A High-Frequency EPR Study on Nanocrystals with Position-Controlled Dopants

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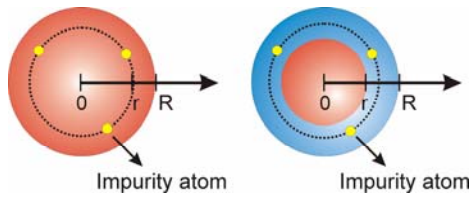
Introduction

The long-term goal of this project is to use high-frequency EPR spectroscopy to study the magnetic properties of doped semiconductor nanocrystals as a function of dopant position inside of these nanocrystals, and the near-tern goal is to investigate detailed the effect of Mn-position inside of CdS/ZnS core/shell nanocrystals (Scheme 1). Recently, we have developed a new approach of using three-step synthesis to achieve radial-position-controlled doping of semiconductor nanocrystals. Based on this new approach, we have successfully synthesized high-quality CdS/ZnS core/shell nanocrystals with Mn-dopants at precise radial positions.[1] Importantly, we have discovered that the room-temperature photoluminescence quantum yield of Mn dopants strongly depends on their radial positions inside the host core/shell nanocrystals.[1] This discovery is the first example that optical properties of nanocrystals strongly depend on Mn radial positions inside nanocrystals. The result opens a new opportunity of using position-controlled dopants to tailor the physical properties of semiconductor nanocrystals, which are important to the development of technological applications in biomedical diagnosis, photocatalysts, solar cells, spintronic devices, etc [2].

Scheme 1. Radial-position-controlled doping of spherical nanocrystals with a homogeneous structure (A) and a core/shell structure (B)



Experimental

First, we have synthesized twelve doped CdS/ZnS nanocrystal samples with Mn at different radial positions inside ZnS shell: at 1st monolayer (ML), 2nd ML, 3rd ML, 4th ML, 5th ML or 6th ML—the surface of core/shell particles. The size of CdS core is 3.1 nm and thickness of ZnS shell is 2.4 nm. Mn-doping levels of these nanocrystals are 1 and 4 Mn per particle, respectively. Second, at the National High Field Magnetic Laboratory, we have used the 17T transmission instrument to study our samples, which was conducted in collaboration with Dr. Jurek Krzystek. To date, we have carried out EPR measurements at various frequencies from 400 GHz to 30 GHz at 20 K.

Results and Discussion

We have found that all these samples with Mn doped inside nanocrystals have two types of Mn sides (tetragonal and hexagonal). Interestingly, the ratio of EPR intensity from these two types of Mn changes alternatively as a function of the change of Mn position from the core/shell interface toward nanocrystal surface. On the basis of current data, we find that the tetragonal Mn sides locate inside CdS/ZnS nanocrystals. This result is consistent with the result from XRD measurements, which show CdS/ZnS nanocrystal with a zinc-blend structure. Second, the hyperfine coupling constant of hexagonal Mn from the samples with Mn inside ZnS shell is different from that of the sample with Mn on the particle surface. In addition, no tetragonal Mn is found from the sample with Mn on the nanocrystal surface. These results indicate that there might be hexagonal Mn site inside the zinc-blend CdS/ZnS core/shell nanocrystals.

Conclusions

First, we have successfully doped Mn into CdS/ZnS nanocrystals. Second, there might be hexagonal Mn site inside the zinc-blend CdS/ZnS core/shell nanocrystals. To further confirm the second conclusion, we need to carry out more experiments to synthesize new samples and to conduct high-frequency EPR measurements with these new samples.

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References

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