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論文の内容の要旨

In recent years colloidal semiconductor nanocrystals become important substances for various applications. Scientific areas such as photovoltaics, biology, electronics and photocatalysis are just a fraction where colloidal semiconductor nanocrystals can be used. The one makes the nanocrystals so attractive is their optical and electrical properties. Systematical control of the absorption and luminescence is an example, which allows integration of the nanocrystals into glass filters. The microscopic phenomenon in general determines the application field in macroscopic dimensions. Moreover, the microscopic phenomenon is often related to nanocrystals sizes and shapes. For example the color variation in nanocrystalline CdSe is size dependent. Just by changing the sizes of the nanocrystals from 2 to 6 nm one can tune the absorption and luminescence spectra from green to red.

Motivated from the unique properties of the nanocrystals and the fact that few is know about their growth, here in this dissertations are given important aspect of the nanocrystal growth as well as studies related to the optical properties of the nanocrystals. Control over the nanocrystal sizes and shapes require maintaining special conditions during the synthesis. In this work are given synthesis conditions for different systems where the nanocrystals were synthesized. Reverse micelles as confined structures are examples where the nanocrystal growth was conducted. Beside reverse micelles, synthesis was also achieved via a method called “hot-matrix”. Structural characterization of the nanocrystals was obtained by using X-ray Diffraction (XRD), Tansmission Electon Microscopy (TEM), absorption spectroscopy, steady state photoluminescence spectroscopy (PL), Electron Paramagnetic Resonance (EPR), transient photoluminescence and photoluminescence excitation spectroscopy. Precursors, which were used for the preparation of the nanocrystals were also analyzed by Nuclear Magnetic Resonance (NMR) and Infrared Spectroscopy (IR). Integration of the colloidal chemistry rules with the nanocrystal synthesis allowed us to obtained unique organic/inorganic nanocomposites. An example of such kind of composites are CdS nanocrystals covered with poly(methacrylic acid). The obtained nanocomposites exhibit good water dispersibility and photoluminescence. The last one is due to the CdS nanocrystals. During the studies were discovered important steps related to mechanism of the nanocrystal

growth. One such kind of indispensable step is the Ostwald ripening process, which controls the polydispersity of the nanocrystals.

During the study two reverse micellar systems were studied. The first system composed of water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/heptane was used to synthesize CdSe nanocrystals. In this system for a first time the kinetics of growth of CdSe semiconductor nanocrystals was reported. Precise size control over the nanocrystals was achieved by controlling the size of the micelles. Relation between the absorption spectra and nanocrystal sizes were established by monitoring the temporal changes in the absorption spectra of CdSe nanocrystals. This allowed us to calculate the respective time constant, which control the nanocrystal growth. The second reverse micellar system was composed of water/cetyltrimethylammonium bromide (CTAB)/benzene. In CTAB system were grown CdSe nanocrystals as well as inorganic(CdSe nanocrystals)/organic(polymer) composites. The motivation for the preparation of nanocomposites was due to the potential application of the nanocomposites in labeling of living cells. As in the AOT system, here the nanocrystal growth also passes through Ostwald ripening process. Especially, when there was dissolved monomer in the reverse micelles, the nanocrystals grew slower and clearly distinguishable changes in the absorption spectra were observed. The latter was explained by the existence of polydisperse nanocrystals in the samples. After the nanocrystals were formed, in-situ polymerization was conducted in the reverse micelles. The agglomerates were further analyzed by TEM and clear evidence for the existence of inorganic/organic nanoparticles was concluded.

Different steps from the reverse micelles method were applied in the case of the hot-matrix method. Here the nanocrystals were synthesized in solvents that have boiling points above 300 °C. In the solvent were dissolved surfactants such as stearic acid and hexadecylamine. At elevated temperatures injection of the precursors containing zinc, manganese (Mn^{2+}), cadmium, selenium or tellurium allowed rapid nucleation of various types of cluster. These nuclei (or clusters) were further grown to well define nanocrystals. By controlling the reaction temperature, reaction time, precursor concentration or surfactant concentration, the size of the nanocrystals were varied.

The nanocrystals synthesized by the hot-matrix method were used for fluorescence resonance energy transfer (FRET) studies. Moreover, for this study we synthesized manganese doped ZnSe nanocrystals. The doping allowed us to achieve long fluorescence lifetimes that are believed to be very useful for transient photoluminescence experiments especially as markers in bio-imaging. To show this remarkable property of the doped nanocrystals we studied the FRET between Mn^{2+} doped ZnSe nanocrystals and photochromic molecules. Because photochromic molecules are unstable in room temperature, the experiments were done at low temperatures.

論文の審査結果の要旨

学位論文は、(1)半導体量子ドットの基礎の概観 (2)ホットマトリクス法およびミセルテンプレート法による単分散 CdTe/S ZnTe/S の合成、(3)反応機構の解明、(4) Mn ドープによる励起寿命の長寿命化、(5) 光励起状態の量子ドットから色素分子への共鳴蛍光エネルギー移動 (FRET) および、(6) 光励起状態の量子ドットからの電子移動を実験的に議論し (7) 半導体量子ドットの分子修飾表面制御と生理学的細胞プローブの可能性を展望した。

この論文で、特に優れている点は、フォトクロミック分子であるスピロピランをエネルギー受容体に用いて、FRET を分子骨格の変化によりゲート制御をはじめて可能とした業績にある。

ZnSe と Spiropyran との間の FRET

直径 8-9nm の ZnSe Q-dot を合成した。この Q-dot 中に Mn^{2+} をドープすると、450 と 580 nm に発光ピークを持つ (図 1)。それぞれ、バンド間再結合発光、 Mn^{2+} (${}^4T_1 \rightarrow {}^6A_1$) である。450nm の発光寿命は、1ns 以下。580nm の発光寿命は 0.5ms 程度にまで長い。これは、 Mn^{2+} のドープにより、発光寿命を 10 万倍長くしたことに相当する。ZnSe: Mn^{2+} からの発光は開環型の Spiropyran 分子 (SPO open; Merocyanine form) の光吸収スペクトルと良く一致する (図 2)。開環型 Spiropyran 分子は、1', 3'-dihydro-1', 3', 3'-trimethyl-6-nitrospiro[2H-1-benzopyran- 2,2'-(2H)-indole] に、紫外線を照射して得られる。図 2 の吸収スペクトルは、紫外線照射時間に従って、開環反応が進み、可視領域の吸収が増加することを示している。ZnSe: Mn^{2+} (${}^4T_1 \rightarrow {}^6A_1$) の発光スペクトルと、SPO open の吸収スペクトルが良く重なることから、両者間で FRET が進むことが予測できる (図 3)。

ZnSe: Mn^{2+} (${}^4T_1 \rightarrow {}^6A_1$) と SPO の間の FRET の最大の特徴は、紫外線照射のよって、Acceptor 分子の数を制御できる点にある。580nm 蛍光寿命を、開環反応を駆動する紫外線照射時間を変えて測定すると、照射時間が長くなるにつれて、寿命が短くなった (図 10)。これは、FRET Acceptor の数を、紫外線予備照射で制御できることを示している。

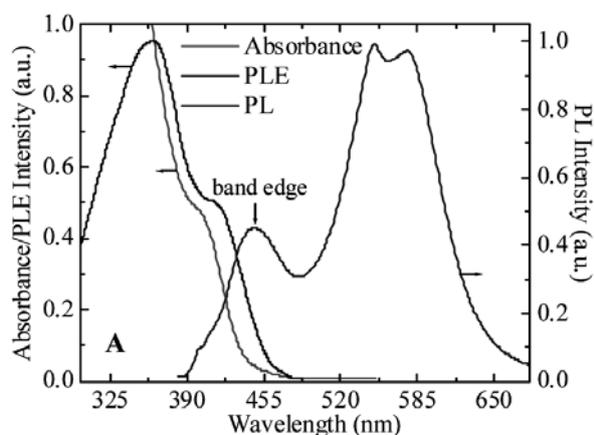


図 1 ZnSe:Mn の吸収、励起、発光スペクトル

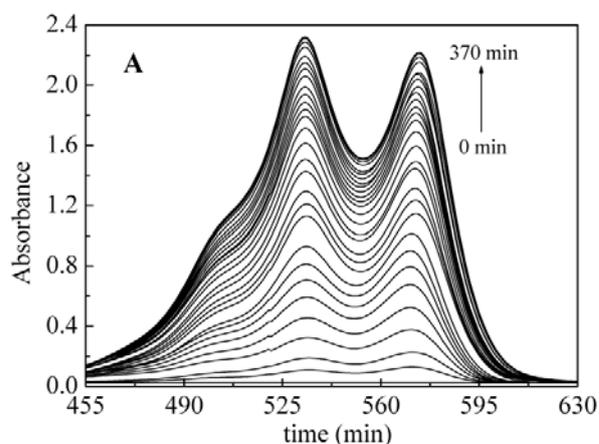


図 2 紫外線照射による SPO 分子の開環

半導体量子ドットの表面修飾

細胞内に取り込まれるために、Q-dot の表面キャップ分子を、1-undecanethiol から、親水性分子に変え、Thioglycolic Acid あるいは、より長鎖類縁体分子での ZnSe:Mn²⁺ の合成を進めた。

半導体ナノ結晶の量子サイズ効果などの光物理過程は、おもに、CdSe などの Cd を含む化合物半導体を用いた研究が多い。カドミウムは、細胞に決定的な毒性を与える。そこで、Cd を Zn に置き換えて、結晶作成をした。

これら水溶性半導体量子ドットを光励起し、表面修飾分子の種類を変え溶存酸素およびメチルビオロジェンへの光誘起電子移動反応のダイナミクスを明らかにした。

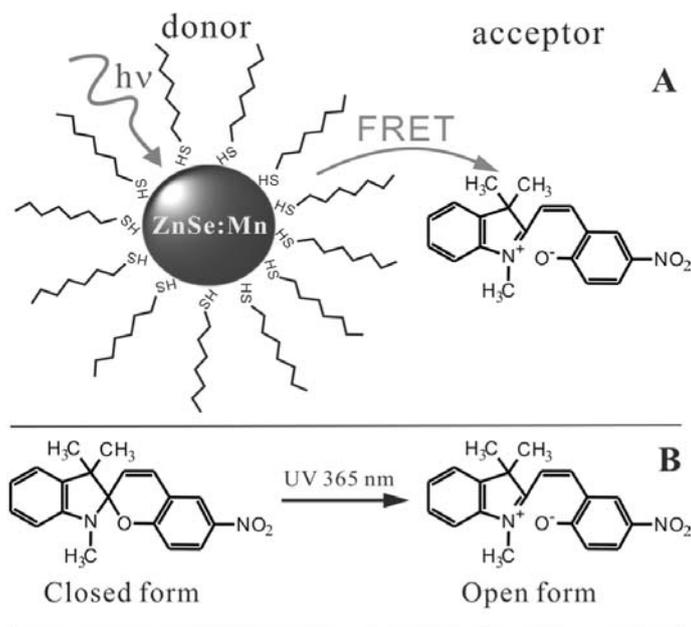


図3 ZnSe:Mn <-> SPOopen 間での FRET