

Visible Light-Induced Charge Retention and Photocatalysis with Hybrid CdSe–Au Nanodumbbells

Ronny Costi, Aaron E. Saunders, Einat Elmalem, Asaf Salant, and Uri Banin*

*Institute of Chemistry and the Center for Nanoscience and Nanotechnology,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

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ABSTRACT

Visible light photocatalysis is a promising route for harnessing of solar energy to perform useful chemical reactions and to convert light to chemical energy. Nanoscale photocatalytic systems used to date were based mostly on oxide semiconductors aided by metal deposition and were operational only under UV illumination. Additionally, the degree of control over particle size and shape was limited. We report visible light photocatalysis using highly controlled hybrid gold-tipped CdSe nanorods (nanodumbbells). Under visible light irradiation, charge separation takes place between the semiconductor and metal parts of the hybrid particles. The charge-separated state was then utilized for direct photoreduction of a model acceptor molecule, methylene blue, or alternatively, retained for later use to perform the reduction reaction in the dark.

Visible light photocatalysis is a promising route for converting solar energy to chemical energy. Semiconductors and metal-semiconductor hybrid materials have been studied as photocatalysts in photochemical water splitting to produce hydrogen,^{1–5} in photoelectrochemical cells,⁶ and in photochemical purification of organic contaminants, and bacterial detoxification.^{7,8} So far semiconductor-metal photocatalysts were based mostly on wide-gap semiconductors limiting their applicability to the UV range, which consists of less than 5% of the solar spectrum. Additionally, they were poorly controlled in terms of the semiconductor particle and metal island size, shape, and location thus limiting their understanding and controlled improvement.^{9–16} Here, we report visible range photocatalytic activity of highly controllable hybrid gold-tipped CdSe nanorods, termed nanodumbbells (NDBs).^{17,18} Following light absorption, rapid charge separation takes place at the semiconductor-metal interface, and the separated charges can perform redox chemistry (Figure 1a). Additionally, nanodumbbells can retain charges during irradiation for later use in redox reactions.^{13,16}

For photocatalysis with semiconductors, it is necessary to suppress the recombination of the electron–hole pair formed following light absorption. In large gap oxide semiconductors such as TiO₂ and ZnO, metal islands deposited on the structures served to promote charge separation and also exhibited charge retention. Recently, a three component CdS–Au–TiO₂ nanojunction system was developed to

achieve vectorial electron transfer and suppress charge recombination, but again the spectral coverage was limited.⁹ Also, CdS–Pt hybrid materials have shown visible light photocatalysis for water splitting.^{5,19} Here, a CdSe system with size-tunable visible absorption was used as a basis for the photocatalyst, taking advantage of its highly developed synthesis allowing production of spherical, rod-, and tetrapod-shaped particles.^{20–22} Charge separation in CdSe nanoparticles was previously demonstrated using molecular complexes or semiconducting polymers.^{23–25} Here, well-controlled growth of Au tips onto the CdSe rods is employed to separate the charges. Previous work on this system showed that upon Au growth, the photoluminescence of the original CdSe rods is quenched.^{17,18} Analysis of the band offsets between Au and CdSe suggests that this is due to rapid electron transfer from the conduction band of CdSe to the Au tips, leading to charge separation (see Figure 1a inset).²⁶

In the previous synthesis approach, the growth of NDBs was performed by reacting CdSe rods with gold precursor in organic solvent.^{17,18} Photocatalysis, however, is most relevant in aqueous solutions. While there is a possibility to transform the solubility of the NDBs from organic to aqueous phase via appropriate ligand exchange,²⁷ this method is time-consuming and difficult to realize for large amounts. Instead, a new method to synthesize NDBs directly in aqueous solution is hereby introduced. This method can be readily expanded to the growth of additional metals aside from Au onto the semiconductor nanoparticles, using the wide selection of available water-soluble metal ion precursors. The

* Corresponding author. E-mail: banin@chem.ch.huji.ac.il.

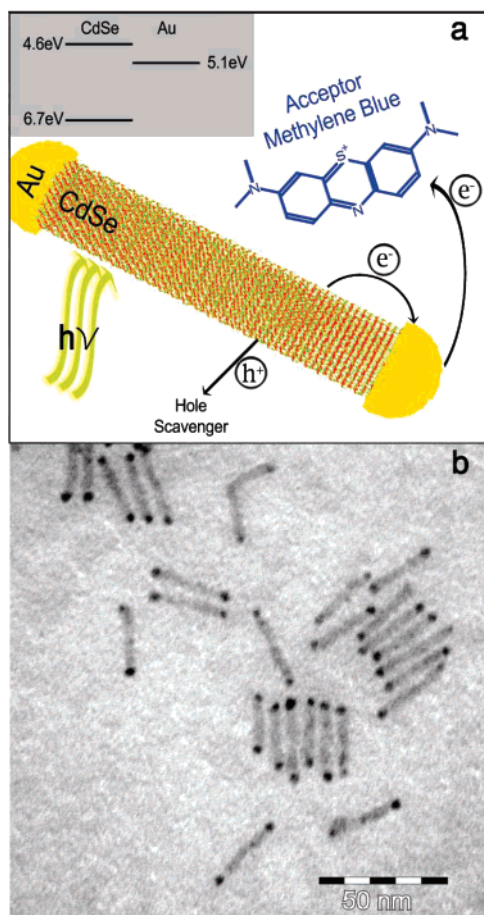


Figure 1. (a) Scheme of a light-induced charge separation mechanism in a nanodumbbell in which the photogenerated electron–hole pair separates so that the electron resides at the gold tip and the hole at the CdSe nanorod. The scheme also depicts the transfer of the hole to the scavenger and the reduction of the MB molecule upon electron transfer from the gold tip. The inset shows the energy band alignment between CdSe (4 nm dots)²⁶ and Au.³⁹ (b) TEM image of CdSe–Au hybrid nanodumbbells synthesized in aqueous solution.

control of the metal tip material is deemed as an essential and powerful knob to tune the photocatalytic activity of this system.

In this new approach, CdSe nanorods ($\sim 38 \times 4$ nm) were grown by high-temperature pyrolysis of suitable precursors in a coordinating solvent containing a mixture of trioctylphosphineoxide and phosphonic acids, as reported previously.²¹ The CdSe nanorods were then transferred to aqueous phase by exchanging the surface ligands to mercapto-undecanoic acid (MUA).^{27–29} This ligand exchange procedure is very fast and with high efficiencies, unlike the ligand exchange procedure for NDBs that is time consuming with low-transfer efficiencies and compromises the Au tip quality.²⁷ Gold growth was performed by preparing 15 mL of dilute nanorod aqueous solution. The concentration of the rods was calculated using the sample's absorbance spectrum to be around 3×10^{-7} M. Gold(III) chloride (Sigma Aldrich) was weighed at a ratio of $\sim 1:8000$ nanorod to gold atoms and was dissolved in 4 mL of TDW (triple-distilled water). The gold solution was added at once to the nanorods solution under vigorous stirring and ambient light. A black precipitate

appeared within 30 s and was left to stir for 2 h after which the black precipitate (nanodumbbells) was collected using centrifuge and was dried. This also serves as a cleaning procedure for excess ions. The precipitate was fully redispersed in a TDW buffer solution of pH 7 after 20 min of sonication. At the neutral pH, a clear and stable solution is obtained, while at more acidic conditions the precipitate does not dissolve well mainly due to the abstraction of the MUA groups from the surface.³⁰

Figure 1b shows a TEM image of CdSe–Au hybrid NDBs prepared as described above. Selective growth of Au at both rod tips was observed, similar to what was achieved previously in organic solution. The average Au particle size was $3.5 (\pm 0.6)$ nm (see size histogram in Figure S1 in Supporting Information). Similar to the previous study, the growth of Au also washed out the excitonic absorption feature of the original CdSe nanorods (see Figure S2 in Supporting Information).

The growth mechanism in this case has to be considered because no reducing agent is added to the reaction solution. The first possible mechanism considered was photoreduction of the gold by electrons generated after light absorption of the semiconductor rod. Control experiments performed under dark conditions also showed similar gold growth (see TEM image in Figure S3 in Supporting Information). Therefore a different reduction mechanism has to be considered. Closer examination of the product NDBs reveals significant shortening compared to the original nanorods. The average length is shortened from 38 nm for the rods in water to 22 nm in the NDBs (see size histogram in Figure S4 in Supporting Information). Se^{2-} from the rods can reduce the Au^{3+} accompanied by etching of the rods, which is consistent with the rod shortening. A similar mechanism of rod etching leading to gold growth was reported for CdTe and PbSe domains on CdSe rods in organic solution.³¹

Two types of experiments were performed to test the charge separation and demonstrate the photocatalytic activity of the NDBs. Methylene blue (MB), a good electron acceptor with a distinctive-shaped absorbance spectrum, was used as the model photocatalyzed compound. Upon reduction by two electrons, MB is transformed to leucomethylene blue (MBH), which is transparent at the visible spectrum, providing a clear spectral signature for MB reduction.³²

In the first set of experiments, termed pre-irradiation experiments, the NDB solution was first irradiated and only then MB was added without further illumination. Aqueous solutions (pH 7) of NDBs with a typical concentration of 5×10^{-8} M and ethanol as a sacrificial hole scavenger³³ were prepared using 1:4 volume ratio of ethanol to buffer solution. Samples, prepared in a dark room, were bubbled with dry nitrogen gas in an airtight cuvette to prevent scavenging of the accumulated electrons by oxygen. MB solution was prepared by dissolving MB crystals (Sigma-Aldrich) in TDW to receive a solution with optical density of 1 at the main absorption peak of the MB at 667 nm. For each experiment, 2 mL of the NDBs aqueous solution was pre-irradiated with a CW laser at 532 nm and a power of 27 mW for variable times with stirring. This irradiation scheme was chosen so

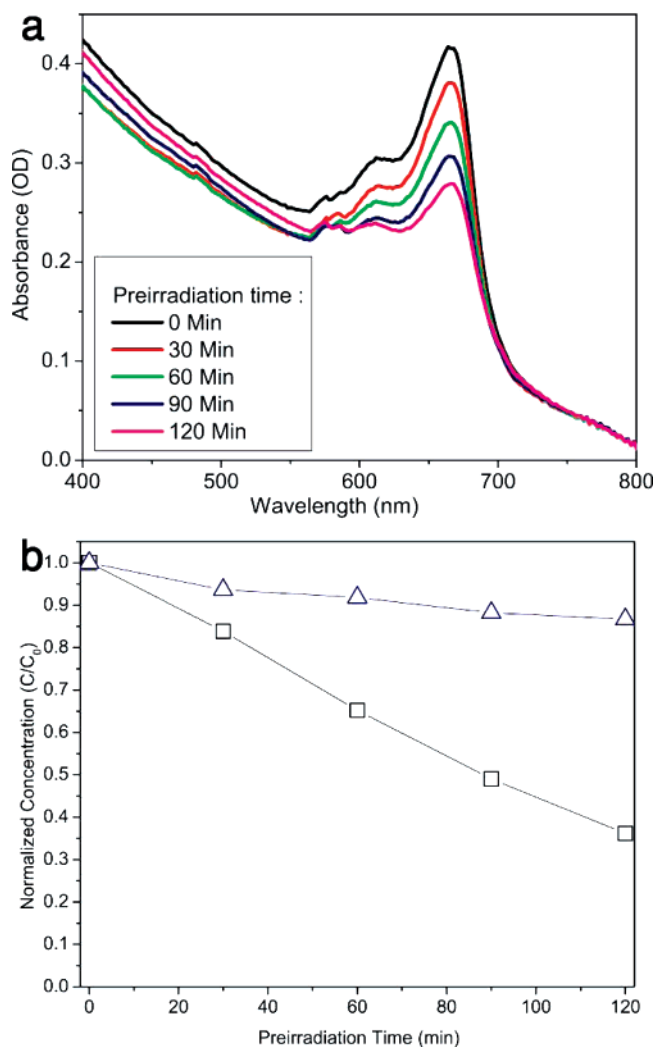


Figure 2. Pre-irradiation experiments for photocatalysis of NDBs (a) Set of absorbance spectra of MB–nanodumbbells solution in which the double peak absorbance feature of the MB is noticeable, and each spectrum relates to a different pre-irradiation time at 532 nm of the NDB solution before the addition of the MB. (b) Normalized concentration of MB dye reduced by CdSe nanorods–gold nanoparticles mixture (open blue triangles) and by hybrid CdSe–Au nanodumbbells solution (open black squares) vs pre-irradiation time. High efficiency of the charge retention in NDBs is demonstrated, leading to activity toward MB reduction.

that the CdSe would effectively absorb the light at a well-defined visible wavelength, and a quantification of photons absorbed can be done. After this irradiation, 1 mL of deaerated MB dye solution was added to the cuvette. It is noted that the NDBs did not show a structural or morphological changes due to the irradiation of the sample (See TEM images in Figure S5 in Supporting Information).

Figure 2a shows a series of absorbance spectra of MB–nanodumbbell aqueous solutions where the double peak feature of the MB (at 609 nm and at 667 nm) is clearly seen. The absorbance spectrum was acquired after letting the mixed sample stir in darkness for 30 min to bring the reaction to completeness as was verified by following the time trace of the absorption profile. The reduction of MB was faster than few tens of seconds, which is the practical limit of the measurement setup.

As the NDBs reduce the MB to MBH, the double peak absorbance feature diminishes as is clearly seen, and longer pre-irradiation leads to a systematic increase in the reduction, indicating more charges were retained on the NDBs. Figure 2b plots the dependence of the reduction activity of the NDBs versus pre-irradiation time, along with the results for a control solution of a mixture of the original CdSe nanorods and Au nanoparticles of diameter 5 nm at a ratio of 1:2 and at similar concentrations to the NDB solution (triangles). The hybrid NDBs have reduced 64% of the MB dye after being pre-irradiated for 120 min, while for the same conditions the mixture has shown only 13% reduction of the MB dye.

Additional control experiments showed that solutions of CdSe nanorods or of gold nanoparticles did not exhibit any photocatalytic reduction effects after being pre-irradiated and hence show no charge retention. It can therefore be concluded that the NDBs exhibit a charge separation under visible illumination consistent with the photoluminescence quenching observed previously; moreover the NDBs have the ability to retain their excited charge-separated state for long times even after the illumination was switched off if a hole scavenger is used to remove the positive charges.^{13,16} The NDBs with the charge retention can then transfer their electron to an electron acceptor in a redox reaction without the presence of light.

From the irradiation parameters, the amount of the NDBs and the amount of reduced MB, the quantum yield of the nanodumbbells–MB photoreduction process, was estimated to be around $\sim 2 \times 10^{-6}$ molecules reduced per two photons absorbed. This is significantly higher than the case of the mixture of CdSe nanorods–Au nanoparticles where the estimated yield was around 3.6×10^{-7} molecules reduced per two photons absorbed.

To better understand the charge retention process, it must first be noted that in the case of the CdSe nanorods and the gold nanoparticles mixture, the charge is retained on the gold nanoparticles in the solution and is transferred through a productive collision from an excited CdSe nanorod. Using the Stokes–Einstein relations, the average collision time between the gold nanoparticles and the CdSe nanorods was estimated at approximately 1 ms, which is significantly longer than the lifetime of the exciton in the CdSe nanorod (~ 10 nsec). However, the presence of ethanol as a hole scavenger at a significant volume fraction in the irradiated solution allows for hole transfer from the excited CdSe nanorod leaving a negatively charged rod that transfers its excess electron to a gold nanoparticle during a collision. In the case of NDBs, the much more effective retention of charge on the gold is assigned to the rapid charge separation between the CdSe and gold parts, accompanied by the hole scavenging by the ethanol, which prevents recombination of charge carriers. The careful design of the photocatalyst therefore enables significantly more effective activity.

The number of retained electrons per NDB can be roughly estimated from the amount of reduced MB and the estimation of the NDB amount using the absorbance spectra. This yields an average retention of about 50 electrons per NDB at the longest pre-irradiation times studied. This large number can

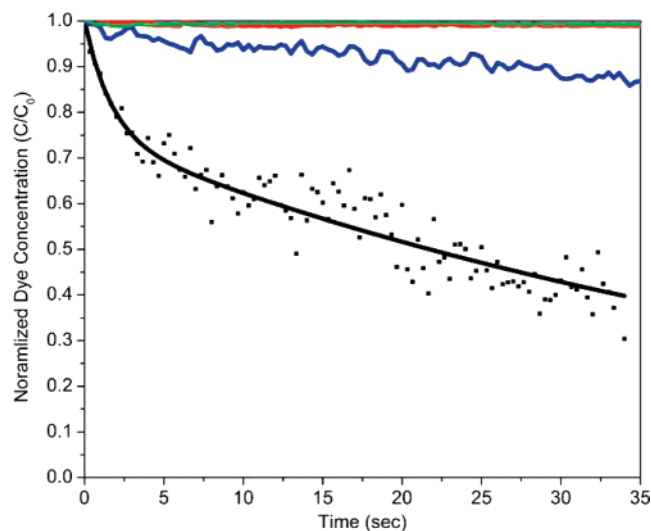


Figure 3. Simultaneous irradiation experiments for photocatalysis of NDBs irradiated at 473 nm. Time trace of normalized concentration of MB dye in MB mixtures with gold nanoparticles of 4 nm (red line), gold nanoparticles of 6 nm (green line), CdSe nanorods (blue line), and CdSe–Au NDBs (black squares and black trend line). In the same time span, NDBs exhibit significant photoreduction activity (61% of the dye reduced) compared to only 15% of the dye reduced by CdSe nanorods and negligible reduction activity of Au particles.

be rationalized by estimating the change in charging energy of the Au tips with addition of an electron. Accumulation of the charge on the Au tips will lead eventually to Fermi level equilibration of the metal with the semiconductor part suppressing further charge separation.^{13,16} Previous scanning tunneling microscopy and spectroscopy measurements of the NDBs on a graphite surface in vacuum³⁴ showed a geometrical charging energy of Au tips of similar size to those here of about 0.1 eV. Taking into account the high dielectric constant of the aqueous solution in the present experiments, the charging energy can be reduced significantly; it is calculated to be about 5 meV for spherical Au particles with diameter of 3.5 nm in water.^{35,36} If 0.5 eV difference between the CdSe conduction band and the Au Fermi level is assumed, accumulation of tens of electrons per tip is possible prior to equilibration, consistent with the observed numbers under long irradiation times.

It is also possible to use the NDBs for direct photocatalysis of the MB reduction. In a second set of experiments, termed simultaneous irradiation, the absorbance (at 667 nm) of MB in a MB–nanodumbbell aqueous solution was followed while irradiating the sample with a 473 nm 30 mW CW laser. This wavelength was chosen because the MB has minimal absorbance in this range, minimizing its direct photobleaching. Samples were prepared as described in the previous experiment, with ethanol as a hole acceptor and MB added. In Figure 3, a normalized time trace of the absorbance of irradiated MB–nanodumbbell solution, MB–CdSe nanorods control solution and of MB–gold nanoparticles control solution, where MUA-coated Au particles of either 4 (± 1.3) nm and of 6 (± 1) nm in diameter were used are shown (See TEM images in Figure S6 and preparation information in Supporting Information). After 30 min of irradiation, the

MB–NDB solution exhibited reduction of 61% of the MB dye. Control Au solutions hardly exhibited any reduction of the MB for both 4 and 6 nm particles, whereas the control CdSe nanorods solution exhibited reduction of 15% of the MB. In another control experiment, only MB solution was used to estimate the amount of photobleaching of the dye under the irradiation. After 30 min of irradiation, only about 5% of the dye has undergone photobleaching. The large decrease of MB dye absorption in the MB–NDB solution can therefore be attributed to a photocatalytic effect that occurs due to the presence of the NDBs. After 30 min of irradiation, the ratio between reduced molecules and pairs of absorbed photons is found to be 1.2×10^{-5} . The average collision time of MB and NDBs is estimated around 4 ms in these conditions. Also here, similar to the case of pre-irradiation discussed above, following light absorption and charge separation between the semiconductor and metal parts, there is hole scavenging by the ethanol followed by charge retention by the Au. The more effective activity in this case, compared to the pre-irradiation experiments, results from the presence of the acceptor MB in the irradiated solution and its rapid collision with the NDB leading to its reduction.

These results demonstrate the use of visible light to activate a photoreduction reaction in a well-defined hybrid nanostructure, as well as the possibility of retaining the charge for later use in reduction reactions, even after the irradiation is shut off. Most previous nanophotocatalyst systems used UV irradiation that could have caused direct photobleaching of the probe molecule, and more importantly the semiconductor could not effectively absorb the solar spectrum in the visible range. The present system provides a high degree of control over the photocatalyst properties, and indeed the rapid development of additional hybrid metal-semiconductor nanoparticles such as CdS–Au³⁷ and Au with IV–VI semiconductors³⁸ was already reported. Future development of additional metal-semiconductor hybrid systems is expected, providing flexibility in tuning the photocatalytic properties. This includes the tuning of the absorption by changing the size, composition, and shape of the semiconductor and changing the metal type and size to change the relative band-offsets of the two materials. This provides adequate pathways to tailor such hybrid nanoparticles for specific visible light photocatalysis reactions and possibly also for photocatalytic water splitting.

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Supporting Information Available: Supporting figures as noted in the text are (S1) size distribution histogram of the Au tips on nanodumbbells, (S2) absorbance spectra of demonstrating the washing out of the excitonic peak in the growth of Au in the rods, (S3) TEM image demonstrating growth under dark conditions, (S4) histogram demonstrating the shortening of the rods due to etching while growing gold, (S5) TEM images demonstrating no structural change of the

nanodumbbells before and after irradiation, and (S6) TEM images of Au nanoparticles and preparation information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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