

Journal of Materials Chemistry A

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COMMUNICATION

Photochemical Oxidation on Nanorod Photocatalysts

revised. Cite this DOI:
10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The combination of photochemical oxidation with colloidal synthesis enables us to re-think the design of photocatalysts with an eye towards overall water splitting. Here, IrO₂ nanoparticle oxidative catalysts that were photodeposited on colloidal CdSe@CdS nanorod photocatalysts revealed a mediated oxidative pathway, and afforded the rods remarkable photochemical stability under prolonged illumination in pure water.

Photocatalysis presents an attractive and promising solution for renewable energy generation and other environmental applications such as water treatment and air purification¹⁻⁵. Solar-driven photocatalytic splitting of water into hydrogen and oxygen can provide clean and renewable fuel; however, systems that are sufficiently stable and efficient for practical use have not yet been realized.

Both photodeposition and semiconductor-mediated photocatalysis rely on photo-generated electron-hole pairs that migrate to the surface in order to promote chemical reactions with various substances. It seems natural to leverage the similarities between these two processes, and utilize one to the benefit of the other. Here, we describe and demonstrate the value photodeposition could offer to the field of photocatalysis, particularly in serving as an advanced synthetic tool⁶⁻⁸ and as a unique probe of redox reactions. We expect our findings to further advance the ability to construct sophisticated nanoparticle heterostructures and ultimately to realize an efficient photocatalyst for direct solar-to-fuel energy conversion.

Photodeposition presents an elegant means for visualization of successful photo-induced charge carrier transfer to the solution⁹⁻¹¹. The deposited metal or metal oxide nanoparticles serve as labels, enabling the use of transmission electron microscopy (TEM) for recognition of the active sites on the semiconductor photocatalysts. Thus, careful examination of the newly formed heterostructures is extremely beneficial and can be utilized for probing the efficiency of photocatalytic reactions. This technique facilitates appealing basic research opportunities: associating structural and chemical reactivity with properties of the individual photocatalyst in question,

formulating a correlation between the activity for O₂ evolution and alterations made to the structure.

We have chosen as our substrate a tunable quantum dot photocatalyst¹² composed of a cadmium sulfide rod with an embedded cadmium selenide seed (CdSe@CdS).¹³⁻¹⁵ This architecture facilitates localization of confined holes¹⁶⁻¹⁷, and control over the degree of charge separation via tuning of the seed size.¹⁸ More importantly, it enables formation of a distinct oxidation reaction site on the rod. We exploit this unique electronic feature in order to deduce the mechanism of the oxidation reactions from examination of oxide markers. This demonstrates an interesting benefit that originates from the combination of photodeposition with cutting-edge colloidal synthesis procedures, which allows for manipulation of photo-induced charge carriers.¹⁹⁻²¹

We focused on IrO₂, as it is known to be an efficient catalyst for water oxidation²²⁻²⁸. Using photochemical oxidation we have successfully grown crystalline IrO₂ nanoparticles on the hybrid CdSe@CdS semiconductor, as can be seen in Figure 1. The TEM micrograph in Figure 1A depicts a representative sample of CdSe@CdS rods, with Ir oxide nanoparticles seen as darker speckles decorating the surface. The high resolution TEM in Figure 1B demonstrates the average size and crystallinity of the oxide, as well as the preservation of the semiconductor substrate. The crystallinity of the CdS rod after photochemical oxidation and deposition of Ir oxide is also evident in the high angle annular dark field (HAADF) micrograph (Figure 1C). Iridium oxide composition and phase were confirmed via X-ray photoelectron spectroscopy (XPS; Figures 1D and S5), which revealed a mix of IrO₂ and Ir₂O₃. X-ray diffraction also indicates the presence of rutile IrO₂ along with corundum Ir₂O₃ (Figure S7). This metastable phase is also thought to be a good oxidative catalyst²⁹, though we expect it will oxidize fully to IrO₂ during catalysis. Chemical compositional analysis by X-ray energy-dispersive spectroscopy (EDS; Figure 1E) was also preformed.

We examined means for control over the characteristics and quality of the deposited oxide co-catalyst, in particularly the particle size, crystallinity, deposition location on the CdS rod, and composition (metallic vs. oxide). For a more detailed account see the SI. While the catalytic activity of IrO₂ towards water oxidation was

proven to strongly depend on size, with smaller particles demonstrating higher activity, most reports only describe particles as small as 10nm²². In this work we report growth of crystalline IrO₂ at much smaller scales, ranging from 0.5nm to about 3nm, as can be seen in the HRTEM in Figure 1B and Figure S1.

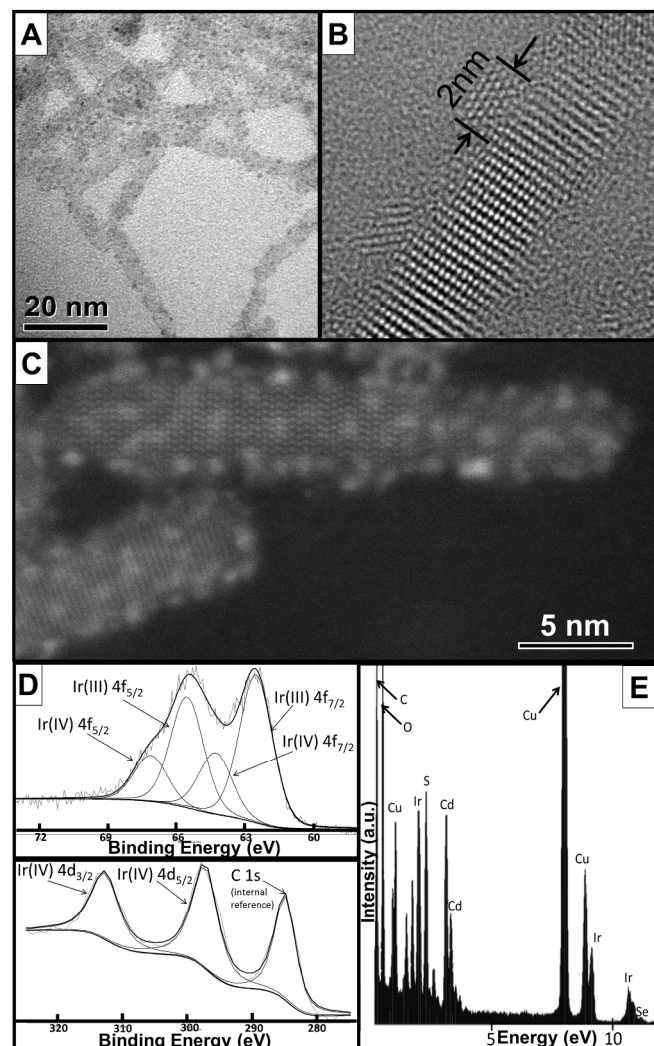


Figure 1. Photochemical oxidation growth of crystalline IrO₂ nanoparticles on hybrid semiconductor nanorods. (A) TEM micrograph of a representative sample of CdSe@CdS rods with Iridium oxide nanoparticles (dark speckles) decorating the surface. (B) High resolution TEM demonstrating the average size and crystallinity of the oxide. (C) High angle annular dark field imaging micrograph demonstrating preservation of the semiconductor substrate. (D) X-ray photoelectron spectroscopy analysis, where the C 1s peak has been used as an internal standard, and (E) X-ray energy-dispersive spectroscopy analysis, both confirming presence of Iridium oxide.

Among the broad range of deposition conditions that were explored were parameters such as the metal precursor type and concentration, electron/hole scavengers, the pH of the solution, solvent environment, degree of holes confinement, illumination intensity and excitation wavelength, and growth time. Figure 2A-B demonstrates the achievable control over the IrO₂ nanoparticles size and level of coverage over the rod (see Figure S1 for more micrographs). Illumination time and excitation wavelength were found to be key parameters for such control, supporting a light induced growth mechanism. This was later confirmed with control experiments in the dark.

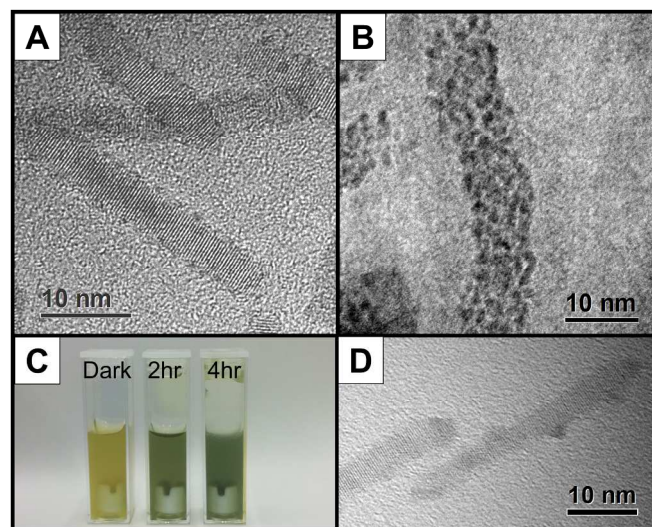


Figure 2. (A-B) TEM micrographs demonstrating the achievable control over the IrO₂ nanoparticles size, and level of coverage over the rod. Illumination time and excitation wavelength were found to be key parameters. (C) Sample color as indirect evidence of growth. Control sample, kept in the dark, retained its original yellow color. During deposition gradual color change was observed to blue, the color of bulk IrO₂ powder. (D) Light induced growth of cobalt oxide.

During deposition a gradual color change was observed from yellow, the color of CdS@CdSe in aqueous solution, to blue, the color of bulk IrO₂ powder. Solutions after 2hr (yellow-green) and 4hr (blue-green) of illumination are shown in Figure 2C, along with a solution that was kept in the dark as a control (yellow), and indeed retained its original color. For TEM of the control see Figure S1.

We have also demonstrated the generalization of the technique to other metal oxides co-catalysts such as cobalt oxide³⁰⁻³² (Figure 2D).

With the addition of a Pt tip, the CdSe@CdS nanorod structure was found to be highly active for hydrogen production.^{12,33,34} However, it is not suitable for overall water splitting since prolonged irradiation of CdS suspensions lead to photocorrosion of CdS into Cd²⁺ and S (sulfate in the presence of O₂). Hampered by photochemical instability, CdS requires the use of sacrificial donors for photochemical H₂ evolution from water, and does not support genuine solar-to-fuel energy conversion. Deposition of a metal oxide catalyst is expected to enhance the structure's stability, due to the oxide's ability to scavenge the holes from the semiconductor and mediate their transfer to water.

Indeed, rods with the addition of IrO₂ demonstrated remarkable photochemical stability under prolonged illumination in pure water (without the addition of any hole scavengers). Figure 3A shows two cuvettes with CdSe@CdS rods (yellow on the left) and CdSe@CdS-IrO₂ (pale green on the right), both in pure water before illumination. Figure 3B depicts the same cuvettes after illumination (identical conditions). While the CdS rods clearly degraded as a result of photocorrosion, the sample with oxide catalysts was protected. Figure 3C shows a representative TEM micrograph of such a CdSe@CdS-IrO₂ rod after illumination. In contrast, and as anticipated, CdSe@CdS rods could not be found in the iridium free samples. In light of their stability, evaluation of the photocatalytic efficiency of our newly developed materials is on-going in our lab.

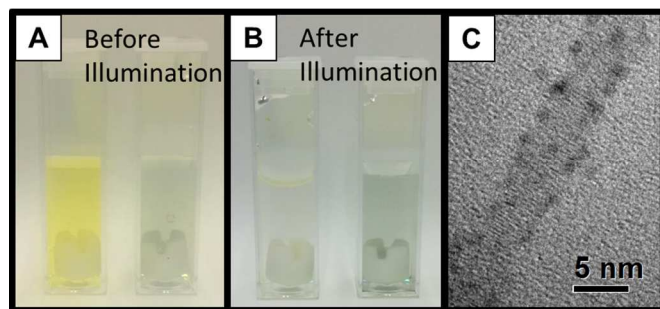


Figure 3. Demonstrating the CdSe@CdS-IrO₂ rods photochemical stability under illumination in pure water. (A) Samples of CdSe@CdS rods with (right) and without (left) IrO₂ before illumination. (B) The same cuvettes after illumination at identical conditions, with significant color loss indicating photocorrosion of the CdSe@CdS sample. (C) A representative TEM micrograph of CdSe@CdS-IrO₂ rod after illumination, which validates particle stability under illumination.

Photodeposition is expected to inherently place the co-catalyst at the location(s) where the photo-induced charge carriers are most readily available for the promotion of photocatalytic reaction. Interestingly, despite having a localized oxidation site, the IrO₂ growth appears to be distributed uniformly along the surface of the nanorod. A similar uniform distribution along the surface was also obtained for cobalt oxide deposition (Figure 2D). This finding sheds light on the possible mechanism for hole transfer to the solution.

Photodeposition is at essence a form of electrochemical deposition. Inspired by electrochemical deposition literature³⁵⁻⁴¹, we hypothesize that the deposition of metal oxides is most likely accomplished via one of two mechanisms: (1) utilization of photo-generated electrons for reduction of the metal ion, followed by oxidation of the deposited metallic particle, or (2) utilization of holes produced in the semiconductor valence band.⁴² A great discussion exists nowadays about the oxidative pathway, which could be performed by direct hole attack or mediated by OH[•] radicals, in their free or adsorbed form.⁴³ In such a chain of events the photogenerated holes are first utilized for water oxidation, which results in the production of OH[•] radicals that can then immediately react with the metal cations in the solution to form an oxide nucleus.

It is imperative that we understand which mechanism controls the deposition of the metal oxide of interest as the appropriate approach and optimized conditions could be vastly different. In this work we have used Na₂S₂O₈, under basic conditions, as an electron scavenger, and hence eliminated (or minimized) the possibility of cation reduction. In the absence of the electron scavenger there was no growth of IrO₂.

Growth of IrO₂ at locations that are far from the CdSe seed, to which holes are three-dimensionally confined, suggests a mediated oxidative pathway, with oxidation intermediate (OH[•] radical) that is mobile, either directly on the semiconductor's surface or within close proximity to it. The suggested deposition mechanism is illustrated in Figure 4.

This finding testifies to the importance of proper design of the photocatalyst, which should be planned not only to promote efficient long lasting charge carriers separation^{44,45}, but also to insure minimal back reaction of intermediates.

The addition of photochemical oxidation to the synthetic toolbox of chemists offers a unique means of material processing, with the potential to create many new hybrid materials. Atomic-level interaction between the deposit and the substrate can allow for production of materials in a non-equilibrium state. Furthermore,

photochemical co-deposition could be exploited for the production of unique complex materials.⁴⁶

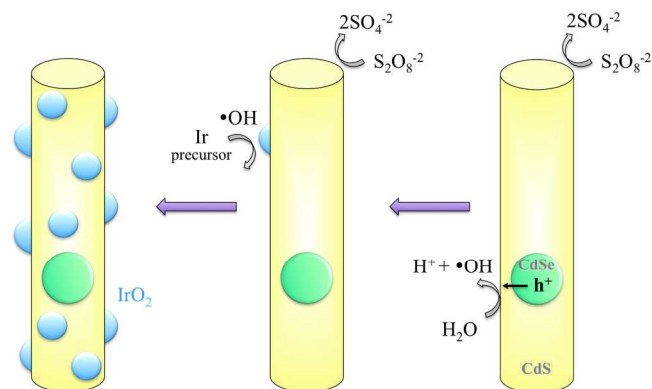


Figure 4. Illustration of the suggested IrO₂ light induced growth mechanism, indicating mobility of the oxidation intermediate.

Conclusions

We coupled photochemical oxidation with colloidal synthesis, for the growth of extra small (1-2nm) crystalline IrO₂ oxidative catalysts on CdSe@CdS nanorod photocatalysts. The addition of iridium oxide nanoparticles afforded the rods photochemical stability under prolonged illumination in pure water. Photochemical oxidation offers visualization of successful charge carrier transfer to the solution, and is harnessed here for a mechanistic study of oxidation reactions. Interestingly, despite the three-dimensional confinement of the holes to the CdSe seed, the IrO₂ growth is distributed uniformly along the surface of the nanorod, revealing a mediated oxidative pathway. This finding is significant for proper design of photocatalysts.

We anticipate that this work will ultimately advance our ability to realize a stable and efficient photocatalyst for solar-to-fuel energy conversion.

Acknowledgments

This research was supported by the I-CORE Program of the Planning and Budgeting Committee and The Israel Science Foundation (Grant No. 152/11). We thank the Schulich Faculty of Chemistry and the Technion – Israel Institute of Technology for the renovated laboratory and startup package. Dr. Kalisman thanks the Schulich postdoctoral fellowship for their support. We thank Dr. Kamira Weinfeld for her assistance with XPS characterization, and Dr. Yifat Nakibli for her valuable contribution to this work. This paper is dedicated to the memory of Rafi Berger.

Notes and references

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Electronic Supplementary Information (ESI) available: detailed description of the typical preparation of Iridium oxide and cobalt oxide coated CdSe@CdS nanorods, the scope of solutions investigated for IrO₂ growth, and techniques used in characterization of these particles. See DOI: 10.1039/c000000x/

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