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# A proof of concept study of preparing ultra bright silicon quantum dots based on synergistic effect of reductants

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ABSTRACT

The concept of synergistic effect has been widely applied into various scientific research areas, ranging from life science to material science, nevertheless it has been rarely adopted in the synthesis of quantum dots (QDs). This proof-of-concept study was the preparation of ultra-bright silicon QDs with a relative quantum yield of up to 84.92% based on the synergistic effect of two reductants, whilst silane coupling agent as the silicon source. Compared with the conventional one-reductant strategy, our as-prepared silicon QDs exhibit greatly enhanced quantum yields with even tunable emission wavelength, meanwhile, inheriting other merits including good pH, salt tolerance, small particle size and amino-rich surface, which is conducive to biological applications. The highly efficient and stable photoluminescence of silicon QDs could definitely facilitate their prospective applications as optical materials.

## 1. Introduction

The synergistic effect is an effect arising between two or more subsystems that produces an effect greater than the sum of their individual effects (1 + 1 > 2). It is ubiquitous in natural and social sciences, and has been widely applied into the life science [1–3], health care [4–12], chemistry and chemical engineering [13–18] and material science [19–36], etc. The discovery of synergistic effect of cytokines and adhesion-dependent signals that leads to long-lived plasma cell is important for our understanding of the mechanism regulating the homeostasis of plasma cells, which can guide the treatment of allergy and autoimmune diseases [1]. The synergistic effect of silver nanoparticles in combination with selected broad spectrum antibiotics against the tested bacteria determined strong growth inhibitory activity, providing an possible emerging strategy to combat disease resistant pathogens in future [4]. Beyond the significance of synergistic effect in the life science and health care, it has been extensively adopted in chemical synthesis for the purpose of reducing reaction temperature, reaction time, possibility of side reaction, enhancing the conversion rate and improving the quality of products. For example, the synthesis of acrylates could be accelerated through an efficacious photoinduced living polymerization due to the synergistic catalysis of $CuBr_2$ and tertiary amine. The near-quantitative monomer conversion (> 95%) is obtained within 80 min (generally take 12–32 h), yielding poly(acrylates) with dispersities as low as 1.05 and excellent end group fidelity (> 99%) [13]. Photocatalysts of g-$C_3N_4$/ $TiO_2$ nanosheets which can degrade almost all RhB under simulated-sunlight irradiation within 50 min were synthesized by a facile biomimetic method. The significantly enhanced photocatalytic activity toward organic pollutant degradation (Rhodamine B) benefited from the synergistic effect of large surface area of nanosheets and small size of $TiO_2$ nanoparticle [14]. In spite of the vital function of synergistic effect in the chemical synthesis, this concept has been rarely practiced in the synthesis of quantum dots (QDs). It is worth noting that the N-S [20–22], N-P [23] and N-B [23–25] co-doped carbon dots (CDs) have already demonstrated improved photochemical activity, such as high quantum yields (QYs) [20], owing to the synergistic effect of multiple elements, thereby expending their potential application areas (eg. photocatalysis [25]). This is indicative of that the synergistic effect has immense potential to improve the character of the QDs.

The silicon QDs (SiQDs) have aroused great attention thanks to their non-toxicity, richness in raw materials and excellent biocompatibility. Recently, a newly developed bottom-to-top method for preparing SiQDs in aqueous phase with silane coupling agent as silicon source and reductant as the catalysis agent becomes popular. Several approaches including microwave route [28–30], hydrothermal route [31–34] and ultraviolet radiation route [35] have been utilized in SiQDs preparation. Meanwhile, multiple silane coupling agents, such as (3-aminopropyl)trimethoxysilane (APTMS) [28,31,32,35], 3-amino-propyltriethoxysilane (APTES) [29,31,36], urea propyl triethoxysilane

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(UPTES) [33], 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (AEEA) [30], and N-[3-(trimethoxysilyl)propyl]ethylenediamine (DAMO) [30,34] have been successfully used to prepare SiQDs. The difference of reductants in their deoxidization ability, mechanism of action, interaction speed, solubility, and reaction product, would greatly impact the optical properties of prepared SiQDs. The blue SiQDs ($\lambda_{em}$ = 445 nm) with super-high QY (82.4%) has been successfully prepared using DAMO as the silicon source and sodium citrate (Na-Citrate) as the reductant [30]. However, with the same silicon source (DAMO), replacing the reductant of Na-Citrate to catechol resulted in green SiQDs ($\lambda_{em}$ = 512 nm) with quite low QY (7.1%) [34]. The green SiQDs can also be achieved by using APTES as silicon source and ascorbate sodium (AS) as the reductant, whilst the maximum emission wavelength was at 530 nm with QY of 21% [36]. Though Na-Citrate is the most commonly used reductant, and the only one that could produce QDs with super-high QY, it can only prepare blue-fluorescence SiQDs. On the other hand, though other reductants could generate QDs with different fluorescence emission wavelengths, the QYs of the products are rather low. The synergistic effect of different kinds of reductants was thus expected to break the bottleneck, and produce SiQDs with both tunable emission wavelength and high QYs.

Utilizing only single reductant in the preparation is not conductive to the improvement of the properties of QDs, which also confines the rational design of high-quality SiQDs under the theoretical guidance. Therefore, in this work, with DAMO as the silicon source, the synergistic effect of reductants in the preparation of SiQDs was systematically explored for the first time. Two pairs of reductant combination were successfully screened out. Under the optimized experimental conditions, the SiQDs with super-high QY (84.92%) have been prepared. Besides, the optical properties, pH tolerance and salt tolerance of the prepared SiQDs with both single-reductant and double-reductant approaches have been compared. What's more, the possible mechanism of synergistic effect of reductants has been proposed. This work demonstrates the broad application prospect of incorporating the concept of synergistic effect into the synthesis of QDs. It is thus expected that the synergistic effect could attract more attention from researches, and be fully utilized in the synthesis of SiQDs as well as other types of QDs in the future.

## 2. Experimental

### 2.1. Materials

DAMO (95.0%) were obtained from Aladdin Chemistry Co., Ltd., Na-Citrate (99.0%), citric acid monohydrate (CA) (≥ 99.5%), sodium borohydride ($NaBH_4$) (≥ 96.0%), sodium oxalate ($Na_2C_2O_4$) (≥ 99.8%), oxalic acid dihydrate ($H_2C_2O_4$) (≥ 99.5%), sodium sulfite anhydrous ($Na_2SO_3$) (≥ 97.0%), urea (≥ 99.0%), thiourea (≥ 99.0%), hydrazine hydrate 85% (HHA) (≥ 85.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Catechol (≥ 99.0%) was purchased from Aladdin Industrial Corporation (China). L-Cysteine (L-Cys) (> 99.9%), Glycine (Gly) (≥ 99%) were purchased from Sigma Corporation (USA). All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared using Milli-Q water (Millipore) as the solvent.

### 2.2. Instrumentation

UV–Vis absorption spectra were recorded on a Lambda-35 UV/ Vis spectrophotometer (PerkinElmer Company). Fluorescence spectra were acquired with a LS55 spectrofluorometer (PerkinElmer Company). All optical measurements were performed at room temperature under ambient conditions. The pH was monitored by a PHSJ-3F pH meter (Shanghai Precision Scientific Instrument Company). The MDS-6 G microwave chemical reactor (Shanghai SINEO Microwave Chemistry Technology Company) was used to synthesize SiQDs. TEM sample was prepared by dropping an aqueous SiQDs solution onto Agar carbon-coated copper grids (400 meshes) with the excess solvent evaporated. TEM image was obtained with a JEM-2100F transmission electron microscope (Japen Electron Optics Laboratory Company). EDS patterns were captured using an FEI Quanta 200 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (FEI Company). Fourier transform infrared spectra were obtained on a Nicolet 6700 (FT-IR) spectrometer (Thermo Fisher Scientific).

### 2.3. Preparation of the SiQDs

The SiQDs were prepared through a microwave-assisted method with DAMO as the silicon source and Na-Citrate, CA, $NaBH_4$, $Na_2C_2O_4$, $H_2C_2O_4$, $Na_2SO_3$, urea, thiourea, HHA, L-Cys, catechol and Gly as the reductants. In a typical preparation procedure, Na-Citrate (0.0621 g, 0.2112 mmol), thiourea (0.0161 g, 0.2112 mmol) and 0.2 ml DAMO (0.88 mmol) were mixed in 20 ml of water under stirring, followed by deaerating with high purity nitrogen gas for 20 min. The precursor solution was adjusted to specified pH value. Finally, the precursor solution was loaded in the microwave oven at 200 °C for 15 min. For other SiQDs, similar procedures were employed except for replacing the reactants of Na-Citrate and thiourea with single or combination of other reactants including CA, $NaBH_4$, $Na_2C_2O_4$, $H_2C_2O_4$, $Na_2SO_3$, urea, HHA, L-Cys, catechol and Gly The molar ratio of DAMO: reductant was 1: 0.48, the concentration of DAMO was 44 mM, the reaction temperature was 200 °C and reaction time was 15 min, unless otherwise specified.

### 2.4. Determination of QYs

The QYs of SiQDs were calculated by comparing the integrated PL intensities and absorbance values of the samples (exited at 360 nm), using quinine sulfate dissolved in 0.1 mol/L $H_2SO_4$ aqueous solution (refractive index (η) of 1.33) as the standard (QY = 54%) [37,38]. All samples dissolved in water (η = 1.33) had absorbance less than 0.1 at 360 nm. The relative QYs can be calculated using the below equation:

$$\Phi_X = \Phi_{ST}(Grad_X/Grad_{ST})\left(\eta_{X^2}/\eta_{ST^2}\right)$$

where Φ is the QY, Grad is the gradient from the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent; ST denotes the standard and X denotes the sample. To obtain more reliable results, a series of solutions of SiQDs and referenced fluorescence dye with low absorbance values (0–0.1) at 360 nm were prepared for QYs calculations.

## 3. Results and discussion

### 3.1. SiQDs prepared by using single reductant

With DAMO as the silicon source, the impacts of various commonly used reductants upon the optical properties of prepared SiQDs have been investigated, including the organic reductants (Na-Citrate, CA, thiourea, urea, $H_2C_2O_4$, $Na_2C_2O_4$, HHA, L-Cys, Gly), and inorganic reductants ($Na_2SO_3$, $NaBH_4$). As shown in Tables 1 and S1, fixing the molar ratio of DAMO to the reductant at 1:0.48, the qualities of SiQDs prepared by using different reductants vary greatly. Only reductant Na-Citrate could produce SiQDs with high QY of 73.27% (Fig. S1b), while SiQDs prepared using other reductants generate relatively low QYs (less than 25%), which might be attributed to the different deoxidization capacities of reductants. It worth nothing that, the QY of SiQDs

**Table 1**
QYs of SiQDs synthesized with different reductants.

| Reductant | $Na_2C_2O_4$ | thiourea | $NaBH_4$ | $Na_2SO_3$ | CA | Na-Citrate |
|---|---|---|---|---|---|---|
| QYs | 1.80% | 2.11% | 11.88% | 12.75% | 24.20% | 73.27% |