Synthesis of CdSe Semiconductor Nanocrystals

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Introduction

Semiconductor nanostructures translate quantum-mechanical phenomena into unique, size-dependent, readily tunable electrical and optical properties.[1] These hold promising applications for photovoltaics and green energy, where nanocrystals have already been applied to engineer highly-efficient, economical solar cells.[2–4] Other inorganic nanostructures have also been found to catalyze CO_2 fixation,[5,6] serve as fluorescent biological imaging tags,[7,8] and even form single-electron transistors in nanoelectronics,[9] all of which have extensive applications in critical technologies and industries in our society.

Sadly, the presence of nanochemistry in modern research and industry dwarfs its presence in the undergraduate curriculum. The wide scope of nanochemistry is seldom discussed in courses, despite its numerous functions in modern chemistry. This set of experiments aims to change that by demonstrating modern synthetic techniques employed to generate nanostructures and educating on the unique electrical and optical properties rising from the both quantum phenomena of nanostructures.

CdX (X = S, Se, Te) semiconductor spherical nanocrystals (i.e. quantum dots) display readily apparent optical properties, and are some of the simplest and most well-studied nanostructures made in the laboratory. Modern one-pot syntheses involving relatively non-

toxic elemental precursors have been well-established by Peng and colleagues, thus making CdX quantum dots ideal targets for study in the undergraduate laboratory.[10,11] Both shape and size are controlled simply by the CdO precursor concentration. At moderate CdO concentrations, monodisperse (i.e. similar to each other in size) spherical nanocrystals are replicably and easily synthesized. This is believed to occur due to diffusion-dependent crystal growth on certain faces of the nanocrystal upon heating.[12]

To provide a gentle introduction into the theory behind the optical properties of nanocrystals, one must first understand what happens during the absorption of a photon. It is well-established that in semiconductors, absorption of a photon results in the formation of a electron-hole pair, which can be roughly visualized as an electron (e) orbiting a positively-charged hole (h).[13,14] This is known as a Wannier-Mott exciton, and typically has a large corresponding Bohr exciton radius, far greater than that of the Bohr radii of the constituent atoms.

Thus, the Hamiltonian of a free Wannier-Mott exciton is trivially related by the expression

$$\hat{\mathcal{H}} = -\frac{\hbar}{2m_h}\nabla_h^2 - \frac{\hbar}{2m_e}\nabla_e^2 - \frac{e^2}{\epsilon|r_e - r_h|}, \tag{1}$$

where m_e (m_h) represents the effective mass of the electron (hole), and ϵ represents the dielectric constant of the semiconductor. This is analogous to the Hamiltonian of the hydrogen atom. However, this equation must fail when the system undergoes quantum confinement, i.e. the nanocrystal radius is less than that of the exciton radius, and the exciton is no longer free. While a full derivation is beyond the scope of this paper, it suffices the mention that an additional polarization term $\hat{V}_{\text{pol}}$ must be included to account for the polarization of electric charge resulting from the formation of the exciton, which obeys a strong dependence on the radius of the spherical nanocrystal R. Following the derivation outlined by Brus, the energy of the lowest excited state of an exciton is approximated by the expression[15]

$$E = E_0 + \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\epsilon R} + \frac{e^2}{R}\overline{\sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R}\right)^{2n}}, \tag{2}$$

where E_0 is the bulk band gap, α is a constant dependent on the dielectric constant of the semiconductor and the surrounding solvent, S is the position of the electron. The bar above the third term denotes that it should be taken as an integral over the entire wavefunction of the electron.

While this equation is certainly complex, it demonstrates the energy of the excited state decreasing monotonically with increasing radius. This is exactly analogous to the particle-in-a-box problem introduced in undergraduate physical chemistry, which also exhibits an inverse dependence between the energy E and the size of the box L.

Pedagogy

In this experiment, students will learn the synthesis of CdS

Hazards

Experimental Procedures

Results and Discussion

Conclusion

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