# Photocatalytic Hydrogen Evolution from Hexaniobate Nanoscrolls and Calcium Niobate Nanosheets Sensitized by Ruthenium(II) Bipyridyl Complexes

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Hexaniobate nanoscrolls (NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) and acid-restacked calcium niobate nanosheets (R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>) were compared as oxide semiconductors in photocatalytic assemblies for H<sub>2</sub> production using ethylenediamine-tetraacetic acid (EDTA) as a sacrificial electron donor and platinum (Pt) nanoparticles as catalysts. Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(bpy)<sub>2</sub>(4,4'-(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>bpy)<sup>2+</sup> (bpy = 2,2'-bipyridine) were employed as visible light sensitizers (abbreviated as Ru<sup>2+</sup> and RuP<sup>2+</sup>, respectively). RuP<sup>2+</sup>, which is anchored by a covalent linkage to the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> surface, functions more efficiently than the electrostatically bound Ru<sup>2+</sup> complex, because of more efficient electron injection from the excited sensitizer to NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>. RuP<sup>2+</sup>-sensitized NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> both produce H<sub>2</sub> photocatalytically using visible light ( $\lambda > 420$  nm) with initial apparent quantum yields of 20–25%. At the optimum sensitizer concentration and Pt loading, the photochemical hydrogen evolution process is primarily limited by the efficiency of light absorption and charge injection from the oxide semiconductor particles. The dependence of the hydrogen evolution rate on Pt loading suggests that the scavenging of conduction band electrons by Pt is substantially faster than charge recombination or EDTA reduction of the oxidized sensitizer under optimized conditions.

## Introduction

Dye-sensitization of wide-gap semiconductor particles, which was demonstrated by Gerischer in 1972,<sup>1</sup> has since been extensively studied as a potential means of producing H<sub>2</sub> from sunlight and water.<sup>2–11</sup> Semiconductor particles mediate the transfer of electrons from photoexcited dye molecules to catalytic species such as platinum (Pt) nanoparticles, where the reduction of water to H<sub>2</sub> competes kinetically with back electron transfer to oxidized dye molecules. The quantum efficiency of dye-sensitized H<sub>2</sub> production is thus strongly dependent on the semiconductor employed, as well as the sensitizer and the catalyst.<sup>2–4,5b,6,7b,9b,10b,11</sup>

Particulate semiconductors that have been studied in these systems are usually "bulk-type" metal oxide particles (such as titanium dioxide), although some anisotropic nanoparticles, such as a carbon nanotubes, have been recently reported as building blocks for dye-sensitized H<sub>2</sub> production.<sup>10</sup> Very recently, we reported that single crystalline nanoscrolls made by acid exchange of potassium hexaniobate (NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) can be sensitized by Ru<sup>2+.11</sup> The negatively charged nanoscrolls bind the cationic  $Ru^{2+}$  complex, and  $H_2$  is produced from aqueous ethylenediaminetetraacetic acid (EDTA) solutions under visible light ( $\lambda > 420$  nm) even without a covalent linkage between the sensitizer and the nanoscroll surface. Dye-sensitized nanoscrolls catalyzed by Pt nanoparticles are more active for H<sub>2</sub> production than analogous composites based on lamellar hexaniobate particles or P25 titania, consistent with efficient mediation of electron transfer by the single-crystalline oxide scrolls. However, the competition of EDTA and  $Ru^{2+}$  for

adsorption sites on the nanoscroll surface limits the quantum yield and turnover number in these systems.

Among ruthenium polypyridyl complexes, phosphonic acidmodified derivatives have been found to be most effective for applications such as dye-sensitized solar cells<sup>12</sup> and photocatalysis, especially in aqueous media.<sup>9a,b</sup> Choi et al. have examined the effects of anchoring groups on sensitized H<sub>2</sub> production using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> derivatives.<sup>9b</sup> RuP<sup>2+</sup> was the most effective of the Ru-based sensitizers they examined. It is thus of interest to compare electrostatic vs covalent anchoring of Ru<sup>2+</sup> and RuP<sup>2+</sup> in the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> system for visible-lightdriven H<sub>2</sub> production from aqueous EDTA solutions.

A Dion–Jacobson type perovskite,  $ACa_2Nb_3O_{10}$  (A = H or K),<sup>13</sup> has been studied by several researchers as a photocatalyst and a photoelectrode for UV light-driven water splitting.14-19 The structure of KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> is schematically illustrated in Figure 1A, along with that of K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (Figure 1B).<sup>13,20</sup> KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> consists of negatively charged calcium niobate sheets that stack along the b axis to form a two-dimensional layered structure, in which K<sup>+</sup> cations are located between the triple perovskite layers.<sup>13c</sup> Upon photoexcitation, electrons and holes are generated in the perovskite blocks, causing redox reactions with reactant molecules adjacent to the layers. Acid exchange of KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> produces HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, which has a higher rate of H<sub>2</sub> production from aqueous methanol due to the hydration of interlayer galleries.14,18 HCa2Nb3O10 is one of the most active niobate photocatalysts,<sup>14a</sup> and it can be exfoliated to unilamellar crystalline sheets by reaction with bulky base molecules.16-19,21 The nanosheet-based materials exhibit enhanced activity for H2 production, most likely because of larger specific surface area and smaller crystallite size.<sup>16a</sup> It is thus expected that crystalline Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub><sup>-</sup> nanosheets will function as effective electron transfer mediators for dye-sensitized H<sub>2</sub> production, as in the case of hexaniobate nanoscrolls.

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Figure 1. Schematic illustration of the structures of (A)  $KCa_2Nb_3O_{10}$  and (B)  $K_4Nb_6O_{17}$ .

The present paper compares two different kinds of exfoliated lamellar niobates (derived from KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) and ruthenium sensitizers (Ru<sup>2+</sup> and RuP<sup>2+</sup>) as photocatalysts for dye-sensitized H<sub>2</sub> production from water-containing EDTA as an electron donor under visible light ( $\lambda > 420$  nm). The efficiency of charge injection and photocatalytic H<sub>2</sub> evolution are compared, and their dependence on the loading of RuP<sup>2+</sup> and Pt provides insight into the relative rates of electron transfer and recombination reactions.

#### **Experimental Section**

Preparation of Hexaniobate Nanoscrolls and Restacked **Calcium Niobate Nanosheets.**  $K_{4-x}H_xNb_6O_{17}$  ( $x \approx 2$ ) and HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> powders were made as described in our previous papers.<sup>11,18</sup>  $K_{4-x}H_xNb_6O_{17}$  ( $x \approx 2$ ) and  $HCa_2Nb_3O_{10}$  were exfoliated using aqueous tetra(n-butyl)ammonium hydroxide (TBA<sup>+</sup>OH<sup>-</sup>, Alfa Aesar, 40 wt % in  $H_2O$ ) at room temperature. Nanoscrolls were obtained by shaking  $K_{4-x}H_xNb_6O_{17}$  ( $x \approx 2$ ) in aqueous TBA<sup>+</sup>OH<sup>-</sup> solution (8.0 wt %) for 1 day.<sup>11</sup> To exfoliate HCa2Nb3O10, the powder was shaken in aqueous TBA<sup>+</sup>OH<sup>-</sup> solution (ca. 7.3 mM) for 1 week according to the method of Ebina et al.<sup>16</sup> In each case, the resulting suspension was centrifuged, and the precipitate was discarded, yielding a colloidal suspension of nanoscrolls or nanosheets. The colloids were restacked by adding aqueous hydrochloric acid (2.5 M). The resulting precipitate was then rinsed several times with pure water to remove excess HCl, followed by drying in an oven at 333 K overnight and grinding into a powder using a mortar and pestle. Energy dispersive X-ray spectroscopy revealed that the acid-precipitated colloids contained only a small amount of residual potassium, with K/Nb ratios of 0.01-0.05. The final products are thus abbreviated below as  $NS-H_4Nb_6O_{17}$  (NS = nanoscroll) and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> (R = restacked).

**Modification with Platinum Nanoparticles.** Nanoparticles of platinum (Pt) as catalysts for  $H_2$  evolution were loaded by an in situ photodeposition method<sup>22</sup> onto the external surface of the as-prepared materials using  $H_2PtCl_6$  as described in our previous paper.<sup>11</sup> The loading of Pt was 0.3 wt % unless otherwise stated.

Adsorption of Sensitizers.  $[Ru(bpy)_2(4,4'-(PO_3H_2)_2bpy)](PF_6)_2$  was synthesized by the method of Schmehl et al.<sup>23</sup> and was used as a visible light sensitizer for H<sub>2</sub> production. For comparison,  $Ru(bpy)_3Cl_2$  (99.95%) was purchased from Aldrich and was used without further purification. The structures of the two complexes are compared in Figure 2.

The spectroscopic and electrochemical properties of  $RuP^{2+}$  and  $Ru^{2+}$  have been reported previously<sup>12c,23</sup> and are summarized in Table 1.

The Ru<sup>2+</sup>-based complexes were adsorbed onto the surface of Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> at room temperature. The solid complex was dissolved in methanol or H<sub>2</sub>O, and the Pt-loaded samples were dispersed in an aqueous solution containing the Ru<sup>2+</sup>-based sensitizers (pH  $\approx$  5.5) under continuous stirring in the dark to establish adsorption—desorption equilibrium. After 1 h, the solid was separated from the suspension by centrifugation, and the resulting supernatant was then analyzed by using a UV—visible spectrometer (Hewlett-Packard, 8452A diode array spectrophotometer). The amount of Ru<sup>2+</sup>-based complex adsorbed was calculated from the difference in absorbance between the initial solution and the supernatant. The resulting solid sample was washed with H<sub>2</sub>O several times, and was dried in an oven at 333 K overnight.

**Characterization of Materials.** Powder X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert MPD diffractometer using Cu K $\alpha$  radiation, and transmission electron micrography (TEM) was obtained using a Jeol JEM-1200EX II microscope. The Brunauer, Emmett, Teller (BET) surface area was measured using a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. Before nitrogen adsorption isotherms were acquired, the samples were evacuated at 353–363 K for at least 24 h.

**Steady-State Luminescence Measurements.** Steady-state luminescence spectra were acquired at room temperature in front-face detection mode under 450 nm excitation using a Spex Fluorolog F212 fluorimeter. The composition of the suspension was identical to that used to measure visible-light-sensitized hydrogen production, as will be described below. The scan rate was 1 nm s<sup>-1</sup>.

Sensitized Hydrogen Production Reaction. The reaction was performed by dispersing 5.0 mg of the sample with adsorbed Ru<sup>2+</sup>-based sensitizer in an aqueous solution (2.0 mL) containing 0.01 M EDTA using a Pyrex reaction cell (10 mL capacity) sealed with a rubber septum unless otherwise stated. EDTA was used as a sacrificial electron donor<sup>5d</sup> in order to study the photochemical hydrogen evolution half-reaction without the possibility of Pt-catalyzed H<sub>2</sub> oxidation by the oxidized electron donor. Because the ultimate goal of this work is to develop visible light water splitting systems, the initial pH of the solution was fixed at 5.5. At pH 5-6, O<sub>2</sub> evolution catalysis on metal oxides (e.g.,  $RuO_2$  and  $IrO_2$ ) coupled with  $Ru(bpy)_3^{2+}$ -based sensitizers proceeds most efficiently.<sup>24</sup> The reactant solution was purged with argon for 5-10 min to remove dissolved air and was then placed in an outer glass jacket where argon gas flowed continuously, to prevent air contamination during reaction. After that, the reaction vessel was irradiated with a 300-W xenon lamp fitted with a cutoff filter ( $\lambda > 420$  nm). Under these conditions, the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> components do not undergo photoexcitation because the band gaps are too wide to absorb visible photons.<sup>14,25</sup> The evolved gases were analyzed by gas chromatography with a thermal conductivity detector and molecular sieve 5A columns at ambient temperature. The reproducibility of the rate of H<sub>2</sub> evolution in this system was confirmed to be within  $\sim 20\%$ under the same reaction conditions.

The turnover number (TON) for  $H_2$  production with respect to the sensitizer was estimated as

$$TON = 2H/S \tag{1}$$



Figure 2. Structures of (A)  $Ru(bpy)_2(4,4'-(PO_3H_2)_2bpy)^{2+}$   $(RuP^{2+})$  and (B)  $Ru(bpy)_3^{2+}$   $(Ru^{2+})_3^{2+}$   $(Ru^{2+})_3^{2+}$   $(RuP^{2+})_3^{2+}$   $(RuP^{2+})_3^{2+}$  (R

TABLE 1:	Spectroscopic	and Electrochemical	Properties of RuP <sup>2+</sup>	<sup>+</sup> and Ru <sup>2+</sup> Co	nplexes <sup>a</sup>
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	MLCT absorption band in H <sub>2</sub> O <sup>12c</sup>				
Ru complex	maximum/nm	coefficient/M <sup>-1</sup> cm <sup>-1</sup>	$pK_{a}^{23}$	$E_{(3+/2+)}/V^{9c}$	$E_{(3+/*2+)}/V^{9c}$
RuP <sup>2+</sup> Ru <sup>2+</sup>	455 452	10200 14400	1.0 $(pK_{a_1})$ 12.0 $(pK_{a_2})$	1.26 1.26	-0.95 -0.86

<sup>a</sup> Superscripts denote cited references.

where H and S represent the number of moles of H<sub>2</sub> produced and sensitizer used in the reaction, respectively. The factor of 2 comes from the assumption that H<sub>2</sub> production takes place when two protons react with electrons injected from the photoexcited sensitizer molecules.

The apparent quantum yield (AQY) was measured using the same experimental setup but with a band-pass filter ( $\lambda = 450 \pm 20$  nm) and was estimated as

$$AQY(\%) = (R/I) \times 100 \tag{2}$$

where *R* and *I* represent the initial rate at which H<sub>2</sub> molecules are evolved and the rate at which photons impinge on the sample, respectively. We assume that one photon forms one H<sub>2</sub> molecule because of a current doubling effect, as discussed in more detail below. It should be also noted that the AQY values are uncorrected for reflection and scattering losses, incomplete electron injection by sensitizer molecules, and for the optical density of sensitizer in the suspension. Therefore, AQY values calculated by eq 2 represent a lower limit and likely underestimate the internal quantum yield (hydrogen yield per photon absorbed) by a factor of  $\sim$ 3–4. The flux of incident photons was measured using a power meter to be ca. 4.08 × 10<sup>19</sup> photons h<sup>-1</sup>.

## **Results and Discussion**

**Physicochemical Properties of Niobate Nanosheets and Nanoscrolls.** Figure 3 shows the XRD patterns of (A) R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and (B) NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, along with the corresponding H<sup>+</sup>-exchanged lamellar materials. The XRD pattern of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> has a broad and weaker (001) diffraction peak, which is shifted to lower angle than the corresponding (002) peak in HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>. There is a complete absence of (00*l*) ( $l \ge$ 2) peaks in contrast to the parent solid, indicating a much less ordered lamellar structure in the restacked material. However, (100) and (110) diffraction peaks corresponding to in-plane lattice directions are preserved in the XRD pattern of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>. This indicates that the in-plane crystalline order of the Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub><sup>-</sup> sheets is preserved after the exfoliationreassembling procedure. The identical behavior has been reported for  $HSr_2Nb_3O_{10}$  nanosheets,<sup>26</sup> which are also in the Dion–Jacobson structural family of layered perovskites. For NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (Figure 3B), a similar tendency in XRD pattern was observed; namely, three-dimensional ordering of the lamellar structure disappeared, but the in-plane crystalline order within the individual nanoscrolls persisted after the exfoliation-reassembling procedure, as reported previously.<sup>11,27</sup>

TEM images of (A) R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and (B) NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> are shown in Figure 4. In R-HCa2Nb3O10 (Figure 4A), individual sheets with edge lengths of several hundred nanometers are randomly restacked to form larger aggregates, although there are some irregularly shaped aggregates in the product. This observation is consistent with the previous report by Osterloh et al.<sup>17a</sup> The thickness of the calcium niobate perovskite layer is 1.16 nm, based on the crystallographic data.<sup>13b</sup> In NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (Figure 4B), on the other hand, addition of HCl to the colloidal suspension results in production of nanoscrolls with diameters of about 30 nm and lengths of several hundred nanometers.<sup>27</sup> Because the Nb<sub>6</sub>O<sub>17</sub><sup>4-</sup> sheets do not have mirror symmetry (i.e., the individual sheet is asymmetric), there is an intrinsic tension in the sheet, which leads to spontaneous scrolling in order to release the strain energy.<sup>27a</sup> The specific surface areas of R-HCa2Nb3O10 and NS-H4Nb6O17 were 50-51 and 250–300 m<sup>2</sup> g<sup>-1,27b</sup> respectively, which are much larger than those of the proton-exchanged parent solids prior to exfoliation (ca.  $1-3 \text{ m}^2 \text{ g}^{-1}$ ).<sup>16,28</sup>

It is important to examine the surface charge of semiconductor particles in the suspension, because electrostatic attraction is one of the driving forces for adsorption of charged sensitizers to the surface of a semiconductor particle.  $\zeta$ -potential measurements for R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> showed a trend similar to that reported previously for NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>.<sup>11</sup> The surface of both materials is negatively charged over the range of pH 3–11, although the surface charge of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> becomes positive from pH 3.3 to 2.3; the point of zero charge (PZC) is thus estimated to be about 2.5 (see Supporting Information, Figure S1). For most "bulk-type" metal-oxides having surface hydroxyl groups (e.g., TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>), the surface charge varies from positive to negative with increasing pH because of the ionization of metal OH groups.<sup>4,9c,29</sup> Although R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> shows the identical tendency to the bulk-type metal oxides, the (estimated) PZC values of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> (ca. 2.5) and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (<2.7) are smaller than that of bulk Nb<sub>2</sub>O<sub>5</sub> (ca. 4.1).<sup>29</sup> At pH 5–6 where these materials could catalyze overall water splitting, the surface charge of the materials is negative. Thus, sensitizers whose net charge is positive could be bound to the surface of both materials by ion exchange.

Adsorption of sensitizers on the metal-oxide surface is in general driven by both electrostatic attraction and chemical bond formation between the sensitizer and the metal oxide.<sup>9a</sup> RuP<sup>2+</sup> has two phosphonic acid groups from which four protons are dissociable, depending on pH.<sup>23</sup> At pH 5.5, two protons (one proton in each phosphonic acid group) are dissociated, and hence the net charge of RuP<sup>2+</sup> is close to zero. The concentration of the predominant (uncharged) form of RuP<sup>2+</sup> at pH 5.5 is approximately 100 and 10 times higher than the forms with overall +2 and -2 charge, respectively. Thus, we expect a dominant covalent interaction of this sensitizer with R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>. It has been reported that  $RuP^{2+}$  can be anchored to the surface of TiO<sub>2</sub> via mono-, bi-, and tridentate binding,<sup>9a</sup> and one expects similar binding on the surface of the niobate particles. After adsorption of Ru<sup>2+</sup>-based complexes onto Pt-loaded materials, the positions of the lowangle layer lines in the diffraction patterns remained unchanged (data not shown), indicating that the complex is not intercalated into the interlayer gallery, but is adsorbed only on the external surface.

The conduction band potential of a semiconductor is one of the important parameters affecting the overall efficiency of dyesensitized H<sub>2</sub> production and should lie at a potential more negative than water reduction potential (<0 V vs NHE at pH 0). Several approximate formulas are available for calculating the flat band potentials ( $E_{FBP}$ ) of metal-oxide semiconductors containing d<sup>0</sup> and d<sup>10</sup> metal ions from band gaps ( $E_g$ ) and average electronegativities of the constituent elements.<sup>30</sup> Matsumoto used data from a large number of oxide semiconductors to obtain the empirical correlation<sup>31</sup>

$$E_{\rm FBP} \approx 1.23 - E_{\rm g}/2 \tag{3}$$

UV-visible diffuse reflectance spectroscopy showed that the band gap energies of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> are 3.50 and 3.33 eV, respectively (see Supporting Information, Figure S2). Thus, we estimate that the conduction band potential of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> is slightly more negative than that of NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, suggesting that electrons in the conduction band of the HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> sample may be more rapidly scavenged by Pt catalyst particles to reduce water to H<sub>2</sub>.

Sensitized Hydrogen Production Using Hexaniobate Nanoscrolls under Visible Light: RuP<sup>2+</sup> vs Ru<sup>2+</sup>. We first compared the activity of the RuP<sup>2+</sup>-sensitized NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> system to the previously reported system sensitized by Ru<sup>2+</sup>.<sup>11</sup> Time courses of H<sub>2</sub> production using NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> and Ru<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>) with visible light ( $\lambda > 420$  nm) are compared in Figure 5. Both systems produced H<sub>2</sub> with visible excitation and the amount of H<sub>2</sub> increased with reaction time. The fact that no reaction takes place in the dark and the TON in both systems far exceeds 1 indicates that the observed H<sub>2</sub> production is derived from photocatalytic cycle. As reported earlier, Ru<sup>2+</sup> is an effective photosensitizer for Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, binding to the surface by simple electrostatic attraction.<sup>11</sup> However, the activity of Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> was 6–7 times higher than that obtained



**Figure 3.** XRD patterns of (A) R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and (B) NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, along with reference patterns of HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and H<sub>x</sub>K<sub>4-x</sub>Nb<sub>6</sub>O<sub>17</sub>•*n*H<sub>2</sub>O ( $x \approx 2$ ).



Figure 4. TEM images of (A) R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and (B) NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>.

using the same amount of  $Ru^{2+}$ .  $RuP^{2+}$  has a slightly smaller molar absorption coefficient of metal-to-ligand charge transfer (MLCT) band than  $Ru^{2+}$  (Table 1), and it is therefore a less efficient visible light absorber than  $Ru^{2+}$ . The higher activity of the  $RuP^{2+}$ -sensitized system is likely to be attributable to a more efficient electron injection process that originates from the strong covalent linkage between hydroxyl groups at the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> surface and phosphonic acid groups of  $RuP^{2+}$ .<sup>9a,32</sup>

The MLCT state luminescence of  $Ru^{2+}$ -based complexes is quenched in the presence of semiconductor particles as a result



**Figure 5.** Time courses of H<sub>2</sub> evolution from 0.3 wt % Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> or Ru<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>) with visible light ( $\lambda > 420$  nm). Data for Ru<sup>2+</sup> are reproduced from ref 11. Reaction conditions: catalyst, 5.0 mg; aqueous EDTA solution (0.01 M, 2.0 mL); light source, xenon lamp (300 W) with a cutoff filter.



**Figure 6.** Luminescence spectra for 0.3 wt % Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> or Ru<sup>2+</sup> with 450 nm excitation. The spectra were acquired at room temperature under Ar atmosphere using aqueous EDTA solution (0.01 M, 2.0 mL) containing 0.3 wt % Pt-loaded NNS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (5.0 mg) adsorbed with RuP<sup>2+</sup> or Ru<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>).

of electron injection into the conduction band.<sup>33</sup> Luminescence spectroscopy was thus employed to study quenching of the MLCT excited-state by NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> for RuP<sup>2+</sup> and Ru<sup>2+</sup>. As shown in Figure 6, the luminescence intensity of the sensitizer decreased upon addition of NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> to the sensitizer solution in each case. Although the scattering of suspended particles may contribute to the reduction of the luminescence intensity to a certain extent, the use of silica powder, which is an insulator (i.e., no electron injection should occur), instead of NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> did not significantly affect the luminescence intensity. One can conclude that the observed decrease in luminescence intensity is mainly attributable to excited-state quenching via electron transfer to NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>. The efficiency



**Figure 7.** Time courses of H<sub>2</sub> evolution from 0.3 wt % Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> sensitized by RuP<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>) with visible light ( $\lambda > 420$  nm). Reaction conditions: catalyst, 5.0 mg; aqueous EDTA solution (0.01 M, 2.0 mL); light source, xenon lamp (300 W) with a cutoff filter.

of quenching was higher for  $RuP^{2+}$  (ca. 90%) than for  $Ru^{2+}$  (ca. 50%). Preliminary time-resolved measurements showed faster luminescence decays for  $Ru^{2+}$ -adsorbed on NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> than in the absence of semiconductors. Very similar results have been reported by Hashimoto et al.<sup>33a</sup> and Kamat et al.<sup>33b</sup> for titania adsorbed with  $Ru^{2+}$ -based complexes. More efficient quenching in the  $RuP^{2+}$ -based system implies stronger electronic coupling between  $RuP^{2+}$  and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> than obtained by electrostatic binding of  $Ru^{2+}$ . A primary requirement for efficient H<sub>2</sub> production by dye-sensitization is strong adsorption of sensitizer molecules onto the surface of the metal-oxide, because the dye excited state is typically too short lived to allow for diffusion of the molecule to the surface.<sup>4,9</sup> The higher quenching efficiency observed in the  $RuP^{2+}$ -based system is consistent with its substantially higher rate of H<sub>2</sub> production.

The photocatalytic activity of the RuP2+/Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>/EDTA system decreased as the reaction progressed, reaching a plateau value of  $30-40 \ \mu mol H_2$  (Figures 7). The same plateau was reached over a range of RuP<sup>2+</sup> and Pt loadings, corresponding to a range of H<sub>2</sub> evolution rates (see Supporting Information, Figure S4), implying that EDTA is the limiting reagent. Indeed, only 20  $\mu$ mol of EDTA is used in the experiment, and each H<sub>2</sub> molecule corresponds to two electrons. The evolution of 40  $\mu$ mol H<sub>2</sub> therefore implies that each EDTA molecule can donate a total of four electrons. In their studies of the analogous RuP2+/Pt-loaded TiO2/EDTA system, Choi et al. reported the generation of  $\sim 140 \ \mu mol H_2$  from 30  $\mu mol$ EDTA,<sup>9b</sup> which is consistent with our observations. To verify that the decrease in H<sub>2</sub> evolution rate with time corresponds to consumption of EDTA, a photolyzed RuP2+/Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>/EDTA suspension was centrifuged and was washed with water. The solid was dispersed in a fresh EDTA solution, and then the activity was tested. In the second and third runs with the same sample, hydrogen was evolved at 40-50% of the initial rate in the first run (see Supporting Information, Figure S3). The loss of activity between the first and second runs is most likely due to the fact that some of RuP<sup>2+</sup> molecules bound to the oxide surface undergo hydrolytic cleavage in the EDTA solution;<sup>34</sup> the activity of this system is strongly dependent on the amount of sensitizer adsorbed (as will be shown in Figure 8). Another possibility is partial decomposition of the sensitizer during the reaction. Choi et al. have observed similar deactivation behavior in the RuP<sup>2+</sup>/Pt-loaded TiO<sub>2</sub>/EDTA system.<sup>9a</sup>

**RuP**<sup>2+</sup>-Sensitized Hydrogen Production under Visible Light: Hexaniobate Nanoscrolls vs Calcium Niobate Nanosheets. Time courses of H<sub>2</sub> production using NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> sensitized by RuP<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>) with visible



**Figure 8.** Initial H<sub>2</sub> evolution rate from 0.3 wt % Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> sensitized by RuP<sup>2+</sup> with visible light ( $\lambda > 420$  nm) as a function of the amount of RuP<sup>2+</sup> added. Reaction conditions: catalyst, 5.0 mg; aqueous EDTA solution (0.01 M, 2.0 mL); light source, xenon lamp (300 W) with a cutoff filter. The amount of RuP<sup>2+</sup> adsorbed is also plotted.

light ( $\lambda > 420$  nm) are shown in Figure 7. Both systems produced H<sub>2</sub> with visible light and in the initial stage of reaction, H<sub>2</sub> evolution was clearly visible to the naked eye as bubbles. The initial H<sub>2</sub> evolution rate obtained using R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> was about 1.5 times higher than that achieved by NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>.

Figure 8 shows the initial H<sub>2</sub> evolution activities of the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>- and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>-based systems as a function of the amount of RuP<sup>2+</sup> sensitizer added in the preparation. The amount of RuP<sup>2+</sup> adsorbed is plotted in the same figures. In both cases, the activity increased markedly with addition of RuP<sup>2+</sup>, reaching saturation at a certain level. The activity of the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>-based system at the saturated level was higher than that of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>; the AQYs were calculated to be ca. 26 (for NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) and 22% (for R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>), respectively. The amount of RuP<sup>2+</sup> adsorbed on the semiconductor was almost quantitative up to 40 and 8.0  $\mu$ mol g<sup>-1</sup> for NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, respectively. The difference in the adsorption capacity between the two oxide semiconductors is primarily due to the difference in their specific surface areas.

Photochemical H<sub>2</sub> production in a Ru<sup>2+</sup>-based dye-sensitized system is ordinarily interpreted according to the following series of reactions<sup>9b,11</sup>

$$*Ru^{2+} \to Ru^{2+} \tag{5}$$

$$*Ru^{2+} \rightarrow \text{semiconductor } (e^{-}) + Ru^{3+}$$
(6)

semiconductor (e<sup>-</sup>) + Ru<sup>3+</sup> 
$$\rightarrow$$
 Ru<sup>2+</sup> (7)

semiconductor (e<sup>-</sup>) + H<sup>+</sup> 
$$\rightarrow \frac{1}{2}$$
H<sub>2</sub> (on Pt) (8)

$$\operatorname{Ru}^{3+} + \operatorname{EDTA}(e^{-}) \rightarrow \operatorname{Ru}^{2+} + \operatorname{oxidized} \operatorname{EDTA}$$
 (9)

AQY values calculated according to steps (4-9) were not reasonable, however, because they imply an internal quantum yield >100% at the optimized RuP<sup>2+</sup> and Pt loadings. A reaction rate of 18  $\mu$ mol h<sup>-1</sup> H<sub>2</sub> at a flux of 4.1  $\times$  10<sup>19</sup> photons h<sup>-1</sup> would correspond to an AQY value of 53%, assuming  $\frac{1}{2}$  H<sub>2</sub> per photon. However, at the optimum sensitizer loading (12  $\mu$ mol g<sup>-1</sup> × 0.005 g/0.002 L = 30  $\mu$ M), the absorbance of the solution at 450 nm (neglecting scattering) is 0.306, meaning that only 51% of the photons are absorbed. Reflection from the front face of the cell corresponds to a  $\sim 15\%$  loss and the quenching efficiency (see below) is  $\sim$ 88%. The combination of these three factors sets the maximum AQY at  $\sim$ 37% without taking scattering into account. The effect of light scattering by the semiconductor particles is more difficult to quantify, but it is not unreasonable to estimate an additional loss of 25-50% through scattering.

One possible explanation for this contradiction is that socalled "current doubling"<sup>35</sup> occurs in this system. Presumably, an intermediate radical species generated by the oxidation of EDTA (eq 10) can inject an electron into the conduction band of the semiconductor, reaction 10

## oxidized EDTA (radical) $\rightarrow$ semiconductor (e<sup>-</sup>) (10)

This injected electron is then consumed by reaction 7 or 8. Current doubling is not observed in the homogeneous [Ru(bpy)<sub>3</sub>]<sup>3+</sup>-EDTA reaction, but it has been reported previously for semiconductor photoelectrodes where EDTA is adsorbed at the surface.<sup>36</sup> We conclude that current doubling can occur in these oxide semiconductor-based photocatalytic systems and perhaps has been overlooked previously because the AQY values are generally low. Our AQY values are thus calculated with the assumption that one photoinjected electron can produce one H<sub>2</sub> molecule through current doubling.

Factors Affecting the Activity for RuP<sup>2+</sup>-Sensitized Hydrogen Production Using NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>. When the same amount of  $\operatorname{RuP}^{2+}(8.0 \,\mu\text{mol g}^{-1})$  was adsorbed onto NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, the activity of the R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>-based system was about 1.5 times higher than that obtained using NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (Figure 7). To examine the efficiency of electron injection from the excited-state RuP<sup>2+</sup>, steady-state luminescence spectra for the two systems were taken and the quenching efficiencies were compared. Table 2 lists the quenching efficiencies for the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>- and the R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>based systems, along with data for H<sub>2</sub> production. The quenching efficiency for the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>-based system is higher than that observed in the R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>-based system, indicating more rapid electron injection in the case of NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>. This is consistent with the idea that the conduction band edge potential of NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> is more positive than that of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>;



**Figure 9.** Initial H<sub>2</sub> evolution rate from Pt-loaded NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> with visible light ( $\lambda > 420$  nm) as a function of Pt loading. Reaction conditions: catalyst, 5.0 mg; sensitizer, 20  $\mu$ mol g<sup>-1</sup>; aqueous EDTA solution (0.01 M, 2.0 mL); light source, xenon lamp (300 W) with a cutoff filter.

 TABLE 2: Luminescence Quenching Efficiencies and

 Activities for H<sub>2</sub> Evolution by the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>- and the

 R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>-Based system<sup>a</sup>

material	quenching efficiency <sup>b</sup> /%	sensitized $H_2$ production activity/ $\mu$ mol $h^{-1}$
$\begin{array}{l} NS\text{-}H_4Nb_6O_{17} \\ R\text{-}HCa_2Nb_3O_{10} \end{array}$	$\begin{array}{c} 88\pm1\\ 64\pm2 \end{array}$	14.4 21.6

<sup>*a*</sup> Reaction conditions: catalyst, 5.0 mg (0.3 wt % Pt-loaded); reaction solution, aqueous solution containing 0.01 M EDTA or 0.1 M methanol (2.0 mL). <sup>*b*</sup> Estimated based on the ratio of the luminescence intensity to the RuP<sup>2+</sup> only case. <sup>*c*</sup> Initial activity sensitized by RuP<sup>2+</sup> (8.0  $\mu$ mol g<sup>-1</sup>) from aqueous EDTA solution ( $\lambda$ > 420 nm).

that is, the driving force for electron injection is larger in NS- $H_4Nb_6O_{17}$  than in R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>. However, it appears to be the opposite of the order of initial hydrogen evolution rates. The difference in activity may come from the different light scattering properties of the two materials; that is, the R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> system harvests more light at a RuP<sup>2+</sup> concentration of 8.0  $\mu$ mol·g<sup>-1</sup> than NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>.

As the amount of adsorbed RuP<sup>2+</sup> was increased, the hydrogen evolution rates of both the NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>- and R-HCa2Nb3O10-based systems increased to a certain level, reaching saturation (Figure 8). Below this plateau value, the increase in activity corresponds to an increase in the fraction of incident light that is absorbed, a general trend in dyesensitized  $H_2$  evolution photocatalysis.<sup>4,6,9b,c</sup> The high AQY values obtained (22% for R-HCa $_2Nb_3O_{10}$  and 26% for NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> at each optimum RuP<sup>2+</sup> loading) suggest that under these conditions photoinjected electrons are very efficiently converted to  $H_2$ . That is, under these conditions, the rate of  $H_2$ evolution is primarily limited by the fraction of incident light absorbed by the sensitizer and the efficiency of charge injection from the excited state. The ratio of AQY values corresponds approximately to the ratio of quenching efficiencies (88 vs 64%, Table 2) for RuP<sup>2+</sup>-sensitized NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, respectively. The slightly different optimum RuP<sup>2+</sup> loadings observed for NS-H4Nb6O17 and R-HCa2Nb3O10 may arise from the slightly different scattering properties of the two materials.

The fate of injected electrons in the conduction band is either to be consumed by water reduction or to recombine with the oxidized sensitizer, and the relative rates of these processes determine the quantum yield for water reduction. The high quantum yield for  $H_2$  formation following electron transfer quenching (reaction 6) suggests that either reactions 8 or 9 are considerably faster than recombination reaction 7 under optimized conditions. While we do not yet have a quantitative measure of any of these rates, the dependence of the initial H<sub>2</sub> evolution rate on Pt loading (Figure 9) shows a clear volcano behavior. The drop in H<sub>2</sub> evolution rate with excess Pt can likely be attributed to an inner filter effect, in which excess Pt absorbs some of the light that would otherwise be absorbed by RuP<sup>2+</sup>. The volcano trend implies that at low Pt loading, neither reactions 8 nor 9 are fast enough to compete with reaction 7, whereas at higher Pt loading, reaction 8 is faster than 7. One can thus conclude that 9, the reaction of EDTA with the oxidized sensitizer, is slower than recombination reaction 7 and also slower than 8 under optimized conditions. The near independence of AQY values on the concentration of EDTA in the range of 0.01–0.05 M (see Supporting Information, Table S1) is consistent with this conclusion.

Several of these rates have been measured in analogous systems and from these we can estimate the order of magnitude of the rates in the case of RuP2+-sensitized NS-NS-H4Nb6O17 and R-HCa2Nb3O10. Zang and Rodgers found that EDTA reduction of  $[Ru(bpy)_3]^{3+}$  in the presence of colloidal TiO<sub>2</sub> was second-order with a rate constant of 6.0  $\pm$  0.2  $\times$  10  $^{6}$   $M^{-1}$   $s^{-1}$   $^{37}$ similar to the value measured for EDTA and  $[Ru(bpy)_3]^{3+}$  in homogeneous aqueous solutions.<sup>38</sup> Under the conditions of our experiments (0.01 M EDTA at pH 5.5) this rate constant would correspond to a time scale of  $\sim 20 \ \mu s$  for 9. We can thus conclude a shorter time scale for 7 and 8. With Pt-loaded eosinsensitized TiO<sub>2</sub> colloids, Moser and Gratzel measured a recombination lifetime of  $\sim$  4  $\mu$ s,<sup>39</sup> and a similar time scale for trapping of electrons by Pt. It is thus reasonable to estimate that 7 occurs on the microsecond time scale with RuP<sup>2+</sup>sensitized niobates and that reaction 8 is significantly faster than reaction 7 under optimized conditions of RuP<sup>2+</sup> and Pt loading. It is interesting to note that electron-hole recombination in HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> nanosheets, which is analogous to reaction 7, has recently been observed on a much faster (as in nanoseconds) time scale by UV flash photolysis.<sup>17</sup> Because the recombination process is second-order, however, it is likely to be much slower under the lower fluences used in continuous photolysis experiments.

#### Conclusions

Dye-sensitized H<sub>2</sub> production from water containing EDTA as a sacrificial electron donor under visible light ( $\lambda > 420$  nm) was studied using hexaniobate nanoscrolls (NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) and acid-restacked calcium niobate nanosheets (R-HCa2Nb3O10) sensitized by  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  ( $\operatorname{Ru}^{2+}$ ) or  $\operatorname{Ru}(\operatorname{bpy})_2(4,4' (PO_3H_2)_2bpy)^{2+}$  (RuP<sup>2+</sup>) complexes. The use of RuP<sup>2+</sup> affords a higher rate of visible-light-driven H<sub>2</sub> production than Ru<sup>2+</sup>, attributed to more efficient electron injection from the MLCT excited state. Platinized NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> was found to be a slightly better electron transfer mediator than R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, with an apparent quantum yield of  $\sim 25\%$  at 450  $\pm$  20 nm under optimized conditions. To adapt these sensitized semiconductor systems for use with nonsacrificial electron donors or with water as the electron donor (i.e., for overall water splitting), it will be essential to maintain the high yields of charge injection and hydrogen evolution observed here but with materials that cannot catalyze the recombination of conduction band electrons or H<sub>2</sub> with the oxidized electron donor. Studies of analogous systems incorporating composite noble metal-metal oxide catalysts are currently in progress.

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**Supporting Information Available:**  $\zeta$ -potential of R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> as a function of the pH of the suspension, results of UV-visible diffuse reflectance spectroscopy and band gap estimation, and H<sub>2</sub> production data for Pt-loaded R-HCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> and NS-H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> sensitized by RuP<sup>2+</sup> with visible light at various reaction conditions. This material is available free of charge via the Internet at http:// pubs.acs.org.

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