CHIROPTICAL PROPERTIES OF CDSE NANOPLATELETS

Maria V MUKHINA[1,*], Vladimir G MASLOV[1], Alexander V BARANOV[1],
Anatoly V FEDOROV[1], Yurii K GUN'KO[1,2]

[1]*ITMO University, 197101, Kronverkskiy pr. 49, St. Petersburg, Russia*

[2]*University of Dublin, Trinity College, Dublin 2, Ireland*

[*]*Corresponding author: mmuxina@gmail.com*

Abstract

Inherent and induced chirality of CdSe quantum nanoplatelets have been investigated using a technique of circular dichroism (CD). It was shown that the nanoplatelets synthesized without using of any chiral reagents possess circular dichroism in their initial condition. The CD can be enhanced up to 30 times by an attachment of the chiral ligands. The attachment of the chiral ligands was obtained via a procedure of the phase transfer from chloroform to water assisted by the chiral molecules of cysteine. The degree of CD increasing depends on thickness of the nanoplatelets. Enhancement of the CD signal is less for thicker nanoplatelets.

Keywords:

chiral nanocrystals, CdSe nanoplatelets, chiroptical properties, circular dichroism, phase transfer, nanoplatelets twisting

1. INTRODUCTION

Chiral nanocrystals are an emerging class of nanostructures that has attracted considerable attention, because chirality of the semiconductor nanocrystals can have a tremendous effect on the nanotechnology field. The key advantage of using artificial nanocrystals is an ability to manipulate the units of matter at the scale close to molecular one [1-3]. If nanocrystal, whose sizes are comparable to the sizes of biomolecules and the pores of cell membranes, also possesses chirality, its «lock and key» interaction with biological objects may be possible [7,8]. Up to date little attention has been paid to chirality of the semiconductor nanocrystals. There were some papers on chirality induced by adsorption of the chiral ligands on the surface of nanocrystals [9], or by using of the chiral ligands in synthesis process [10-16].

Here, we use a technique of circular dichroism (CD) to investigate inherent and induced chirality of CdSe nanoplatelets. The nanoplatelets are 2D nanocrystals with anisotropic optical properties [17]. As it was shown in [18], the nanoplatelets tend to roll up into tubes, and the probability of rolling-up into a tube is less for thicker nanoplatelets [19]. It is reasonable to suggest that CdSe nanoplatelets like single-walled carbon nanotubes [20,21] possess large optical activity what makes these nanocrystals are promising object for studying of the chiroptical properties.

2. METHODS

CdSe nanoplatelets. Semiconductor CdSe quantum nanoplatelets were synthesized by a method described in the reports [22,23] without using any chiral chemicals. The samples of nanoplatelets (NPL) used for the experiments had the first absorption peak at 460 nm and 507 nm. The nanoplatelets had a mean lateral dimension of 17 nm and thickness of the nanoplatelets was 4 monolayers of CdSe, or 2.4 nm (NPL 460), and 5 monolayers of CdSe, or 3 nm (NPL 507). As-prepared CdSe nanocrystals were surface capped by achiral trioctylphosphine oxide (TOPO).

Phase transfer. For the samples capped with chiral ligand, 15 mg of nanocrystals were dissolved in 750 mkl of chloroform. Then 10 vol. % of methanol solution of D- or L-cysteine (8 mg of cysteine dissolved in 300 mkl of methanol) was added to the nanocrystals solution followed by stirring. After 1-2 min of solubilization, 750 mkl of distilled water with pH 10-11 were added to the solution. pH was varied by adding of aqueous solution of KOH. To initiate the phase transfer, the mixture was vigorously shaken and left for 1-2 minutes. After complete separation, the aqueous phase was collected in separate vial.

CD measurements. The spectra of circular dichroism and absorption were studied using a Jasco J-1500 spectrometer. The spectra of CD were measured at 20 ˚C. Quartz cuvettes with a 1 cm path length were used for all experiments.

3. RESULTS AND DISCUSSION

The CD spectrum of as-prepared NPL 460 is shown in **Figure 1** (the black line). As-prepared nanocrystals were surface capped by TOPO. As one can see, the NPL even capped with achiral TOPO possess chiroptical activity around 1-2 mdeg. It increases dramatically after adsorption of the chiral ligands on the surface of the nanocrystals. The green line in **Figure 1** shows the CD spectrum of the NPL 460 after the phase transfer from chloroform to water assisted by L-cysteine. At this case, the CD is almost 30 times stronger than in the case of the as-prepared NPL 460 capped with TOPO. The most probable explanation for a weak signal from the TOPO-capped NPL is that they slightly twisted (as in the case described in [19]). When the nanoplatelets transfer from chloroform to water, they adsorb the chiral molecules of cysteine. Adsorption of cysteine molecules may lead to tighter folding, because, as it was shown in [19], the folding of CdSe nanoplatelets is strongly affected by asymmetric capping of ligands on a large nanoplatelets' surface. This may result in increasing of the CD signal observed by us in the experiments.

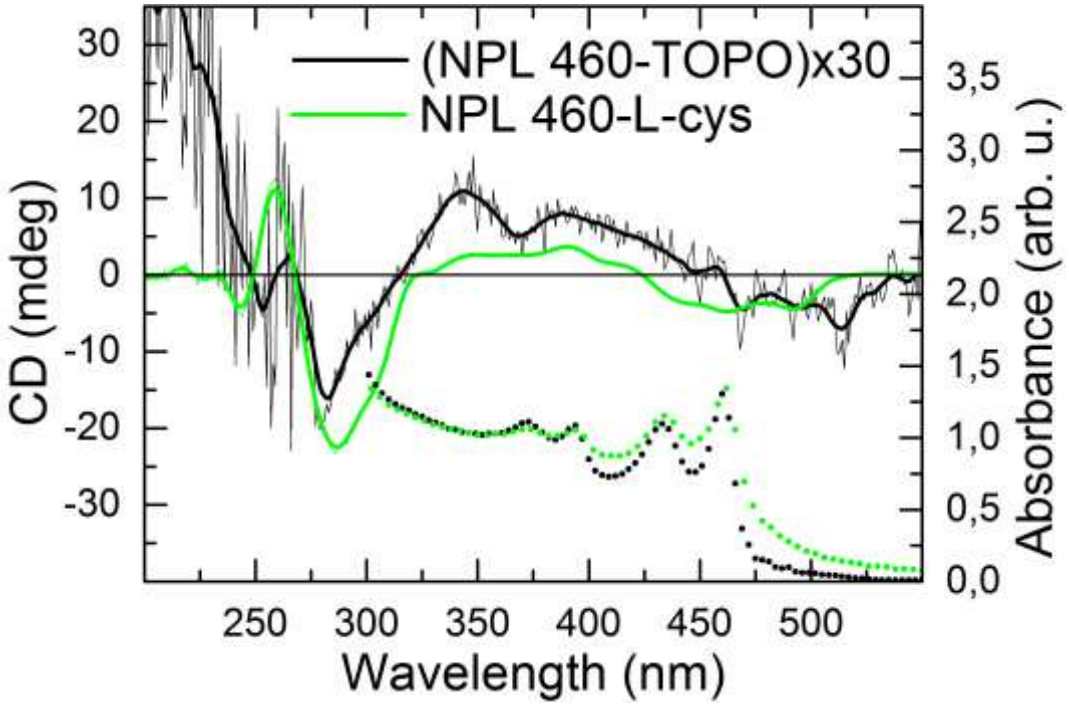

Fig. 1 The CD (solid lines) and absorption (dotted lines) spectra of aqueous solutions of the NPL 460 before and after capping with chiral ligand L-cysteine (L-cys).

The phase transfer assisted by molecules of D-cysteine also leads to increasing of initial CD signal, but with the sign, opposite to initial one. As shown in **Figure 2**, the samples of the NPL 460 capped with L- and D-cysteine exhibit near mirror-image signals. At the case of the quantum dots reported in [9,13], the values of

the phase transfer induced CD are the same for L- and D-cysteine. But in the case of the NPL, the sample capped with L-cysteine exhibits 3-5 times stronger signal. Also L-capped sample possesses CD spectra with sharper bands. The differences between L- and D-cysteine capped samples may arise from the intrinsic chiroptical activity of nanoplatelets.

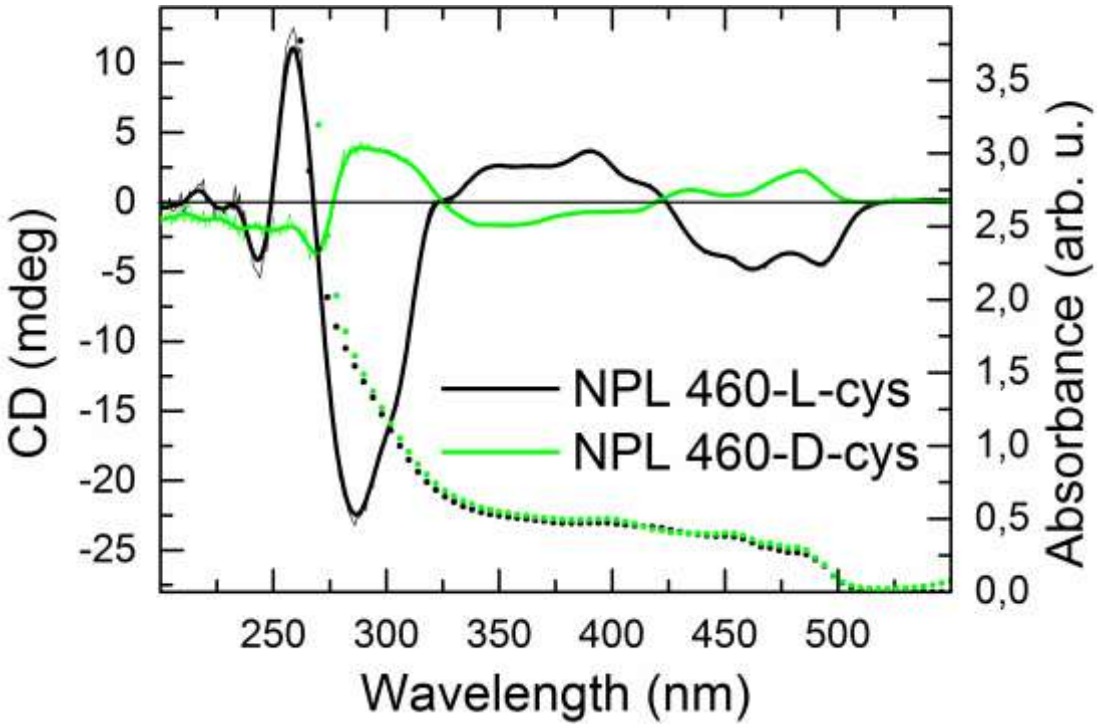

Fig. 2 The CD (solid lines) and absorption (dotted lines) spectra of aqueous solutions of the NPL 460 measured after capping with L- and D-cysteine.

Figure 3 displays the absorption (dotted lines) and CD (solid lines) spectra for the NPL of different thickness. As expected, the CD bands wavelengths depend on size of the NPL that is in a good agreement with data for CdS quantum dots [24]. The first CD band of the NPL 507 is red-shifted for 43 nm compared with the NPL 460, what is correlated with size shift of absorption band.

Figure 3 also shows dependence of CD increasing coefficient on thickness of the nanoplatelets. In the case of the NPL 507, increasing of chiroptical activity induced by attachment of L-cysteine is not so strong as in the case of the NPL 460. Weaker CD enhancement for thicker nanoplatelets is in a good correlation with data reported in [19]. According to [19], thicker nanoplatelets do not tend to fold on themselves and form nanoscrolls regardless of type of the ligands attached to their surfaces.

Results of the observation of inherent and induced chirality of CdSe nanoplatelets reported here can be discussed in light of previously suggested mechanisms for induction of chiroptical activity in spherical nanocrystals [9-11, 24]. In these reports experimental data and theoretical calculations to support the induction of chiroptical activity via distortion of the nanocrystals' surface by binding with chiral ligands have been brought. The nanoplatelets tend to twist into tubes [19], similarly to carbon nanotubes [20,21]. Such folding into helical structures necessarily should affect their chiroptical activity because of breaking symmetry. Here we provide indirect evidences of correlation between chiroptical activity and folding of the nanoplatelets that should be supported by data of transmission electron microscopy.

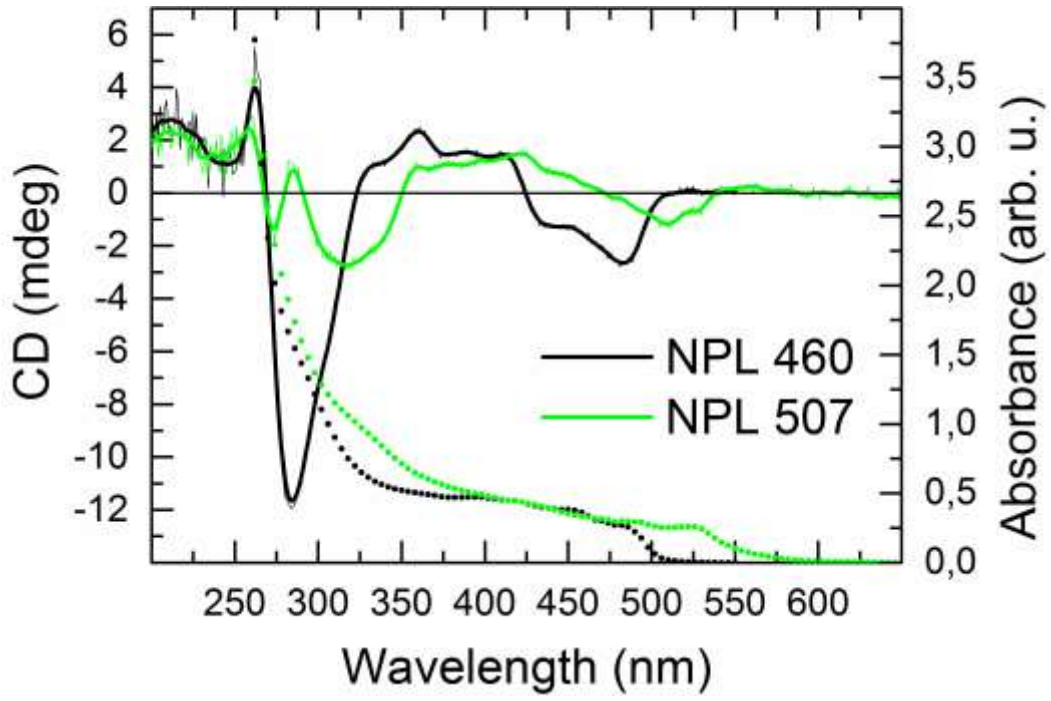

Fig. 3 The CD (solid lines) and absorption (dotted lines) spectra of aqueous solutions of the NPL 460 and the NPL 507 measured after capping with L-cysteine.

4. CONCLUSION

We have shown that CdSe quantum nanoplatelets possess inherent chiroptical activity. The phase transfer of the nanoplatelets from chloroform to water assisted by chiral molecules of cysteine leads to an enhancement of CD up to 30 times. Weaker CD enhancement for thicker nanoplatelets has been also observed that is in good correlation with data on folding of the nanoplatelets reported in [19]. This observation allow us to suggest that folding of the nanoplatelets in combination with surface distortion produced after binding with chiral ligands is the mechanism of induction of CD enhancement.

ACKNOWLEDGEMENTS

This work was supported by the Government of Russian Federation (Grant 074-U01), and the Ministry of Education and Science of the Russian Federation (Grant no. 14.B25.31.0002).

LITERATURE

[1] JASIENIAK, J.; SMITH, L.; van EMBDEN, J.; MULVANEY, P., CALIFANO, M. Re-examination of the Size-Dependent Absorption Properties of CdSe Quantum Dots *J. Phys. Chem. C,* 2009, year 113, page 19468-19474.

[2] YU, W. W.; QU, L.; GUO, W., PENG, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals *Chem. Mater,* 2003, year 15, page 2854-2860.

[3] RESCH-GENGER, U.; GRABOLLE, M.; CAVALIERE-JARICOT, S.; NITSCHKE, R., NANN, T. Quantum dots versus organic dyes as fluorescent labels *Nat. Methods,* 2008, year 5, page 763-775.

[4] MUKHINA, M.; DANILOV, V.; ORLOVA, A.; FEDOROV, M.; ARTEMYEV, M.; BARANOV, A. Electrically controlled polarized photoluminescence of CdSe/ZnS nanorods embedded in a liquid crystal template. *Nanotechnology,* 2012, year 23, page 325201.

[5] BAKER, J.; WIDMER-COOPER, A.; TONEY, M.; GEISSLER, P.; ALIVISATOS, A. Device-Scale Perpendicular Alignment of Colloidal Nanorods. *Nano Lett.,* 2010, year 10, page 195-201.

[6] JONES, M. R.; MACFARLANE, R. J.; LEE, B.; ZHANG, J.; YOUNG, K. L.; SENESI, A. J.; MIRKIN, C. A. DNA-nanoparticle superlattices formed from anisotropic building blocks. *Nat. Mater.,* 2010, year 9, page 913-917.

[7] BOOTH, T. D.; WAHNON, D.; WAINER, I. W. Is chiral recognition a three-point process? *Chirality,* 1997, year 9, page 96-98.

[8] KUEHNLE, A.; LINDEROTH, T. R.; HAMMER, B.; BESENBACHER, F. Chiral recognition in dimerization of adsorbed cysteine observed by scanning tunnelling microscopy. *Nature,* 2002, year 415, page 891-893.

[9] TOHGHA, U., DEOL, K., PORTER, A., BARTKO, S., CHOI, J., LEONARD, B., VARGA, K., KUBELKA, J., MULLER, G., BALAZ, M. Ligand induced circular dichroism and circularly polarized luminescence in CdSe quantum dots. *ACS nano*, 2013, year 7, nr. 12, page 11094–11102.

[10] ELLIOTT, S. D.; MOLONEY, M. P., GUNKO, Y. K. Chiral Shells and Achiral Cores in CdS Quantum Dots. *Nano Lett.,* 2008, year 8, page 2452-245.

[11] MOLONEY, Mi. P.; GUN'KO, Y. K., KELLY, J. M. Chiral highly luminescent CdS quantum dots. *Chem. Commun.,* 2007, year 38, page 3900-3902.

[12] ZHOU, Y.; YANG, M.; SUN, K.; TANG, Z., KOTOV, N. A. Similar topological origin of chiral centers in organic and nanoscale inorganic structures: effect of stabilizer chirality on optical isomerism and growth of CdTe nanocrystals. *J. Am. Chem. Soc.,* 2010, year 132, page 6006-6013.

[13] NAKASHIMA, T.; KOBAYASHI, Y., KAWAI, T. Optical activity and chiral memory of thiol-capped CdTe nanocrystals *J. Am. Chem. Soc.,* 2009, year 131, page 10342-1034.

[14] BEN-MOSHE, A.; GOVOROV, A. O., MARKOVICH, G. Enantioselective Synthesis of Intrinsically Chiral Mercury Sulfide Nanocrystals. *Angew. Chem.,* 2013, year 125, page 1313-1317.

[15] BEN-MOSHE, A.; WOLF, S. G.; SADAN, M. B.; HOUBEN, L.; FAN, Z.; GOVOROV, A. O., MARKOVICH, G. Enantioselective control of lattice and shape chirality in inorganic nanostructures using chiral biomolecules *Nature Comm.,* 2014, year 5, page 1-9.

[16] GOVAN, J. E.; JAN, E.; QUEREJETA, A.; KOTOV, N. A.; GUN'KO, Y. K. Chiral luminescent CdS nano-tetrapods. *Chem. Commun.,* 2010, year 46, page 6072-6074.

[17] MUKHINA, M.; MASLOV, V.; BARANOV, A.; FYODOROV, A.; ARTEMYEV, M., PRUDNIKOV, A. Anisotropy of light absorbed by an ensemble of CdSe quantum nanoplates *J Opt. Technol.,* 2013, year 80, page 642-644.

[18] SHEN, Q.; JIANG, L.; MIAO, J.; HOU, W., ZHU, J.-J. Sonoelectrochemical synthesis of CdSe nanotubes. *Chem. Commun.,* 2008, page 1683-1685.

[19] BOUET, C.; MAHLER, B.; NADAL, B.; ABECASSIS, B.; TESSIER, M. D.; ITHURRIA, S.; XU, X., DUBERTRET, B. Two-dimensional growth of CdSe nanocrystals, from nanoplatelets to nanosheets. *Chem. Mater.,* 2013, year 25, page 639-645.

[20] STRANO, M. S. Carbon nanotubes: Sorting out left from right. *Nature Nanotech.,* 2007, year 2, page 340-341.

[21] PENG, X.; KOMATSU, N.; BHATTACHARYA, S.; SHIMAWAKI, T.; AONUMA, S.; KIMURA, T., OSUKA, A. Optically active single-walled carbon nanotube. *Nature Nanotech.,* 2007, year 2, page 361-365.

[22] ITHURRIA, S., DOUBERTRET, B. Quasi-2D colloidal CdSe platelets with thicknesses controlled at the atomic level. *J. Am. Chem. Soc.*, 2008, year 130, page 16504.

[23] ACHTSTEIN, A. W., SCHLIWA, A., PRUDNIKAU, A., HARDZEI, M., ARTEMYEV, M. V., THOMSEN, C., WOGGON, U. Electronic structure and exciton–phonon interaction in two-dimensional colloidal-CdSe nanosheets. *Nano Lett.*, 2012, year 12, page 3151.

[24] BEN MOSHE, A., SZWARCMAN, D., MARKOVICH, G. Size Dependence of Chiroptical Activity in Colloidal Quantum Dots. *ACS nano,* 2011, year 5, page 9034-9043.