

Photocatalytic reduction of aromatic azides to amines using CdS and CdSe nanoparticles†

Manoj Warriar,^a Michael K. F. Lo,^b Harold Monbouquette^{*b} and Miguel A. Garcia-Garibay^{*a}

^a Departments of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095-1569. E-mail: mgg@chem.ucla.edu; Fax: 1 310 825 0767; Tel: 1 310 825 3159

^b Chemical Engineering Department, University of California, Los Angeles, Los Angeles, CA 90095-1592. E-mail: hmonbouq@ucla.edu; Tel: 1 310-825-8946

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We have shown that CdS and CdSe nanoparticles can act as very efficient and highly chemoselective photocatalysts for the reduction of aromatic azides to aromatic amines. In several cases, the reaction proceeds with quantum yields near 0.5, which approaches the theoretical maximum for a two-electron process. The wide scope of the reaction was confirmed with compounds containing electron withdrawing ($-\text{NO}_2$, CO_2R , COR) and electron donating groups ($-\text{OMe}$, $-\text{R}$, $-\text{Cl}$) at the *para*-, *meta*-, and *ortho*-positions. Remarkably, the reaction is relatively insensitive to the electron demands of the substituent. However, azides with *meta*-substituents give slightly lower yields than those with the same substituent at the *ortho*- or *para*-position.

Introduction

Semiconductor nanoparticles, nanocrystals, or quantum dots (Q-dots), belong in a state of matter in transition between discrete supramolecular entities and bulk solid.¹ When particle aggregates are decreased in size to that of their characteristic exciton diameter, they exhibit properties markedly different from those of the bulk.² One of those changes is a shift of the onset of absorption to shorter wavelengths as the particles decrease in size.^{2,3} When semiconductor particles absorb light, electrons are promoted from the valence band of the particle to its conduction band, generating delocalized electron-hole pairs, or excitons. In bulk particles, the gap between valence and conduction bands is very small, and the electrons and holes can recombine efficiently. As the particles shrink beyond the threshold for quantum confinement effects, the band gap increases and the charge separation between the hole and the electron becomes pronounced. A high surface to volume ratio insures that electrons and holes have ready surface access, thereby enhancing their photocatalytic action for efficient oxidation and reduction processes which are not available to bulk material.⁴

There have been many reports addressing various aspects of photoinduced electron transfer involving semiconductor nanoparticles to redox species in solution.^{5,6} Motivations for these studies have ranged from the development of solar cell technologies, to the clean up of organic pollutants from the environment.⁷ However, their potential as electron transfer sensitizers in common organic transformations has been the subject of very few investigations.⁸ In this report, we describe the photocatalyzed reduction of several aryl azides using CdS and CdSe in aqueous solutions (Fig. 1; procedures for azide synthesis and details of their characterization are given in the ESI†). It is shown that reduction occurs in high quantum yields and with complete selectivity towards aniline formation, even for examples where additional products have been observed under homogeneous photoinduced electron transfer and electrochemical methods.

† Electronic supplementary information (ESI) available: The preparation of CdS and CdSe nanoparticles, the synthesis of aromatic azides, procedures for the photocatalyzed reduction of aromatic azides, and procedures for the quantum yield measurements. See <http://www.rsc.org/suppdata/pp/b4/b404268a/>

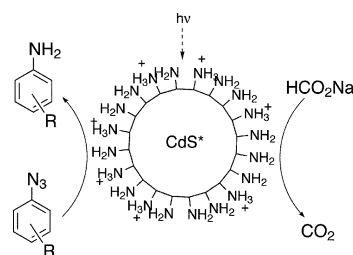


Fig. 1 Simplified model for the reduction of azides to amines using CdS or CdSe as photocatalyst and sodium formate as a sacrificial electron donor.

Results and discussion

Nanoparticle preparation

A pictorial representation of the reaction investigated in this study is shown in Fig. 1. It involves an aqueous solution with an aromatic azide substrate ArN_3 , the nanoparticle (CdS or CdSe) photocatalyst, sodium formate (HCO_2Na), which is sacrificially oxidized, and light of wavelengths that are exclusively absorbed by the nanoparticle. For efficient control of excitation energies, redox properties, and substrate binding, it is necessary to control the size and surface coverage of the nanoparticle. While many techniques to accomplish this have been developed in recent years,⁹ we adopted a simple self-assembly procedure using Na_2S or Na_2Se with CdCl_2 in the presence of a suitable aminothiol as a capping ligand for colloidal stabilization and surface coverage.¹⁰ This procedure provides a reasonably narrow size distribution and control of average particle diameter while allowing for simple changes of surface functionality.¹¹ Nanoparticle preparations with 2-aminoethanethiol hydrochloride, *N,N*-dimethyl-2-aminoethanethiol hydrochloride, and *N,N*-diethyl-2-aminoethanethiol hydrochloride gave rise to pale yellow solutions with absorption and emission spectra characteristic of nanoparticles with average sizes of 2.2 and 2.5 nm for CdS and CdSe, respectively (Fig. 2).^{6,9} Nanoparticles obtained in this manner are estimated to have an average composition of *ca.* $\text{Cd}_{32}\text{S}_{50}$ ^{10b} at a concentration of *ca.* 6×10^{-6} M. Amine terminated thiols were selected with the expectation that the nanoparticle surface would be positively charged at neutral pH and offer a strong binding interaction to the polar azide group (Fig. 1).

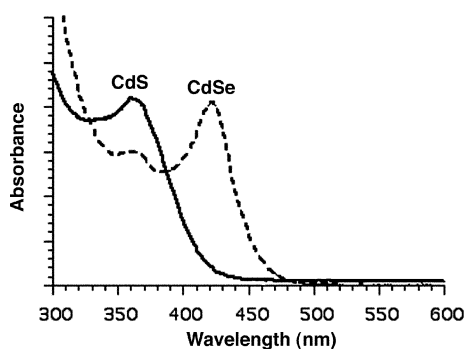
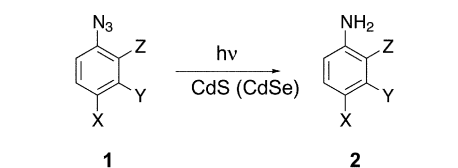


Fig. 2 UV-Vis spectra of CdS and CdSe nanoparticle solutions, illustrating their difference in λ_{max} .

Photocatalysis

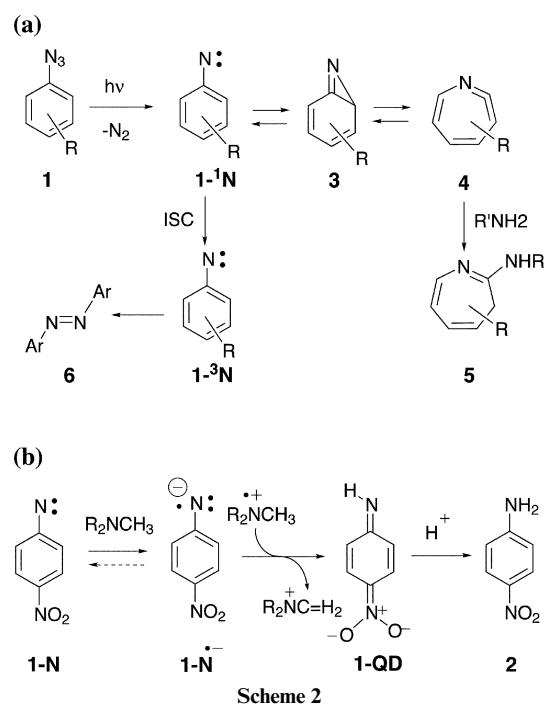
Initial experiments were carried out with solutions containing CdS nanoparticles and *para*-chlorophenyl azide **1i** (Scheme 1) in the presence HCO_2Na . Satisfyingly, photolysis of the reaction mixture with a 1 kW Hg-Xe lamp using a $\lambda \geq 400$ cut-off filter smoothly reduced the azide to the amine in the expected manner. The cut-off filter was used to prevent direct excitation of the aryl azide, which is known to result in the formation of highly reactive singlet aryl nitrenes by photodissociative elimination of a nitrogen molecule [Scheme 2(a)].¹² The chemistry of photogenerated aryl-substituted nitrenes is very rich and depends strongly on the reaction conditions.¹³ Steady-state irradiation and flash photolysis experiments in solution at ambient temperature indicate that singlet aryl nitrenes (**1-¹N**) reversibly rearrange to benzazirines **3** and keteneimines **4**. Reactions carried out in the presence of amines trap the latter to give 2-amino-3H-azepines **5** as the main photoproduct.^{14,15} In inert solvents, the nitrenes can reach the triplet state to give high yields of azobenzene derivatives **6**. The formation of amines **2** in the presence of electron-rich amines in solution at ambient temperature has also been observed.¹⁴ The reaction was suggested to occur by single electron transfer from the electron-rich amine to form the nitrene radical anion **1-N⁻**, which is followed by sequential H-atom and proton transfers to form quinodiiimine **1-QD** and aniline **2** as indicated in Scheme 2(b).¹⁶ In general, the relative yields of **2**, **5**, **6** and other products depend on the nature of the aryl azide and the reaction conditions, usually giving complex mixtures.^{13,14,16}



Azide ^a	X	Y	Z	$\lambda_{\text{tail}}/\text{nm}^b$
1a	NO_2	H	H	450
1b	H	NO_2	H	420
1c	H	H	NO_2	420
1d	CO_2H	H	H	350
1e	H	CO_2H	H	380
1f	COMe	H	H	380
1g	H	OMe	H	450
1h	OMe	H	H	400
1i	Cl	H	H	390
1j	$(\text{CH}_2)_2\text{OH}$	H	H	450
1k	MeO	NO_2	H	380
1l	MeO	CO_2Me	H	410

^a All the aromatic azides used in the study were prepared by diazotization of commercially available aromatic amines with sodium nitrite/HCl followed by addition of sodium azide. ^b Onset of absorption spectrum (long-wavelength tail).

Scheme 1



To ensure that nanoparticles are required for the observed transformation we carried out several control experiments. First we left the reactants in a test-tube with no light exposure and found no dark reactions. Second, we showed that no photoreduction occurs in the absence of nanoparticles if filters are used to block light at wavelengths absorbed by the azides. However, we discovered that direct excitation of **1i** (and other aromatic azides) with $\lambda \geq 290$ nm (Pyrex glass) in the presence of sodium formate and a large excess of 2-aminothiol does indeed lead to formation of the amine. This result suggests that the (presumably triplet) nitrene is capable of reacting with the electron-rich aminothiol groups¹⁷ under the conditions of the experiment, perhaps by a mechanism similar to that in Scheme 2(b). This observation emphasizes the importance of avoiding direct excitation of the azide while quantifying the efficiency of nanoparticle-photocatalyzed photoreduction.

Scope of the photocatalytic reaction

Once the photocatalytic nature of the reaction had been demonstrated with *para*-chlorophenyl azide **1i** under conditions where the CdS nanoparticles were the only light absorbers, we selected a test set of aromatic azides possessing a relatively wide variety of functional groups (Scheme 1). Compounds with electron-withdrawing ($-\text{NO}_2$, $-\text{COOH}$, $-\text{COCH}_3$, $-\text{Cl}$) or electron-donating ($-\text{OCH}_3$, $-\text{CH}_2\text{CH}_2\text{OH}$) substituents were analyzed along with a few compounds possessing two of these groups (**1k**, **1l**). The effect of functional groups at positions *ortho*, *meta* or *para* to the azide were also investigated. We hoped that these substituents would help us to determine the scope of the reaction in terms of: (a) the selectivity for azide reduction in the presence of other functional groups, and, (b) the effect of other functional groups on the photocatalytic efficiency of azide reduction. In addition, we hoped to find possible correlations involving the redox properties of the azide group and/or potential differences in binding of the azide to the nanoparticle surface.

Having exposed the importance of selective nanoparticle excitation to quantify the effects substituents on the efficiency of the reaction, we documented the UV-Vis spectra of all the azides in Scheme 2. It was shown that several azides have absorption spectra with a strong overlap, and sometimes even a longer absorption wavelength than that of CdS. An example is shown in Fig. 3 where the absorption spectrum of 4-methoxy-3-

Table 1 Percentage conversions of phenyl azide to phenyl amine when photolyzed for 15 min in the presence of nanoparticles^a

Azide	With CdS ^c	With CdSe ^d
1a	— ^f	33 ^e
1b	— ^f	3 ^e
1c	12	13
1d	15	13
1e	6	4
1f	7	15
1g	— ^f	— ^f
1h	12	12
1i	8	6
1j	15	10
1k	— ^f	3 ^e
1l	11	12

^a Reaction mixtures were photolyzed for 15 min. Reported conversions are an average of 3 independent runs. Estimated error limits are $\pm 2\%$. The ratio of the catalyst (nanoparticle) to the substrate (aromatic azide) is *ca.* 1 : 1000. ^b The percentage conversions were computed by NMR analysis. ^c Photolyses carried out at a $\lambda \geq 360$ nm. ^d Photolyses carried out at a $\lambda \geq 400$ nm. ^e Photolyses carried out at a $\lambda \geq 420$ nm. ^f Reactions were not carried out due to overlap in absorption spectra of the nanoparticles and the aromatic azide.

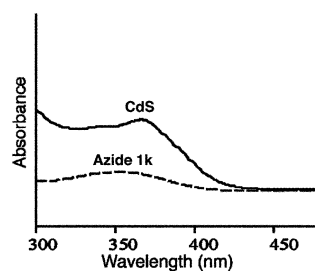


Fig. 3 Comparison of the UV-Vis spectra of a CdS nanoparticle solution and azide **1k**.

nitro-phenylazide **1k** is overlaid with that of CdS. With very similar absorption maxima ($\lambda_{\max} \approx 350$ nm) and tails that extend up to ≈ 450 nm, it would be essentially impossible to prevent absorption by the azide while exciting the nanoparticle. Fortunately, a solution to this problem should be possible by using CdSe nanoparticles as they have an absorption maximum significantly red-shifted ($\lambda_{\max} \approx 425$ nm), and an absorption tail that extends up to ≈ 500 nm (Fig. 1). Thus, spectral overlap permitting, we analyzed the photocatalytic reduction of each phenyl azide with both CdS and CdSe particles. Depending on the long-wavelength tail of azide absorption, filters were used with cut-offs at 360, 400 or 420 nm. Parallel photolysis experiments were carried out with solutions lacking the nanoparticles to ensure the absence of product formation by direct azide photolysis. Table 1 shows the percentage conversion of azides to their corresponding amines under standard conditions that included 15 min irradiation at 298 K. With solutions that are 6×10^{-6} M in nanoparticle and 3.7×10^{-3} M azide and mean conversion values of 15%, we can estimate turn over numbers ≥ 100 . Notably, the results with CdS and CdSe were qualitatively consistent with each other when comparisons could be made using the same azide. Given that they share the same surface groups, binding interactions should be identical for both nanoparticle types towards any given azide, thus revealing very similar redox activities. The high chemoselectivity of the photocatalyzed reaction stands out from the results in Table 1. While the reduction of $-\text{NO}_2$, and $-\text{Cl}$ aromatics has been previously reported,¹⁸ only the azide group of **1a–1l** is reduced under the conditions of our experiments.

Quantum yields of the photocatalyzed reductions

The high chemoselectivity for azide reduction is strongly suggestive of a high reaction quantum yield as compared to

Table 2 Quantum yields for photocatalytic reduction of aromatic azides with CdSe nanoparticles

Azide used	Quantum yield ^a
1d	0.60
1e	0.17
1h	0.56
1i	0.18
1j	0.51

^a The photolyses were done using a 400 nm filter. Reported quantum yield numbers are an average of 5 independent runs. Estimated errors are *ca.* 20%.

those for reaction of other functional groups. In order to test this hypothesis, we measured the quantum yields of the reaction using Reinecke's salt actinometry.¹⁹ We selected Reinecke's salt as an actinometer based on its ideal spectral absorption window, essentially constant quantum yield values, and what turned out to be a suitably high quantum yield of the actinometric reaction ($\Phi = 0.31$) to match the quantum yields of the photocatalytic reductions studied here.²⁰ Representative examples of the photocatalytic reduction quantum yields with CdSe nanoparticles are shown in Table 2.

An approximate correlation between the chemical yields in Table 1 and the quantum yields in Table 2 suggests that meaningful comparisons can be made between sets of values within either table. Across the board, the quantum yields for azide reduction are remarkably high, and very close to the maximum of $\Phi_{\max} = 0.5$ expected for a reaction involving a two electron, two photon reduction. In general, the *para*-substituted azides show higher yields as compared to those with *meta*-substituents. Irrespective of the quantum yield, the reaction is still very selective for the azide reduction, as required for a mild method to reduce the azide group in the presence of a wide range of functionalities.

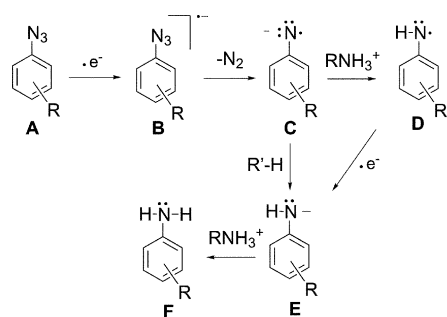
Effect of azide substituents on reaction efficiencies

It is rather surprising that chemical and quantum yields do not depend strongly on the electron withdrawing or electron donating nature of the functional groups in the aromatic ring.²¹ For example, while **1d** has an electron withdrawing *para*-carboxylic acid ($-\text{COOH}$), **1h** and **1j** have *para*-donating methoxy and hydroxyalkyl groups ($-\text{OCH}_3$, $-\text{CH}_2\text{CH}_2\text{OH}$). However, all three compounds have high chemical and quantum yields with CdSe. Substitution at the *meta*-position with respect to the azide group reduces the quantum and chemical yields, but not dramatically. This is illustrated by substrates **1b** and **1e** with *meta*- NO_2 and *meta*- COOH groups, respectively. While the chemical yield of **1b** is about one tenth as large as that of **1a** (Table 1), the quantum yield of **1e** is about a third as large as that of **1d**, its *para*- COOH isomer. The effect of *ortho* substitution in the case of nitro compound (**1c**) is to bring the reaction efficiency close to that of the *para*-isomer. Most substrates with two substituents had their UV-Vis spectra so strongly shifted to the red that direct irradiation could not be avoided. In general, these results suggest that *ortho* and *para* substituents on the phenyl azide ring favor photocatalysis while *meta* substitution appears to reduce the reaction efficiency.

Reaction mechanism

The efficiency of the photocatalytic process depends on the cumulative effect of several sequential steps. First of all, the substrate should be at the nanoparticle surface within the lifetime of the charge-separated excited state. It is well known that end-chain substituents on chemisorbed thiols can influence the surface character, which in turn impacts properties vital to photocatalytic applications, such as excitation lifetimes,²² surface charge and ionicity,²³ particle solubility²⁴ and flat-band

redox potentials.²⁵ Surface groups also affect the surface concentration of reactant molecules by adsorption effects. It is known that reactant and product concentrations on the nanoparticle surface greatly affect the rate of electron transfer, and therefore the photocatalytic efficiency.²⁶ A high quantum efficiency in the presence of a relatively broad range of functional groups suggests generally favorable binding interactions. Electron transfer from the nanoparticle to the azide to generate an azide radical anion **B** (Scheme 3) must be faster than electron-hole recombination, which is known to occur within ≈ 40 ps for 20 Å particles.²⁷ Fast electron transfer is an indication of a suitable thermodynamic driving force. Unfortunately, literature information regarding the reduction potential of azides appears to be extremely limited.²⁸ A one-electron reduction potential of -0.23 V vs. CdCl₂/Cd(Hg) [-0.59 V vs. NHE] in CH₃CN for *p*-NO₂-phenylazide was reported in 1990 by Herbranson and Hawly.²⁹ Another hint of facile reduction can be found from a later study by Moutet *et al.*, who reported the reduction of wide range of alkyl azides with a weakly negative electrode potential [$E_{\text{red}} = 0.5$ V vs. SCE (0.26 vs. NHE)] using Pt and Pd microparticles dispersed in poly(pyrrole) films electrodeposited on carbon felt electrodes.³⁰ Given that the potential of photoexcited electrons in ≈ 20 Å CdS particles has been estimated to be ≈ -1.7 V vs. NHE,⁶ it is not surprising that reduction occurs with high efficiency for all the aryl azides in Table 1. Regarding the fate of the postulated azide radical anion **B**, one may speculate whether it may be rapidly protonated, abstract a hydrogen atom from surface groups, or accept a second electron to give a doubly charged species. However, a rapid loss of a N₂ to generate a nitrene radical anion (**C**) is more likely.²⁹ Nitrene radical anion **C** may subsequently be protonated to give an aminyl radical (**D**) or abstract a hydrogen to form the amide anion **E**. Given that quantum yields suggest a two electron transfer process and the high proton density on the particle surface, the sequential formation of **C**, **D** and **E** appears more likely. As the two electrons are transferred from the nanoparticle to the substrate, the holes left behind must be filled by electrons from a sacrificial donor that is oxidized in this process, thus preventing the nanoparticles from getting corroded. Although the results in Tables 1 and 2 were obtained with sodium formate as sacrificial electron donor, one may speculate that other species present in the reaction mixture may also serve as a sacrificial reductants.³¹ Test reactions carried out in the absence of sodium formate proceeded very sluggishly, suggesting the need for a good reducing agent.



Scheme 3

Conclusions

The results reported in this article indicate that semiconductor nanoparticles may be used as photocatalysts for the reduction of aromatic azides to aromatic amines in very clean, and potentially synthetically useful transformations. The reaction occurs under mild conditions at neutral pH, at room temperature, and the product amine can be easily separated from the reaction mixture after photolysis. A great advantage of this reaction is the high chemoselectivity for azide reduction in the presence of several other functional groups on the aromatic ring. An

interesting observation comes from the modest effect of different functional groups on photocatalytic efficiency. Similarly, the position of the functional group affects the reaction rather modestly. Further studies with different reaction types will be required to establish the potential of this method for synthetic transformations involving other types of azides and other types of reactions.

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