

Supporting Information for:

**Silicon quantum dots (SQDs) catalyzed visible-light-induced ATRP
and its application for controlled surface modification**

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Experimental section

Materials

Ascorbic acid (AA, 99%), 3-(aminopropyl)trimethoxysilane (APTMS), *tert*-butyl acrylate (BA, 99%), methyl acrylate (MA, 99%), methyl methacrylate (MMA, 99%) were purchased from Aladdin and used after removing the inhibitor. *o*-phenylenediamine (98%), ethyl α -bromoisobutyrate (EBiB, 98%), tris(2-pyridylmethyl)amine (TPMA, 99%) and copper(II) bromide (CuBr₂, 99%), APTMS were purchased from Macklin and used as received. Solvents of N,N-dimethyl formamide (DMF, 99%), Dimethyl sulfoxide (DMSO, AR) and N,N-Dimethylacetamide (DMA, 99%), Tetrahydrofuran (THF) and cyclohexane (CYH, 99%) were purchased from Aladdin and purified to remove H₂O before using. Blue-light-emitting diode (LED) light strips (6 W, $\lambda_{\text{max}} = 460 \text{ nm}$, 2 mW cm^{-2}) was purchased from Rishang Optoelectronics Co., Ltd.

Characterization

The gel permeation chromatography (GPC) analyses were performed with THF as the eluent, on the equipment of SFD2000. ¹H-NMR (Bruker Avance 400MHz) was applied to measure the monomer conversion, using CDCl₃ as the solvent. Thermo Evolution was used to collect the data of UV-vis absorption spectra, and Thermo Lumina fluorescence spectrometer was used for the analyzing of photoluminescence (PL) behavior. FT-IR results were obtained from a Thermo Scientific™ Nicolet™ iS5. The morphologies of particles were observed with transmission electron microscopy (JEM-2100). Thermal gravimetric analyses (TGA) were performed with METTLER

TOLEDO thermogravimetric analyzer (TGA Q5000). The zeta potentials of different nanoparticles were measured using a laser particle size instrument from Microtrac Inc.

Hydrothermal synthesis of SiQDs

The general synthetic procedure is described as follows. First, 10 mL of APTMS and 40 mL of ultrapure water were added to a 250 mL flask equipped with a magnetic stirrer bar, and then the reaction system was loaded in an oil bath at the temperature of 40 °C. After that, 0.2202 g of AA was added to the above mixture and continued to stir for 3.5 h. After cooling naturally, the resulting solution was transferred into a dialysis bag (molecular weight cutoff = 1000) and dialyzed for 3 days.

Synthesis of SiO₂@SiQDs

50 mg SiQDs was first dissolved in 20 mL H₂O with the assistance of ultrasonic. 100 mg SiO₂ was then added to the solution. After stirring for 12h, the solution was centrifuged (8000 rpm min⁻¹, 15 min) to collect the precipitates. The precipitates were washed with water for several times to remove unanchored SiQDs, resulting in the final product UCNP@SiO₂@CDs.

General procedure of SiQDs-catalyzed photoATRP

A mixture of MMA (2 mL, 18.6 mmol), EBiB (13 μL, 0.093 mmol), PMDETA (10 μL, 0.046 mmol) and CuBr₂ (2.7 mg, 0.0093 mmol) with a ratio of 200/1/0.5/0.1 was put into a 10 mL Schlenk tube with 2 mL DMF and 10 mg SiQDs. The reaction mixture was degassed with three freeze-pump-thaw cycles and finally filled with nitrogen. The reaction system was irradiated with visible light at room temperature. Samples were characterized by GPC and ¹H-NMR.

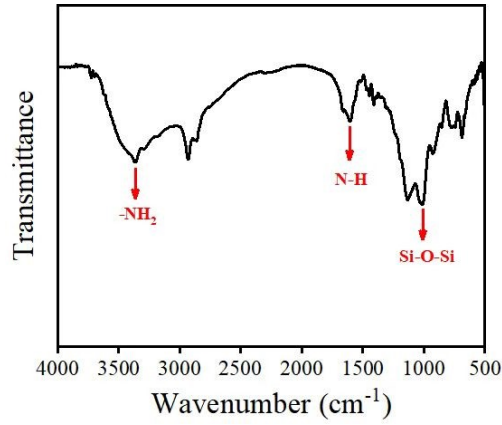


Figure S1. FT-IR spectra of SiQDs.

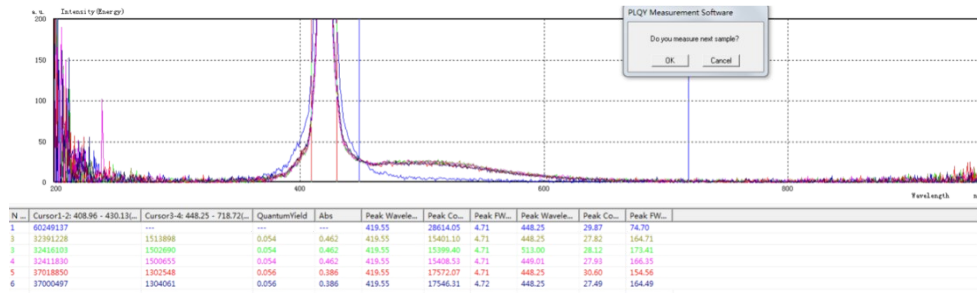


Figure S2. Original data of SiQDs' quantum yield obtained from quantum yield measurement system.

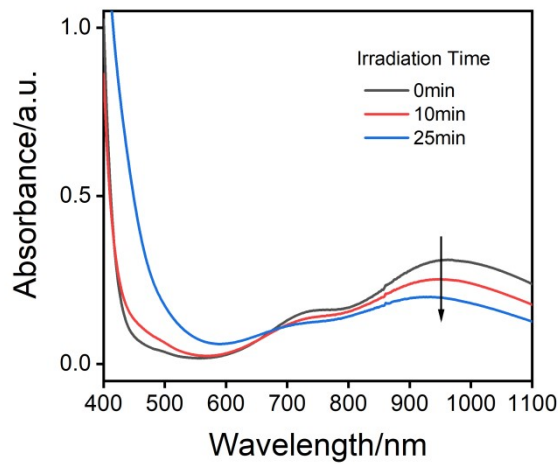


Figure S3. UV-Vis-NIR spectra of CuBr₂/PMEDTA in the presence of SiQDs at varied irradiation time.

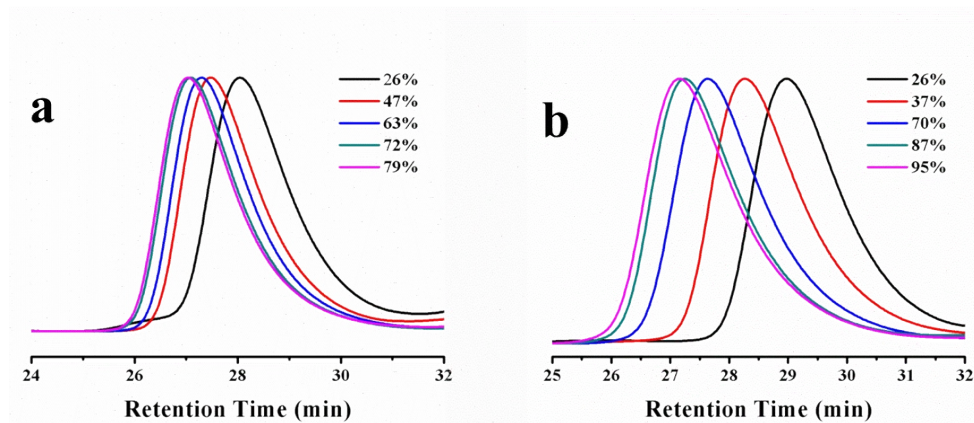


Figure S4. GPC traces in the kinetic study of PMMA synthesized via SiQDs catalyzed photoATRP with different concentration of Cu^{II} : (a) 200 ppm and (b) 500 ppm.

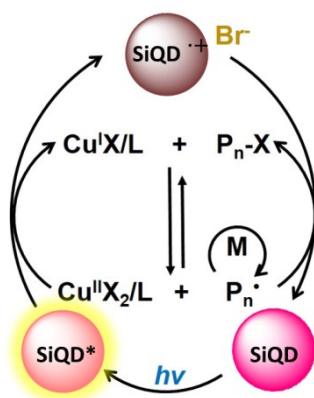


Figure S5. Mechanism for SiQDs catalyzed photoATRP.

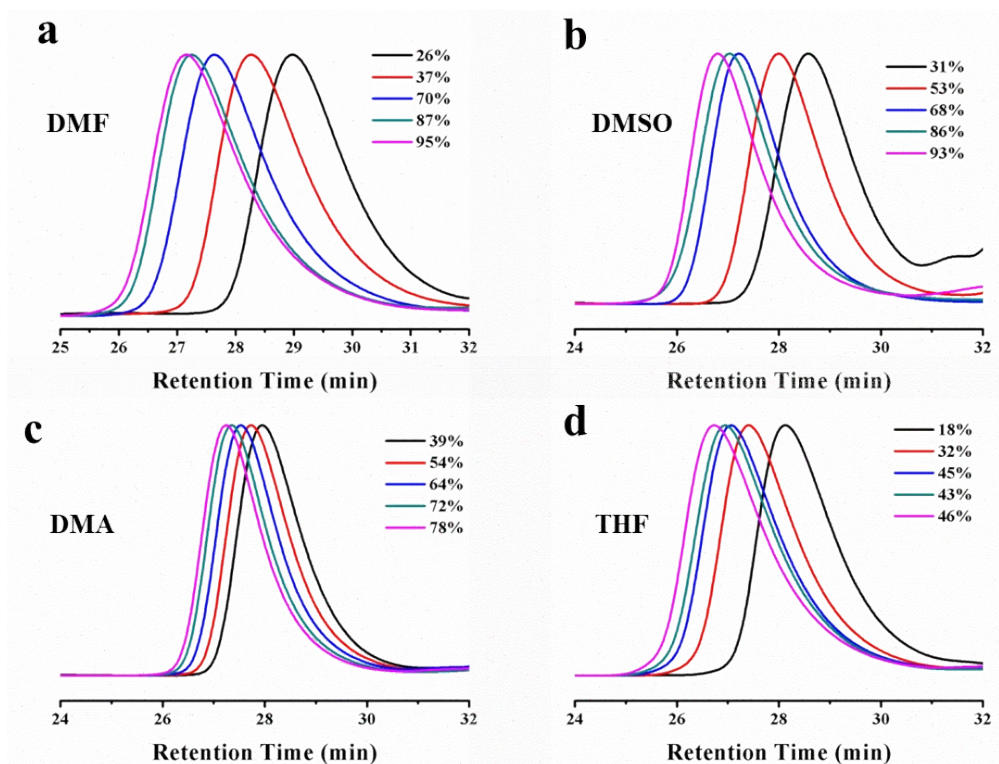


Figure S6. GPC traces in the kinetic study of PMMA synthesized via SiQDs catalyzed photoATRP with different solvents: (a) DMF, (b) DMSO, (c) DMA and (d) THF.

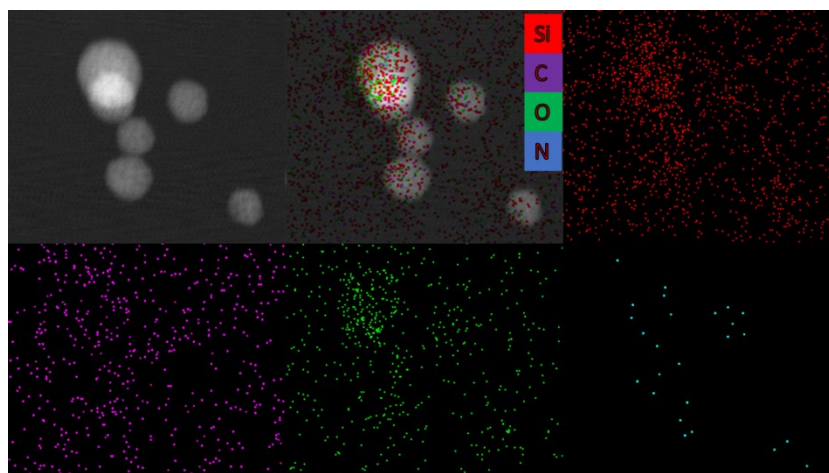


Figure S7. EDS mapping for SiO₂@SiQDs nanoparticles.

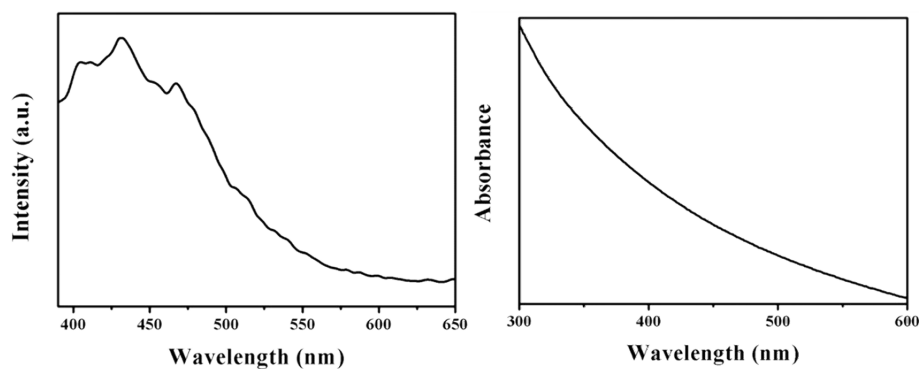


Figure S8. (a) Fluorescence spectra with 365 nm excitation and (b) UV-vis absorption spectrum for SiO₂@SiQDs.

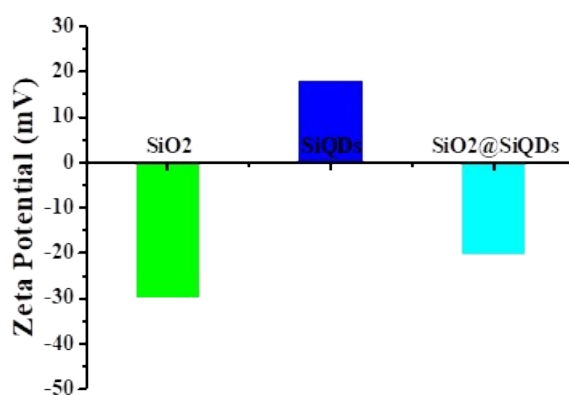


Figure S9. Zeta potential analysis for the aqueous dispersions of SiO₂, SiQDs and SiO₂@SiQDs.

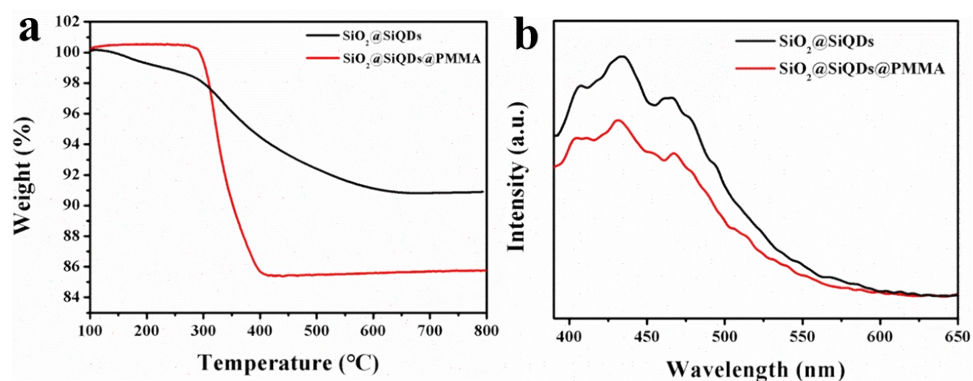


Figure S10. (a) TGA curves and (b) fluorescence spectra of SiO₂@SiQDs and SiO₂@SiQDs@PMMA.

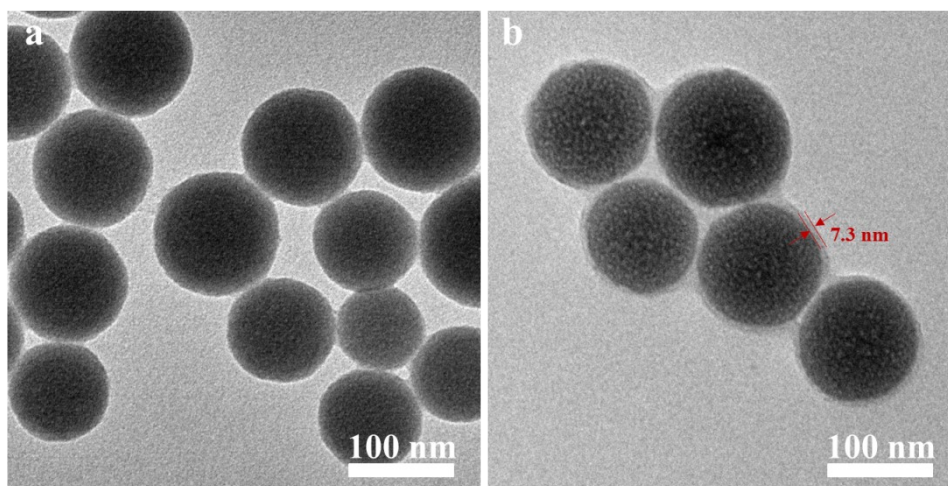


Figure S11. (a)TEM image of pure silica nanoparticles; (b) TEM image of SiO₂@SiQDs@PMMA nanoparticles.

Table S1 Comparison of grafted polymers on SiO₂ surface and free polymers

| Entry | polymers | $M_{n, \text{GPC}} \text{ (g mol}^{-1}\text{)}$ | M_w/M_n |
|-------|------------------|---|-----------|
| 1 | grafted polymers | 89700 | 1.20 |
| 2 | free polymers | 90900 | 1.17 |