Supporting Information

Platinum@Hexaniobate Nanopeapods: A Directed Photocatalytic Architecture for Dye-Sensitized Semiconductor H₂ Production Under Visible Light Irradiation

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SYNTHESIS OF CHROMOPHORES AND CATALYST STARTING MATERIALS

Materials. K$_2$CO$_3$ (99%) and Nb$_2$O$_5$ (99%) were acquired from Alfa Aesar. Oleylamine (OAm) (technical grade, 70%), platinum (II) acetylacetonate (Pt(acac)$_2$) (97%), L-ascorbic acid ($\geq$99%), 6 M hydrochloric acid, and tetrabutylammonium hydroxide (TBAOH) 30-hydrate were purchased from Sigma-Aldrich. Toluene (certified ACS, 99.8% anhydrous), hexane (95% anhydrous), and absolute ethanol (200 proof) were purchased from Fisher Scientific.

Synthesis of K$_4$Nb$_6$O$_{17}$

Crystalline samples of the layered metal oxide K$_4$Nb$_6$O$_{17}$ were prepared via a high-temperature ceramic method. Nb$_2$O$_5$ was dried for 1 hour at 900 °C and stored under argon. K$_2$CO$_3$ and Nb$_2$O$_5$ (molar ratio 1.4:1) were ground for 10 minutes using a ball-milling apparatus (Spex 8000 Mixer/Mill, zirconia ball media) and placed in an alumina crucible. An initial 10% molar excess of K$_2$CO$_3$ was included to compensate for volatilization during the high-temperature synthesis. The mixture was heated at 900 °C for 1 hour. After cooling to 700 °C in the oven and to room temperature in the open air, a further 10% excess of K$_2$CO$_3$ was added to prevent the formation of potassium-deficient phases; this mixture was ground again for 10 minutes via ball-milling. The sample was then heated for 2 days at 1050 °C, followed by 1 hour at 1100 °C. After cooling to room temperature, the sample was washed via centrifugation with de-ionized water and acetone and dried overnight at 75 °C.

Protonation of host to H$_x$K$_{4-x}$Nb$_6$O$_{17}$

Protonation was performed by placing 8 mL of 6 M HCl and 1 g of K$_4$Nb$_6$O$_{17}$ in a 23 mL capacity PTFE liner within a stainless steel autoclave (Parr model 4749A) and heating at 90 °C for 2 d. The product was washed via centrifugation with de-ionized water and acetone and then dried overnight at 75 °C.
Figure S1. XRD spectra of as-synthesized host material $\text{K}_4\text{Nb}_6\text{O}_{17}$ (bottom) and protonated $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$ (top). The increase in d-spacing of the [040] peak after protonation indicates a decrease in the interlayer distance in the $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$, confirming successful replacement of the large $\text{K}^+$ interlayer cations with the smaller $\text{H}^+$. 
**Synthesis of Ru(II) bipyridyl complexes**

In this study, two different ruthenium(II) bipyridyl compounds were used to sensitize catalyst materials for visible light absorption. The phosphorous hexafluoride salts of tris(2,2’-bipyridine)ruthenium(II) ([Ru(bpy)$_3$]$^{2+}$) and (4,4’-dicarboxy-2,2’-bipyridine)ruthenium(II)$^{2+}$ ([Ru(bpy)$_2$(dcbpy)]$^{2+}$) were synthesized by published methods, and will hereafter be referred to as Ru(bpy) and Ru(dcbpy), respectively.$^{1,2}$ Formation of the target compounds was verified via nuclear magnetic resonance (NMR) spectroscopy and visible absorbance spectroscopy. As seen in **Figure S2**, both absorbance spectra show peaks in good agreement with literature.$^{3,4}$

![UV-Vis spectra of Ru(bpy) and Ru(dcbpy) chromophores with absorbance peaks at expected locations.](image)

**Figure S2.** UV-Vis spectra of Ru(bpy) and Ru(dcbpy) chromophores with absorbance peaks at expected locations.
**Synthesis of platinum nanoparticles and nanoseeds via microwave heating**

Cubic, 8-nm Pt NPs were synthesized via a microwave heating method recently reported by our group.  

\[ 200 \text{ mg Pt(acac)}_2, 50 \text{ mg L-ascorbic acid, 5 mL OAm, and 5 mL toluene were added to a microwave-transparent glass reaction vessel along with a PTFE stir bar and a Weflon\textsuperscript{TM} button. The vessel was sealed with a 15-bar pressure responsive cap, then heated under an applied power of 1200 W at 3.5 °C/minute to 135 °C and held for 30 minutes. After cooling to room temperature, dark brown Pt NPs were isolated from solution by adding 25 mL EtOH, followed by centrifugation for 10 minutes at 6000 rpm. The light yellow-brown supernatant was discarded, and the precipitate was redispersed in toluene. This precipitation-redispersal procedure was repeated 3 times to obtain OAm-capped Pt NPs. Finally, the Pt NPs (yield ~ 200 mg) were dispersed in 10 mL of toluene, sonicated, and transferred to a glass scintillation vial. The highly dispersible 8-nm Pt nanocubes formed a colloidal suspension that was used to synthesize Pt@HNB NPPs. Small, irregular Pt NPs (2 – 4 nm) were also synthesized via MW heating under the same conditions except with temperature reduced to 120 °C. The small, seed-like Pt NPs were then used to form extPt-HNB NScs.**

Composition, size, and morphology of the Pt nanocubes and nanoseeds was examined via XRD and TEM. As seen in Figure S3, peak position and intensity for both samples was in good agreement with the Pt reference pattern, which confirmed the successful formation of Pt NPs. The Pt nanocubes show diffraction peaks that are well-defined and symmetrical, with peak intensities that correspond to a random three-dimensional ordering of polyhedral Pt NPs. The broad, lower intensity peaks of the Pt nanoseeds is consistent with their smaller size and lack of defined crystallographic facets.
Figure S3. X-ray diffraction pattern of MW-synthesized 8-nm Pt nanocubes (top) and 2–4 nm Pt nanoseeds (middle) compared to the reference pattern for Pt* (bottom).
Synthesis of extPt-HNB NScs and empty hexaniobate nanoscrolls
ExtPt-HNB NScs were synthesized from crystalline hexaniobate and the Pt nanoseeds. 100 mg of crystalline H$_x$K$_{4-x}$Nb$_6$O$_{17}$, 200 mg TBAOH, 5 mL OAm, and 3 mL toluene were added to the reaction vessel. A colloidal toluene suspension of OAm-capped Pt nanoseeds (20 mg/mL) was briefly sonicated, after which 5 mL (100 mg of NPs) were added to the mixture in the glass reaction vessel. The reaction mixture was heated to 135 °C at a rate of 3.5 °C/minute and held at that temperature for 105 minutes. To ensure optimal distribution of heat and chemical species throughout the reaction mixture, magnetic stirring at 650 rpm was maintained consistently throughout the reaction. After the reaction, the vessel was cooled to room temperature at 10 °C/minute. Washing the silvery-brown product and isolation of the extPt-HNB NScs was performed using the method for isolating Pt@HNB NPPs described in the main text. ExtPt-HNB NScs were dried overnight at room temperature in preparation for surface passivation and photolysis. Empty hexaniobate NScs (Figure S4) were synthesized the same method, but substituting pure toluene for the Pt NPs suspension.
Figure S4. TEM image of empty hexaniobate nanoscrolls synthesized via MW method.
SURFACE PASSIVATION OF AS-SYNTHESIZED CATALYSTS VIA UV IRRADIATION

Confirmation of OAm removal was conducted via ATR-FTIR (Figure S5). In Figure S5a, the presence of OAm ligands on the surface of the as-synthesized Pt@HNB NPPs is confirmed by the appearance of characteristic amine peaks including NH$_2$ bends at 722 and 1574 cm$^{-1}$, asymmetric and symmetric C—H stretches at 2921 and 2852 cm$^{-1}$ (respectively), and a bend of the C—H group near the C=C at 3006 cm$^{-1}$. As shown in Figure S5b, the catalyst surfaces can be effectively passivated by UV irradiation for removal of the OAm groups. The strong peaks characteristic of amine C—H and NH$_2$ groups are absent, and the appearance of a strong broad band near 3500 cm$^{-1}$ indicates the presence of hydroxyl groups. The hydroxyl groups could have adsorbed to the passivated hexaniobate surface from the EtOH suspension in which the UV irradiation was performed. Significantly increased dispersibility of the passivated catalysts in EtOH and MeCN further supports thorough removal of the amine.
Figure S5. ATR-FTIR spectra showing Pt@HNB NPPs (a) before and (b) after passivation via UV irradiation to remove OAm groups from the surface.
PHOTOLYSIS PREPARATION

Table S1. Samples prepared using 5 mg of dried, UV-passivated solid catalysts dispersed in photolysis solution; samples irradiated 210 minutes; 50 μL headspace withdrawn every 30 minutes for GC analysis.

| Component               | Type                           | Amount       |
|-------------------------|--------------------------------|--------------|
| Solvent                 | Acetonitrile                   | 3.2 – 3.9 mL |
| Chromophore             | [Ru(bpy)$_3$](PF$_6$)$_2$       | 260 μM       |
|                         | [Ru(bpy)$_2$(dcbpy)](PF$_6$)$_2$|              |
| Sacrificial Electron Donor | Triethylamine (TEA)         | 0.05 M       |
| Reductive Quencher      | Trimethylaniline (TMA)        | 0.4 M        |
| D.I. Water              | Proton source                 | 100 – 800 μL |

**Photosystem optimization**

In order to ensure reproducibility of photolysis results, catalyst photosystems were optimized to maintain a homogeneous colloidal dispersion and prevent clumping or settling during photolysis. Catalyst surfaces were pre-treated with UV irradiation to remove residual hydrophobic groups and maximize dispersibility in the MeCN-based photosystem. When assembling the photolysis reaction mixture, micro-stir bars were added to each vial before degassing. The prepared vials were subsequently placed on a stir plate situated within the photoreactor. Continuous gentle stirring was performed for the duration of photolysis to ensure that the catalysts maintained a homogeneous colloidal dispersion. Figure S6 shows examples of prepared vials.
Figure S6. Examples of prepared photolysis vials. Samples were able to maintain homogeneous colloidal suspensions when agitated or stirred, as seen above.
Determination of Hydrogen Production

Number of moles H$_2$ were derived from thermocouple readings (mV) vs. time (s) output by the gas chromatograph during photolysis, using the method of Shan and Fontenot.$^{8,9}$ Hydrogen production was determined by integrating the area under the peak for H$_2$, which occurred at a retention time of 65 s after injection in each GC measurement. H$_2$ peak area was multiplied by a constant (m) representing the slope of the GC calibration curve in units of μL/area to find volume of H$_2$ (in μL). The percentage of H$_2$ in the photolysis vial headspace was found by dividing μL H$_2$ by the volume of injected gas (50 μL). These calculations were repeated for GC data collected at 30-minute intervals over the 210-minute photolysis period. Total volume H$_2$ produced was calculated by multiplying percent H$_2$ in the headspace by total headspace volume (4.7 mL), and then adding that quantity to the sum of cumulative H$_2$ volumes (converted to mL) observed at each 30-minute interval. This value of H$_2$ volume (in L) was then converted into moles of H$_2$ via the ideal gas law.
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