

Video Article

Photochemical Oxidative Growth of Iridium Oxide Nanoparticles on CdSe@CdS Nanorods

Philip Kalisman¹, Yifat Nakibli¹, Lilac Amirav¹
¹Schulich Faculty of Chemistry, The Russell Berrie Nanotechnology Institute, The Nancy and Stephen Grand Technion Energy Program, Technion – Israel Institute of Technology

Correspondence to: Lilac Amirav at lilac@technion.ac.il

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Abstract

We demonstrate a procedure for the photochemical oxidative growth of iridium oxide catalysts on the surface of seeded cadmium selenide-cadmium sulfide (CdSe@CdS) nanorod photocatalysts. Seeded rods are grown using a colloidal hot-injection method and then moved to an aqueous medium by ligand exchange. CdSe@CdS nanorods, an iridium precursor and other salts are mixed and illuminated. The deposition process is initiated by absorption of photons by the semiconductor particle, which results with formation of charge carriers that are used to promote redox reactions. To insure photochemical oxidative growth we used an electron scavenger. The photogenerated holes oxidize the iridium precursor, apparently in a mediated oxidative pathway. This results in the growth of high quality crystalline iridium oxide particles, ranging from 0.5 nm to about 3 nm, along the surface of the rod. Iridium oxide grown on CdSe@CdS heterostructures was studied by a variety of characterization methods, in order to evaluate its characteristics and quality. We explored means for control over particle size, crystallinity, deposition location on the CdS rod, and composition. Illumination time and excitation wavelength were found to be key parameters for such control. The influence of different growth conditions and the characterization of these heterostructures are described alongside a detailed description of their synthesis. Of significance is the fact that the addition of iridium oxide afforded the rods astounding photochemical stability under prolonged illumination in pure water (alleviating the requirement for hole scavengers).

Video Link

The video component of this article can be found at <https://www.jove.com/video/53675/>

Introduction

Photocatalysis presents an attractive and promising solution for renewable energy generation and other environmental applications such as water treatment and air purification¹⁻³. Overall water splitting, driven by solar energy, could be a source of clean and renewable hydrogen fuel; however, despite decades of research, systems that are sufficiently stable and efficient for practical use have not yet been realized.

Both photodeposition and semiconductor-mediated photocatalysis rely on the same mechanism of separating photo-generated electron-hole pairs and driving them to the surface where they can initiate redox reactions. The similarities between these two processes make photodeposition an attractive synthetic tool for the field of photocatalysis⁴⁻⁶. This method is expected to take photocatalyst production to new and unexplored frontiers. It might potentially offer pristine control over the spatial arrangement of the different components in a heterostructures, and advance the ability to construct sophisticated nanoparticle systems. Ultimately the method will bring us one step closer to realizing an efficient photocatalyst for direct solar-to-fuel energy conversion.

We investigated the growth of IrO₂ as a co-catalyst, as it is known to be an efficient catalyst for water oxidation⁷⁻¹¹. A tunable structure of quantum dot (CdSe) embedded in a rod (cadmium sulfide)^{12,13} was used as our photocatalyst substrate^{14,15}. It is currently undetermined whether the oxidative pathway occurs via a mediated pathway, or by a direct hole attack. Here, our knowledge and control over the photogenerated holes in the semiconductor heterostructure can be harnessed for a mechanistic study of oxidation reactions. This is made possible by the substrate architecture, which facilitates localization of confined holes^{16,17} and formation of a distinct oxidation reaction site on the rod. The use of nanoscale materials with localized charge carrier can be exploited for mechanistic studies of redox reactions by simple examination of the products. In this way photodeposition can be used as a unique probe of both reduction and oxidation reaction pathways. This is one example of the new and exciting possibilities afforded by the combination of photodeposition and cutting edge colloidal synthesis¹⁸⁻²⁰.

The quest to develop an efficient photocatalyst for water splitting and renewable energy conversion has become an important thrust within the materials community. This has spurred worldwide interest in CdS, which is known to be highly active for hydrogen production, though it is hampered by photochemical instability. Our work here treats the Achilles heel of the material. IrO₂ decorated CdSe@CdS rods demonstrate remarkable photochemical stability under prolonged illumination in pure water.

Protocol

1. Synthesis of Quantum Dots²¹

1. Preparation of TOP:Se Precursor
 1. Combine 58 mg of Se powder with 0.360 g of Tri-n-octylphosphine (TOP) in a vial with a septum.
 2. Sonicate the TOP:Se mixture until it is clear with no solids.
2. Synthesis of CdSe
 1. Combine 3.0 g trioctylphosphine oxide (TOPO), 280 mg n-octadecylphosphonic acid (ODPA), and 60 mg CdO with a 3 mm x 8 mm cylindrical stir bar in a 25 ml 3-neck round bottom flask equipped with a thermocouple (inserted in a custom glass adapter), a reflux condenser with a T-joint (center neck), and a rubber septum. Assemble all glass-to-glass joints with high temperature vacuum grease. Connect the T-joint to a Schlenk line on one end that can be switched between a clean inert gas and vacuum, while connecting the other end to a bubbler.
Caution: CdO is very toxic and should be weighed and added to the round bottom flask inside an enclosed environment such as a glovebox.
 2. Place the round bottom flask apparatus in a heating mantle, and purge with inert gas.
 3. Heat the solids in the round bottom flask to 150 °C, making sure to start stirring vigorously once the compounds melt (around 60-80 °C). In order to avoid overshooting the target temperature, heat to 100 °C and then 150 °C once the heating rate slows down or stabilizes.
 4. Degas the mixture under vacuum (at 150 °C) for at least 1 hr while still stirring. Make sure the T-joint is not open to the bubbler or the oil will get sucked into the flask and Schlenk line. When moving from gas to vacuum be careful to transition slowly to avoid more than a rolling boil.
 5. Refill the flask with inert gas (and continue to flow gas over the sample) and increase the temperature to 350 °C. The solution should turn clear as it heats up, and excess solids on the flask wall can be collected by careful swirling of the flask.
 6. Inject 1.5 g of TOP into the flask through the septum. Allow the solution temperature to stabilize before proceeding.
Note: Try to minimize the amount of air/moisture injected by keeping the TOP in a septa vial under inert atmosphere, and injecting it as quickly as possible.
 7. Inject all of the TOP:Se mixture (prepared in section 1.1) into the flask through the septum, using a wide needle to inject the TOP:Se as quickly and uniformly as possible.
 8. Let the reaction proceed for the desired time, and remove from the heating mantle.
 1. For very small seeds remove from heat just before injecting. For larger seeds remove the flask from heat immediately after injecting TOP:Se or after waiting up to 3 min. Longer wait result in larger seeds.
 9. Let the reaction cool to approximately 100 °C and inject approximately 5 ml of degassed toluene. Transfer the solution to a vial under inert atmosphere for cleaning.
Note: To simplify this process 10 ml of toluene can be placed in a 20 ml vial with a septa under constant flow of inert gas. Use approximately half of this toluene to inject into the cooling mixture, and then transfer the cooled mixture back into this vial.
 10. Cleaning of seeds
 1. Put the solution in a 50 ml centrifuge tube.
 2. Add methanol (approximately 5 ml) to precipitate out the seeds from the toluene mixture.
 3. Centrifuge at 3,400 x g for 5 min.
 4. Decant clear supernatant and re-dissolve the pellet in toluene (5-10 ml).
 5. Repeat steps 1.2.10.2 through 1.2.10.4 at least three times total.
 11. Dilute a small aliquot of the seeds in toluene in order to measure Ultraviolet-Visible (UV-Vis) absorbance between 350-800 nm. Use the peaks to determine the concentration and size of the CdSe seeds as described in the literature²².

2. Synthesis of Seeded Rods²¹

1. Preparation of TOP:S Precursor
 1. Combine 1.2 g of S with 15 g of TOP in a vial with a stir bar.
 2. Stir until clear with no solids (usually at least 24 hr).
 3. Measure 0.62 g of this mixture into a vial with a septum.
2. Preparation of TOP:CdSe Precursor
 1. Measure the appropriate volume of CdSe seeds from step 1 (based on UV-Vis peak) into a vial with a septum.
Note: For a calculated concentration of 5×10^{-5} with 2.25 nm seeds (both values calculated from the UV-Vis spectra²²), use 300 μ l of solution.
 2. Evaporate the toluene using a vacuum line until the seeds are dry. Do not leave under vacuum for more than 5-10 min once dry, as this can degrade the quality of the seeds.
 3. Re-dissolve all of the dried seeds in 0.5 g of TOP.
3. Synthesis of CdSe@Cds
 1. Combine 60 mg propylphosphonic acid (PPA), 3.35 g TOPO, 1.080 g ODPA, and 230 mg CdO with a 3 mm x 8 mm cylindrical stir bar in a 25 ml 3-neck round bottom flask equipped with a thermocouple (inserted in a custom glass adapter), a reflux condenser with a T-

- joint (center neck), and a rubber septum. Assemble all glass-to-glass joints with high temperature vacuum grease. Connect the T-joint to a Schlenk line on one end that can be switched between a clean inert gas and vacuum, while connecting the other end to a bubbler. Caution: CdO is very toxic and should be weighed and added to the round bottom inside an enclosed environment, such as a glovebox. PPA is regulated in some countries and can be replaced by butylphosphonic acid (BPA, 72 mg) or hexylphosphonic acid (HPA, 80 mg), though BPA and HPA usually result in shorter rods.
- Place the round bottom flask apparatus in a heating mantle, and purge with inert gas.
 - Heat the solids in the round bottom flask to 120 °C, making sure to start stirring vigorously once the compounds melt (around 60-80 °C). In order to avoid overshooting the target temperature, heat to 90 °C and then 120 °C once the heating rate slows down or stabilizes.
 - Degas the mixture under vacuum (at 120 °C) for at least ½ hr while still stirring.
 - Make sure the T-joint is not open to the bubbler or the oil will get sucked into the flask and Schlenk line. When moving from gas to vacuum be careful to transition slowly to avoid more than a rolling boil. Use a cold trap with liquid nitrogen (LN₂) for a better vacuum.
 - Refill the flask with inert gas (and continue to flow gas over the sample) and increase the temperature to 320 °C. The solution should turn clear as it heats up, and excess solids on the flask wall can be collected by careful swirling of the flask.
 - Cool back down to 120 °C and degas under vacuum as in step 1.2.4.
 - Refill and reheat the flask as in step 1.2.5.
 - Inject 1.5 g of TOP into the flask through the septum. Allow the solution temperature to stabilize at 340 °C before proceeding.

Note: Try to minimize the amount of air/moisture injected by keeping the TOP in a septa vial under inert atmosphere, and injecting it as quickly as possible.
 - Inject the TOP:S mixture into the flask through the septum, using a wide needle to inject the TOP:S as quickly and uniformly as possible. Start a timer.
 - Exactly 20 sec after injecting the TOP:S, inject the TOP:CdSe mixture into the flask through the septum, using a wide needle to inject the TOP:CdSe as quickly and uniformly as possible.

Note: The temperature should have dropped to below 330 °C by this point due to the addition of RT TOP solutions.
 - Set the temperature to 320 °C and let the reaction proceed for the desired time (8-15 min), and remove from the heating mantle.
 - Let the reaction cool away from the heating mantle and inject approximately 5 ml of degassed toluene when the temperature reaches approximately 100 °C. Transfer the solution to a vial under inert atmosphere for cleaning.

Note: To simplify this process 10 ml of toluene can be placed in a 20 ml vial with a septa under constant flow of inert gas. Use approximately half of this toluene to inject into the cooling mixture, and then transfer the cooled mixture back into this vial.
 - Cleaning of rods
 - Put the solution in a 50 ml centrifuge tube.
 - Add methanol (approximately 5 ml) to precipitate out the seeds from the toluene mixture.
 - Centrifuge at 3,400 x g for 5 min.
 - Decant clear supernatant and re-dissolve the pellet in approximately 10 ml hexane.
 - Add 1-2 ml each of n-octylamine and nonanoic acid to the solution. The solution should be transparent.
 - Add 5 ml methanol and centrifuge for 5 min at 3,400 x g.
 - Repeat steps 2.3.13.4 through 2.3.13.6 at least twice more.
 - Re-dissolve pellet in 10 ml of toluene. If the pellet does not easily dissolve, more cleaning steps are likely needed, in which case repeat steps 2.3.13.4 through 2.3.13.6.
 - Add approximately 7 ml of IPA, 1 ml at a time, until the solution is slightly cloudy even when mixed.
 - Centrifuge for 30 min at 2,200 x g in order to separate longer rods from everything else.
 - Re-dissolve pellet in 10-15 ml of toluene.
 - Dilute a small aliquot of the seeds in toluene in order to measure UV-Vis absorbance and/or photoluminescence (PL) of the rods.

Note: Any aliquot volume is acceptable as long as the dilution factor is known, however, a typical dilution factor would be 20. For PL, the absorption should be at or below 0.1 at the chosen excitation wavelength (typically use 450 nm).

3. Transfer of Seeded Rods to Aqueous Solution

- Preparation of Methanol Solution
 - Pour approximately 10 ml of methanol into a centrifuge tube.
 - Add approximately 250 mg mercaptoundecanoic acid (MUA) and 400 mg tetramethylammonium hydroxide (TMAH).
 - Vortex or let sit until all solids fully dissolved.
- Ligand Exchange
 - Add methanol (5-10 ml, or enough to precipitate the rods) to ¼ to ½ of rods synthesized from step 2 in a centrifuge tube.

Note: The volume of rods used will be dependent on the amount of toluene used to dissolve the rods for storage. If 10-15 ml are used as suggested in step 2.3.13.11, then 3-6 ml of the rod solution should be appropriate.
 - Centrifuge at 3,400 x g for 5 min.
 - Decant the clear supernatant.
 - Add all of the methanol solution from section 3.1 to the pellet.
 - Vortex or shake by hand to fully dissolve. Allow the solution to sit at least 1 hr to allow maximum ligand exchange to occur.

Note: The solution should be allowed to sit for at least 1 hr even if it appears to dissolve immediately and completely
 - Separate the solution into two halves in two centrifuge tubes.

Note: Save the centrifuge tube used for step 3.1 and transfer half of the solution into there.
 - Add 20 ml of toluene to each half. If there is a phase separation between the alcohol and toluene add methanol drop wise until the phases recombine.

8. Centrifuge at 7,700 x g for 15 min.
9. Very carefully decant the clear supernatant from pellet.
10. Invert the centrifuge tube carefully in order to dry the sample.
11. Add 5 ml ultrapure water to the pellet and store in a vial wrapped well in Al foil (or other opaque covering).

Note: Once moved from toluene to water, the rods are not photostable, which is why they are covered. Even if kept in the dark the rods should be used as soon as possible, and it is not recommended to store rods in water for more than one month.

4. Growth of Iridium Nanocrystalline Particles

1. Sodium Hydroxide
 1. In a plastic vial weigh out 1,450 mg NaOH. Dissolve NaOH in 20 ml ultrapure water. Solution should be clear with no solids.
2. Sodium Persulfate
 1. In a plastic vial weigh out 950 mg NaS₂O₈. Dissolve NaS₂O₈ in 20 ml ultrapure water. Solution should be clear with no solids.
3. Sodium Nitrate
 1. In a plastic vial weigh out 300 mg NaNO₃. Dissolve NaNO₃ in 18 ml ultrapure water. Solution should be clear with no solids.
4. Iridium Precursor Solution
 1. In a plastic vial weigh out 50 mg Na₃IrCl₆. Dissolve Na₃IrCl₆ in 5.0 ml ultrapure water. Solution should be transparent brown (like scotch) with no solids.
5. Preparation of sample
 1. Place a spectroscopic stirrer in a standard polystyrene cuvette.
Note: Because the solution is very basic, quartz and other glass cuvettes should not be used.
 2. Add 0.20 ml iridium precursor solution from step 4.4.1.
 3. Add 0.50 ml nitrate solution from step 4.3.1.
 4. Add 0.30 ml of seeded rods in water from section 3 (trace toluene from the ligand exchange may cause clouding of the cuvette wall).
 5. Add 0.50 ml of persulfate solution from step 4.2.1.
 6. Add 0.50 ml of sodium hydroxide solution from step 4.1.1.
6. Illumination of sample
 1. Place the cuvette in a holder with stirring capabilities.
 2. Illuminate with 450 nm light at 100 mW for up to 4 hr. The solution should turn green and later blue.
7. Collecting sample
 1. Pour solution (but not stir bar) into a centrifuge tube.
 2. Centrifuge at 7,700 x g for 10 min.
 3. Carefully decant the supernatant from the pellet, which should be green or blue depending on the reaction time selected.
Note: The pellet can now be collected or dispersed in a polar solvent through sonication for use in other experiments.

Representative Results

Transmission electron micrographs (TEM) were collected in order to see the distribution of iridium oxide on the seeded rods (**Figure 1**). TEM samples were prepared by pipetting a drop of dissolved particles onto a TEM grid. X-ray diffraction (XRD, **Figure 2**) and X-ray photoelectron spectra (XPS, **Figure 3**) were used to characterize the observed growth as a mix of crystalline IrO₂ and Ir₂O₃. Preparation of XRD and XPS samples was done by the drying of particles on glass slides. Enough sample was used so that a thick film developed (**Figure 4**). The illumination time was found to correspond with the particle size (**Figure 5**), which can be estimated visually. As the iridium oxide particles grow the color transitions (**Figure 4**) from yellow-orange (the color of bare rods) to green (medium coverage of ~1 nm particles) to blue (full coverage of ~2 nm particles).

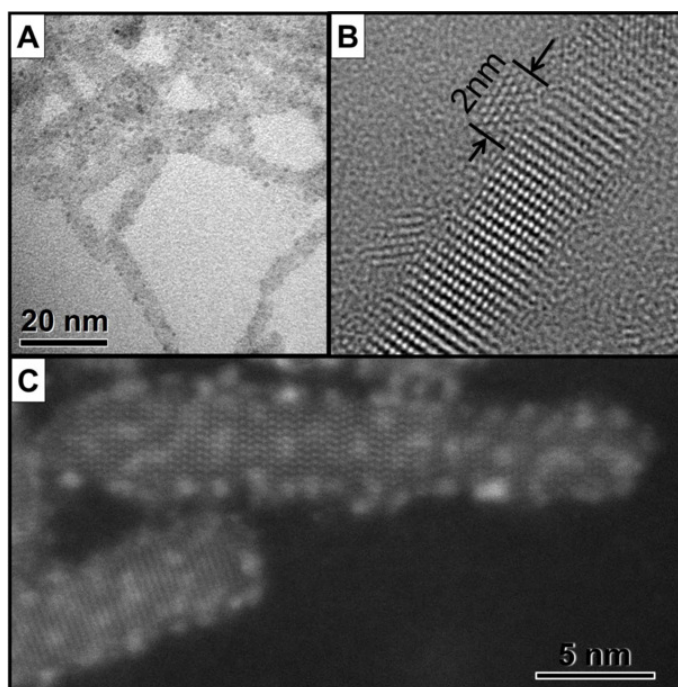


Figure 1. Electron Micrographs of Iridium Oxide Coated Rods. Seeded rods covered in iridium oxide as seen in TEM at lower magnification (A) and higher magnification (B) as well as using high angle annular dark field imaging (C) (adapted from Ref. [9] - Reproduced by permission of The Royal Society of Chemistry). [Please click here to view a larger version of this figure.](#)

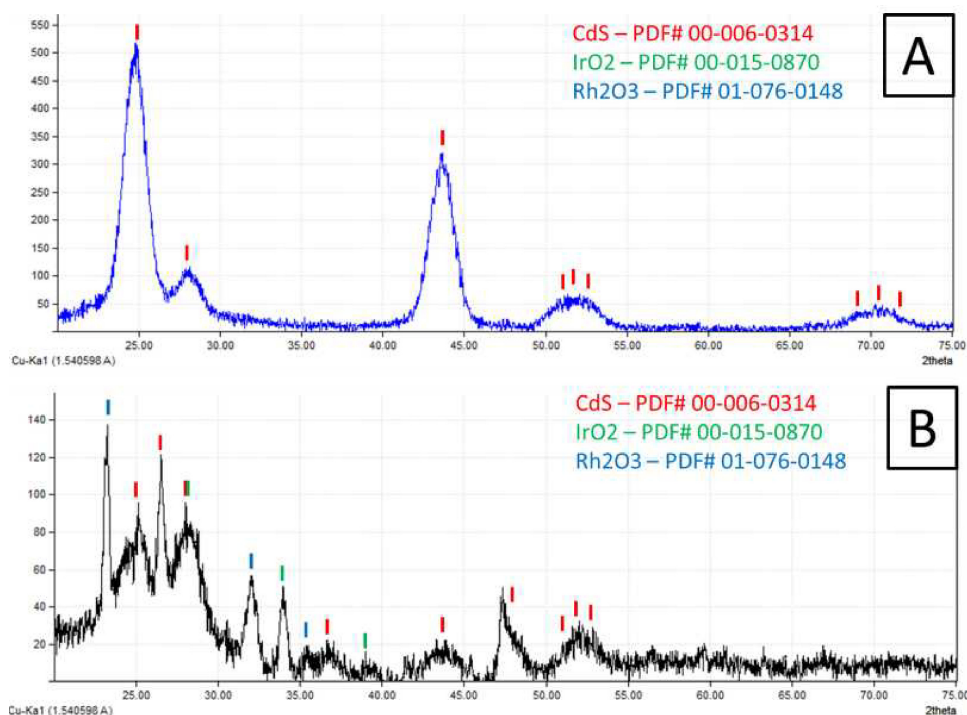


Figure 2. X-ray Diffraction Patterns. XRD patterns for (A) bare CdSe@CdS rods (B) CdSe@CdS rods after 2 hr growth of iridium oxide. These XRD patterns show the emergence of crystalline IrO₂ and Ir₂O₃. Indexed patterns for CdS (red) IrO₂ (green) and Rh₂O₃ (blue) are overlaid on the diffraction patterns. Ir₂O₃ was matched using the powder diffraction file for Rh₂O₃ because it is too unstable in bulk to characterize, yet has been predicted using theoretical modelling to have an almost identical structure (adapted from Ref. [9] - Reproduced by permission of The Royal Society of Chemistry). [Please click here to view a larger version of this figure.](#)

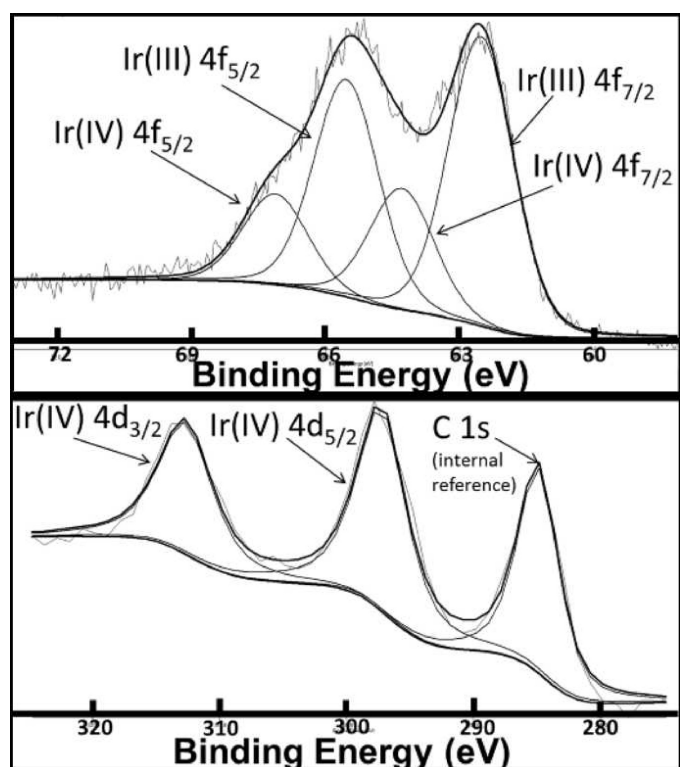


Figure 3. X-ray Photoelectron Spectrum. XPS was used to support the presence of both IrO_2 and Ir_2O_3 . Both plots are from a typical XPS spectrum, for a sample of CdSe@CdS after 2 hr photochemical growth of iridium, over different energy ranges. Signatures of both Ir(III) (at around 65 eV) and Ir(IV) (at around 300 eV) were observed as shown in the spectral peak deconvolutions (adapted from Ref. [9] - Reproduced by permission of The Royal Society of Chemistry). [Please click here to view a larger version of this figure.](#)

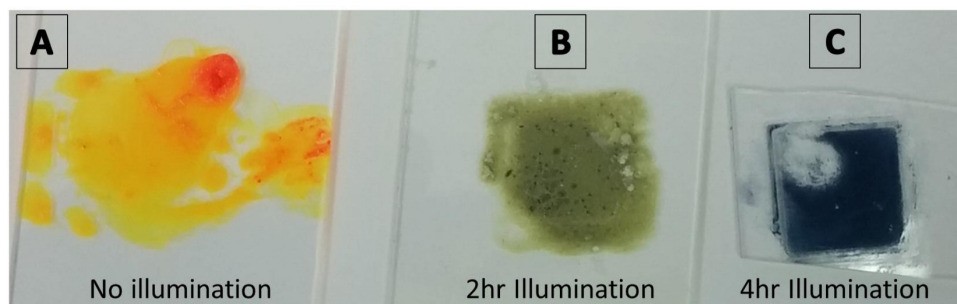


Figure 4. Visual Appearance of Sample After Different Growth Times. Powder samples prepared for XRD showing dried particles of (A, orange-red) bare rods (B, green) rods after 2 hr of illumination (C, blue) rods after 4 hr of illumination. [Please click here to view a larger version of this figure.](#)

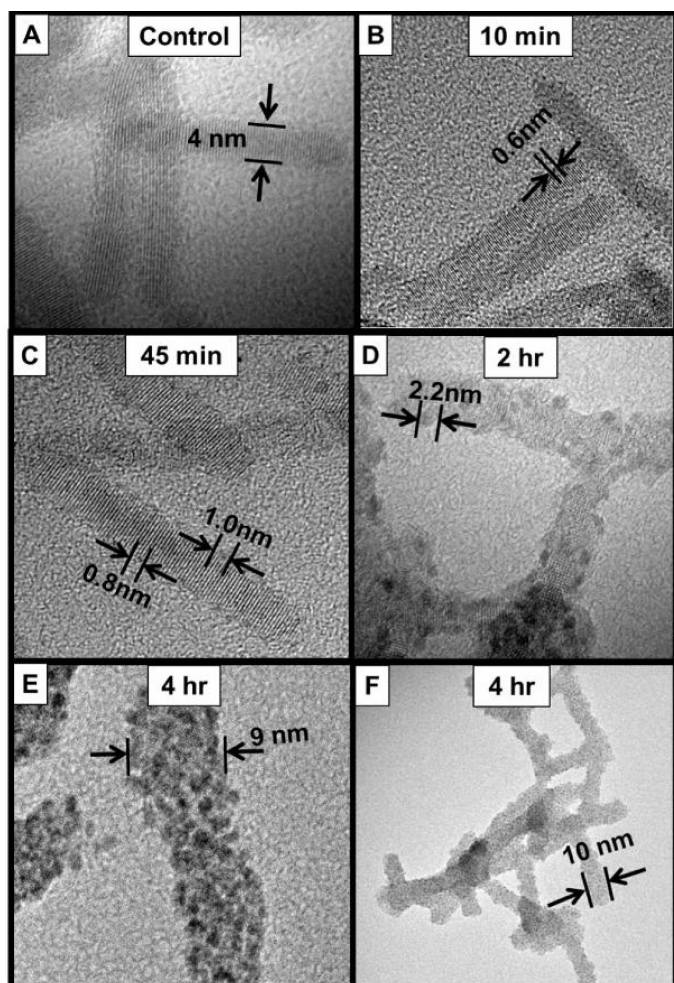


Figure 5. Iridium Oxide Growth Over Time. TEM micrographs, showing the growth of iridium oxide particles over time. (A) Control, kept in the dark. The control shows no iridium oxide growth, and rods of 4-5 nm diameter, unchanged from before the experiment. (B-F) Samples illuminated with unfiltered lamp light for (B) 10 min, (C) 45 min, (D) 2 hr, (E-F) 4 hr. This series shows the progression from small (<0.5 nm) iridium oxide particles, to larger (0.5-2 nm) particles, to a full coating of iridium oxide. The rods that were illuminated for 4 hr have a total diameter of 9-10 nm, indicating a 2-3 nm thick coating of iridium oxide is present (adapted from Ref. [9] - Reproduced by permission of The Royal Society of Chemistry). [Please click here to view a larger version of this figure.](#)

Discussion

The synthesis of CdSe seeds and CdSe@CdS seeded rods has been well studied^{21,24,25}. Slight modifications to the amounts, temperatures, and times for steps of the synthesis of these substrate particles can be used to tune their length, diameter, and/or morphology. The synthetic protocol described herein yields highly photoluminescent seeded-rods of uniform dimensions.

The ligand exchange procedure allows for the use of seeded rods in polar environments, in this case water. At the final stages of the ligand exchange, when the pellet is being collected for dissolution (after precipitation by toluene) the pellet often adheres poorly to the surface of the centrifuge tube. It is very important to decant and dry this pellet very carefully, otherwise there is a risk of throwing out or contaminating the pellet that has been formed. Seeds and rods in toluene and methanol are easy to precipitate and collect through the use of a non-solvent, however, once rods are put in water they are very hard to collect or move if they are soluble. This difficulty comes from the immiscibility of water with non-polar non-solvents such as toluene and hexane.

Once iridium oxide has been grown on the surface of seeded rods they become much harder to deal with as they aggregate. This made working with them and then analyzing them a challenging endeavor. Sonication in methanol or water produces a suspension that can be maintained by stirring.

Dried samples were used for XRD analysis. XRD patterns taken after different illumination times showed a growing peak near $2\theta=23^\circ$ (Figure 2), indicating time dependent growth of a crystalline material. High resolution spectra taken for clean rods, and rods after 2 hr of photochemical growth of iridium oxide were also taken. Signal from the CdSe@CdS rod sample shows a match with the expected pattern for CdS [PDF# 00-006-0314], with missing peaks attributed to the preference for the clean rods to lay flat on the substrate. Signal from CdSe@CdS rods after growth of iridium oxide show the characteristic CdS peaks, along with extra peaks, including the one seen in Figure 2. Peaks in the XRD pattern were very small (see Figure 2), and required long scans (at least 8 hr) because of the small crystallite size. Some peaks match well with IrO_2 [PDF# 00-015-0870], while others match well with Rh_2O_3 [PDF# 01-076-0148] (which has been theorized to have a structure nearly identical to

Ir_2O_3 — the pattern for Ir_2O_3 is not reported in the JCPDS database because it is relatively unstable²³). Similar to the XPS data, this XRD data confirms the presence of IrO_2 , and suggests the iridium growth is a mix of IrO_2 and Ir_2O_3 .

Photochemical oxidation as a synthetic tool expands the methods by which chemists can create new hybrid materials. While new synthetic procedures must be developed for photodeposition of each target material, our work shows that photochemical oxidation is possible with cadmium chalcogenide materials. It offers unique means of material processing that can be applied to the intelligent design of complex photocatalysts. It might allow for production of materials in a nonequilibrium state (e.g., formation of the metastable phase Ir_2O_3), presumably due to the unique atomic-level interaction between the deposit and the substrate. In addition, intermediates produced during the various redox reactions might have interesting effect on the oxide formation; bring about photochemical co-deposition to produce exclusive complex materials. The synthetic method described herein is the first time oxidative photodeposition has been realized with CdS. We anticipate that this synthetic methodology will ultimately allow for the development of stable and efficient solar driven photocatalysis of water.

Disclosures

The authors have nothing to disclose.

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