

論文 / 著書情報  
Article / Book Information

題目(和文)	特異な金属カルコゲン化物コロイドナノ結晶の合成、構造ならびに電気特性
Title(English)	Syntheses, Structures and Electronic Properties of Unconventional Metal Chalcogenide Colloidal Nanocrystals
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

## 論文要旨

THESIS SUMMARY

系・コース : Department of, Graduate major in	Materials Science and Engineering	系 コース	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	(Philosophy)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

In this thesis, synthesis, structure, and electronic properties of unconventional metal chalcogenide colloidal nanocrystals (NCs) including core@shell lead chalcogenide and tin chalcogenide semiconductor is reported. It consists of 7 chapters as shown below.

Chapter 1 introduced the fundamental theory and motivation of this study. The general overview of core@shell lead chalcogenide colloidal NCs, particularly core@shell consisting of Lead Telluride (PbTe) core and Lead Sulfide (PbS) shell is described. The overview of environmentally friendly Tin Sulfide (SnS) semiconductor NCs are also provided. Then the outline and chapter overview of this study is explained.

In chapter 2, the charge carrier transport of core@shell PbTe@PbS colloidal NCs assembly was successfully demonstrated using Field Effect Transistor (FET) device. The core@shell NCs assemblies are cross-linked by molecular ligand ethane-1,2-dithiol (EDT), which replaced the native insulating oleic acid ligand. To perform the direct comparison, the FET device of EDT cross-linked core-only PbTe colloidal NCs assembly was also prepared. The number of the deposited layers of PbTe@PbS and PbTe assemblies were identical. PbTe@PbS FETs exhibit like an entirely n-type transistor with no sign of hole accumulation. This behavior was distinct from the core-only PbTe NC FETs which exhibited signature of ambipolar transport, where both electron and hole current were observed. The comparison of FET properties between the PbTe@PbS and the constituent core-only PbTe NC revealed that the hole transport was entirely suppressed by the shelling with PbS.

Chapter 3 provided more precise measurements on intrinsic properties of core@shell NCs assembly by electron double layer transistor (EDLT). Compare to conventional solid-gated FET, EDLT provided very high accumulation up to  $10^{14}$  cm<sup>-2</sup> sheet carrier density. This could fill most of the available carrier trap sites, therefore more intrinsic transport at the corresponding HOMO and LUMO level of the NCs could be probed. Consistent with the solid-gated FET, EDLT demonstrated that PbTe@PbS NCs exhibit complete n-type transporting. The electron mobility ( $0.62$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and the electron current modulation ratio as high as  $10^4$  are among record high for core@shell NC assembly. Moreover, in this measurement, the suppression of hole transport becomes more apparent. Counter-experiment using p-type doping ligand Na<sub>2</sub>S and TB(OH) was also performed. Due to the strong hole localization, both S and OH cross-linked PbTe@PbS persisted its n-type

transport behavior and did not show any indication of hole transport. Both of complete suppression of the hole transport and enhancement of electron transport indicate that the shelling PbTe NCs using PbS results in the formation of a type-II internal heterojunction.

In chapter 4 approach to achieve improvement in conductivity and excellent stability of PbTe@PbS FET was successfully demonstrated. Here, PbTe@PbS assembly was cross-linked by iodide as passivation ligand. As a comparison, the corresponding EDT cross-linked PbTe@PbS assembly was also prepared. The numbers of the deposited layer were identical between these two groups' assembly. The FET of PbTe@PbS NCs assembly cross-linked by iodide ligand showed a higher maximum electron current compare to that of EDT-capped. The extracted electron mobility of iodide capped PbTe@PbS FET was as high as  $2.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  which is two times higher than the value in the EDT capped PbTe@PbS. It is found that FET of PbTe@PbS cross-linked by iodide ligand exhibited more stable electron transport characteristics, maintained the electron mobility and on/off current modulation ratio even being stored for 7 to 20 days. These results indicated that iodide ligand plays a role as a passivating ligand on the remaining Pb dangling bond. Thus, it prevents the formation of the electron trap states that usually occur in the EDT-capped NCs.

Chapter 5 focused on the synthesized route, the study on the structure, and the size-dependent optical band gap of lead-free Tin Sulfide (SnS) colloidal NCs. The conventional hot injection methods, which are usually used for synthesis colloidal NCs was unsuccessful to produce SnS NCs with small diameter and narrow diameter distribution. Thus, it was remained difficult to obtain the size-dependent quantum confinement effect in this SnS colloidal NCs. The new method proposed in this study was successfully synthesized SnS colloidal NCs with a minimum average diameter of 4.6 nm and narrow diameter distribution. As a result, the size-dependent quantum confinement effect in the SnS colloidal NCs could be observed. The optical band gap increased as the diameter of SnS NCs could be reduced smaller than 7 nm. It was found that the SnS NCs showed optical absorption spectra with absent of excitonic peak as the consequence of the indirect transition band structure of SnS semiconductor.

Chapter 6 summarize and generally conclude the research results obtained in this study.

Chapter 7 focuses on the discussion of the philosophical viewpoint, contribution, and prospect. In general, this study proposed a new synthesis method and clarify the electronic properties of unconventional metal chalcogenide colloidal NCs such as core@shell and lead-free colloidal NCs. The result obtained in this study provided fundamental knowledge that contributes to the development of this research field.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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