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Thiol ligand capped quantum dot as an efficient and oxygen tolerance photoinitiator for aqueous phase radical polymerization and 3D printing under visible light

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Abstract: We report here a rapid visible-light-induced radical polymerization in aqueous media photoinitiated by only ppm level thiol ligand capped cadmium selenide (CdSe) quantum dots (QDs). Simple ligand exchange procedures with various bifunctional thiol ligands facilitate the dispersion of CdSe QDs in water, thus expanding the scope of aqueous photocatalysts. The polymerization showcased excellent oxygen tolerance, giving low dispersity (*Đ*) of 1.27. Additive thiol molecules were proposed to act as the coinitiating species, oxidized by photoexcited CdSe QDs to form the thiyl radicals and further initiate the polymerization. More importantly, successful thiol-ene click reactions were achieved by scaling up the thiol to olefine ratio to 1, solidifying the thiol ligand coinitiating mechanism and meanwhile demonstrating the great potential of QDs photocatalysts in organic transformations. Furthermore, the photoinitiation system using CdSe QDs could be readily employed for photo 3D printing of photocurable resin poly(ethylene glycol) diacrylates, opening up vast opportunities for fabricating advanced polymer-inorganic hybrid materials.

Introduction

Light-mediated polymerizations have gained significant interest because of the ability to provide both spatial and temporal control over reaction kinetics via external stimulus, showing great potential to harness solar energy for chemical transformations.[1–5] Indeed, light-mediated polymerization techniques have been well demonstrated for reversible addition-fragmentation chain transfer (RAFT) polymerization,[6–10] atom transfer radical polymerization (ATRP),[11–17] radical ring-opening polymerization,[18,19] cationic polymerization,[20–22] and conventional/uncontrolled radical polymerization.[23–27] Conventional/uncontrolled radical polymerization, although lacks living characteristics,[28] is still a buttress process for industrial polymer synthesis[29] and 3D-printing[30,31]. The development of efficient photocatalysts (PCs)/photoinitiators (PIs) for radical polymerization offers the advantage of mild reaction conditions and low energy consumption. Especially, photo 3D printing, an advanced technique that can rapidly transfer reactive liquid monomers into solid printing objects at ambient temperature, requires efficient photoinitiators/initiation systems to provide high polymerization rate and monomers conversion.[32–36] Recent advances in employing photoinduced electron/energy transfer RAFT polymerization for 3D printing provide spatial control and the post-printing transformation of printed objects.[37–42] Yet, most PIs currently used in radical polymerization and photo 3D printing, only absorb in the UV range (300 nm to 400 nm).[31] Of course, UV light does not represent a significant part of the solar spectrum and is also costly in generation and maintenance.[24] This challenge has promoted interest in developing visible light as the source of irradiation for photo-polymerization[4,5] and photo 3D-printing[31,43]. Particularly, the development of visible-light PIs has revolutionized the photo 3D printing process by lowering energy consumption, heat generation and operating costs, leading to vast opportunities for industrial application.[43,44] One method to increase the absorbances of PIs to long wavelengths is through chemical modification,[45] for example, to extend the π-conjugation of the molecular.[46,47] However, this method usually requires extensive synthesis and purification efforts. For commercial PIs with absorption in visible light, the use of multiple component (three components system,[48–50] etc.) are sometimes required to achieve high initiation efficiency, which complicated the reaction set-up and operations. Therefore, in order to further propel the photo-3D printing techniques to the forefront, there is still of general interest to discover novel and simple visible-light photoinitiation systems which enable the fast and efficient curing of resin with the easy experimental operation and simple synthesis of PIs.

Efforts toward sustainability and considerations of ecological consequences have also resulted in tremendous interest in developing polymerization methods that can proceed in water, an environmentally-friendly solvent, as an alternative to hazardous and volatile organic solvents.[51] Furthermore, polymerization in aqueous media provides access to functional hydrophilic polymers that have a broad range of applications in medical engineering,[52] nanotechnology,[53] and electronic materials.[54] While successful examples of photo-induced aqueous polymerizations have been reported, only a handful of photocatalysts (PCs)/PIs have been employed for both controlled and uncontrolled radical polymerization.[6,51,53,55–60] The major limitation of photopolymerizations in the aqueous medium is the lack of solubility of organic or organo-metallic PCs/PIs in water.[25] Thus, the development of new photoinitiation systems that are compatible with water is needed to expand the scope of aqueous phase visible light photoinitiated polymerization.

Semiconductor quantum dots (QDs), a commercially available nanomaterial[61] with a narrow emission peak (full width at half maximum < 20 nm)[62] and high fluorescence quantum yield (quantum yield = 40–50%),[62] have been intensively studied in light-emitting devices[63,64] and widely applied in biological studies.[65] The unique electronic and optical properties such as large extinction coefficients (over 10^{-6} M^{-1} cm^{-1} for CdSe QDs et.al.),[66] broad absorption spectrum (ranging from 200 nm to 560 nm for 3.2 nm CdSe QDs)[67] and multiple binding sites[67] make QDs beneficial for photon absorption and charge/energy transfer.[68–70] Besides, the solubility of QDs can be adjusted simply by changing the ligand shell,[71,72] rendering the QDs dissolve in both organic and aqueous solvents.[73] All the aforementioned characteristics make QDs as good candidates for photoredox agents in small molecular[74–80] and polymer synthesis[7,53,59,81–87]. Particularly for QDs-initiated photopolymerizations,[84] QDs may provide an added advantage by minimizing side reactions that can occur when using organic dye PIs, because extra radical species originating from photodegradation of organic dyes usually leads to undesired reaction.[25] Furthermore, the usage of QDs/nanomaterials photoinitiated polymerization is often favorable because of the in-situ fabrication of polymer nanocomposites,[88–91] which have various applications in optical/electrical sensors,[92] batteries,[93,94] absorption[95,96] and light-emitting diodes[97]. However, some drawbacks of QDs photoinitiated polymerizations involve low monomer conversion (< 10%) and poorly controlled polydispersity (*Đ*) over 2.0.[81,98] Additionally, many QDs photoinitiated polymerizations could not process in the presence of oxygen,[81,98] especially under low concentration of PIs (<0.2 μM). Therefore, developing highly efficient and oxygen tolerance QDs photoinitiation systems is highly desirable. Besides, we foresee that the integration of the 3D printing technique and the in-situ photopolymerization can help form the polymer-nanocomposites with various macroscopic structures and sizes.

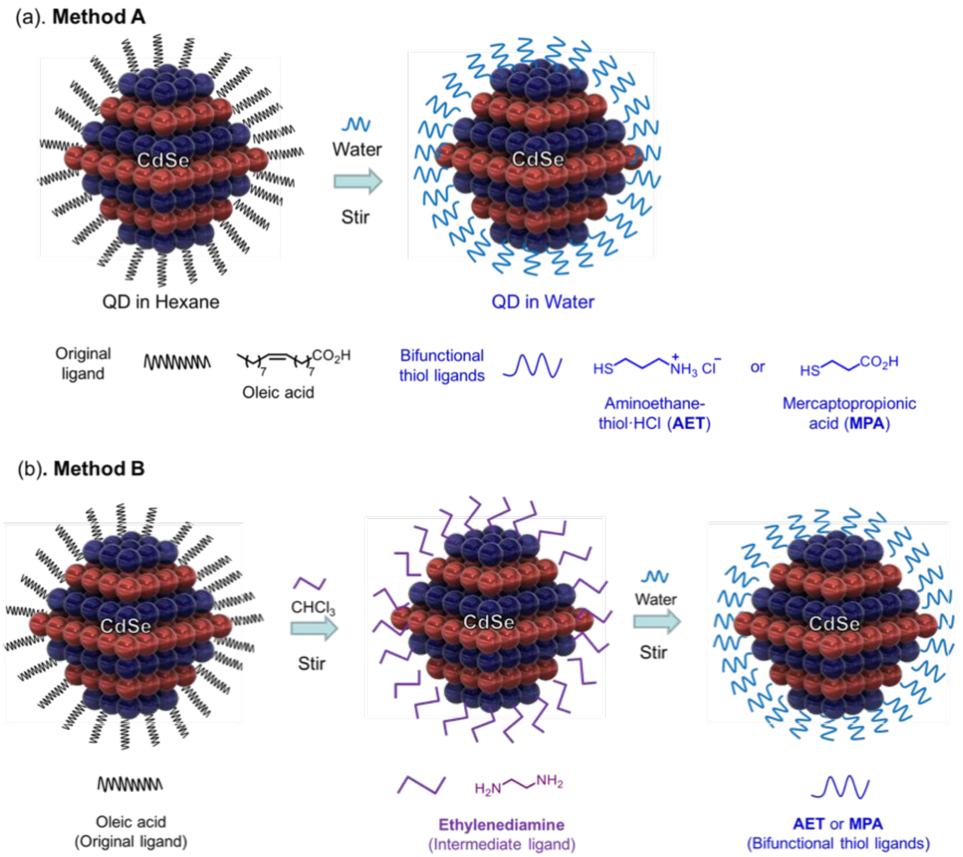
Herein, we described an efficient radical polymerization in aqueous media using thiol ligand capped CdSe QDs as a new class of PIs under visible light. The polymerization could be operated with only several ppm catalyst loading, giving *Đ* as low as 1.27 with excellent oxygen tolerance. The use of hydrophilic ligands such as 3-mercaptopropionic acid (MPA) with two kinds of ligand exchange methods provided CdSe QDs a very good water solubility, therefore, expanding the scope of water-soluble PCs/PIs. Besides, thiol molecules may act as the coinitiators to help CdSe QDs form a catalytic cycle, due to its' strong binding ability towards CdSe QDs core and easy to be oxidized nature. This unique mechanism was further elucidated on the basis of the fluorescence quenching study and capture of thiyl radical using thiol-ene reactions. The presence of thiol additives also provided the polymerization unprecedented tolerance towards oxygen.[99] The influence of different conditions on reactions such as QDs catalyst loading, thiol to monomer ratio and different functional groups on the monomers were well demonstrated. This efficient photopolymerization system was subsequently employed in digital light processing (DLP) 3D printing of polymeric materials.

Results and discussion

Ligand exchange and characterization of thiol ligands capped CdSe QDs in water

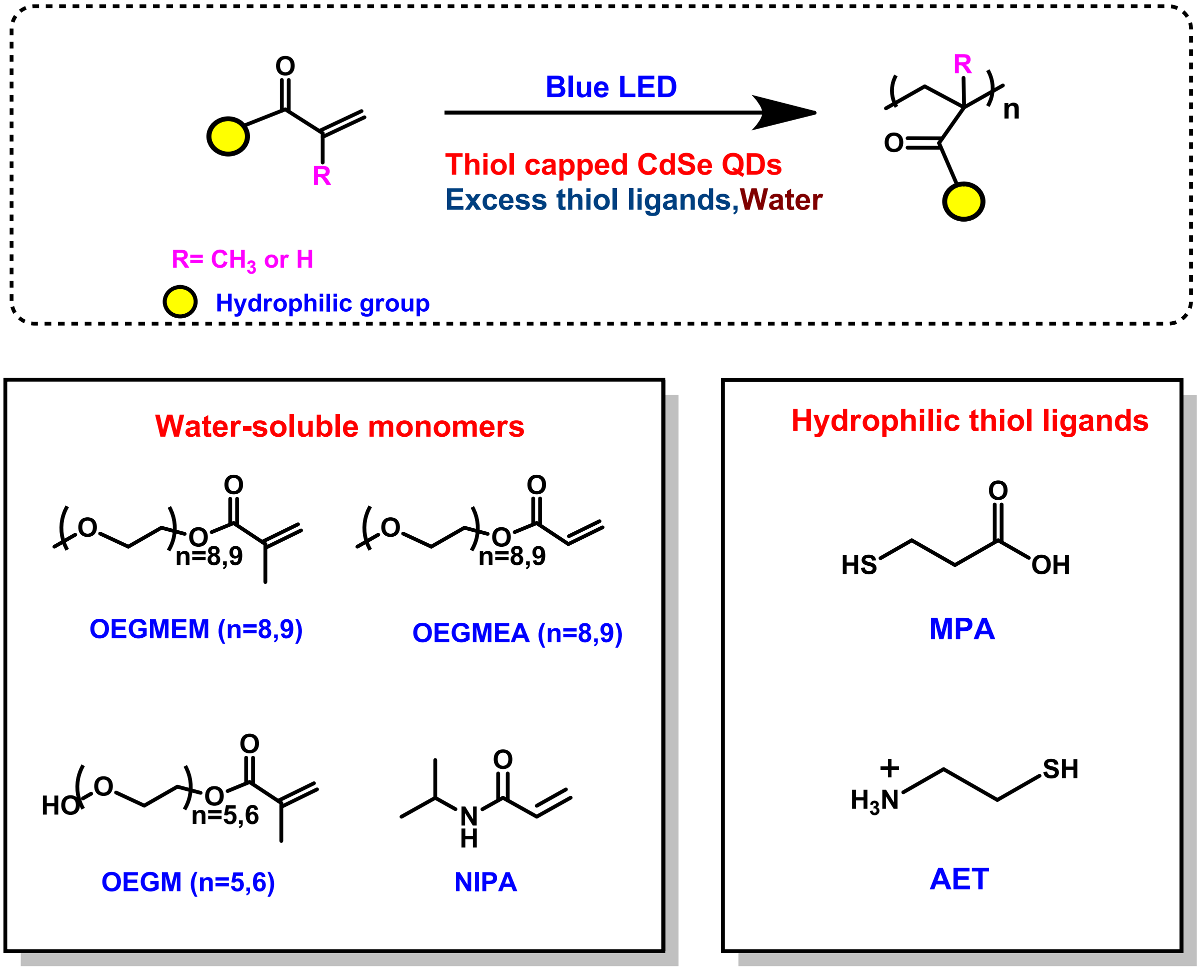
The hot-injection approach in noncoordinating solvents remains the most powerful tool to synthesize monodisperse QDs with high-level control of sizes.[100] However, the QDs synthesized via hot injection are usually capped with nonpolar ligands such as oleic acid (OA), which would not enable the dissolving of QDs in water.[101] Thus, efficient ligand exchange methods are necessary for the transformation of QDs to the aqueous phase. During the preparation of this work, Weiss's group described a biphasic ligand-exchange method to tune the solubility of CdSe QDs into the water with MPA as the ligand, and further applied the QDs as PCs for aqueous RAFT polymerization.[53] However, the aggregation of QDs was reported after ligand exchange,[53] which might weaken the photocatalytic performance.[85] The aggregation phenomenon is consistent with what we observed when a biphase ligand exchange with MPA ligand was applied with 3.2 nm CdSe QDs (**Method A, Scheme 1a** and **Figures S1-2**). Dynamic light scattering (DLS) spectrum of AET capped QDs showed mono-dispersed size distribution (mean size of 27.2 nm), while the MPA capped QDs obtained from methods A showed micro-scale aggregation (**Figure S3**). We suspect that the oleate ligands on the CdSe QDs surface were just partially replaced, hence the poor solubility which traps the QDs at the phase boundary.[101] On the other hand, utilizing aminoethanethiol hydrochloride (AET) via method A offers enhanced dispersion of CdSe QDs water solution (**Figures S1-2**), given that the ammonium salt group has better solubility in water than the carboxylic acid group on MPA. Another possible reason is that positively charged AET ligands could increase the electrostatic repulsion and prevent QDs from aggregation.[102]

Scheme 1. Two ligand exchange method used in this study (a) biphase-ligand exchange (b) EDA-assisted ligand stripping method.



Although method A resulted in a well-dissolved AET-capped QDs aqueous solution (**Figure S1**), excess of AET ligands were required to maintain the stability of CdSe QDs. Attempts to wash out the extra thiol ligands led to the aggregation of QDs. To get a stable and better dissolved QDs aqueous solution, an alternative strategy, ligand-stripping (**Method B**) assisted by ethylenediamine (EDA) was also examined using MPA as the ligand (**Scheme 1b**).[101] The detailed procedure of Method B and ligand exchange mechanism is outlined in the **Supporting information**. Encouragingly, ligand exchange was rapid and successful, yielding a well dissolved CdSe QDs aqueous solution. The absence of light scattering in the UV-vis spectra (**Figure S2**) of QDs after ligand exchange indicates that MPA-capped CdSe are fully dispersed and stable in water. A slight blue shift in the first excitonic peak by about 7 nm was observed and attributed to surface etching from the excess of MPA ([MPA]:[CdSe] is around 10^4).[101] MPA-capped CdSe QDs via method B is stable even aging for 2 months without the addition of excess MPA. Therefore, MPA-capped QDs prepared by Method B were chosen for the following studying.

Scheme 2. Visible light-initiated radical polymerization using CdSe semiconducting quantum dots in aqueous medium and water-soluble monomers.



Photoinduced polymerization initiated by CdSe QDs and control experiments

We subsequently examined the photocatalytic activity of the water-soluble CdSe QDs prepared by Methods B, using water-soluble monomer oligo-(ethylene glycol) methyl ether methacrylate (OEGMEM,

M_n= 500 g/mol) in distilled water under the irradiation of a household blue LED lamp (460 nm, 10W) at room temperature (**Scheme 2**). We initially tested the activity of MPA-capped CdSe QDs prepared using Method B in the polymerization of OEGMEM, and excess of thiol molecules (2 mol% to OEGMEM) was added as the additive. We hypothesized that the excess thiols could stabilize the QDs by replenishing the photo oxidized ligands,[103] and meanwhile, could also be oxidized by photoexcited QDs[104] and act as co-initiators to initiate monomers. Encouragingly, with only 3 ppm QDs loading, the polymerization proceeded rapidly and full conversion was achieved after 3 hours, resulting in M_n of 39.5 kDa and $Đ$ of 1.70 (**Table 1, entry 1**), showing the robust photoinitiation efficiency of CdSe QDs. We performed a range of control experiments to verify and examine the role of each component in the polymerization, including thiol ligands, light, and CdSe QDs (**Table 1, entries 2-4**). In contrast to the successful polymerization in the presence of 2 mol% MPA, only trace amount of polymer was obtained without externally adding MPA as coinitiators (**Table 1, entry 2**). This suggests the excess MPA is essential for the polymerization and might act as the coinitiator. Besides, precipitation of CdSe QDs was observed after irradiation. The precipitation of QDs might be due to the oxidization of the MPA ligands.[103] The oxidized thiol ligand (R-S-H) formed a disulfide (R-S-S-R) that becomes ineffective in coordinating with CdSe QDs.[103] Meanwhile, in the absence of either light or CdSe QDs, the polymerization did not proceed, demonstrating a photo-mediated polymerization that is catalyzed by CdSe QDs (**Table 1, entries 3-4**). Interestingly, the polymerization proceeded in non-purified monomer (e.g.OEGMEM contains 100 ppm MEHQ as inhibitor) without the need for cumbersome filtering procedure (**Table 1, entry 5**), resulting in comparable M_n (39.8 kDa) and OEGMEM conversion (95.3 %) to the polymerization carried out with purified monomers (**Table 1, entry 1**). This powerful ability highly simplifies the reaction setting up, and therefore we did not purify the monomers in the following study.

Table 1. Results of photoinduced radical polymerization initiated by CdSe QDs obtained by ligand exchange method B[a]

Entry	[QD]:[M][b] (ppm)	Conv (%)[c]	M_n (kDa)[d]	$Đ$
1	3	100	39.5	1.70
2[e]	3	trace	/	/
3	0	0	/	/
4[f]	3	0	/	/
5[g]	3	95.3	39.8	1.62

a. Reaction condition: 3 ppm QDs, 2 mol% MPA, 0.54 ml OEGMEM and 2 ml water, were mixed in a 20 ml silicon vial under 3 hours irradiation by the blue LED household lamp (λ_{max} = 460 nm) b.[M] stands for monomer molar concentration c.Conversion determined by proton nuclear magnetic resonance (^{1}H NMR) d.Determined by GPC in THF, based on linear polystyrene as calibration standard e. No MPA was added. f.Reaction was operated in the dark, covered with aluminum foil g.Monomer was not purified

Influence of catalyst loading on polymerization

We further investigated the photocatalyst loading by varying the concentration of MPA-capped CdSe QDs via Method B from 0.2 ppm to 5 ppm. Generally, an increase in QDs loading led to a faster reaction rate and an increase in OEGMEM conversion (**Table 2, entries 1-4**), which could be attributed to an increased concentration of excited states QDs (QD*).[105] A high CdSe QDs loading of 5 ppm resulted in a rapid polymerization with a OEGMEM conversion of 90.3% in just 20 minutes (**Table 2, entry 1**). Polymerization operated in both catalyst loading of 1 ppm and 0.4 ppm fully converted monomers into polymers within 3 hours, while reactions with 0.2 ppm QDs showed a comparatively slower rate, yielding 83.5% OEGMEM conversion in the same time frame. (**Table 2, entries 2-4**). Generally, we observed in this system that varying in the catalyst loading did not yield an obvious change on M_n. These results prompted us to further probe the role of MPA.

Table 2. Results of photoinduced radical polymerization initiated by different concentration MPA-capped CdSe QDs[a]

Entry	[QD]:[M][b](ppm)	Reaction Time (h)	Conv(%)[c]	M_n (kDa)[d]	*Đ*
1	5	0.33	90.3	40.5	1.47
2	1	3	100	37.8	1.70
3	0.4	3	100	41.8	1.64
4	0.2	3	83.5	46.9	1.43

a. Reaction condition: 0.54 ml OEGMEM, 2 ml water, 2 mol% MPA and different loading of QDs were mixed in a 20 ml silicon vial, irradiated by the blue LED household lamp (λ_{max} = 460 nm) for 1 hour. b. [M] stands for monomer molar concentration c. Conversion determined by ^1H NMR. d. Determined by GPC in THF, based on linear polystyrene as the calibration standard

Influence of MPA amount on polymerization

To systematically investigate the role of excess MPA, we used MPA-capped CdSe QDs prepared by Method B, and systematically varied the concentration of MPA added to that system. With CdSe QDs loading of 0.4 ppm, MPA concentrations ranging from 0.6 mol % to 12 mol % to OEGMEM were tested (**Table 3, entries 1-4**). Generally, we found that an increase in MPA to OEGMEM ratio results in an increase in the polymerization rate and a decrease in M_n as well as *Đ*. For example, increasing MPA to OEGMEM ratio from 2 mol % to 6 mol % resulted in M_n decreasing from 30.1 kDa to 19.4 kDa (**Table 3, entries 2-3**), and further increasing to 12 mol % led to a 13.3 kDa (**Table 3, entry 4**). Meanwhile, *Đ* decreased from 1.74 to 1.34 and the OEGMEM conversion increased from 27.4% to 63.7% in the same time frame. These results suggest that MPA might serve as a co-initiator as well. We proposed that MPA could be easily oxidized by excited state QDs, forming a thiyl radical and further initiate polymerization. We also suspect that the excess MPA protects the CdSe QDs from photodegradation[103] and therefore offers low dispersity (as low as 1.34). It is notable to mention that the reaction does not proceed with a low concentration of MPA (0.6 mol %, **Table 3, entry 1**), which suggests non-efficient initiation. Under a low concentration of MPA, the thiyl radical may prefer to form a bithiol instead of initiating the polymerization.[77] Besides, the aggregation and precipitation of QDs were observed after irradiation when 0.6 mol% MPA was used, indicative of the relatively low stability of QDs with small amount of MPA.[103]

Table 3. Results of photoinduced radical polymerization initiated by MPA-capped CdSe QDs from ligand strip method with different amount of additive MPA[a]

Entry	[MPA](mol %)	Conv[b](%)	M_n [c](kDa)	$Đ$[c]
1	0.6	0	/	/
2	2	27.4	30.1	1.74
3	6	56.1	19.4	1.36
4	12	63.7	13.3	1.34

a.Reaction condition: 0.54 ml OEGMEM, 2 ml water, 0.4 ppm MPA-capped QDs loading, irradiated by the blue LED household lamp (λ_{max} = 460 nm) for 1 hr. b. Conversion determined by ^{1}H NMR. c. Determined by GPC in THF, based on linear polystyrene as calibration standard

Oxygen tolerance ability of MPA-capped CdSe QDs photoinitiated polymerization

The inability to perform polymerization in the air is one of the major challenges hindering the potential to apply current radical polymerization techniques at industry scale or low volumes.[106] Particularly for photopolymerization, oxygen can quench the excited state of PIs and further lead to their degradation,[106,107] resulting in low initiation efficiency and OEGMEM conversion. Herein, in order to test the sensitivity of our polymerization towards oxygen, a range of experiments were performed at different degrees exposing to oxygen. Three conditions were studied: in a sealed vial without degassing, totally open vessel, and purging reaction mixture with continuous oxygen flow (presence of oxygen in the reaction increases from left to right). Encouragingly, successful polymerizations were all demonstrated under the above conditions in the presence of 1 ml water. A minor difference was observed between polymerization after 20 mins in the sealed vial and open vessel, which achieved 17.4 % and 17.6 % OEGMEM conversion, respectively (**Table 4, entries 1-2**). Meanwhile, polymerization running in the oxygen flow even showed a slightly higher OEGMEM conversion (23.5%), resulting in polymer with M_n of 22.9 kDa and a low dispersity 1.27 (**Table 4, entry 3**). Furthermore, after 1.5 hours, almost full conversion, similar M_n near 20 kDa and $Đ$ around 1.35 were achieved among the three different conditions, indicating the excellent oxygen tolerance ability of our polymerization (**Table 4, entries 4-6**). We presume that the oxygen is perhaps consumed by the reductant species of MPA.[108] Besides, we also suspect that singlet oxygen may accept one electron from excited states QDs,[59] help QDs form a catalytic cycle and accelerate the CdSe QDs turnover. The detailed discussion will be further presented in the mechanism part. The excellent oxygen tolerance under an extremely low catalyst loading (1 ppm) provides an unanticipated advantage of our polymerization for potential industrial-scale applications where deoxygenation procedures are costly and challenging.[106] Furthermore, it is worthwhile to mention that $Đ$ = 1.27 is an unusually low dispersity for photoinitiated radical polymerization, comparing to other PIs including organic dyes or semiconductor nanoparticles, that typically yield $Đ$ of 2.0.[25]

Table 4. Results of photoinduced radical polymerization by CdSe QDs in the oxygen [a]

Entry	Degree of opening to O_2	Reaction Time (h)	Conv (%)[b]	M_n (kDa)[c]	*Đ*
1	Sealed vial	0.33	17.4	19.9	1.29
2	Open vessel	0.33	17.6	20.1	1.32
3	Purging O_2	0.33	23.5	22.9	1.27
4	Sealed vial	1.5	100	20.2	1.37
5	Open vessel	1.5	95.6	19.5	1.30
6	Purging O_2	1.5	98.0	19.4	1.30

a.Reaction condition: 0.54 ml OEGMEM (non-purified), 1 ml water, 6 mol% MPA, 1 ppm MPA-capped QDs in stocked solution with irradiation by the blue LED household lamp (λ_{max} = 460 nm) b.Conversion determined by ^{1}H NMR c. Determined by GPC in THF, based on linear polystyrene as calibration standard

Expanding scope of monomers

We further evaluated the scope of this polymerization method by expanding the range of the water-soluble monomers. Oligo(ethylene glycol) methacrylate (OEGM, M_n = 360 g/mol), oligo(ethylene glycol) methyl ether acrylate (OEGMA, M_n = 480 g/mol) and *N*-Isopropylacrylamide (NIPA) monomers were polymerized with 0.4 ppm MPA-capped CdSe QDs prepared obtained from Method B. After three hours of irradiation, polymerization of OEGM resulted in a 95.2% conversion (**Table 5, entry 1**), yielding an insoluble polymer gel. This is maybe due to the hydroxyl groups forming intra-chain and inter-chain hydrogen bonding that results in polymer hydrogels. Meanwhile, polymerization of OEGMA reached 62.5% conversion and *Đ* as low as 1.30 (**Table 5, entry 2**). Furthermore, functional polymer poly-NIPA, a stimuli-responsive biopolymer widely applied in drug release and tissue cultures,[109] was synthesized using our polymerization method with only 0.4 ppm catalyst loading. NIPA conversion of 91.3 % was achieved, yielding polymers with M_n of 1.7 kDa and a $Đ$ of 1.80 (**Table 5, entry 3**). The ability to polymerize different functional monomers showcased the versatility and broad applicability of our techniques.

Table 5. Results of photoinduced radical polymerization by CdSe QDs with different monomers [a]

Entry	Monomer	[QD] (ppm)	Ligand Exchange Method	Conv^b(%)	M_n ^{c}(kDa)	$Đ^c$
1	OEGM	0.4	Method B	95.2	gel^d	gel^d
2	OEGMEA	0.4	Method B	62.5	18.7	1.30
3	NIPA	0.4	Method B	91.3	1.7	1.80

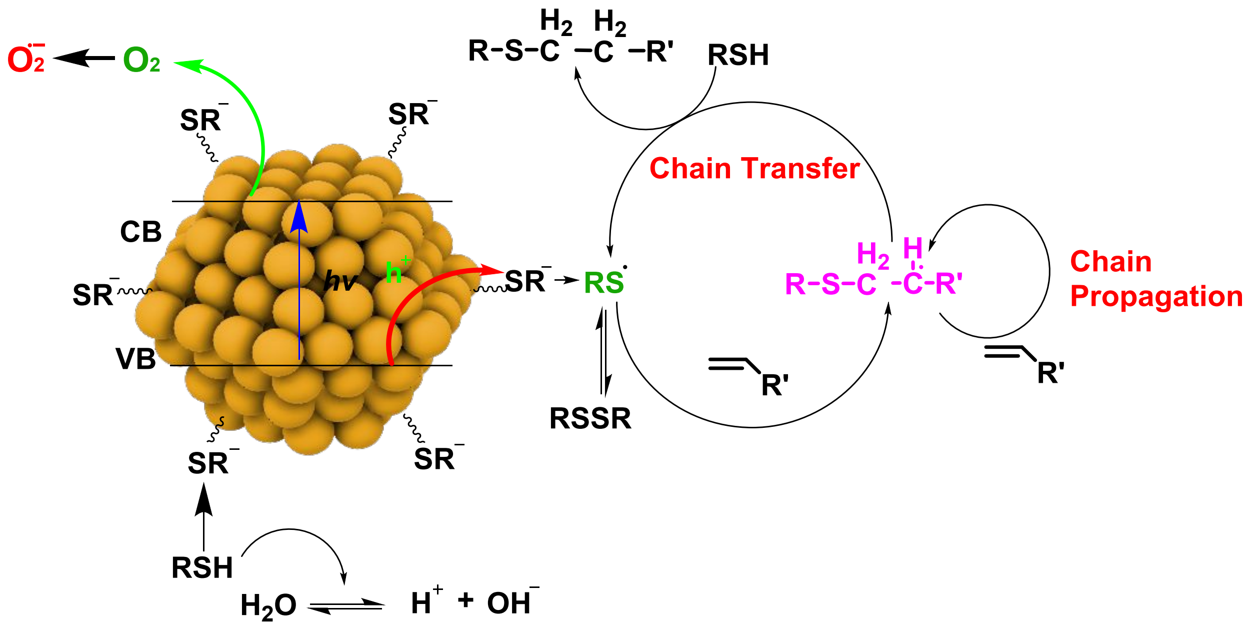
a.Reaction condition: 1.16 mmol monomer, 2 ml water, with MPA-capped QDs water solution and 6 mol% MPA after 3 hours irradiation by the blue LED household lamp (λ_{max} = 460 nm) unless other noted b. Conversion determined by ^{1}H NMR.c. Determined by GPC in THF, based on linear polystyrene as calibration standard d. polymer gel is not soluble in THF

Proposed mechanism

To lend support to this mechanism, we evaluated the fluorescence quenching of CdSe QDs in the presence of MPA and monomer. Addition of MPA to a MPA-capped CdSe QDs aqueous solution resulted in completely quenching of the fluorescence of QDs, whereas addition of the same molar concentration of OEGMEM did not lead to any significant quenching in the fluorescence (**Figure S4**). These results further suggest that there is a possible charge transfer between CdSe QDs and MPA rather than with the OEGMEM. Valence band maximum of MPA capped QDs was calculated to be 0.456 V vs saturated calomel electrode (SCE) using X-ray photoelectron spectroscopy (XPS, **Figure S5**). Besides, in the presence of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), polymerization completely halted, suggesting a possible radical propagation mechanism during polymerization (**Table S1, entries 3-4**).

On the basis of the fluorescence quenching results (**Figure S4**), control experiment (**Table 1, entry 4**) and the influence of thiol concentration over polymerization (**Table 3**), we proposed MPA might play a role as a co-initiator and initiate the polymerization (**Scheme 3**). The first step of the considered mechanisms is the absorption of visible light by CdSe QDs to generate electron-hole pair in excited-state QDs (QD*). As the redox potential of MPA (0.30 to 0.35 V vs SCE[110]) is more positive than that of the valence band of CdSe QDs (0.456 V vs SCE, **Figure S5d**), the photoexcited hole could be transferred from QDs to MPA, generating the thiyl radicals.[111,112] The generated thiyl radical cation may lose a proton to give a thiyl radical in the presence of water,[112] which can add to the alkene, initiating the propagating process in the presence of a large amount of alkenes.[99] Furthermore, the excited state electron may be captured by oxygen in the system and help the catalysis turnover,[113] which further explained the excellent oxygen tolerance of our technique. We also suspect the resultant thiyl radicals can also participate in a chain-transfer reaction with excess thiol ligand. Considering the only 2 mol% MPA used in the polymerization, we suspect that polymerization is more likely undergoing a chain-growth propagation/homopolymerization mechanism.[114] Additionally, ^{1}H NMR of the polymer product (poly-(ethylene glycol) methyl ether acrylate) exhibited broad peaks ranging from 2.6-2.8 ppm (**Figure S6**), which might originate from MPA capped on the polymer chain end.

Scheme 3. Proposed mechanism of radical polymerization photoinitiated by CdSe QDs.



Thiol-ene addition and thiol-ene step-growth polymerization using CdSe QDs as photocatalysts

Thiol-ene "click" reaction, as a highly efficient, rapid methodology, has been widely applied for organic and polymer synthesis/post-functionalization.[99,115–117] To further confirm our initiation mechanism and expand the scope of reactions where CdSe QDs could be employed as PCs, we performed a thiol-ene reaction between norbornene and MPA with a molar ratio equal to 1 in the acetonitrile (MeCN) (**Scheme 4a**). The reaction was operated under household blue LED with 15 ppm as-synthesized MPA-capped CdSe QDs via Method B and 5 mol % dimethylaniline as a redox mediator according to Yoon's report.[118] The reaction was very rapid, reached full conversion in 1 hour without executing any side product according to the crude ^{1}H NMR spectrum (**Figure S7**). This result suggests the thiyl radical could be produced from photooxidation of a thiol ligand by CdSe QDs*, further consolidating thiyl radicals initiating mechanism for the radical polymerization. More importantly, to best our knowledge, this is the very first example of semiconducting QDs photocatalyzed thiol-ene click reaction, and very few example of QDs photocatalyzed organic transformation.[74,75,77,78]

Encouraged by the successful thiol-ene click reactions photoinduced by CdSe QDs, we further envisioned a step-growth thiol-ene polymerization to prepare a linear polymer with MPA-capped CdSe QDs as PCs (**Scheme 4b**). 1,5-hexadiene (HD), 2,2′- (ethylenedioxy)diethanethiol (EDDT), p-toluidine (5%) and 10 ppm QDs were mixed in *N*-Methyl-2-pyrrolidone, and then irradiated upon blue LED in the presence of air. Not surprisingly, polymerization was rapid, obtained a full conversion of olefin within an hour, and provided polymers with M_n of 4.0 kDa and a moderate *Đ* equal to 1.50, showing the versatility of this approach towards different type of reactions. ^{1}H NMR spectrum further confirmed the formation of poly-ethylenedioxy thioether (**Figure S8**). Meanwhile, without addition of QDs, no polymerization was observed after 1 hour irradiation under the same blue LED (**Table S2**). These results suggest CdSe QDs could also serve as an efficient photocatalyst for thiol-ene step-growth polymerization.

Scheme 4. Thiol-ene click reaction and polymerization photoinduced by CdSe QDs

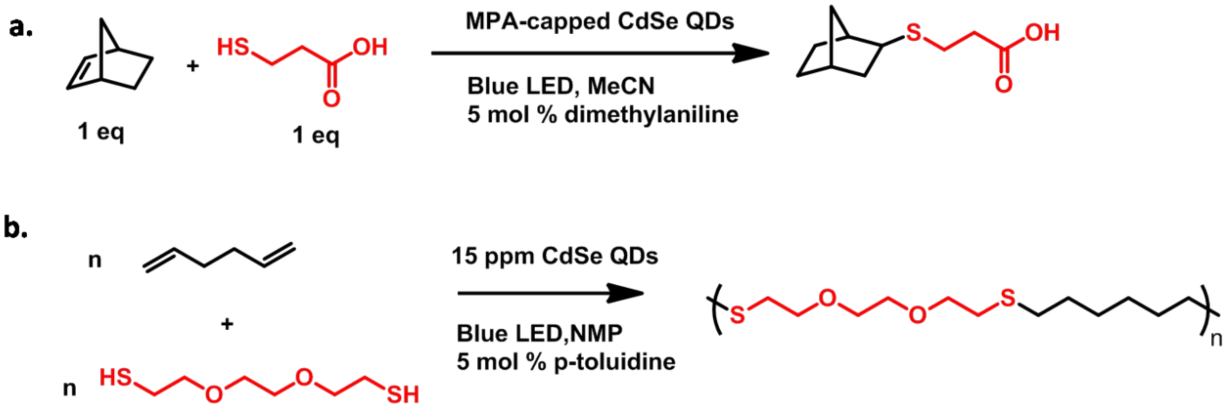


Photo 3D printing via MPA-QDs photoinitiated radical polymerizations.

One of the key challenges in photo-3D printing is lacking robust PIs which enable the printing process with high oxygen tolerance under low catalyst concentration.[30,31] As the CdSe/MPA system exhibits formidable performance in polymerizing different acrylate monomers and rapid gelation without degassing, we sought to explore the applicability of MPA-capped QDs as PIs in photo-3D printing. Poly(ethylene glycol) diacrylate (PEGDA, M_n = 700 g/mol) was used as the difunctional monomer in 3D printing resin to increase the cross-linking density and accelerate the gelation. The photopolymerization process of PEGDA using 14 ppm MPA-CdSe-QDs was monitored by Fourier-transform infrared spectroscopy (FTIR). Encouragingly, the polymerization could achieve considerable PEGDA conversion of 86% in 8 minutes (**Figure S9**). The photopolymerization of PEGDA photocatalyzed by CdSe QDs was further used for photo 3D printing. Under a DLP printer with relatively low visible light intensity (2 mW/cm^2) and a wavelength centered at 410 nm, a hydrogel tag with our university logo "RICE" (the dimension of 35 mm x 20 mm x 3 mm.) was successfully printed utilizing PEGDA/CdSe QDs water solution/MPA resin system in the air **(Figure 1)**. Furthermore, the catalyst loading of the 3D printing resin is very low (14 ppm), while using commercially available PI Eosiny Y[119] under identical conditions failed to print any objects. Additionally, we also explored the possibility to print the polymer/carbon nanotube nanocomposites. Polymer/carbon nanotube nanocomposites are a class of advanced materials that have shown good mechanical property[120] and high conductivity[121]. By adding 0.22 wt% single-wall carbon nanotubes into the resin, objects with different sizes and shapes could be easily printed using the MPA-CdSe QDs photoinitiation system (**Figure 1 c-g and SI for size detail**). The excellent performance of CdSe QDs/MPA initiating system in 3D printing photocurable material PEGDA opens up great opportunities for fabricating polymer-nanocomposites via photo 3D printing process.

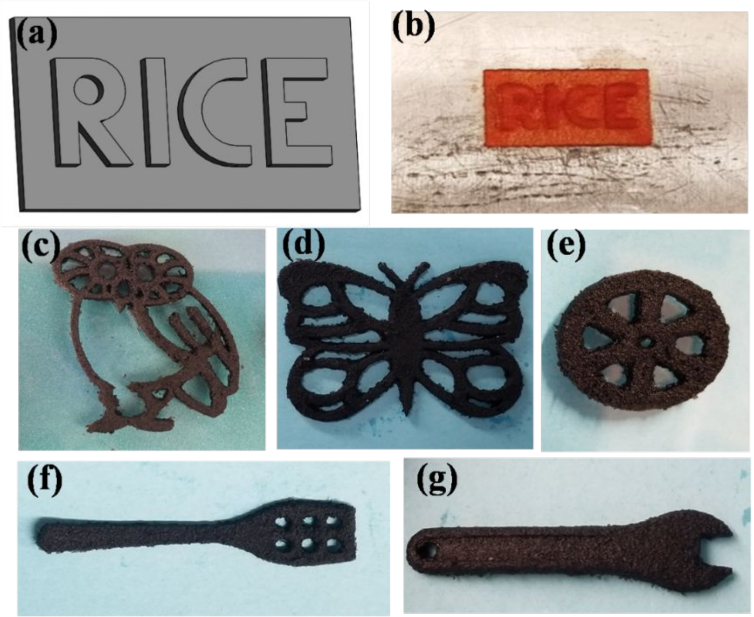


Figure 1. (a) 3D model of the tag (b) 3D printed hydrogel tag (35 mm x 20 mm x 3 mm) using PEGDA/CdSe QDs water solution/MPA as a photoinitiating system (c-g) different 3D printed objects with different sizes

Conclusion

In conclusion, we have demonstrated an effective aqueous phase radical polymerization and successful photo 3D printing using thiol ligand capped CdSe QDs as PIs. The various ligands and ligand exchange methods render CdSe QDs soluble in water, thus offering the ability to synthesize various water-soluble functional monomers. Generally, MPA-capped CdSe QDs prepared using ligand-stripped method exhibited superior catalytic activities in the radical polymerization, achieving almost full monomer conversion in an hour with high oxygen tolerance. The thiyl radicals from additive MPA were proposed to be the initiating species, which is further supported by the fluorescence quenching study of CdSe QDs and successful thiol-ene click reactions. Besides, resulting M_n and $Đ$ of the polymer could be easily tunned by additive/monomer ratio, yielding dispersity as low as 1.27. Furthermore, the successful application of CdSe QDs-MPA photoinitiation systems for the 3D printing of photocurable resin illustrates the enormous potential in designing advanced polymer nanocomposites.

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Notes

The authors declare no competing financial interest

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