1-2012

Photocatalytic Hydrogen Production at Titania-Supported Pt Nanoclusters that are Derived from Surface-Anchored Molecular Precursors

Rony S. Khnayzer

Lucas B. Thompson

Mikhail Zamkov
Bowling Green State University, zamkovm@bgsu.edu

Shane Ardo

Gerald J. Meyer

See next page for additional authors

Follow this and additional works at: https://scholarworks.bgsu.edu/physics_astronomy_pub

Part of the Astrophysics and Astronomy Commons, and the Physics Commons

Repository Citation
Khnayzer, Rony S.; Thompson, Lucas B.; Zamkov, Mikhail; Ardo, Shane; Meyer, Gerald J.; Murphy, Catherine J.; and Castellano, Felix N., "Photocatalytic Hydrogen Production at Titania-Supported Pt Nanoclusters that are Derived from Surface-Anchored Molecular Precursors" (2012). Physics and Astronomy Faculty Publications. 5.
https://scholarworks.bgsu.edu/physics_astronomy_pub/5

This Article is brought to you for free and open access by the Physics and Astronomy at ScholarWorks@BGSU. It has been accepted for inclusion in Physics and Astronomy Faculty Publications by an authorized administrator of ScholarWorks@BGSU.
Photocatalytic Hydrogen Production at Titania-Supported Pt Nanoclusters That Are Derived from Surface-Anchored Molecular Precursors

Rony S. Khnayzer,†,§ Lucas B. Thompson,‖ Mikhail Zamkov,‖ Shane Ardo,‖ Gerald J. Meyer,‖ Catherine J. Murphy,‖ and Felix N. Castellano*,‖§

†Department of Chemistry, ‡Department of Physics, §Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States
‖Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States
§Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, United States

Supporting Information

ABSTRACT: Degussa P-25 TiO2 bearing surface-anchored Pt(dcbbpy)Cl2 [dcbbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine] prepared with systematically varied surface coverage produced Pt0 nanoparticles under bandgap illumination in the presence of methanol hole scavengers. Energy-dispersive X-ray spectroscopy confirmed the presence of elemental platinum in the newly formed nanoparticles during scanning transmission electron microscopy (STEM) experiments. According to the statistical analysis of numerous STEM images, the Pt0 nanoclusters were distributed in a segregated manner throughout the titania surface, ranging in size from 1 to 3 nm in diameter. The final achieved nanoparticle size and net hydrogen production were determined as a function of the Pt(dcbbpy)Cl2 surface coverage as well as other systematically varied experimental parameters. The hybrid Pt/TiO2 nanomaterials obtained upon complete decomposition of the Pt(dcbbpy)Cl2 precursor displayed higher photocatalytic activity (300 μmol/h) for hydrogen evolution in aqueous suspensions when compared with platinized TiO2 derived from H2PtCl6 precursors (130 μmol/h), as ascertained through gas chromatographic analysis of the photoreactor headspace under identical experimental conditions. The conclusion that H2 was evolved from Pt0 sites rather than from molecular Pt(dcbbpy)Cl2 entities was independently supported by Hg and CO poisoning experiments. The formation of small Pt nanoparticles (1.5 nm in diameter) prevalent at low surface coverage of Pt(dcbbpy)Cl2 on TiO2 (0.5 to 2% by mass) that exhibit enhanced turnover frequencies with respect to all other materials investigated, including those produced from the in situ photochemical reduction of H1PtCl6. Pt4+ precursor absorption in the ultraviolet region appeared to be partially responsible for attenuation of the H2 evolution rate at higher Pt(dcbbpy)Cl2 surface coverage. The nanoparticle size and hydrogen evolution characteristics of the surface-anchored materials generated through photodeposition were directly compared with those derived from chemical reduction using NaBH4. Finally, Degussa P-25 thin films deposited on FTO substrates enabled electrochemically induced (−1.0 V vs Ag/AgCl, pH 7.0, phosphate buffer) electron trapping (TiO2(e−)) throughout the titania. After removal of the applied bias and the anaerobic introduction of Pt(dcbbpy)Cl2, the accumulated electrons reduce this molecular species to Pt0 nanoparticles on the titania electrode surface, as confirmed by TEM measurements, with the concomitant production of H2 gas. The combined experiments illustrate that TiO2(e−) generated with bandgap excitation or via electrochemical bias affords the reduction of Pt(dcbbpy)Cl2 to Pt0 nanoparticles that in turn are responsible for heterogeneous hydrogen gas evolution.

INTRODUCTION

The utilization of solar photons for the generation of energy-rich chemical fuels from abundant energy-deficient molecules requires the development of new catalytic systems and redox assemblies.1–5 Of particular interest is the utilization of sunlight to produce H2 by the reduction of water, thereby providing an environmentally sensible fuel from naturally abundant precursors.1–9 The challenge in designing catalysts to promote these reactions lies in the fact that single-photon-driven electron transfer must somehow be coupled to a multielectron fuel-forming step. In other words, the reduction of protons to H2 requires the coupling of two protons and two electrons to produce one molecule of the desired combustible fuel. The catalyst serves to bring all reacting species together, permits H2 evolution, and must ultimately be regenerated to repeat the sequence. Surprisingly, efficient photo-initiated multielectron-transfer chemistry remains largely unrealized in photocatalysis despite decades of research on the subject. The use of metal complexes as molecular photocatalysts for...
hydrogen evolution in homogeneous systems has gained widespread popularity due to both fundamental mechanistic questions and its possible transformative potential.\textsuperscript{10–13} Originally, we were inspired by the notion that molecular catalysts could be readily linked to heterogeneous nanoparticles to yield materials that both absorb light and drive the two-electron reduction of protons to hydrogen gas. During the course of this work, evidence began accumulating that molecular Pt- and Pd-containing complexes were susceptible to photolytic reduction, forming their corresponding metallic nanoparticles, which were ultimately responsible for the majority of H\textsubscript{2} evolution observed in these systems.\textsuperscript{16,17} This was not too surprising given the fact that Finke and coworkers previously also noted that the molecular Pt\textsuperscript{II} species Pt(1,5-COD)Cl\textsubscript{2} and Pt(1,5-COD)(CH\textsubscript{3})\textsubscript{2} (COD is 1,5-cyclooctadiene) both form Pt\textsuperscript{0} nanoclusters in situ, the latter being ultimately responsible for substrate hydrogenation catalysis.\textsuperscript{18,19} During the course of these studies, we linked Pt(dcbbpy)Cl\textsubscript{2} (dcbbpy is 4,4′-dicarboxy-2,2′-bipyridine), originally believed to be a viable molecular hydrogen evolution catalyst,\textsuperscript{10–15} to the surface of Degussa P-25 TiO\textsubscript{2}, which serve as electron storage reservoirs in the presence of bandgap excitation and appropriate hole scavengers such as methanol.\textsuperscript{20} Whereas these composites were indeed superior hydrogen-evolving photocatalysts when directly compared with more conventional materials, they did not function via molecular chemistry at the surface-anchored Pt\textsuperscript{II} complexes.\textsuperscript{20} Rather, the Pt\textsuperscript{IV} complexes served as molecular precursors that yielded highly segregated nanoscopic Pt\textsuperscript{0} particles decorating the TiO\textsubscript{2} surface and formed from bandgap illumination. Notably, this system has been used for aerobic water detoxification under visible-light illumination where the Pt\textsuperscript{IV} complex acted as a dye sensitizer that injected electrons into titania initiating a cascade of mineralizing decomposition chemistry of the prototypical 4-chlorophenol.\textsuperscript{21}

The work related to nanoparticle-based photodeposition (PD) served as a caveat to researchers employing noble metal-containing complexes as H\textsubscript{2}-generating catalysts that photodecomposition of these complexes could in fact occur and that the identity of the true catalysis needs to be rigorously addressed. The present study revealed that surface-bound molecular Pt(dcbbpy)Cl\textsubscript{2} complexes were photochemical precursors to segregated Pt\textsuperscript{0} nanomaterials that displayed enhanced hydrogen evolution from TiO\textsubscript{2} surfaces under bandgap illumination. We view this latter result as significant because the electrocatalytic activity of platinum clusters toward the four-electron reduction of oxygen to water has recently been demonstrated to exhibit drastic size-dependent behavior; smaller nanoparticles (1 to 1.2 nm in diameter) promote enhanced catalytic activity.\textsuperscript{22} Variation in Pt\textsuperscript{0} particle size may indeed be the reason for the wide variation of H\textsubscript{2} evolution rates we observed as a function of Pt(dcbbpy)Cl\textsubscript{2} surface coverage on TiO\textsubscript{2} in the original study,\textsuperscript{20} and the current effort develops this concept further through photochemical, chemical, and electrochemical reduction processes to prepare nanoscopic Pt\textsuperscript{0} clusters on the surface of titania. We chose these three distinct reduction methods based on previous work by Pichat and coworkers, who extensively studied the nanoporous deposition of Pt on TiO\textsubscript{2} prepared from a variety of codissolved precursors.\textsuperscript{23–25} It should also be noted that the ligands present in the Pt(dcbbpy)Cl\textsubscript{2} precursor likely help stabilize the resultant Pt\textsuperscript{0} nanoparticles distributed on the titania surface. The nature of the titania support renders any surface study of the Pt\textsuperscript{0} sites experimentally tedious; therefore, research on the aqueous suspended nanoparticles is underway to better understand the nature of the analogous materials produced on titania.\textsuperscript{18,26–29}

We clearly demonstrate from heterogeneous poisoning experiments\textsuperscript{30,31} that hydrogen-evolving catalytic activity in these hybrid materials emanates from the nanoparticulate catalysts rather than molecular compounds. The combined data revealed that the H\textsubscript{2} evolution yields monitored as a function of Pt(dcbbpy)Cl\textsubscript{2} surface coverage could be rationalized in terms of three distinct variables: (1) the mass of Pt\textsuperscript{0} deposited, (2) the Pt\textsuperscript{0} nanoparticle size, and (3) undecomposed Pt\textsuperscript{II} precursors that competitively absorb ultraviolet photons.\textsuperscript{32,33}

### EXPERIMENTAL SECTION

**General.** \textsuperscript{1}H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) or Bruker Avance III 500 (500 MHz) spectrometer. All chemical shifts were referenced to the residual solvent signals, and splitting patterns were designated as s (singlet) or d (doublet). UV–vis absorption spectra were measured on a Cary 50 Bio spectrophotometer. A VWR 75HT sonicator was used to sonicate the colloidal suspensions. Raman spectra were acquired on a Renishaw inVia Raman Microscope using 442 nm He–Cd Laser excitation, and IR spectra were measured using an FT-IR spectrometer (JASCO FT/IR-4100) equipped with an ATR accessory. All electrochemical measurements were performed using a BAS Epsilon electrochemistry workstation using a traditional three electrode arrangement.

**Materials.** P-25 TiO\textsubscript{2} (ca. 80% anatase, 20% rutile; BET area, ca. 50 m\textsuperscript{2} g\textsuperscript{–1}) was obtained from Degussa and used as received. Potassium tetrachloroplatinate, hexachloroplatinic acid hexahydrate, 4,4′-dimethyl-2,2′-bipyridine, and sodium borohydride (NaBH\textsubscript{4}) were purchased from Aldrich and used without further purification. Fluorine-doped tin oxide (FTO) conducting glass substrates (TEC 15) were purchased from Hartford Glass. Water was deionized using a Barnstead nanopure system. All reagent grade solvents and reactants were used as received. cis-Pt(DMSO)\textsubscript{2}Cl\textsubscript{2} was synthesized in 90% yield according to the established literature procedure.\textsuperscript{34}

**TiO\textsubscript{2} Film Formation.** FTO conducting glass substrates were cleaned by sonication using a solution of HCl in isopropanol, a solution of soap in water, then finally acetone. The FTO glass was then dried in an oven. A mixture of 3:1 by volume H\textsubscript{2}O/CH\textsubscript{3}COOH (glacial acetic acid) was mixed slowly with TiO\textsubscript{2} (Degussa P-25) (12 wt %) and hydroxypropylcellulose (6 wt %). This mixture was sonicated and stirred vigorously overnight. The resultant paste was doctor bladed on FTO glass between three Scotch tape layers resulting in a material with ~20 μm thickness and a TiO\textsubscript{2} electrode area of 1 cm\textsuperscript{2}. The electrode was sintered at 500 °C for 30 min at a heating rate of 5 °C per min and finally cooled to room temperature.

**Synthesis.** Pt(dcbbpy)Cl\textsubscript{2}. This complex was synthesized according to a slightly modified literature procedure.\textsuperscript{35} 4,4′-Dicarboxy-2,2′-bipyridine (dcbbpy) was prepared as described in the literature from 4,4′-dimethyl-2,2′-bipyridine.\textsuperscript{36} A suspension of 98 mg dcbbpy and 212 mg of cis-Pt(DMSO)\textsubscript{2}Cl\textsubscript{2} were mixed with 40 mL of methanol and refluxed for 8 h in an oil bath at 80 °C. The yellow solid was filtered, washed with methanol and hot ethanol, and then dried under vacuum (77% yield). Anal. Calc. for C\textsubscript{22}H\textsubscript{24}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{4}Pt: C, 28.25; H, 1.58; N, 5.49. Found: C, 28.53; H, 1.81; N, 5.09. \textsuperscript{1}H NMR (300 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): 9.72 (d, J = 6 Hz, 2H), 9.04 (s, 2 H), 8.24 (d, J = 5.7 Hz, 2H). \textsuperscript{1}H NMR (500 MHz, D\textsubscript{2}O-NaOD, δ): 8.50 (d, J = 6 Hz, 2H), 8.09 (s, 2H), 7.60 (d, J = 5.8 Hz, 2H). FT-IR (ATR, ν(cm\textsuperscript{–1}): 1730, 1619, 1553, 1440, 1412, 1320, and 1232. Raman spectroscopy...
Photocatalytic Hydrogen Production. Pt(dcbbpy)Cl₂/TiO₂ Photodeposition. Photocatalytic reactions were performed in a 50 mL Pyrex round-bottomed flask equipped with a stir bar. All mixtures were sonicated for 1 min before PD and stirred at the same speed during the measurements. A suspension of 25 mg of the Pt(dcbbpy)Cl₂/TiO₂ catalyst at a specific % loading by mass and 25 mL of methanol/water (1:6 by volume) was degassed using the freeze–pump–thaw technique and maintained under an argon atmosphere in a gas-tight Schlenk line directly linked to a gas chromatograph (GC, Shimadzu GC-8A, argon carrier gas, 5 Å molecular sieve column (Restek), thermal conductivity detector, 0.5 mL gas sample injection, calibrated against known H₂/argon gas mixtures). Under our experimental conditions, the retention time of H₂ was 1.5 min, well-separated from N₂ and O₂. Detection of CO₂ from the reaction headspace was accomplished using a custom-made column for gas separation (Supelco). The excitation light source was the broadband output of a 300 W Xe arc lamp (Oriel). The broadband incident power density on each reactor. The hydrogen was detected from the headspace; samples of gas were taken at different time intervals using a 100 μL gastight syringe (Hamilton) and analyzed using the GC system described above.

CO Poisoning. Because CO is a highly toxic gas, the CO poisoning test was performed in a well-vented fume hood. We degassed 10 mg of 1% by mass Pt(dcbbpy)Cl₂/TiO₂ isolated after complete PD using the same procedure described above, and STEM of the powders was taken. The full decomposition of Pt(dcbbpy)Cl₂ was indicated by the negligible absorption of the supernatant after 5 h of continuous photolysis. Because Pt(dcbbpy)Cl₂ and H₂PtCl₆·6H₂O have comparable molecular weights, the weight percent of Pt metal is approximately the same in both cases (0.4 wt % Pt in a 1% by mass sample).
resuspended in ~200 μL of DI H2O, and ~20 μL of this solution was dropcasted onto holey carbon transmission electron microscopy (TEM) grids and then dried under ambient laboratory conditions. High-resolution images were acquired with a JEOL model 2200-FS electron microscope operated at 200 keV. EDS scans were acquired with a 50 mm² Oxford INCA detector on the 2200FS. High-resolution transmission electron microscopy (HR-TEM) measurements were carried out using a JEOL 3011UHR or 2010 transmission electron microscopes, operated at 300 and 200 kV, respectively.

### RESULTS AND DISCUSSION

Pt(dcbpy)Cl₂ was designed to surface anchor on TiO₂ nanoparticles owing to the carboxylic acid groups present on 4,4’-dicarboxylic acid-2,2’-bipyr dine (dcbpy) ligand. This yellow complex exhibits a modest extinction coefficient at its absorption peak in the near-visible (λ = 377 nm, ε = 2770 M⁻¹ cm⁻¹), which overlaps the titania band edge. This creates a situation where Pt(dcbpy)Cl₂-induced absorbance of bandgap excitation can have a pronounced effect on the resultant material. Minute amounts of aqueous base deprotonates the acids forming carboxylates, promoting the solubility of this complex in water. After stirring mixtures containing Pt(dcbpy)Cl₂ in water and TiO₂, Pt(dcbpy)Cl₂ adsorbed onto TiO₂ was readily obtained, whose loading by mass was easily determined by adsorption isotherms derived from UV−vis spectra of the supernatant solutions. When required, 0.1 M KOH was used to desorb surface-anchored Pt⁰ species. (See the Supporting Information for more details.) The various Pt(dcbpy)Cl₂/TiO₂ materials were tested for hydrogen production upon TiO₂ bandgap excitation (3.0 to 3.2 eV) in the presence of hole scavengers, which resulted in the photodeposition (PD) of Pt⁰ nanoparticles in all instances. Alcohols such as methanol and ethanol have been widely used as hole scavengers due to the thermodynamic and kinetic favorability of alcohol oxidation by TiO₂ valence band holes.¹⁷,43−46 In the current work, we used aqueous media composed of 1:6 MeOH/H₂O by volume for all photocatalytic hydrogen-evolving experiments. These experimental conditions ensured efficient hole scavenging during bandgap illumination that positioned the composition to accumulate electrons at titania, termed TiO₂(e⁻) throughout this manuscript. In some instances, Pt⁰ nanoparticles were formed via chemical deposition (CD) using direct NaBH₄ reduction of select Pt(dcbpy)Cl₂/TiO₂ compositions, which were compared with the corresponding photodeposited materials.

Atomic resolution STEM images of the 1% Pt(dcbpy)Cl₂/TiO₂ sample after 5 h of bandgap illumination indicated the presence of Pt nanoparticles (distinguishable as bright areas in Figure 1a), with characteristic lattice fringes indexed to the fcc (111) crystal phase. The high-resolution image in Figure 1a confirms that the lattice spacing is 2.2 Å, whereas the expected value for Pt(111) is a/√3 (2.26 Å), where a (3.92 Å) is the lattice constant of bulk Pt.⁴⁷ Statistical analysis of multiple STEM images revealed that the formed nanoparticles at 1% loading were ~1.5 nm in diameter, with a size dispersion of ±0.2 nm. Energy-dispersive X-ray (EDX) spectroscopy measurements confirmed the presence of elemental platinum in these particles (Figure 1b). Most of the remaining signals emanated from the holey carbon substrate and the TiO₂ support.

Figure 2 presents the hydrogen evolved versus irradiation time measured as a function of Pt(dcbpy)Cl₂ catalyst precursor (mass percent) originally loaded onto the TiO₂ surface. These samples contained 25 mg of each Pt(dcbpy)Cl₂/TiO₂ composition suspended in 25 mL of MeOH/H₂O (1:6), ultimately subjected to 300 W broadband Xe lamp illumination. It is important to note that the precursor loading in these samples does not represent the final Pt nanoparticle catalyst loading; the latter is quantified from surface desorption of remnant PtII molecular species subsequent to 5 h of continuous photocatalysis. The hydrogen evolution yield increases with decreasing surface coverage, exhibiting optimal performance with the 1 to 2% Pt(dcbpy)Cl₂/TiO₂ composition (Figure 2). The first hour of hydrogen evolution in the in situ photodeposited materials was characterized by a slightly lower rate than the later time periods, behavior attributed to an induction period necessary to form the catalytically active Pt nanoparticles (Figure 2). For this reason, the turnover frequency calculation (TOF = [mol H₂ produced] × [mol decomposed PtII precursors]⁻¹ × s⁻¹) is reported over the time range between 1 and 5 h for these in situ photodeposited materials (Table 1). The 0.5% loading was characterized by a lower hydrogen evolution rate (240 μmol/h) relative to the 1 to 2% loading (800 μmol/h). This observation can be rationalized by the lower surface coverage of the Pt catalyst on TiO₂ at loadings below 1%. Related previous optimized systems require the use of ~0.5 to 1 wt % Pt on TiO₂ to achieve optimal catalysis and when translated into the current composition mandates 1 to 2% by mass Pt(dcbpy)Cl₂ on TiO₂.⁵⁰,2,12,25,43

An important factor contributing to optimal hydrogen production at 1 to 2% Pt loading and the decrease in catalytic activity

Figure 1. (a) Atomic resolution STEM of 1% Pt(dcbpy)Cl₂/TiO₂ after 5 h of bandgap illumination, showing nanoscopic platinum particles with high crystallinity indexed to the fcc (111) crystal face, with lattice spacing of 2.2 Å. (b) EDX measurement of the same sample indicating the presence of platinum.
at higher precursor loadings potentially emanates from the absorbance of leftover molecular Pt+ species resident on the titania surface. As previously mentioned, Pt(dcbpy)Cl2 is a yellow complex possessing a broad charge transfer absorption band centered at 377 nm with a modest extinction coefficient (ε = 2770 M–1 cm–1), which can serve to attenuate photon flux in the vicinity of the bandgap. We postulated that the observed decrease in hydrogen evolution rates as a function of increased surface coverage might simply be reflecting a systematic attenuation in light absorbed by the TiO2. To test this possibility, we used 0.1 M KOH to desorb quantitatively any surface-bound Pt+ complexes remaining after 5 h of photocatalytic reaction; specifically, 25 mg of the TiO2/Pt sample (after catalysis) was treated with 25 mL of 0.1 M KOH. The corresponding solutions were centrifuged (10 min, 10 000 rpm) and filtered using a 0.2 μm pore size filter. The photoinitiated hydrogen evolution of the collected solid catalyst was then monitored by GC. This base treatment did not increase the catalytic activity at ≤2% loading. However, the complete removal of the remaining molecular surface-anchored Pt+ precursors markedly enhanced the hydrogen evolving activity from 180 to 240 μmol/h of the deposited Pt at 7.05% initial loading (Figure 3a). The same data also imply that the presence of molecular Pt+ species on the surface of titania is responsible for a significant amount of light absorption in the vicinity of the bandgap. In fact, the calculated amounts of Pt+ precursors remaining on the surface of TiO2 after 5 h of catalysis suggest that only ~10% of the originally present Pt(dcbpy)Cl2 at high surface coverage (7.05% loading) actually decomposed, whereas ~75% of this same molecule decomposed at low surface coverage (1% loading) (Figure 3b). Ultimately, at low surface coverage (~2% by mass of Pt(dcbpy)Cl2), the decomposition was complete after prolonged photolysis (>7 h). The combined results suggest that molecular Pt(dcbpy)Cl2 is more efficiently decomposed to Pt0 at low surface coverage and exerts a rather substantial UV bandgap absorbance at higher surface coverage.

The data presented in Figure 4 are representative of catalytic hydrogen-evolving samples formed from complete decomposition of the molecular precursors present. In these instances, 1% molecular precursor loading (either Pt(dcbpy)Cl2 or H2PtCl6), followed by broadband irradiation resulted in quantitative Pt0 deposition, as ascertained by negligible detection of any molecular precursors desorbed from the titania surface. Subsequent to washing, these materials were resuspended in 1:6 MeOH/H2O and tested for their hydrogen photocatalytic activity. Notably, the material isolated after complete PD of Pt(dcbpy)Cl2 (300 μmol/h) significantly outperformed that photodeposited from H2PtCl6 (130 μmol/h) (Figure 4). The hydrogen evolution rate is lower in these particular molecules as a result of the catalyst being present in smaller quantities (12 mg as opposed to 25 mg used to obtain the data in Figure 2) and from postphotolysis processing (washing, drying, etc.). The combined data associated with catalytic samples formed from quantitative decomposition of the Pt-based molecular precursors (1% by mass on titania) are collected in Table 2.

In another set of experiments, chemically deposited platinum nanoparticle performance (produced from NaBH4 reduction) was directly compared with that generated from PD (Figure 5). These measurements were also acquired with 12 mg of each sample suspended in 25 mL of 1:6 MeOH:H2O. Prior to photocatalysis experiments, each solid was isolated immediately after platinum nanoparticle deposition, after washing and vacuum drying. The sample generated from CD clearly operates at a lower catalytic activity with respect to the one produced via PD (200 and 300 μmol/h, respectively). Because the surface coverage was the same, the TOF follows the same trend (0.24 and 0.36 s–1, respectively) (Figure 5 and Table 2).

Another possible explanation was experimentally tested to rationalize the observation that the 1 to 2% loaded samples

![Figure 2. Photochemical hydrogen evolution from 25 mg samples of Pt(dcbpy)Cl2/TiO2 at varied initial surface coverage (specified in legend) suspended in 25 mL of MeOH/H2O (1:6).](Image)

<table>
<thead>
<tr>
<th>Table 1. Summary of Relevant Materials Parameters and In Situ Photocatalytic Activity of 25 mg Pt(dcbpy)Cl2/TiO2 Samples at Different Initial Surface Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface coverage (%)</td>
</tr>
<tr>
<td>0.5%</td>
</tr>
<tr>
<td>1%</td>
</tr>
<tr>
<td>2%</td>
</tr>
<tr>
<td>4.27%</td>
</tr>
<tr>
<td>7.05%</td>
</tr>
</tbody>
</table>

a Photocatalytic activity (μmol H2/h) was measured by GC headspace analysis. b Amount of decomposed Pt precursor (milligrams and micromole, respectively) was deduced from the quantitative desorption of Pt4+ precursors. c Turnover frequencies TOF = [mol H2 produced] × [mol decomposed Pt4+ precursors] × 1 s−1. d Number “N” of Pt(0), crystallites per milligram of TiO2 was calculated from obtained data. e Average nanoparticle size (nanometer) was measured by STEM. f Pt nanoparticle shell number “n” and the magic number of surface atoms “10n² + 2” were calculated based on nanoparticle diameter. g Total number of atoms per nanoparticle was calculated from size distribution data. h % of surface atoms which was assumed to be catalytically active. i Surface TOF (s−1) was calculated from TOF and % of surface atoms; see the text for details.

Figure 3. (a) Hydrogen evolution increases after removal of the remaining molecular PtII complexes from the surface of TiO2 at higher surface coverage, illustrating the absorbance of undecomposed PtII precursors in the UV region of this sample. (b) Normalized percent transmittance at 377 nm (black line and data points) of five different solutions and the calculated mass of PtII precursors remaining on the TiO2 surface (red line and data points), where the unreacted PtII precursors are systematically desorbed at each percentage loading from the surface of titania after 5 h of photocatalysis.

Figure 4. Photochemical hydrogen evolution from 12 mg of Pt/TiO2 (1% by mass prepared from complete photodeposition (PD) of Pt(dcbpy)Cl2 on TiO2, red line and data points) versus the benchmark Pt/TiO2 (1% by mass prepared by 5 h photodeposition of H2PtCl6 on TiO2, black line and data points) both suspended in 25 mL of MeOH/H2O (1:6).

outperformed all others in hydrogen production activity (Figure 2); namely, smaller nanoparticles with enhanced catalytic activity25 were formed at lower surface coverage. Dark-field STEM images of Pt particles at varied surface coverage were quantitatively analyzed. At low loading of Pt(dcbpy)Cl2 (0.5 to 2%), the resulting particles were 1.5 ± 0.2 nm in diameter, whereas at higher coverage (4.27 and 7.05%), they were measurably larger: 1.9 ± 0.3 and 2.5 ± 0.4 nm, respectively. Both the Pt(II) precursor and deposition method influence the Pt particle size. The 1% sample resulting from CD yields Pt(0) nanoparticles that were 2 ± 0.5 nm in diameter, whereas the 1% H2PtCl6 photodeposited sample results in the generation of 3 ± 0.6 nm particles (Figure 6). Therefore, a clear variation in the efficiency of hydrogen production with the ultimate size of resultant nanoparticles was observed. In theory, small nanoparticle clusters have more exposed platinum surface area potentially leading to higher catalytic efficiencies.27 This notion is consistent with the current experimental data and quantified further in Tables 1 and 2. In summary, the higher photocatalytic efficiency of the photodeposited Pt0 catalysts from Pt(dcbpy)Cl2 precursors at lower loadings was shown to be correlated to the formation of smaller particles and the absence of possible contaminants when PtII is formed photochemically in situ.

Because of the complexity of heterogeneous photocatalytic materials, the activity in terms of micromoles per hour under defined experimental conditions was used as a metric for the relative performance of different samples throughout the literature as summarized in the cited review article.9 We also calculated turnover frequencies and surface turnover frequencies for comparative purposes in this study, and these data are summarized in Tables 1 and 2. Assuming spherical Pt(0) nanoparticles, one can estimate the average number of Pt atoms (x) present in the nanoparticles in each sample. Full shell nanoparticles are thermodynamically stable and possess lower reactivity for surface growth, so it is expected that transition-metal nanoparticles are centered around “magic number” clusters: Pt(0)13, Pt(0)15, Pt(0)17, Pt(0)30, Pt(0)50, Pt(0)92, and so on.48 Therefore, using the “magic number” formula for the number of surface atoms (10n² + 2, where n is the number of shells), we can estimate the percentage of surface atoms (assumed to be catalytically active) in each sample and subsequently calculate a surface turnover frequency, the observed induction period for nanoparticle formation present in the in situ photodeposited samples (Figure 2 and Table 1). In addition, the number (N) of Pt(0) nanoparticles per mass of TiO2 (milligram) were calculated (Tables 1 and 2) using eq 1

\[ NPt(0) = n \times N_s \times x^{-1} \times (mass \ of \ TiO_2)^{-1} \]

Here n is the number of moles of decomposed Pt precursor, Ns is Avogadro’s number, and x is the number of Pt atoms per Pt(0) cluster.

The trends found for the photocatalytic activities in terms of both TOF and surface TOF clearly reflect changes in catalytic behavior in different samples resulting from two main factors discussed throughout this report. The first relates to the absorbance in the UV due to undecomposed PtII precursors at high surface coverage ultimately resulting in diminished catalytic
The Journal of Physical Chemistry C

Table 2. Summary of Relevant Materials Parameters and Photocatalytic Activity of 12 mg Pt0/TiO2 Composites Formed from Different Molecular Precursors (1% Pt(dcbpy)Cl2 or H2PtCl6) Subsequent to Recovery Following Photodeposition (PD) or Chemical Deposition (CD)

<table>
<thead>
<tr>
<th>Pt0 deposition method</th>
<th>activity (μmol·H2/h)a</th>
<th>precursor decomposed (mg)b</th>
<th>precursor decomposed (μmol)b</th>
<th>TOF (s−1)c</th>
<th>Pt(0)x per mg “N”d particle size (nm)e</th>
<th>shell number f</th>
<th>surface Pt atoms (%g)</th>
<th>surface TOF (s−1)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD from Pt(dcbpy)Cl2</td>
<td>300</td>
<td>0.12</td>
<td>0.23</td>
<td>0.36</td>
<td>7.7 × 1011 ∼ 1.5</td>
<td>3</td>
<td>92</td>
<td>∼ 150</td>
</tr>
<tr>
<td>CD from Pt(dcbpy)Cl2</td>
<td>200</td>
<td>0.12</td>
<td>0.23</td>
<td>0.24</td>
<td>3.7 × 1011 ∼ 2</td>
<td>4</td>
<td>162</td>
<td>∼ 310</td>
</tr>
<tr>
<td>PD from H2PtCl6</td>
<td>130</td>
<td>0.12</td>
<td>0.23</td>
<td>0.16</td>
<td>1.3 × 1011 ∼ 3</td>
<td>6</td>
<td>362</td>
<td>∼ 920</td>
</tr>
</tbody>
</table>

a Photocatalytic activity (μmol H2/h) was measured by GC headspace analysis. b Amount of decomposed Pt precursor (milligram and micromole, respectively) based on complete decomposition of Pt+ precursors. c Turnover frequencies TOF = [mol H2 produced] × [mol decomposed Pt+ precursors]−1 × s−1. d Number “N” of Pt(0)x crystallites per milligram of TiO2 was calculated from obtained data. e Average nanoparticle size (nanometer) was measured by STEM. f Pt nanoparticle shell number n and the magic number of surface atoms 10n + 2 were calculated based on nanoparticle diameter. g Total number of atoms per nanoparticle was calculated from size distribution data. h % of surface atoms which was assumed to be catalytically active. i Surface TOF (s−1) was calculated from TOF and % of surface atoms; see the text for details.

Figure 5. Comparison of hydrogen evolution from 12 mg of Pt(dcbpy)Cl2/TiO2 using photodeposition (PD) (red line and data points) and chemical deposition (CD) (black line and data points), respectively. Both samples were isolated after complete decomposition of Pt(dcbpy)Cl2 on the titania surface.

activity. To elucidate further this concept, surface TOF values can be useful because these values are corrected for the fraction of exposed Pt atoms. For comparative purposes, refer to the surface TOF of the in situ photodeposited samples at different surface coverage (Table 1). The surface TOF is clearly higher at low catalytic loadings (≤ 2%). Second, the larger number of surface atoms produced in smaller nanoparticles exhibit higher catalytic activity and improved TOFs, consistent with the materials produced from photodecomposition of Pt(dcbpy)Cl2 resident on titania at 1 to 2% by mass. The inadequate surface coverage of Pt on TiO2 at 0.5% loading is deemed responsible for the lower catalytic activity (240 μmol/h) because the TOF, which corrects for the amount of Pt decomposed on TiO2 is 0.35 s−1, greater than the TOF obtained in the 4.27 and 7.05% samples, 0.2 s−1 and 0.14 s−1, respectively. This trend would be anticipated given that the samples at higher loading suffer from Pt0 precursor-induced competitive absorbance of bandgap photons and the subsequent formation of larger Pt0 nanoparticles.

In two distinct experiments operated under different conditions, liquid Hg and gaseous CO (at 1 atm) were introduced into the photoreaction mixture, and the hydrogen evolution was significantly attenuated (Figure 7). Hydrogen evolution catalysis at Pt0 is known to be poisoned by mercury because of the formation of a Hg/Pt amalgamate. In the present compositions, the Hg strongly interacted with these samples to the point that most of the suspended material accumulated and bound to the mercury at the bottom of the photoreactor. Platinum is also known to have high surface adsorption capacity for CO, which easily passivates the surface upon binding. At 1 atm pressure (gas bubbled through the aqueous suspension), the CO substantially inactivates the photocatalytic evolution of H2 gas from the samples. The two combined heterogeneous poising tests strongly suggest that the catalysis responsible for H2 generation is indeed heterogeneous in nature and results from the Pt nanoscopic particles embedded on the titania surface rather than from any remnant molecular Pt0 species. Similar data were obtained after aqueous base was utilized to remove all molecular Pt0 complexes from the titania surface after several hours of photoreaction.

DFT and TD-DFT calculations have suggested that Pt(dcbpy)Cl2 is stable upon one electron reduction. However, photoexcitation of this reduced compound with visible light is expected to result in Pt0 agglomerates when these molecules are in solution. Such a mechanism is qualitatively consistent with the PD of Pt nanoparticles seen in all of the materials presented herein. Whereas this mechanism justifies the photodecomposition of Pt0 molecular complexes under light illumination, Pt nanoparticle formation has also been observed from Pt0 salt precursors, starting with the reduction of Pt+ into Pt0 by the conduction band electrons of TiO2 upon bandgap excitation, where Pt0 adsorbed on the titania surface ultimately agglomerates into small crystallites. Under equilibrium conditions, the flatband potential of TiO2 at the TiO2/electrolyte interface is defined by Vfb = −0.2 − 0.059 pH = −0.613 V at pH 7,52,53 In a qualitative experiment, electrons on titania (TiO2(ε−))s were produced electrochemically in an argon-saturated H-cell by biasing a TiO2 film on a FTO electrode at −1000 mV versus Ag/AgCl in 0.1 M sodium phosphate buffer at pH 7, in conjunction with a Pt wire counter electrode in a standard three-electrode arrangement. At this potential, which roughly supplies 390 mV overpotential for hydrogen evolution at pH 7.0, electrons become trapped rapidly in the conduction band of TiO2, and because TiO2 is not a good electrocatalyst for hydrogen evolution itself, the resultant film turns from white to blue, indicating the presence of TiO2(ε−).
Figure 6. (a) Variation of particle size as a function of Pt(dcbpy)Cl$_2$ initial surface coverage on TiO$_2$. (b) Comparison of particle size from 1% Pt(dcbpy)Cl$_2$ photodeposited (PD), chemically deposited (CD), and the 1% H$_2$PtCl$_6$ PD benchmark.

Figure 7. (a) Mercury poisoning test performed on samples produced via photolysis of 1% Pt(dcbpy)Cl$_2$ by mass adsorbed on titania with Pt(0) formed in situ. (b) CO (1 atm) inhibition experiment performed on photodeposited catalytic samples subsequent to Pt(0) photodeposition. Hydrogen evolution decreases dramatically in the presence of Hg and CO in 1% Pt(dcbpy)Cl$_2$/TiO$_2$ suggesting that the catalyst is indeed heterogeneous and has its origin in the formed Pt nanoparticles.

Figure 8. (a) Qualitative electron trapping experiment showing the color change of the white TiO$_2$ film into blue due to trapped electrons resulting from −1000 mV versus Ag/AgCl applied bias in 0.1 M sodium phosphate buffer at pH 7.0. Ultimately, this material turns gray after the addition of Pt(dcbpy)Cl$_2$ to the solution and removal of the bias. (b) TEM image of the scraped film after the experiment indicates the presence of Pt nanoparticles (black) on the TiO$_2$ support (lighter), 5 nm scale bar.

(Figure 8). The electrochemical bias was removed after 5 min, then Pt(dcbpy)Cl$_2$ in slightly basic water was injected in the working side of the electrochemical cell under an argon atmosphere in the dark, turning the TiO$_2$ film into a gray cast signaling
the formation of metallic platinum. Hydrogen could be readily detected from the headspace by GC after the injection of this molecular precursor and the subsequent formation of platinum nanoparticles, ultimately confirmed using TEM. This experiment verifies that TiO₂(e−) are likely responsible for the reduction of the surface-anchored Pt₄⁺ complex into Pt⁰, which ultimately leads to heterogeneous hydrogen production as a dark reaction. However, this does not necessarily imply that the one-electron reduced Pt(dcbpy)Cl₂ complex is unstable, as multiple electrons can be simultaneously delivered to the molecules under these experimental conditions.

Meyer and coworkers have reported a similar observation on Ru(dcbq)(bpy)₃/TiO₂ and hemin/TiO₂ systems where TiO₂(e−) afforded the reduction of these surface-anchored compounds. In a separate experiment, Pt(dcbpy)Cl₂/TiO₂ (1%) in pure water was irradiated using broadband white light illumination from a Xe lamp, and the solid isolated after irradiation possessed a gray cast suggesting the formation of Pt nanoparticles. This experiment confirmed that TiO₂(e−) derived from a photochemical reaction can reduce Pt(dcbpy)Cl₂ into Pt⁰ nanoparticles in the absence of hole scavengers. Similar results have been described in the photochemical Pt deposition on TiO₂ from various Pt complexes in aqueous media. It is important to note that in the current photocatalytic H₂ production experiments over titania, CO₂ was also qualitatively detected in the reactor headspace by GC, verifying the oxidation of MeOH by hole migration to the surface of TiO₂. For more details of methanol decomposition products generated (HCHO, CO₂, etc.) and the associated plausible mechanisms, please refer to the literature.

CONCLUSIONS

Bandgap excitation of TiO₂ containing surface-anchored Pt-(dcbpy)Cl₂ molecules in 1:6 methanol/water results in the formation of Pt⁰ nanoparticles that subsequently photocatalyze the reduction of protons into hydrogen. Some of the lowest Pt(dcbpy)Cl₂ surface coverage (1 to 2% loading by mass) produced materials exhibiting the highest photocatalytic performance, which significantly outperformed all other surface coverage and the benchmarks. The CD of this catalyst via NaBH₄ reduction on TiO₂ gave rise to slightly inferior catalytic materials, promoting the economic usage of noble metals in the area of hydrogen production catalysis, as demonstrated by using modest amounts of the surface-anchored molecular precursor Pt-(dcbpy)Cl₂ for the generation of high activity and monodisperse Pt⁰ nanoparticles on titania surfaces.