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COMMUNICATIONS

Photochemical Size Reduction of CdSe and CdSe/ZnS Semiconductor Nanoparticles Assisted by $n\pi^*$ Aromatic Ketones

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Semiconductor nanoparticles, such as CdSe quantum dots (QDs) have been used for cellular imaging, light-emitting diodes, and more recently for solar cells applications, owing to their unique optical properties and tunable band edge.[1] In addition, it has been previously reported that benzophenone (BP, Chart 1) acts as a capping ligands of CdSe nanoparticles.[2]

In the present communication, we report a novel role of $n\pi^*$ aromatic ketones with respect to core and core−shell QDs in order to induce their size reduction upon UV−visible light irradiation, preserving their luminescence and crystalline quality. By controlling some experimental conditions such as time of irradiation, presence of air in the media, hydrogen donor capacity of the solvent, irradiation wavelength, and nature of the aromatic ketone lowest triplet excited state, we can resize as convenient core and core−shell CdSe QDs.

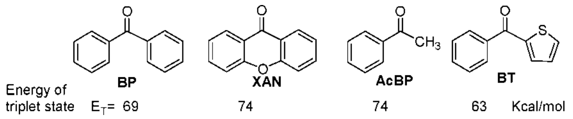
Core CdSe QDs of two different sizes, capped with trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) as ligands, were synthesized following the methodology reported by Peng et al.[3] Their absorption and emission properties are reported in Table S1 in the Supporting Information. The peak absorption wavelength and the emission peak width (full width at half-maximum, fwhm) were used to estimate QDs diameter and polidispersity, respectively.[4] To extend these studies to other nanoparticles, commercial core shell quantum dots (CS QDs) with two different sizes were purchased from Evidenttech.[5]

Addition of increasing BP concentrations to aerated toluene solutions of the QD practically did not affect their absorption spectrum at $\lambda > 400$ nm. By contrast, an important hypsochromic shift was observed upon irradiation with a 355 nm laser (Nd:YAG). For CS QD-2, the first exciton absorption peak shifted 3 and 10 nm after 1 and 5 min irradiation, respectively. Especially noteworthy was the advance of the process in the dark. So, a global 25 nm shift was measured for CS QD-2 after 5 min irradiation and 24 h dark storage (Figure 1). In accordance, the QD fluorescence emission showed a blue shift (581−565 nm), going from an orange to a green fluorescence as can be observed in the inset of Figure 1.

The influence of the air on this process was evaluated. A large shift of the absorption peak (61 nm) was registered after 30 min irradiation (355 nm laser pulses) of an aerated toluene solution of QD-1 in the presence of BP (Figure S1), compared with the 10 nm shift in anaerobic conditions (Figure S2).

The effect of the irradiation wavelength was analyzed using different irradiation sources (355 and 532 nm laser pulses, UVA, and visible illumination). Data of the absorption peak for irradiated (1 min) aerated toluene solutions of QD-1 in the presence of BP are summarized in Table S2. The results revealed the involvement of the BP in the process, since the absorption blue shift was only detected when irradiating at wavelengths where BP absorbs. In fact, selective excitation of the QD at 532 nm did not produce any change on the first exciton peak. Table 1 summarizes the data for all the QDs upon irradiation with UVA lamps, measured immediately after the exposure and 24 h later.

Chart 1. Aromatic Ketones Used in This Work



It is well-known the high efficiency of $n\pi^*$ aromatic ketones to abstract hydrogen efficiently from good hydrogen donors, such as toluene, leading to ketyl radicals.[6] By contrast, $\pi\pi^*$ aromatic ketones have low capacity for direct hydrogen abstraction.[7] Therefore, the influence on the process of the nature of aromatic ketone lowest triplet state was analyzed using benzophenone, (BP, $n\pi^*$), xanthone (XAN, $n\pi^*$ no polar solvents), acetophenone (AcBP, $n\pi^*$ no polar solvents), and 2-benzoylthiophene (BT, $\pi\pi^*$), see Chart 1. XAN and AcBP induced the reaction though with lower efficiency than BP. So, after 1 min irradiation (UVA lamp) of aerated toluene solutions of QD-1

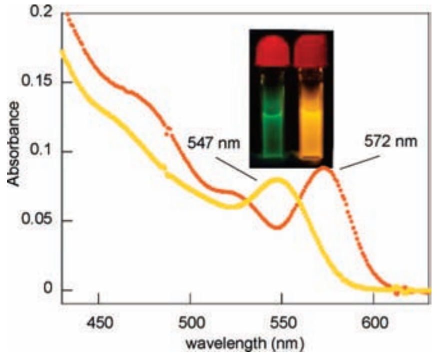


Figure 1. UV−visible spectra of aerated toluene solutions of CS QD-2 (0.7 μM) in the presence of BP (18 mM), before (orange) and after 5 min of irradiation with 355 nm laser pulses, recorded after 24 h dark storage (yellow). Inset: pictures illustrate the corresponding fluorescence of theses samples.

Table 1. **Blue Shift of the First Exciton Pick ($\Delta\lambda$) for Core and Core-Shell QDs upon Irradiation with an UVA Lamps[a]**

	$\Delta\lambda$ (nm)	
QDs	1 min irrad.	24 h dark storage
QD-1[b]	28	72
QD-2[b]	9	40
CS QD-1[c]	0	20
CS QD-2[c]	11	34

[a] Conditions: aerated toluene solutions. [b] Concentrations: QD (2 μM) and BP (18 mM). [c] Concentrations: QD (0.5 μM) and BP (9 mM).

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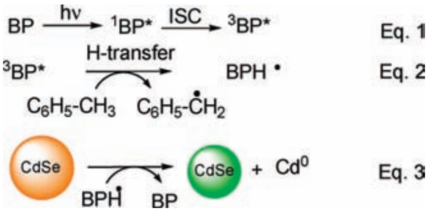
Scheme 1. Plausible Mechanism for the BP-Photosensitized Size Reduction of the Nanoparticles



in the presence of XAN and AcBP, 11 nm (XAN) and 1 nm (AcBP) blue shifts were registered, compared with 28 nm for BP. However, no changes were detected when using a $\pi\pi^*$ aromatic ketone such as BT. The low efficiency of AcBP can be attributed to the well-known isoenergetic lowest n,π^* and $\pi\pi^*$ triplet states.[8] These data demonstrated the dependence of the reaction on the nature of the ketone lowest triplet state and the plausible involvement of the ketyl radicals in the observed changes.

Later on, reactions were carried out in dichoromethane (DCM), a poor hydrogen-donor solvent. A 5 nm blue shift of the exciton peak was measured upon 1 min irradiation (355 laser pulses) of aerated dichloromethane solutions of QD-1 in the presence of BP, compared with an 11 nm shift in toluene. Transient absorption experiments (not shown) indicated that no ketyl radicals were formed upon irradiation of deaerated solutions of BP in dichoromethane, but they were detected in the presence of increasing amounts of TOPO. It must be taken into account that the nanoparticles possess organic capping ligands (TOPO for core QDs or long chain amine for CS QDs), which could act as hydrogen donors to produce the ketyl radicals needed for the process.

The reduction of Ag(I) and Au(III) by ketyl radicals has been recently reported to play a key role in the synthesis of Ag and Au nanoparticles[9–11] and Ag, Au, and Cu crystallites.[12] Therefore, a plausible mechanism for the QD size reduction could be attributed to electron transfer processes between the benzophenone ketyl radical ($E_{ox} = -0.25$ V vs SCE in acetonitrile)[13] and the Cd^{2+} ($E_{red} = -0.41$ V),[14] see Scheme 1.

The formation of light absorbing transients (LATs) arising from ketyl radicals coupling upon UV irradiation of BP in the presence of a good hydrogen donor has been reported.[15] These transients were detected after irradiation of anaerobic toluene solutions of QDs in the presence of BP (Figure S3, the UV-absorption in the range 300−350 nm increased and the band maximum shifted from 340 to 318 nm). However, the involvement of LATs in the change of QDs optical properties can be ruled out; indeed, the nanoparticle size reduction was accelerated in the presence of air, where LATs formation is quenched.

All these results are consistent with BP-photoinduced QD size reduction as confirmed by high resolution transmission electronic microscopy (HRTEM). For example, an aerated toluene solution of QD-2 was irradiated (355 nm laser pulses) in the presence of BP for 10 min, and the new QDs were precipitated by the addition of methanol and washed several times with methanol (see UV−visible spectra in Figure S4). The HRTEM images support the reduction of the nanoparticle diameter from 3.5 to 3 nm as well as their crystallinity (Figure S5). In addition, the ^{1}H NMR spectrum of the isolated nanoparticles did not show the presence of BP or ketyl coupling products.[16]

Interestingly, the nanoparticles were photostable when irradiated in the above-mentioned conditions but in the absence of BP. Moreover, they showed a remarkable stability in solution for a couple of months.

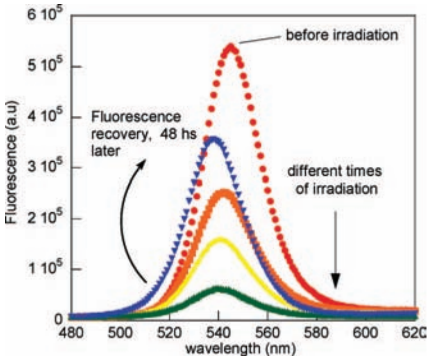


Figure 2. Fluorescence spectra of aerated DCM solutions of QD-1 (2.2 μM) in the presence of BP (18 mM), before irradiation (red) and after 1 (orange), 2 (yellow), and 4 min (green) laser (355 nm) exposure. The emission spectrum of the last sample was recorded after 24 h dark storage (blue).

The fluorescence time evolution of the irradiated nanoparticles was also followed. Strikingly, though a remarkable quenching of the emission was detected immediately after laser (355 nm) illumination, the fluorescence was slowly recovered after dark storage (see Figure 2 for QD-1). A total recovery was measured when the sample was irradiated during a short time (30 s) and the QD emission was registered after 48 h dark storage (Figure S6). Consequently, it was possible to transform homemade and commercial QDs into smaller nanoparticles preserving their luminescent properties.

In summary, we report an easy and reproducible resize of core and core−shell QDs promoted by nπ^* aromatic ketones. Among others, one advantage of the reported procedure is to allow the preparation of different size nanoparticles using batches from the same QD preparation, by controlling the irradiation time, the hydrogen donor capacity of the solvent, and the presence of oxygen. New applications for QDs are based in suitable methods for the preparation of monodisperse and size-controlled nanoparticles.

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Supporting Information Available: Additional UV−visible, emission spectra, and HRTEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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