Inflight Synthesis and Functionalization of Silicon Nanocrystals

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Abstract: In this study, silicon nanocrystals were synthesized and functionalized with 1-decene and 1-hexanol ligands in a nonthermal, low-pressure plasma. This functionalization can enhance the quantum yield and the solubility of the nanocrystals in different nonpolar solvents. Furthermore, the effect of solvents was analyzed in different samples.

1. Introduction

Silicon nanocrystals (Si NCs) have attracted growing interest over the past few decades due to silicon's abundance, biocompatibility, and low toxicity [1]. Among the various methods for synthesizing these particles, nonthermal plasmas stand out as an effective technique for producing luminescent Si NCs with high crystallinity and uniform size distributions [2]. However, as-synthesized Si NCs from plasma processes often suffer from low photoluminescence quantum yield (PLQY) and poor colloidal stability in solvents. To address this, surface functionalization becomes crucial for enhancing PLQY, particularly for applications that demand strong PL. A promising alternative is to carry out synthesis, functionalization, and processing entirely in the gas phase. This approach not only eliminates the use of solvents but also benefits from the efficiency of avoiding transitions between different processing media [3]. This work focuses on the inflight synthesis and functionalization of Si NCs and examines how aging in the solvents affects the PLQY.

2. Methods

Si NCs were synthesized and functionalized using a nonthermal RF plasma reactor. The main plasma region excited a gas mixture of 30 sccm argon and 14 sccm silane (5% in He), while 1-decene and 1-hexanol were introduced in the afterglow region, carried by 100 sccm of hydrogen flowing through a bubbler. 13.56 MHz RF power was applied to a pair of copper ring electrodes positioned before the afterglow region. The resulting Si NCs (about 3.2 nm diameter) were collected and transferred to a nitrogen-purged glovebox. Then, they were dissolved in various solvents, including chloroform, toluene, and mesitylene, to investigate the effect of solvent choice on PLQY over time. During the aging process, all samples were stored in the glovebox under dark conditions to minimize external factors influencing PLQY changes.

3. Results and Discussion

PLQY of the samples was measured immediately after dissolving them in solvents (time zero) and for nine days thereafter using an Ocean Optics USB 2000 spectrometer. All samples exhibited a PL peak wavelength between 825 and 850 nm, which remained almost constant after aging, indicating that the Si cores were unchanged. Figure 1 shows the PLQY increased in all samples over time. Notably, hexanol-grafted samples consistently exhibited higher PLQYs compared to those functionalized with decene, regardless of the solvent used. Among the solvents, samples dissolved in chloroform showed the highest PLQYs for both surface ligands. This trend can be attributed to differences in surface coverage by ligands, as surface chemistry at the nanoscale can significantly influence the electronic and optical properties of nanomaterials. To explore this further, FTIR spectra of decene and hexanol-grafted Si nanocrystals were analyzed before and after dissolving in different solvents. The FTIR results revealed a marked reduction in the intensity of SiH_x peaks, which were almost eliminated in samples dissolved in chloroform. This reduction likely contributed to the observed PLQY enhancements. These findings highlight the critical role of both surface functionalization and the solvent environment in the PLQYs of Si NCs.

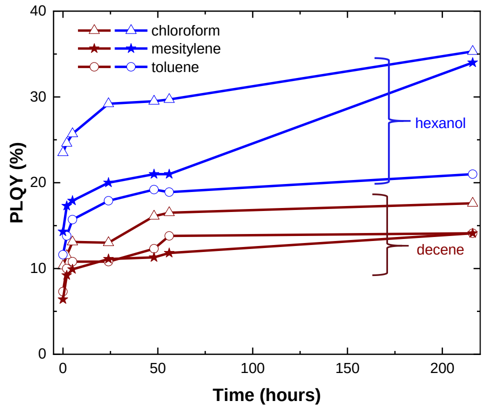

Fig. 1. PLQY of decene and hexanol-capped samples during aging in different solvents.

4. Conclusion

Here, inflight synthesis and functionalization of Si NCs were investigated in a nonthermal plasma reactor. The effect of surfactants and solvents on the PLQY was studied. Both ligand and solvent choice influenced the PLQY of samples as they altered the surface of the Si NCs.

References

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[3] Y. Lee et al., ACS Applied Nano Materials **7(18)**, 21728-21734 (2024).