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Novel synthesis of covalently linked silicon quantum dot–polystyrene hybrid materials: Silicon quantum dot–polystyrene polymers of tunable refractive index

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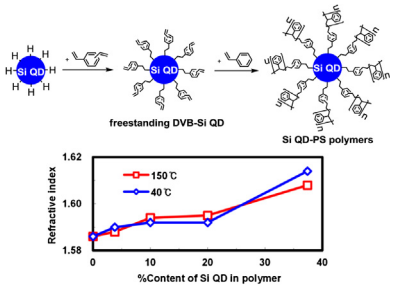
HIGHLIGHTS

- A new material design concept, Si QD polymer, is presented.
- Freestanding vinyl-functionalized Si QD was synthesized as a monomer for polymer.
- Si QD–PS polymers were synthesized by polymerization of styrene with vinyl-Si QD.
- Concentration of Si QD in the polymer was well controlled by amount of Si QD used.
- Refractive index of polymer thin films linearly increased with concentration of Si QD.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a new material design concept, silicon quantum dot (Si QD) polymers, for which surface-functionalized Si QDs can be regarded as a large monomer in the polymers. As a prototypical example, vinyl-functionalized Si QDs, i.e., divinylbenzene-capped Si QDs (DVB-Si QDs) synthesized by adopting divinylbenzene (DVB) capping molecule to the hydride-terminated Si QD (H-Si QD) via Pt-catalyzed hydrosilylation was introduced and polymerized with a styrene monomer to yield Si QD–polystyrene (Si QD–PS) polymers. To demonstrate controllability of the content of Si QDs in the polymers as in conventional polymers, three Si QD content varied Si QD–PS polymers were systematically prepared, named as Si QD–PS-A, Si QD–PS-B, and Si QD–PS-C. It has been demonstrated that the content of the Si QDs in the Si QD–PS polymers was well controlled by the amount of the DVB-Si QD used, as found to be 3.8 wt% (Si QD–PS-A), 10.0 wt% (Si QD–PS-B), 20.0 wt% (Si QD–PS-A), and 37.4 wt% (DVB-Si QD), which was deduced from TGA results. Thin films of the Si QD–PS polymers and the free-standing DVB-Si QDs were successfully fabricated by a spin-coating method and it was found that the refractive index of the thin films dried at 40 °C was linearly increased as the content of the Si QD in the polymers was increased from 1.586 (0 wt%), to 1.590 (3.8 wt%), to 1.592 (10.0 wt%), to 1.592 (20.0 wt%), and to 1.614 (37.4 wt%).

1. Introduction

Semiconductor nanocrystals (NCs) sized in nano-regime, comparable to or smaller than the Bohr radius, are commonly referred

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to as quantum dots (QDs) because the QDs display the quantum confinement effect, where electronic structure becomes discrete as opposed to continuous electronic structure of bulk counterparts, in addition band gap is altered in the QDs [1–3]. Such size-dependent electronic structures and hence optical and electrical properties of the semiconductor QDs have attracted extensive scientific and industrial interest. The synthesis, properties, and further applications of compound II–VI and III–V semiconductor QDs such as CdS, CdSe, PbSe, and InP have been widely investigated [4–6]. However, despite their outstanding properties, these semiconductor QDs have critical and fundamental drawbacks, including cytotoxicity and a scarcity of the elemental materials, which restrict their utilization for practical applications [7]. As a promising replacement material, silicon QD (Si QD) of group IV semiconductor has gathered much attention due to its nontoxicity and abundance as well as the ease of integration into well-established industrial silicon processes [8,9].

Despite the advantages mentioned, Si QDs still encounter some serious obstacles that must be addressed for practical applications, such as the ease of oxidation converting them to thermodynamically stable SiO_2 and difficulties controlling the size as well as mass-production. The former oxidation issue of the Si QD can partly be overcome by modification or protection of the QD surface with a cap of organic molecular layers. Unlike the compound semiconductor QDs, the surface of Si QDs can be mostly protected by organic molecules via covalent bonds, e.g., Si–C, Si–O, etc. further tailoring the QD surface structure enables altering chemical and physical properties such as solubility and optical properties [10–13]. Recently there have been some advances in the synthetic methodology of the Si QDs, partly allowing size control and mass-production on a gram scale [14–16]. The annealing of Si-rich SiO_x powders at high temperatures followed by etching with HF, is seen as the most promising to date because the size of the Si QDs is controllable by adjusting the annealing and HF-etching conditions. The resultant Si QDs exhibit clear luminescent properties in the visible range [15–17].

In addition to the passivation of the QDs by organic molecules protecting against environmental degradation (oxidation in case of the Si QDs), encapsulation of the QDs with polymeric matrix materials is common and useful. This also allows for modification of chemical properties, such as solubility, and allows the addition of functionalities from matrix materials, to produce improvements in physical and chemical properties, thermal stabilities, and tunable mechanical properties [18–25]. For the Si QDs, encapsulation with matrices has been also applied in the manner of physical mixing between the Si QDs and matrices [26–30]. However, this encapsulation method based on the weak interactions may limit the stability of materials; phase separation due to aggregation or agglomeration of the Si QDs may occur. The best way to guarantee the material's stability is to incorporate the Si QDs into the matrix via strong covalent bonds. To our knowledge, there have been few attempts to incorporate covalently bonded Si QDs into polymeric matrices [31,32].

As a prototypical example, we have previously demonstrated the synthesis of Si QD–polystyrene nanocomposite created by a thermally initiated one-pot hydrosilylation/polymerization reaction in hydride-terminated Si QDs (H-Si QDs) and styrene monomer. The H-Si QDs were surface-functionalized with polystyrene arising from the polymerization of the styrene monomer, with its memory functionality in a thin film transistor (TFT) device structure based on the thermally robust charge trap (hole trap in this case) property of the Si QDs surrounded by insulating polystyrene through strong covalent bond [31]. Although this one-pot synthetic approach gave rise to enhanced stability of the Si QDs and new functionality as well, it possessed fundamental limitations in fine control of content and concentration of the Si QDs in the nanocomposite. On the other hand, Yang et al. [32] also reported the synthesis of Si QD–polystyrene nanocomposite (or Si NC/polystyrene hybrid, as named in the report) by the similar reaction manner, in which highly luminescent well-defined Si NCs were used. Though the authors demonstrated the variation of Si NC concentration in the nanocomposite (or hybrid) by simply varying the amount of H-Si QD which was reacted with the styrene monomer, the variation of the Si NC concentration was limited in a few weight% (wt%) range such as 0.8, 1.6, and 2.4 wt%, and longer reaction time was required for the higher Si NC-concentrated nanocomposites (e.g., 15 h and 59 h for the 0.8 and 2.4 wt% cases, respectively) [32].

In this study, to overcome this limitation, a new synthetic strategy has been demonstrated; freestanding organic-capped Si QDs designed to contain surface functional groups (vinyl groups) for post-functionalization were synthesized and utilized for the reaction with the styrene monomer to produce Si QD–polystyrene nanocomposite. The content (or concentration) of the Si QDs in the nanocomposite was able to be easily controlled by the ratio between the surface-functionalized Si QD and styrene monomer. In fact, from the viewpoint of conventional polymer science, the surface-functionalized Si QDs that can be bonded with monomers, e.g., styrene, could be regarded as a monomeric component of a polymer, especially considering that the surface-functionalized Si QD is able to be polymerized and be selectively used to control its content or concentration in the resultant polymers by simply varying the amount used.

Based on the considerations above, herein we term such a Si QD nanocomposite as a “Si QD polymer”. As an introductory research on realization of such a novel material design concept of Si QD polymer, Si QD–polystyrene (Si QD–PS) polymers, in which surface-functionalized Si QDs were polymerized with styrene monomer, were synthesized with varying concentrations of the Si QDs and their structures and properties were investigated.

The Si QD–PS polymers were synthesized by following two steps, as schematically described in Scheme 1; (a) preparation of freestanding divinylbenzene-capped Si QD (DVB-Si QD) which possesses vinyl functional groups on the outermost surface of the Si QD for post-functionalization and (b) co-polymerization of the DVB-Si QD and styrene monomer in a single phase to yield the Si QD–PS polymers, in which the content or concentration of the Si QD in the polymers was controlled by varying the mixing ratio of the reagents, freestanding DVB-Si QD and styrene.

2. Materials and methods

2.1. Materials

Silicon tetrachloride ($SiCl_4$, 99.998%), lithium aluminum hydride solution ($LiAlH_4$, 2 M in THF), toluene (anhydrous, 99.8%), methanol (anhydrous, 99.8%), divinylbenzene (DVB, 80%), and chloroplatinic acid hydrate ($H_2PtCl_6 \times H_2O$, ≥99.9%) were purchased from Sigma–Aldrich and used as received without further purification. Styrene (≥99%) was also purchased from Sigma–Aldrich and purified by distillation prior to use. Copper sulfate ($CuSO_4$, anhydrous, >98.0%) and magnesium sulfate ($MgSO_4$, anhydrous, >99.0%) were purchased from Yakuri Pure Chemicals (Kyoto, Japan) and Duksan Pure Chemicals (Ansan-si, South Korea), respectively.

2.2. Synthesis of divinylbenzene-capped Si QD (DVB-Si QD)

The freestanding divinylbenzene-capped Si QD (DVB-Si QD) was obtained by introducing the DVB molecule to hydride-terminated Si QD (H-Si QD) via Pt-catalyzed hydrosilylation, in