

Mechanistic Insights into the Interface-Directed Transformation of Thiols into Disulfides and Molecular Hydrogen by Visible-Light Irradiation of Quantum Dots**

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Abstract: Quantum dots (QDs) offer new and versatile ways to harvest light energy. However, there are few examples involving the utilization of QDs in organic synthesis. Visible-light irradiation of CdSe QDs was found to result in virtually quantitative coupling of a variety of thiols to give disulfides and H_2 without the need for sacrificial reagents or external oxidants. The addition of small amounts of nickel(II) salts dramatically improved the efficiency and conversion through facilitating the formation of hydrogen atoms, thereby leading to faster regeneration of the ground-state QDs. Mechanistic studies reveal that the coupling reaction occurs on the QD surfaces rather than in solution and offer a blueprint for how these QDs may be used in other photocatalytic applications. Because no sacrificial agent or oxidant is necessary and the catalyst is reusable, this method may be useful for the formation of disulfide bonds in proteins as well as in other systems sensitive to the presence of oxidants.

Colloidal semiconductor nanocrystals (quantum dots; QDs) have attracted widespread interest because their physical properties are quite different from those of bulk materials.^[1–3] Owing to their quantum confinement effects, rich surface binding properties, high surface-to-volume ratios, broad and intense absorption spectra in the visible region, and low cost, QDs offer new and versatile ways to harvest light energy. However, few examples involving the utilization of QDs in organic synthesis have been reported, and many of the details

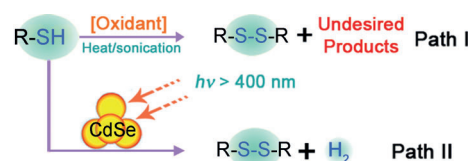
concerning how QDs function in specific processes are unclear. Miguel and co-workers, for example, applied CdS and CdSe QDs in the photocatalytic reduction of aromatic azides to amines.^[4] Niemeyer and Ipe employed QD/enzyme nanohybrids for photocatalyzing the transformation of myristic acid to α - and β -hydroxymyristic acid.^[5] Most recently, Ford and co-workers found that 1,1-dithiooxalate bound to the surfaces of CdSe QDs can be converted into carbon disulfide under aerobic conditions through oxidative cleavage.^[6] Herein, we report that visible-light irradiation of CdSe QDs leads to virtually quantitative coupling of a variety of thiols to give disulfides and molecular hydrogen without the need for sacrificial reagents or external oxidants and with relatively high turnover numbers (TONs). The mechanistic insights presented offer a blueprint for how these QDs may be used in other applications.

Coupling reactions are useful in the synthesis of new molecules, as well as for various medical, biological, materials, and nanotechnological applications. For this reason, extensive efforts have been made over the years to find efficient methods for coupling the atoms of two unlinked molecular species.^[7–11] Among these is the selective coupling of thiols to produce disulfides, a seemingly simple synthetic procedure that is, in fact, not simple at all. Such reactions play an important role in the tertiary and quaternary structure and the function of proteins, and as in drug delivery systems and smart materials.^[12–15] Disulfides are also of interest as protecting groups in synthetic applications and as vulcanizing agents for rubber. A broad range of reagents (e.g., molecular oxygen, metal complexes, peroxides, halogens, and organic oxidants) has thus been employed to synthesize disulfides by the coupling of thiols in both heterogeneous and homogeneous systems.^[16–23] However, most of these procedures suffer from low selectivity and overoxidation of the thiols to give undesired products such as sulfoxides and sulfones (Path I of Scheme 1) and/or involve very expensive reagents.^[24–26]

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Scheme 1. Two general approaches for the conversion of thiols into disulfides.

In 2010, Yoon and co-workers introduced a photooxidative coupling method that is not catalytic and is applicable to a limited number of aromatic thiols.^[27] Later, Ando and co-workers reported the aerobic photocoupling of thiols to give disulfides by using rather toxic diaryltellurides as catalysts.^[28] Notably, Fan and co-workers were able to convert thiols into disulfides and molecular hydrogen for the first time by using a $[\text{Mn}(\text{CO})_5\text{Br}]$ complex as the photosensitizer, but the reported TON of the coupling reaction is less than 20, and UV irradiation and molecular oxygen are required.^[29] Herein, we report a simple, clean, recyclable, and efficient photocatalytic ($\lambda > 400$ nm) method for the virtually quantitative and selective conversion a variety of thiols into disulfides and molecular hydrogen at room temperature by visible-light irradiation of CdSe-QD/thiolate conjugates (Path II of Scheme 1). Given that no sacrificial agent or oxidant is necessary and that the catalyst is reusable, this method may be attractive for the formation of disulfide bonds in proteins, as well as in other systems sensitive to the presence of oxidants.

Typically, an aqueous stock solution of water-soluble CdSe QDs (see Figures S1 and S2 in the Supporting Information) was treated with hydrochloric acid (0.1 M) to aggregate and precipitate the QDs (Figure S3), which were isolated by centrifugation and washed with water to remove any residual ligands not bound to the surface of the QDs. The precipitate was then redispersed in water and a thiol, such as 3-mercaptopropionic acid (MPA), was added. After the pH value was adjusted to be near the pK_a value of the thiol (9.0 in the case of MPA), the reaction mixture was deaerated by bubbling with nitrogen and then irradiated ($\lambda > 400$ nm) at room temperature for a specified period either in the air or under a nitrogen atmosphere. Significantly, the disulfide and H_2 were the only products detected; the yields in Table 1 are based on the amount of thiol reacted. As expected, the

conversion and yield increased when the irradiation time was increased (Table 1, entries 1,2). However, the conversion of MPA was lower and slower when the pH value was lower or higher than 9.0 (Table 1, entries 3–7). Disulfide production was not observed in the absence of irradiation or the CdSe QDs (Table 1, entry 8).

Because the reaction proceeded smoothly without added oxidants and H_2 was evolved in a virtually quantitative yield, we expected (and found) that coupling could be facilitated by the presence of a cocatalyst for H_2 evolution. Upon the addition of a small amount of a nickel(II) salt such as NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, or $\text{Ni}(\text{OAc})_2$ (which were recently reported to be exceptional photocatalysts for H_2 evolution^[30,31]), both the conversion of thiols into disulfides and the rate of H_2 evolution improved dramatically. Within 1.5 h, the conversion approached 99% and the yields of the disulfide and H_2 photoproducts were near 100% (Table 1, entry 9). Even under aerobic condition, 92% and 95% yields of the disulfides and H_2 , respectively, could be achieved (Table 1, entry 10). Clearly, the combination of CdSe QDs and nickel(II) ions under visible-light irradiation is a promising approach for the conversion of thiols into disulfides.

As shown in Table 2, the protocol can be used to convert a broad range of thiols into their corresponding disulfides while leaving carboxyl, amino, methoxy, and halide substitu-

Table 1: Variation of the conditions for the coupling of MPA to give 3,3'-dithiodipropionic acid and H_2 in water.^[a]

$2 \text{ HOOCCH}_2\text{SH} \xrightarrow[\text{water; } \lambda > 400 \text{ nm; RT}]{\text{CdSe QDs}} \text{HOOCCH}_2\text{S-SCH}_2\text{COOH} + \text{H}_2$						
Entry	pH value	t [h]	Conv. ^[b]	Yield [%]		TON ^[e]
				disulfide ^[c]	H_2 ^[d]	
1	9.0	5.0	86	83	86	990
2	9.0	8.0	91	88	91	1040
3	3.0	5.0	15	12	15	170
4	5.0	5.0	50	44	50	580
5	7.0	5.0	73	70	73	836
6	10.0	5.0	83	79	83	950
7	12.0	5.0	34	30	34	390
8 ^[f]	9.0	5.0	0	0	0	0
9 ^[g]	9.0	1.5	99	95	99	1150
10 ^[h]	9.0	5.0	95	92	95	1092

[a] Conditions: MPA (0.23 mmol) and acid treated QDs (0.02 mm) in 10 mL H_2O under a 500 W high-pressure mercury lamp with a 400 nm cutoff filter. [b] Based on the starting amount of MPA. [c] Determined by ^1H NMR spectroscopy with diphenylacetonitrile as an internal standard. [d] Determined by GC with CH_4 as an internal standard. [e] TON: mmol substrate converted/mmol CdSe QDs. [f] Without irradiation or the QDs. [g] In the presence of 0.1 mM NiCl_2 . [h] Under aerobic conditions in the presence of 0.1 mM NiCl_2 .

Table 2: Substrate scope and TONs for the conversion of thiols into disulfides and H_2 .^[a]

$2 \text{ R-SH} \xrightarrow[\text{solvent; } \lambda > 400 \text{ nm; RT}]{\text{CdSe QDs, Ni}^{2+}} \text{R-S-S-R} + \text{H}_2$				
entry	Substrate	Yield [%]		TON ^[d]
		disulfide ^[b]	H_2 ^[c]	
1	HOOCCH_2SH	99	96	2500
2	$\text{HOOCCH}_2\text{CH}_2\text{SH}$	99	98	2500
3	$\text{C}_6\text{H}_5\text{SH}$	99	99	2500
4	$4\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$	83	86	2075
5	$4\text{-MeC}_6\text{H}_4\text{SH}$	99	97	2500
6	$4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{SH}$	99	96	2500
7	$4\text{-MeOC}_6\text{H}_4\text{SH}$	88	91	2150
8	$4\text{-ClC}_6\text{H}_4\text{SH}$	95	96	2375
9	$4\text{-CF}_3\text{C}_6\text{H}_4\text{SH}$	96	98	2380
10	$3\text{-MeOC}_6\text{H}_4\text{SH}$	ND ^[e]	trace	< 100
11	$2\text{-MeOC}_6\text{H}_4\text{SH}$	NR ^[f]	0	0
12	$2\text{-ClC}_6\text{H}_4\text{SH}$	NR ^[f]	0	0

[a] Conditions: thiol (0.5 mmol), NiCl_2 (0.1 mM) and QDs (0.02 mm) at a pH value near the pK_a value of the corresponding thiol in 10 mL of water or a mixture of water and THF, irradiated for 4.0 h ($\lambda > 400$ nm). [b] Yield of isolated product. [c] Determined by GC. [d] TON based on the product yields. [e] Not determined owing to extremely low conversion. [f] No reaction.

ents unaffected. Aliphatic thiols bearing a carboxyl group were converted into the corresponding disulfides in excellent yields (99%; Table 2, entries 1 and 2). Varying the length of the alkyl chain on the thiols did not perceptibly affect the coupling reaction. For substrates that are not soluble in water, such as thiophenol, the reaction was carried out in a 1:1 (v/v) mixture of water and tetrahydrofuran (THF); again, the corresponding products were obtained in virtually quantita-

tive yields (Table 2, entry 3). Thiophenols with electron-donating groups (Table 2, entries 4–7) or electron-withdrawing groups (Table 2, entries 8,9) at the *para*-position were converted into the corresponding disulfides in excellent yields. Despite the absence of a clear electronic-substituent effect among these groups, there is a strong steric effect. When the methoxy group was moved from the *para* to the *ortho* or *meta* positions of thiophenol, the chemical yields decreased dramatically (Table 2, entries 10,11) and like the *ortho*-chloro derivative (Table 2, entry 12), these compounds were nearly unreactive.

To assess the economic and environmental attractiveness of the method, the same batch of QD/Ni²⁺ catalyst was used to convert four aliquots of MPA sequentially. After each run, the catalyst was precipitated and separated from the liquid by centrifugation. A loss of activity of only approximately 5% between the first and last runs, based on the yields of both products (Figure 1), was observed and can be attributed to mild photocorrosion (Figure S4) and/or some loss of catalyst during physical transfers.

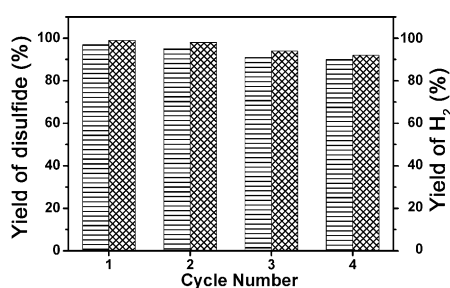


Figure 1. Recycling efficiency of the CdSe-QD catalyst for the coupling of MPA as measured by yields of disulfide (left-hand columns) and H₂ (right-hand columns). Each run was conducted with 0.23 mmol of MPA under the conditions of Entry 9 in Table 1.

In order to elucidate the reaction mechanism, the interaction between the thiols and the CdSe QDs was studied in some detail. Samples of CdSe-QD solutions with different amounts of MPA at pH 9.0 were prepared and placed in the dark for sufficient time to allow maximal complexation before steady-state and dynamic-decay emission data were collected. The band-edge emission of the QDs was significantly diminished and the rate of emission decay was accelerated (Figure S5) by the MPA, perhaps as a result of hole transfer from excited QDs to bound thiolates (thus leading to the formation of surface-bound sulfenyl radicals or radical-like species; see below).^[32] In solutions at pH values near the pK_a value of the thiol groups (4–7 for aromatic thiols and 9–11 for aliphatic thiols),^[33,34] thiolates, which can coordinate easily to cadmium(II) ions at the QD surfaces,^[35,36] are present.

Since the size of the CdSe QDs is about 1.9 nm, as determined by high resolution TEM, and the estimated area per surface cadmium site is about 0.2 nm²,^[37] the average number of thiolate binding sites on the surface of each CdSe QD after acid treatment is approximately 57. This number is very close to the experimentally determined number of thiolates bound per QD (Figure S6 in the Supporting

Information). Given that the TONs of the QDs are more than 10³, each cadmium ion on a QD surface was able to convert at least 20 thiolates into disulfides.

The photoinduced formation of sulfenyl radicals was confirmed by electron paramagnetic resonance (EPR) spectroscopy. Although an attempt to directly observe sulfur-centered radicals failed, the spin adducts of sulfenyl radicals with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were successfully detected. Before irradiation, no spectral signal was observed (Figure 2a). After irradiation ($\lambda > 400$ nm) for 10 s,

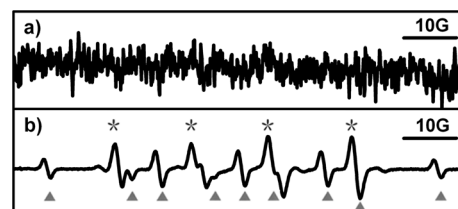


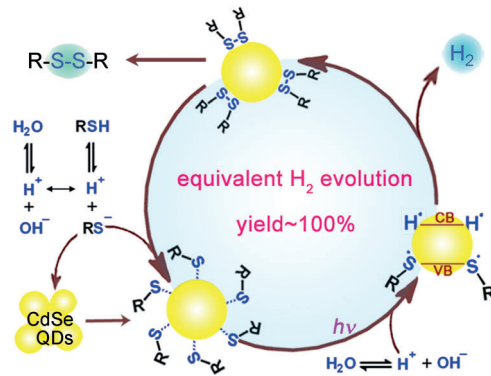
Figure 2. EPR signals from an aqueous solution containing MPA (0.023 M), QDs (0.02 mM), and DMPO (0.02 M) at pH 9.0 before (a) and after (b) irradiation at $\lambda > 400$ nm for 10 s.

however, the spectrum contained spin-adduct spectral features for DMPO (labeled with *) which are typical for the trapping of a sulfenyl radical (RS[•]; $a_N = 15.2$ G, $a_H = 17.0$ G). Simultaneously, another set of signals appeared (marked by gray ▲), which are ascribed to an adduct of hydrogen radicals (H[•]) with DMPO ($a_N = 16.6$ G, $a_H = 22.6$ G) (Figure 2b). The coupling constants of both set of signals are consistent with reported values.^[38,39] When a small amount of nickel(II) ions were present, identical signals with relatively stronger intensities were observed (Figure S7).

In addition, evidence for the homocoupling of thiols to give disulfides and H₂ (i.e., coupling on a single QD) was found. CdSe QDs with adsorbed MPA or *p*-toluenethiol were prepared separately. After removal of the solvent by rotary evaporation under vacuum, the two QD samples were dispersed together in a mixture of H₂O and THF (1:1, v/v) and then irradiated until no more H₂ was evolved. No cross-coupled disulfides of the two thiols were detected (Figure S8). The photogenerated sulfenyl radicals thus couple to form disulfide products on their QD surface of origin before being able to diffuse into the solution. The high efficiency of the catalytic homocoupling also implies that the desorption of thiolates from the surface is very slow and is more difficult than the desorption of disulfides. This assumption is further supported by the fact that the coupling reaction of MPA was nearly absent when CdSe QDs were not prepared with acid treatment (Figure S9). All of these observations suggest that the catalytic reaction takes place on the surface of the QDs rather than in the solvent.

When the reaction was conducted in D₂O (instead of H₂O), D₂ was generated (instead of H₂) as the only byproduct, and with no alteration in the reaction efficiency. Furthermore, only a trace amount of H₂ was evolved when the reaction was carried out in neat [D₆]acetone (Figure S10). These results indicate that the source of the H atoms in the product H₂ is the aqueous solvent.

Based on the accumulated experimental evidence, the mechanism in Scheme 2 is proposed for the photocatalytic transformation of thiols into disulfides and molecular hydrogen on the QD surfaces. When the water-soluble CdSe QDs



Scheme 2. Proposed mechanism for the photocatalytic conversion of thiols into disulfides and molecular hydrogen.

are treated with acid, ‘vacant sites’ are created on the surface of the QDs. Deprotonated thiols bind to the surface through cadmium–sulfur bonds to form QD/thiolate conjugates. Visible-light excitation of the CdSe QDs results in the promotion of electrons to the conduction band (CB), thereby leaving holes in the valence band (VB; Figure S11). The excited states of the QDs are subsequently reductively quenched by the bound thiolates, thereby producing sulfur-centered radicals (RS^\bullet) or radical-like species, which couple to form the corresponding disulfides on the surface of the QDs. The disulfides are released into the solvent and then additional thiolates from the solution bind to the vacant sites and complete the reaction cycle. At the same time, the CB potential of CdSe (> 2.0 V) is sufficiently negative to reduce H^+ to H^\bullet radicals.^[40] We hypothesize that the H^\bullet radicals are stabilized on the QD surfaces as well, thereby allowing two putative H^\bullet radicals to combine and generate one molecule of H_2 . Nickel(II) ions on the QD surface provide even more efficient sites for proton reduction.

The coupling of thiols in this system is a surface-directed process. As a result, it possesses several interesting and synthetically advantageous characteristics: 1) The reaction occurs on the QD surfaces, rather than by diffusive coupling of the sulfenyl radicals in solution. Acid treatment of the QDs improves the yields of the disulfides and their rates of formation by providing more vacant surface sites for the adsorption of thiolates. 2) When the pH value of the solution is near the pK_a value of the thiol, the thiolate population is large and the thiolates are easily adsorbed onto the QD surfaces. 3) Because the disulfides are bound much more weakly on the QD surfaces than the corresponding thiolates, overoxidation of the initially produced disulfides is avoided; the disulfides become unbound from the surface before additional reaction can occur. 4) The simple catalyst, which is generated in situ, can be reused several times with very little loss of activity.

In conclusion, we have established an attractive and clean catalytic approach for the selective oxidative coupling of thiols to give disulfides; the ‘reduction product’ is molecular hydrogen. The protocol does not require sacrificial agents or oxidants and proceeds efficiently under visible light irradiation at room temperature. In fact, some reactions have been conducted successfully by exposing the solutions to sunlight under aerobic conditions. Upon the addition of nickel(II) salts to the system, the efficiency and rate of conversion dramatically improve because the formation of hydrogen atoms is facilitated, thereby leading to faster regeneration of the ground-state QDs. Because of these attributes, this method offers an attractive alternative to existing procedures for synthesizing disulfides from thiols. The mechanistic information obtained, which demonstrates that the CdSe QDs have many active surface sites ready to induce photochemical transformations, will facilitate the exploration and exploitation other potential photocatalytic applications of QDs in the future.

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