoms. Furthermore, the process of the surface exchange reaction was experimentally studied by the HRS technique and electroconductivity measurements, and their results were in good agreement. Also, the significance of these investigations consists in indicating directly that HRS technique is sensitive tool for characterization of nanoparticle surface structure and polarity.

Acknowledgements

This work was supported by the National Science Foundation of China (Nos. 10074023, 69890225, and 69890220).

References

- [1] G. Richmond, J.M. Robinson, V.L. Shannon, *Prog. Surf. Sci.* 28 (1988) 1.
- [2] Y.R. Shen, *Ann. Rev. Phys. Chem.* 40 (1989) 327.
- [3] K.B. Eisenthal, *Ann. Rev. Phys. Chem.* 43 (1992) 627.
- [4] H. Wang, E.C.Y. Yan, E. Borguet, K.B. Eisenthal, *Chem. Phys. Lett.* 259 (1996) 15.
- [5] H. Wang, E.C.Y. Yan, Y. Liu, K.B. Eisenthal, *J. Phys. Chem. B.* 102 (1998) 4446.
- [6] F.W. Vance, B.I. Lemon, J.A. Ekhoftand, J.T. Hupp, *J. Phys. Chem. B* 102 (1998) 1845.
- [7] D.G. Fu, Y. Zhang, X. Wang, J.Z. Liu, Z.H. Lu, *Chem. Lett.* (2001) 328.
- [8] M. Jacobsohn, U. Banin, *J. Phys. Chem. B.* 104 (2000) 1.
- [9] Y. Zhang, X. Wang, D.G. Fu, J.Q. Cheng, Y.C. Shen, J.Z. Liu, Z.H. Lu, *J. Phys. Chem. Solids* 62 (5) (2001) 903.
- [10] Y. Zhang, D.G. Fu, J.Q. Cheng, X. Wang, Y.C. Shen, J.Z. Liu, Z.H. Lu, *Mol. Cryst. Liq. Cryst.* 363 (2001) 207.
- [11] Y. Zhang, X. Wang, D.G. Fu, J.Z. Liu, Y.P. Cui, Z.H. Lu, *Chem. Lett.* (2001) 46.
- [12] B.S. Santos, G.A.L. Pereira, D.V. Petrov, C.M. de Donegá, *Opt. Commun.* 178 (2000) 187.
- [13] P. Galletto, P.F. Brevet, H.H. Girault, R. Antoine, M. Broyer, *Chem. Commun.* (1999) 581.
- [14] N. Herron, Y. Wang, H. Eckert, *J. Am. Chem. Soc.* 112 (1990) 1322.
- [15] K. Clays, A. Persoons, *Rev. Sci. Instrum.* 63 (1992) 3285.
- [16] K. Clays, A. Persoons, *Phys. Rev. Lett.* 6 (1991) 2980.
- [17] H. Weller, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 41.
- [18] K. Clays, E. Hendrickx, A. Persoons, *J. Mol. Liq.* 67 (1995) 133.
- [19] J.I. Dadap, J. Shan, K.B. Eisenthal, T.F. Heinz, *Phys. Rev. Lett.* 83 (1999) 4045.
- [20] C.B. Murry, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* 115 (1993) 8706.
- [21] Y. Wang, *Acc. Chem. Rev.* 24 (1991) 133.
- [22] Y. Zhang, D.G. Fu, J.Z. Liu, Z.H. Lu, *J. Nanoparticle Res.* 2 (2) (2000) 299.
- [23] Y. Zhang, D.G. Fu, J.D. Cai, M. Li, J.Z. Liu, Z.H. Lu, *J. Fouc. Mater.* 31 (4) (2000) 380 (Chinese).
- [24] J.L. Oudar, D.S. Chemla, *J. Chem. Phys.* 66 (1977) 2664.
- [25] U. Resch, A. Eychmiiller, M. Haes, H. Weller, *Langmuir* 8 (1992) 2215.