Visible Light Induced Photocatalytic Activity of TiO_2 Nanowires Photosensitized with CdSe Quantum Dots

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Abstract

In this study the photocatalytic efficiency of CdSe quantum dot photosensitized TiO_2 nanowires (~50 nm diameter) was examined under visible light irradiation. The sensitizer CdSe nanocrystals featured 3.1, 4.0, 4.6 and 6.0 nm mean diameter and a wurtzite crystal structure. The co-sensitization of the nanowires using the smallest and the largest nanocrystals was also investigated and these co-sensitized nanowires performed in almost the full visible-range spectrum. To attach the quantum dots onto the TiO_2 surface, either a direct deposition method from toluene solution or an indirect linker molecule-assisted method with thioglycolic acid were applied. The photosensitized nanowires showed appreciable activity in a model photocatalytic test reaction. The best result was 71% decrease of the initial methyl orange concentration with the co-sensitized nanowires after 6 hours of visible light irradiation with a relatively low, 40 W output performance light source.

Keywords: CdSe, quantum dot, TiO_2, nanowires, photosensitization, photodegradation

Introduction

The removal of non-biodegradable organic pollutants from contaminated media is a crucial environmental problem today. Semiconductor photocatalysts are extensively studied as potential solutions [1]. TiO_2 is a widely used and efficient photocatalyst for the degradation of organic chemicals under UV-light irradiation. It is a relatively low cost, environmentally friendly material with high oxidative power and stability. Its one drawback is the relatively high band gap (3.2 eV for anatase TiO_2), which renders the decomposition of organic compounds effective only under UV irradiance (wavelength shorter than 387.5 nm). The proportion of UV radiation in sunlight is only 3-4%, therefore, it is important to improve the pollutant degradation capacity of TiO_2 under visible light. This can be achieved by using sensitizer materials to improve the generation of excitons under visible light or by hindering the recombination of the photoinduced electrons and holes.

Major efforts were made to photosensitize TiO_2 structures with e.g. organic dyes [2, 3, 4] or with different nanocrystals as inorganic dyes. Narrow band gap semiconductors such as quantum dots (QDs) are good alternatives to organic dyes because of their unique optical and electronic properties. Quantum dots are fluorescent semiconductor nanocrystals. Their absorption and emission wavelengths can be tuned by controlling their elemental composition and particle size. Their most attractive benefit is that they can be used to tune the light absorption properties of a wide band-gap semiconductor. TiO_2 structures photosensitized by QDs are promising materials in third generation solar cells [5, 6] as well as in visible light photocatalysis [7, 8, 9, 10]. Semiconductor QDs and nanocrystals that have been studied recently as sensitizers of different TiO_2 structures are CdS [11, 12, 13, 14], CdSe [15,16], CdTe [17], PbS [18], InP [19] and InAs [20].

Ever since the first reports on one-dimensional TiO_2 nanostructures (TiO_2 nanotubes) were published [21, 22], they received considerable attention because of their potential applications. One-dimensional TiO_2 structures (nanotubes and nanowires) have been shown to be more effective light harvesters than TiO_2 nanoparticles in photovoltaic applications because of the more efficient transport of the charge carriers [23, 6, 24, 25]. Therefore, it is important to study the photosensitization of this kind of nanostructures with quantum dots of different types and sizes.

Co-sensitization means using two different types (or sizes) of sensitizers with complementary absorption properties to cover a broader part of the solar spectrum. TiO_2 had been co-sensitized with organic dyes [26, 27] or in K. Prabakar's work [28] with different sized CdSe QDs and N719 dye. They observed that the 3.3 nm CdSe and the 6.3 nm CdSe QDs had the highest power conversion efficiency (3.65 and 3.52 %), whereas TiO_2 nanotubes (NTs) sensitized with six different sized QDs exhibited lower efficiency (3.1%). W. Lee et al. co-sensitized TiO_2 nanotubes with two different sized CdSe nanocrystals to absorb in a broad spectral range in the visible region [29]. In Lee's work the co-sensitization of nanotubes was carried out with ~2.6 and ~3.0 nm CdSe nanocrystals and the co-sensitized NTs showed higher power conversion efficiency (1.20%) than the NTs with individual CdSe nanocrystals (0.91% for 2.6 and 0.86% for 3.0 nm CdSe).

Several methods were suggested to anchor sensitizer nanocrystals onto the TiO_2 surface. In most cases bifunctional linker molecules were used to facilitate the attachment of hydrophobic QDs to the hydrophilic surface of TiO_2. It was observed that the chemical nature of the linker molecules plays an important role [5] and the chain length of the molecules is also very important, because with increasing chain lengths the electron injection efficiency decreases dramatically [30]. Guijarro and co-workers [31] studied the IPCE (incident photon-to-current efficiency) and QD coverage on comparing the direct and linker molecule mediated adsorption methods with CdSe QDs. They observed that the direct contact between the QDs and the oxide nanoparticle is beneficial for the efficiency of the photoanode, but a high QD coverage leads to a drop in the IPCE which was attributed to QD aggregation. In contrast, in the case of MPA (mercaptopropionic acid) mediated attachment they found that the IPCE monotonously increases with coverage.

Most of the available studies on CdSe sensitized TiO_2 structures discuss solar cell applications. In this contribution we focus on the utilization of QD-sensitized TiO_2 nanowires as potential environmental photocatalysts working with visible illumination.

Experimental

Chemicals: CdO (99.5%, Sigma-Aldrich), Se (99.99%, Sigma-Aldrich), trioctylphosphine (TOP) (90%, Sigma-Aldrich), oleic acid (90% Sigma-Aldrich), oleylamine (70%, Sigma-Aldrich), octadecene (ODE) (90%, Sigma-Aldrich), thioglycolic acid (TGA) (98%, Sigma-Aldrich), acetonitrile (99%, Reanal), anatase TiO_2 powder (99,8%, Sigma-Aldrich), sodium hydroxide (99,5%, Molar Chemicals Kft.). All chemicals were used as received.

Synthesis of CdSe nanocrystals with 3.1 nm and 4.0 nm diameter: CdSe QDs were synthesized by the standard one-pot method under inert atmosphere. The Cd stock solution was prepared by dissolving 0.5 mmol CdO in 1 mL oleic acid and 15 mL ODE in the presence of 0.2 mL oleylamine. The Se stock solution was prepared by dissolving 1 mmol Se in 1.5 mL TOP and 1.5 mL oleylamine. The reaction mixture was heated up to 245 °C before the Se stock solution was injected. The nanocrystal growth temperature was set to 225 °C. Samples were taken after 30 and 90 s and injected into cold hexane to terminate the growth of nanocrystals. QDs samples were purified by repeated extraction with hexane and precipitation with 1:1 methanol and acetone while centrifuging at 3200 rpm for 15 minutes. The nanocrystals were finally dispersed in toluene for further characterization.

Synthesis of CdSe nanocrystals with 4.6 nm and 6.0 nm diameter: The red-emitting larger sized nanocrystals were synthesized by the „reverse injection” method based on a previous work [32] with slightly different stock solution compositions. The Se stock solution contained 0.6 mmol Se dissolved in 1 mL TOP with 10 mL oleylamine. The Cd stock solution was made by dissolving 0.8 mmol CdO in 1 mL TOP with 1 mL ODE. This solution was injected into the Se stock solution at 300 °C. The synthesized quantum dots featured 4.6 and 6.0 nm diameter after 1 minute and 10 minutes of reaction time, respectively.

Synthesis of TiO_2 nanowires with anatase crystal structure: The synthesis of TiO_2 nanowires (NWs) was based on the hydrothermal method described by Horváth et al. [33]. In a typical synthesis, 50 g anatase TiO_2 powder was placed into an autoclave with 1 L 10 M NaOH solution. The autoclave was kept at 185 °C for 24 h while it was rotated around its short axis at 28 rpm. Once the autoclave was cooled down to room temperature, the obtained $Na_2Ti_3O_7$ nanowires were washed with dilute aqueous HCl solution and distilled water. Finally, the nanowires were filtered on a glass filter and annealed at 600 °C for 12 h to convert the trititanate structure into anatase.

Anchoring CdSe QDs onto the surface of the nanowires: Two methods were used to anchor QDs to the surface of the NWs. Nanocrystals were either adsorbed directly on the TiO_2 NWs surface from toluene solution (direct method), or they were attached to the surface by the bifunctional linker molecule thyoglicolic acid (indirect method).

In direct QDs adsorption, 180 mg NWs were placed for 8 hours in the toluene solution of QDs with CdSe:TiO_2 weight ratio of about 1:20. Concentration estimations of the QD solutions were based on Yu et al.’s work. [34]. After 8 hours of stirring the CdSe decorated TiO_2 nanowires were filtered on a membrane filter with 0.45 μm pore size and washed extensively with toluene.

In TGA-mediated adsorption the NWs were treated in 1 M TGA acetonitrile solution for 24 h, then filtered and washed with acetonitrile and toluene. 180 mg of this TGA functionalized NWs were mixed for 48 h with CdSe QDs suspensions while stirring intensively. The functionalized nanowires were then filtered on a membrane filter and washed with toluene.

Sample Characterization: Transmission Electron Microscopy (TEM) performed on Philips CM10 and FEI Tecnai G^2 F20 X-Twin microscopes was used for nanoparticle size measurements. UV-VIS spectra were recorded using an Ocean Optics USB4000 spectrometer with a DH-2000-BAL UV-Vis-NIR light source. The photoluminescence measurements were performed on a Hitachi F-2000 spectrofluorometer utilizing 390 nm excitation wavelength. The crystal structure of the synthesized QDs was analyzed by X-ray Diffraction (XRD) on a Rigaku MiniFlex II system operating with Cu Kα radiation. The composition of the nanocrystals was characterized by Energy Dispersive X-ray Spectroscopy (EDX) on a Hitachi S-4700 Cold Field Emission Scanning Electron Microscope (SEM) system. Brunauer-Emmett-Teller (BET) specific surface area measurements were performed on a Quantachrome NOVA 3000e surface area & pore size analyzer.

Photocatalytic model reaction: In the methyl orange (MO) degradation reaction 10 mg of photosensitized NWs were sonicated for 30 min in the dark with 10 mL MO solution of 9.6 mg/L concentration. The MO-nanowire suspensions were then irradiated by visible light for 3 and 6 hours under vigorous stirring by placing a 40 W Hg-vapour quartz UV-lamp (Medicor Ltd.) with a 400 nm cut-off filter 12 cm above the reaction vessel. After centrifugation for 15 minutes at 3200 rpm the UV-Vis absorbance spectrum of supernatant was recorded and the concentration of the remaining MO was calculated from the absorbance value of the spectrum at $\lambda = 462$ nm.

Results and discussion

CdSe QDs of four different mean diameters were synthesized by the two methods described above. The smaller ones featured 3.1 nm mean diameter and 10% standard deviation after 30 s reaction time, while after 1.5 minutes, nanocrystals with 4.0 nm mean diameter and 10% standard deviation were obtained. The „reverse injection” method yielded nanocrystals of 4.6 nm mean diameter with 7% standard deviation after 1 minute of crystal growth and particles measuring 6.0 nm mean diameter with 10% standard deviation after 10 minutes. All four nanocrystal types exhibited similar size and shape with spherical morphology. TEM images of the four samples with the corresponding diameter distribution histograms are presented in **Fig. 1.**.

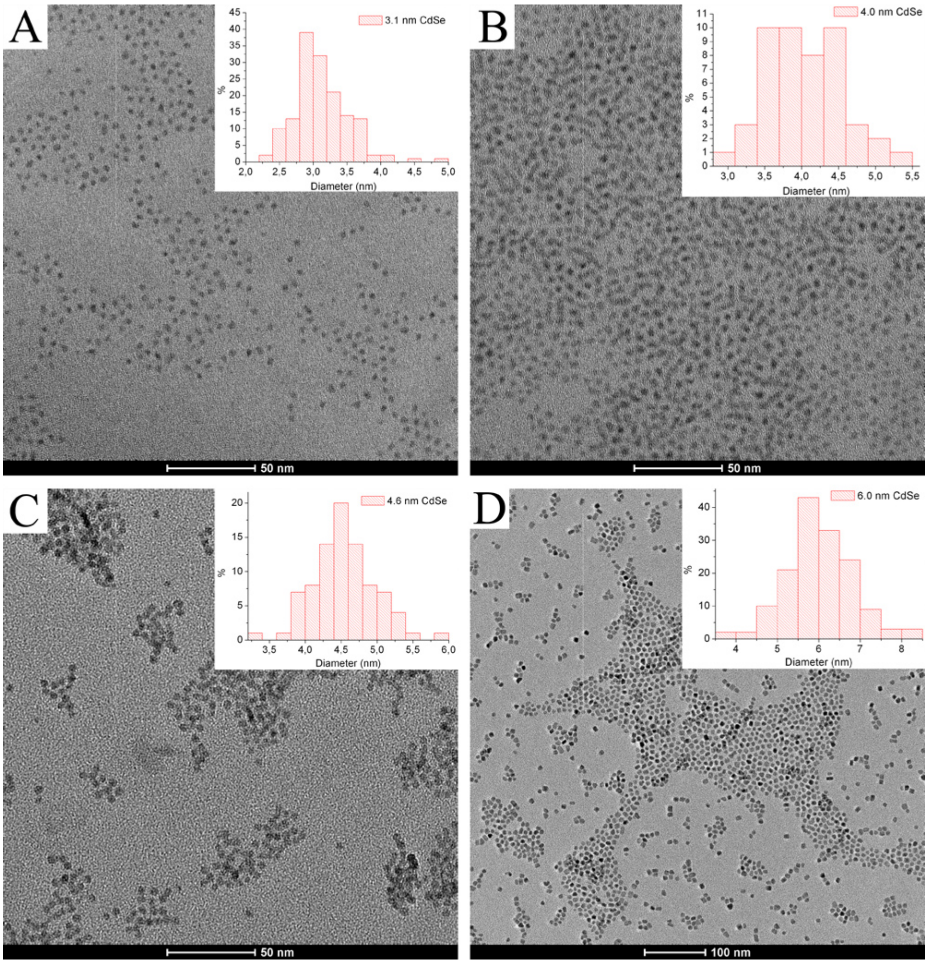

Figure 1. Transmission electron microscopy images of the CdSe QDs samples. (A) 3.1 nm, (B) 4.0 nm, (C) 4.6 nm and (D) 6.0 nm mean diameter. The insets show the corresponding particle diameter distribution histograms as calculated by TEM image analysis.

The XRD patterns of the nanocrystals are shown in **Fig 2. (A)** with bulk wurtzite CdSe reflections marked at the bottom of the graph for reference. The nanocrystals had a uniform hexagonal wurtzite crystal structure. With increasing crystal size the intensity of the diffraction peaks increased gradually. In the 6.0 nm diameter QD sample even the peak at 2θ = 45.8° (associated with the (103) lattice plane) is identifiable because of the improved crystallinity of these larger nanocrystals.

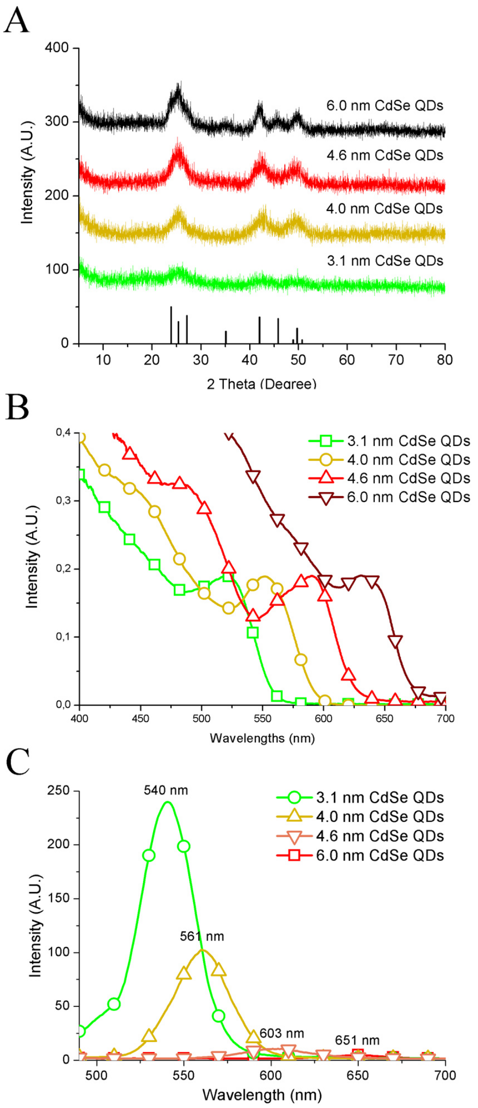

Figure 2. XRD patterns (A), UV-Vis absorption spectra (B) and photoluminescence spectra (C) of CdSe QDs. The characteristic reflections of buld wurtzite CdSe are denoted by line markers in figure (A) for reference.

The absorption spectra of the QDs are presented in **Fig. 2. (B).** The absorption peaks are in the visible range and they exhibit the typical size quantizitation effects of QDs, namely, they shift towards longer wavelengths with increasing particle size. The values of the first absorption excitonic peaks with increasing diameter were 520, 551, 590 and 632 nm.

Photoluminescence spectra of the QDs are depicted in **Fig. 2. (C).** Emission maxima shift towards higher wavelengths and gradually lose intensity with increasing particle size. The PL peak maxima for the 3.1, 4.0, 4.6 and 6.0 nm QDs are found at 540, 561, 603 and 651 nm, respectively. QDs with 6.0 nm size had the weakest PL intensity at 651 nm as demonstrated by **Fig. 2. (C).** These nanocrystals have a quantum yield below 2 percent, which could be attributed to the weak quantum confinement effect. This is due to the fact that the physical size of the particle exceeds the Bohr-exciton radius of CdSe.

Comparing the size-dependent optical properties of the synthesized CdSe QDs to literature results we found good agreement between the crystal size and the adherent first absorption peaks. In our studied crystal size regime and spectral window (from 3.1 nm to 6.0 nm; first absorption peaks from 520 nm to 632 nm) the correlation between the crystal size and optical properties is linear. However, graphing the position of the first absorption peaks as a function of crystal size in a wider size range (1.5 – 8 nm in the work of Jasieniak et al. [35]) revealed that the experimental data is somewhat better described with a polynomial curve. Our own results fitted very well to this curve insofar as the size of our QDs was underestimated only by an average 0.4 nm (3.1-4.0-4.6-6.0 nm vs. calculated 2.7-3.2-4.3-6.2 nm).

The anatase NWs were obtained from the as-synthesized sodium trititanate ($Na_2Ti_3O_7$) nanowires by washing and calcining them at 600 °C. The TEM images of the TiO_2 nanowires reveal that the wire structure was maintained after the 12 hours of heat treatment (see Supplementary material, **Fig. S1**). These NWs are approx. 750 nm long, 50 nm in diameter and have anatase crystal structure as confirmed by XRD measurements (**Fig S2**.).

The goal of using an 8 hour long reaction time in the direct QD attachment was to avoid the aggregation of the nanocrystals. Guijarro and co-workers have found [31] that aggregation can become a problem in long direct QD adsorption from dichloromethane, hence in our case the moderate treatment duration of 8 hours was chosen and the solvent was changed to toluene. On the other hand, in TGA-mediated indirect QD adsorption the treatment time was 48 hours, since Guijarro and co-workers observed that the incident photon to current efficiency (IPCE) increased with the loading in the case of MPA-mediated adsorption. The

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degree of QD aggregation was found to be lower in indirect adsorption than in direct QD attachment.

TEM images presented in **Fig. 3.** indicate that nanocrystals cover the surface of the nanowires fully and uniformly. This finding agrees well with the observation of color change from the original TiO_2 white to a reddish color after the filtration of the sensitized nanowires. X-ray diffraction peaks related to the CdSe nanocrystals are not observable in **Fig. S3**, which can be attributed to the low nanocrystal to nanowire weight ratio and the consequential suppression of the wide and low intensity CdSe nanocrystal peaks by the anatase reflexions.

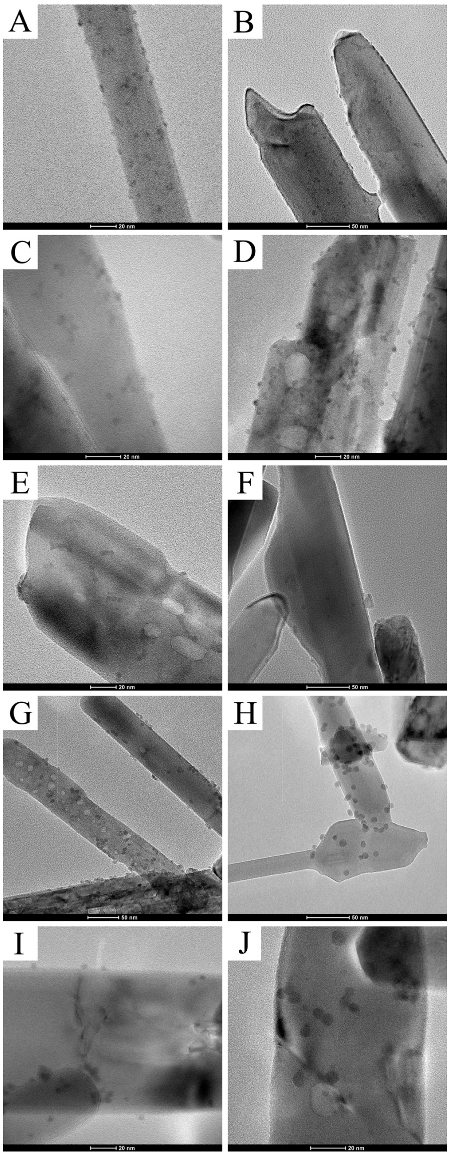

Figure 3. TEM images of CdSe-decorated TiO_2 nanowires prepared by direct (left column) and TGA-mediated (right column) attachment. Samples: 3.1 nm CdSe (A), (B), 4.0 nm CdSe (C), (D), 4.6 nm CdSe (E), (F), 6.0 nm (G), (H), and co-sensitized NWs (I), (J).

Cadmium contents determined by EDX were somewhat higher in samples obtained by TGA-mediated adsorption (1.2 vs. 1.6 atom% Cd by direct and indirect attachment, respectively). CdSe contents calculated from measuring EDX at three points per sample were as follows. 3.1 nm CdSe: TGA 3.4 weight%, direct 2.1 weight%; 4.0 nm CdSe: TGA 3.8 weight%, direct 3.8 weight%; 4.6 nm CdSe: TGA 3.9 weight%, direct 2.9 weight%; 6.0 nm CdSe: TGA 4.2 weight%, direct 1.2 weight%; co-sensitized (3.1+6.0 nm CdSe): TGA 4.8 weight%, direct 2.6 weight%.

The photocatalytic degradation of methyl orange (MO) under visible light illumination was utilized as a model reaction to verify the successful photosensitization of nanowires and study their photocatalytic activity. The irradiance spectrum of the light source is depicted in **Fig S4.** in the Supplementary Information. Since wavelengths shorter than 400 nm were cut off by the filter, MO degradation over the nanowires was attributed to the succesful electron injection from the sensitizer QDs into the conduction band of the NWs.

The four most intense peaks of the light source were at 404, 436, 547 and 578 nm. The first absorption maxima of the four different sized dots were at 520 (3.1 nm), 551 (4.0 nm), 590 (4.6 nm) and 632 nm (6.0 nm), therefore, the first two irradiation wavelengths have enough energy to excite all QDs. The 547 nm peak of the lamp had the strongest intensity, two times higher than the second one at 436 nm. This largest peak has enough energy to excite all but the 3.1 nm diameter QDs samples.

UV-Vis spectra of the supernatants obtained after centrifuging the reaction mixtures are presented in **Fig S5.** The absorbance value at $\lambda = 462$ nm was used to calculate remaining MO concentration. The amount of methyl orange adsorbed on the surface of TiO_2 NWs was found to be 0.7 mg after 6 hours in an independent experiment, hence all measured MO concentrations were corrected by this factor. TiO_2-catalyzed photodegradation of different dyes follows the Langmuir-Hinshelwood kinetics, which can be simplified as apparent first-order kinetics at low dye concentrations. It can be described with the $\ln(c_0/c) = k_{app}t$ equation, where c is the concentration of the dye at time t, c_0 is the initial concentration and k_{app} is the apparent reacton rate constant [36]. Linearized kinetic plots of photocatalytic MO removal are presented in **Fig. 4.** where solid and dashed lines correspond to results achieved with indirectly and directly functionalized QDs, respectively.

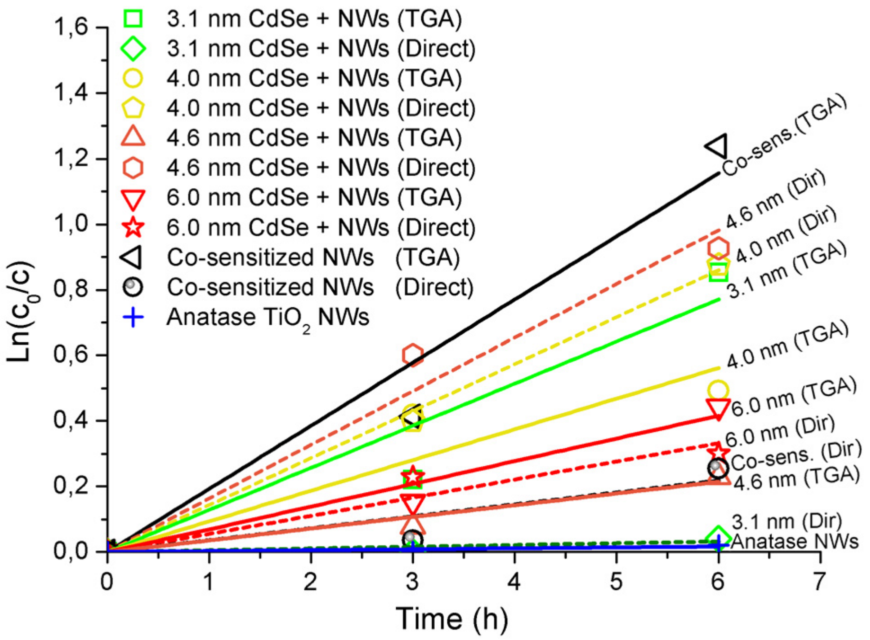

Figure 4. Linearized kinetic plots of the methyl orange degradation speed using different types of QDs as photosensitizer. Lines denote pseudo-first rate kinetics fits to the data to derive the apparent rate constant values (k_{app}) listed in Table 1.

Undecorated anatase nanowires exhibited minimal photocatalytic activity, while co-sensitized NWs prepared by using the TGA linker decomposed 71.0 % of the initial MO during 6 hours of visible light irradiation. Interestingly, co-sensitized NWs prepared by the direct attachment method exhibited considerably worse efficiency (22.5% MO oxidized within 6 hours). It should be mentioned though that this direct sensitized sample contained somewhat less CdSe as discussed above. Nanowires decorated with 4.6 nm QDs using direct attachment exhibited the second best performance at 60.4% – almost three times higher than the corresponding TGA-linked sample, even though the CdSe content of the latter was higher. The direct sensitized 4.0 nm CdSe NW sample also outperformed its TGA-sensitized counterpart with about the same CdSe loading. However, the 3.1 nm TGA attached CdSe NWs with 3.4 weight% CdSe decomposed 57.4% of the MO, whereas their directly synthesized pair performed weakly with only 4% MO degradation at 2% CdSe content. The MO degradation values with the correspondng CdSe weight ratios are summarized in **Table 1.**

Based on EDX data and specific surface area measurements, the specific QD concentrations of the decorated nanowires were calculated by assuming the quantum dots to be spherical and monodisperse. In the case of co-sensitized NWs with 3.1 and 6.0 nm CdSe, the anchored amounts of QD types on the surface were considered to be equal. The calculated fractional coverage values were obtained by assuming the nanocrystals to cover a circular area equivalent in diameter with the QDs. The light-absorbing surface area of the QDs on the nanowires was calculated by considered them as half spheres with the corresponding diameter. These values along with the measured MO degradation performance after 6 hours and the MO degradation efficiencies normalized to 1 m^2/g nanocrystal surface coverage are summarized in **Table 1.** The BET surface area for the bare anatase TiO$_2$ nanowires was measured to be 103 m^2/g.

	CdSe QDs weight ratio (%)	Particle concentration (x10^{10} particles*cm^{-2})	Fractional coverage	Calculated QD surface area (m^2/g)	MO degradation after 6 hours (%)	Normalized MO degradation after 6 hours (%)	k_{app} (x10^{-3} (min^{-1})
3.1 nm CdSe + NWs (TGA)	3.41	36.4	0.027	5.7	57.4	10.1	2.14 ± 0,324
3.1 nm CdSe + NWs (Direct)	2.06	22.0	0.017	3.4	4.0	1.2	0.089 ± 0.031
4.0 nm CdSe + NWs (TGA)	3.79	18.8	0.023	4.9	38.9	8.0	1.56 ± 0,271
4.0 nm CdSe + NWs (Direct)	3.83	19.0	0.024	4.9	58.3	11.8	2.39 ± 0.060
4.6 nm CdSe + NWs (TGA)	3.92	12.8	0.021	4.4	20.5	4.7	0.595 ± 0.056
4.6 nm CdSe + NWs (Direct)	2.91	9.49	0.016	3.3	60.4	18.3	2.73 ± 0.216
6.0 nm CdSe + NWs (TGA)	4.18	6.14	0.017	3.6	35.8	10.0	1.16 ± 0.108
6.0 nm CdSe + NWs (Direct)	1.23	1.81	0.005	1.1	26.0	23.6	0.922 ± 0.123
Co-sens. NWs (TGA)	4.8	12.4	0.022	4.6	71.0	15.4	3.21 ± 0,323
Co-sens. NWs	2.64	6.81	0.014	2.5	22.5	9.0	0.605

(Direct)	± 0.143

Table 1. CdSe weight ratio, particle concentration, fractional coverage, QD surface area, MO degradation and k_{app} values for the different QD decorated nanowires

The apparent reaction rate constants of the sensitized NWs are summarized in **Table 1.** and depicted in **Fig. 5.** as a function of nanocrystal diameter and the anchoring method of the QDs onto the TiO_2 NWs surface.

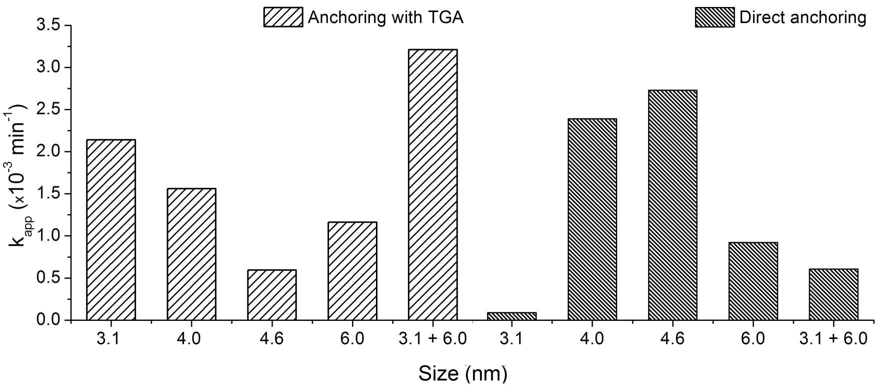

Figure 5. The values of apparent rate constants as a function of QDs diameter and the anchoring method onto the NWs surface

The undecorated nanowires exhibited minimal catalytic activity ($k_{app} = 0.0468*10^{-3} \pm 0,00165*10^{-3}$) under visible light irradiation, while the highest degradation rate obtained on co-sensitized TGA-attached NWs was 68.6 folds higher ($k_{app} = 3.21*10^{-3} \pm 0,323*10^{-3}$). It is revealing to compare this result to the MO degradation performance obtained under UV illumination using similar experimental parameters and nanofibers with similar dimensions [37]: TiO_2 NWs have just 25.5 folds higher activity under UV-light ($k_{app} = 0.082 \pm 0.003$) than CdSe QDs sensitized NWs under visible-light irradiance.

It is difficult to directly compare the performace of the CdSe sensitized NWs to literature results, however, with this 40 W visible light source the 60-70 % degradation of the initial MO can be considered as good performance after 6 h irradiation. W. Ho and co-workers [7] synthesized CdSe photosensitized TiO_2 nanoparticles with sonochemical method and the photocatalytic activities were measured by 4-chlorophenol degradation with a 300 W tungsten halogen lamp with 400 nm cut off filter. 200 mg photocatalyst was suspended in 200 mL $2.5x10^{-4}$ mol/L 4-chlorophenol aqueous solution. The sensitized catalyst degradated the 32% of the initial 4-chlorophenol concentration after 8 hours of irradiation. Lim and co-workers [8] synthesized CdSe-TiO_2 photocatalyst with solvothermal method. Their photocatalytic activity measurements were performed with 50 mg catalyst in 50 ml $1x10^{-6}$ mol/L methylene blue solution with a λ=420 nm visible- and λ=365 nm UV-light source with 8 W output. They observed 42% degradation in visible light and 59% in UV-light after 4 hours of illumination. In the case of CdS QDs Zhu et al [9] sensitized TiO_2 nanotubes with CdS nanocrystals and this NTs were degradated the 83.7% of the initial methylene blue concentration with a 150 W xenon arc lamp (with 50 mg catalyst and 100 mL 20 mg/L MB solution) after 6 hours of irradiation. L. Mao and co-workers [10] sensitized 20 nm TiO_2 nanoparticles with CdS QDs. These NPs (with 25 mg catalyst, and 100 mL 60 mg/L Rhodamine B solution) degradated the 92.2% of RhB after 60 min under a 160 W high pressure mercury lamp irradiation with a 400 nm cut off filter.

It is interesting to analyze the MO degradation efficiency normalized to 1 m^2/g nanocrystal surface coverage (**Table 1**). In this representation NWs decorated by the largest (6.0 nm) CdSe QDs with direct attachment exhibit the best specific MO degradation performance, followed by the directly attached 4.6 nm CdSe sensitized NWs. The TGA attached co-sensitized NWs exhibit 65% of the efficiency of the 6.0 nm CdSe sensitized NWs, the 4.0 nm directly attached NWs perform at 11.8% and the worst value in this representation belongs to the smallest (3.1 nm) directly attached QDs sensitized NWs at 1.2%. In most cases the direct adsorption of the QDs onto TiO_2 nanowires produced better results than the TGA-mediated attachment which was attributed to the reduction of the electron injection efficiency in the presence of the linker molecule. This finding is in good agreement with Guijarro's work [31] where the IPCE values were higher in the case of direct adsorption than with MPA linker molecule.

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It is worth noting that our light source had a line spectrum and the smallest 3.1 nm QDs could only be excited with the 436 nm wavelength part of the spectrum, which had only half the intensity of the 547 nm line. Although it is difficult to factor this information into the analysis accurately, our preliminary calculations indicate that even by considering the lamp spectrum intensity differences, the 6.0 nm directly attached NWs would remain the most efficient nanowires, followed by the 4.6 nm directly attached and the co-sensitized TGA-attached NWs.

As a final observation it can be said the direct attachment of the nanocrystals to the TiO_2 surface yields better degradation efficiencies in most cases and the co-sensitization of the nanowires to absorb a wider spectral window is also feasible. The good performance of the larger nanocrystals when normalizing the efficiency to equal QDs surface area for 1 gram of NWs could be explained by the better absorption in the visible region of the larger nanocrystals and with a decreasing electron injection rate to the TiO_2 with decreasing size. This hypothesis is in good agreement with the works of Prabakar work [28] and of Mora-Seró and co-workers' [38] if we assume the electron injection rate efficiency to be independent of the QD diameter. However, it is to be noted that Kongkanand et al. reported a decreasing electron transfer rate with increasing CdSe diameter [6].

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Conclusion

TiO_2 nanowires photosensitized with CdSe quantum dots were prepared successfully both with the direct and the indirect QD attachment method. The attachment of wurtzite CdSe QDs onto the anatase TiO_2 nanowires was verified by EDS and TEM and the efficiency of photosensitization was investigated by the methyl orange degradation model reaction. The absolutely most efficient nanowires were the co-sensitized NWs containing both 3.1 and 6.0 nm QDs in an equal ratio. These co-sensitized NWs decomposed 71% of the initial MO within 6 hours, whereas the performance of all other samples was 60% or less. Normalizing the MO decomposition efficiencies to QD surface area on 1 g nanowire revealed that the direct attachment of quantum dots to the TiO_2 nanowire was preferable to TGA-mediated anchoring. Furthermore, the specific photocatalytic performance increased with increasing QD size, which could be attributed to the better absorption capacity of larger CdSe QDs.

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