Enhanced Photocatalytic Hydrogen Evolution from Transition-Metal Surface-Modified TiO₂

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ABSTRACT: This study describes the UV solution photodeposition of several earth-abundant 3d transition metals (Co, Ni, and Cu) onto the surface of nanoparticle TiO₂. Irradiated methanolic metal dichloride solutions with suspended Degussa P25-TiO₂ (1–2 wt % metal to TiO₂) yield visibly colored titanias, whereas the bulk TiO₂ structure is unchanged; X-ray photoelectron spectroscopy confirms that metals are present on the titania surface in either reduced metal (Cu/Cu⁺) or metal cation states (Co²⁺ and Ni²⁺), and UV-vis diffuse reflectance spectroscopy shows new visible absorbance features. The analyzed bulk metal contents (~0.04–0.6 at. %, highest for copper) are lower than the nominal metal solution content. Mixed-metal solution photodeposition reactions roughly parallel observations for single metals, with copper deposition being most favored. These 3d metal surface-modified titanias show significant (~5–15×) improvement in UV photocatalytic H₂ evolution versus unmodified TiO₂. H₂ evolution rates as high as 85 μmol/h (8500 μmol h⁻¹ g⁻¹) were detected for Cu-coated TiO₂ using continuous monitoring of reactor headspace gases by portable mass spectrometry. Control experiments verify the necessity of the methanol sacrificial oxidant in both metal deposition and H₂ evolution. In situ metal surface deposition is quickly followed by enhanced H₂ evolution relative to TiO₂, but at lower levels than isolated metal surface-modified titanias. The photodeposited 3d metal species on the TiO₂ surface likely act to reduce electron–hole recombination by facilitating the transfer of photoinduced TiO₂ conduction band electrons to protons in solution that are reduced to H₂. This study demonstrates a facile method to modify photoactive TiO₂ nanoparticles with inexpensive 3d transition metals to improve photocatalytic hydrogen evolution, and it shows the utility of quantitative real-time gas evolution monitoring by portable mass spectrometry.

INTRODUCTION

Titanium dioxide (TiO₂) is a well-studied semiconducting material for photocatalysis and has promise in solar energy conversion.1−4 Anatase TiO₂ (Eg = 3.2 eV) can perform the photolysis of water into hydrogen and oxygen gases in an electrochemical cell.5 The deposition of platinum metal on the surface of anatase TiO₂ forms a highly active UV photochemical water-splitting catalyst.6−8 Platinum metal regions on titania act as a surface catalyst that funnels photoexcited TiO₂ conduction band (CB) electrons to protons in solution that are reduced to H₂. In these types of photocatalytic reactions, a sacrificial oxidant is needed to remove photogenerated holes from the semiconductor valence band (VB) and maintain overall charge balance.9,10 However, even at low catalyst concentrations (~1 wt %), platinum has disadvantages related to its high cost and low abundance.

There have been extensive efforts to improve the photochemical properties of TiO₂-based materials that do not involve noble metal cocatalysts and may also enable absorption of solar radiation for water-splitting hydrogen production.11 A wide range of metals (Cu, Ni, Co, Cr, Fe, Mo, V, and W16) and nonmetals (N, P, and S20) have been doped into the bulk structure of TiO₂ by solution or solid-state methods to modify the bulk titania band structure and improve visible light absorption or electron–hole charge recombination kinetics. Most prior work has used gas-phase H₂ or solution-phase NaBH₄ reduction of metal ions mixed with TiO₂ precursors. We previously incorporated ~5–10 at. % of several 3d metals into rutile TiO₂ via exothermic solid-state metathesis reactions.21 These metathesis-derived titanias showed lower photoactivity versus undoped materials, though 3d metals gave visible color to the products. Modifying TiO₂ with two metals in its bulk structure, such as Co/Ni or Cu/Ce, has been studied for photocatalytic applications in dye degradation and water splitting.22,23 CuO coatings or intimate copper oxide mixtures with TiO₂ exhibit partial reduction of copper oxide during observed enhanced photocatalytic hydrogen evolution.24,25 Photodeposition has been utilized for the removal of metal ions from aqueous environments with semiconducting WO₃ or TiO₂ as photocatalytic substrates.26−31 In addition to environ-
mental remediation, photoassisted deposition can also function as a potentially facile low-temperature method to modify photoactive surfaces such as TiO₂ with metal or metal oxide cocatalysts. Copper and nickel have shown promise as photodeposited cocatalysts or as in situ catalysts for photocatalytic hydrogen evolution using high-surface area titania nanotubes or mesoporous structures. This paper describes the UV photodeposition of several 3d metals (Co, Ni, and Cu) onto the surface of commercial photoactive Degussa P25-TiO₂ (primarily anatase) using a method analogous to noble metal (e.g., Ag and Pt) photoreduction processes. The bulk titania structure and particle morphologies after 3d metal surface modification are unchanged. The surface and optical properties of the modified TiO₂ were investigated using X-ray photoelectron spectroscopy (XPS) and UV-vis spectroscopy. XPS surface compositions are compared to bulk chemical analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) to better analyze the metal deposition process. Real-time reactor headspace gas analysis by portable residual production. The 3d metal surface-modified TiO₂ materials show significant improvements in the photoreduction of water to hydrogen gas to levels approaching half of that of similarly prepared platinum-coated titanias.

RESULTS AND DISCUSSION

Photochemical M:TiO₂ Synthesis. Commercial Degussa P25-TiO₂ nanoparticles (∼50 nm, 80:20 anatase–rutile) were surface-modified with the 3d metals nickel, cobalt, and copper using solution UV photoreduction in the presence of a sacrificial methanol oxidant. P25-TiO₂ was dispersed in a 50 vol % aqueous methanol solution containing dissolved metal dichlorides. The solution was degassed with argon prior to UV irradiation to favor inert (nonoxidizing) conditions. The initial solutions contained sufficient metal chlorides to deposit either 1 or 2 wt % metal onto the suspended titania powder. Following UV exposure, the titania suspension had darkened in color (e.g., gray Ni:TiO₂ and purple Cu:TiO₂) and the washed and dried M:TiO₂ solids were light gray (Ni) or light blue (Co and Cu). When two different metals were present in the photodeposition solution (Co/Ni, Co/Cu, and Ni/Cu), the M:TiO₂ products had a light blue coloration, similar to the Cu and Co products. Comparable visible titania colorations were observed for the nominal 1 and 2 wt % metal loadings. Each product is identified by metal and nominal metal loading as M(x%):TiO₂, for example, Ni(1%):TiO₂.

M:TiO₂ Structure, Composition, and Surface Analysis. Powder X-ray diffraction (XRD) of the photodeposited M:TiO₂ products shows predominately anatase TiO₂ with a small rutile component in ratios that are unchanged from the starting P25-TiO₂ (Figure S1). No additional XRD peaks corresponding to other metals or metal oxide phases were observed, suggesting that they are present in amounts below the few percent XRD detection limits or they are on the surface in a noncrystalline form. The photochemical reactions between P25-TiO₂ and metal halide solutions also did not lead to detectable physical changes in the titania powders. A Brunauer–Emmett–Teller (BET) surface area of 44.8 m²/g was measured for P25-TiO₂, which is essentially the same as the 44.6 m²/g surface area measured for a surface-modified Cu(1%):TiO₂ sample. Scanning electron microscopy (SEM) analysis also showed that the original TiO₂ particle sizes near 50 nm are retained in the Cu(1%):TiO₂ photoproduct (Figure 1). Aggregated small particles near 50 nm are similarly observed for Ni and Co deposition products (Figure S8).

Bulk elemental analysis using ICP–OES detected the metals deposited onto TiO₂ and the M:Ti atomic ratios are summarized in Table 1. At the targeted 1 wt % metal loading, the ideal M:Ti atomic ratio would be 1.3:98.7 (2.6:97.4 for 2 wt %) if all of the metal present in solution was deposited onto the P25-TiO₂ particle surface. Cobalt and nickel were detected at less than 10% of the ideal 1 wt % loading value, whereas copper approached half of the ideal loading. In the mixed-metal samples, the cobalt and nickel content remained low (<0.07 at. % vs Ti), whereas the amount of copper was closer to its ideal content based on solution concentrations; thus, the photodeposition of copper onto semiconducting TiO₂ is favored over the other metals. A doubling of the metal chloride solution concentration to 2 wt % did not result in a doubling of metal product content. Similar metal deposition trends have been observed in related photochemical contexts. These surface deposition results are consistent with metal activity series trends and reduction potentials (M²⁺ + 2e⁻ → M with ease of reduction Cu > 2H⁺ → H₂). For example, copper is the most easily reduced of the three metal cations and protons. Copper is also the only one of the three metal cations that is easier to reduce than H²⁺ to H₂. In the photoassisted solution reduction process, it is generally accepted that a sacrificial methanol oxidant interacts with the VB holes in photoexcited TiO₂ while the photoexcited CB electrons in TiO₂ are used for solution H⁺ to H₂ reduction and also surface metal reduction (e.g., Cu²⁺ → Cu⁺/Cu⁰). This catalytic redox cycle parallels the mechanisms used for platinum-coated titanias produced by UV photoreduction of PtCl₆²⁻ in methanol solutions.
Surface composition and chemical environment were examined for select M:TiO\textsubscript{2} products using surface-sensitive XPS. For the nominal 1−2 wt % metal concentrations, signals were observable for Co, Ni, and Cu, though the Co and Ni contents were low and required longer sampling times to detect weak signals for these metals above the baseline.

Figure 2 shows the 2p\textsubscript{3/2} spectra for Ti, Co, Ni, and Cu peaks in representative M(2\%):TiO\textsubscript{2} samples (additional spectra are in Supporting Information Figure S2). Table 1 summarizes the XPS peak positions and relative atomic ratios of the surface metal species. As compared to the bulk ICP composition results, XPS shows higher M:Ti surface atomic ratios. Because the metal species are photodeposited on the surface, rather than being homogeneously distributed through the TiO\textsubscript{2} structure, it is consistent that the XPS surface composition yields a higher M:Ti atomic ratio than bulk analysis. For the mixed-metal samples, Co(1%)/Ni(1%):TiO\textsubscript{2} has Co and Ni contents similar to what was observed in the individual Co(1%) and Ni(1%):TiO\textsubscript{2} samples. In contrast, the mixed-metal samples containing Cu showed no detectable Co or Ni, which is consistent with the bulk ICP results showing decreased photodeposition of Co and Ni when Cu is present in solution. The mixed-metal results provide further support for the ease of copper ion photoreduction onto semiconducting TiO\textsubscript{2} as compared to Co and Ni ions.

In addition to surface-sensitive compositions, XPS provides useful information about the nature of the metals deposited on the surface. As shown in the results in Table 1, in all M:TiO\textsubscript{2} samples, the Ti 2p\textsubscript{3/2} peak is between 458.4 and 459.0 eV, agreeing with a Ti\textsuperscript{4+} environment for TiO\textsubscript{2}. For reference, the starting P25-TiO\textsubscript{2} has a Ti 2p\textsubscript{3/2} peak centered at 458.2 eV. The O 1s spectra show a major peak at 530.2 eV in all samples, also consistent with the oxide anion for TiO\textsubscript{2}. The other metal peak positions were used to help determine their chemical states on the TiO\textsubscript{2} surface. The 2p\textsubscript{3/2} peak in Cu samples indicates that the metal has been reduced on the

<table>
<thead>
<tr>
<th>Sample</th>
<th>M:Ti (at. %) ICP</th>
<th>M:Ti (at. %) XPS</th>
<th>M 2p\textsubscript{3/2} (eV)\textsuperscript{a}</th>
<th>Ti 2p\textsubscript{3/2} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1%):TiO\textsubscript{2}</td>
<td>0.04:99.96</td>
<td>0.3:99.7</td>
<td>780.0</td>
<td>458.5</td>
</tr>
<tr>
<td>Co(2%):TiO\textsubscript{2}</td>
<td>0.07:99.93</td>
<td>1.3:98.7</td>
<td>780.8, 786.6</td>
<td>458.6</td>
</tr>
<tr>
<td>Ni(1%):TiO\textsubscript{2}</td>
<td>0.08:99.92</td>
<td>0.5:99.5</td>
<td>855.3, 861.5</td>
<td>458.5</td>
</tr>
<tr>
<td>Ni(2%):TiO\textsubscript{2}</td>
<td>0.08:99.92</td>
<td>3.4:96.6</td>
<td>855.8, 860.9</td>
<td>458.6, 461.3</td>
</tr>
<tr>
<td>Cu(1%):TiO\textsubscript{2}</td>
<td>0.44:99.56</td>
<td>1.7:98.3</td>
<td>932.3</td>
<td>458.4</td>
</tr>
<tr>
<td>Cu(2%):TiO\textsubscript{2}</td>
<td>0.64:99.36</td>
<td>3.5:96.5</td>
<td>932.6</td>
<td>458.4</td>
</tr>
<tr>
<td>Co(1%)/Ni(1%):TiO\textsubscript{2}</td>
<td>Co:Ni:Ti 0.05/0.06/99.89</td>
<td>Co:Ni:Ti 0.6/0.4/99.0</td>
<td>Ni: 855.8, Co: 782.0</td>
<td>458.5</td>
</tr>
<tr>
<td>Co(1%)/Cu(1%):TiO\textsubscript{2}</td>
<td>Co/Cu:Ti 0.02/0.97/99.01</td>
<td>Co/Cu:Ti 0/5.2/94.8</td>
<td>Cu: 932.2</td>
<td>458.4</td>
</tr>
<tr>
<td>Ni(1%)/Cu(1%):TiO\textsubscript{2}</td>
<td>Ni/Cu:Ti 0.03/1.02/98.95</td>
<td>Ni/Cu:Ti 0/6.0/94.0</td>
<td>Cu: 933.0</td>
<td>458.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Literature values for M 2p\textsubscript{3/2} from NIST XPS database:\textsuperscript{36} Co(0/+2/+3) 778.1/780.2/781.3,\textsuperscript{37,38} Ni(0/+2) 852.8/853−856,\textsuperscript{39} and Cu(0/+1/+2) 932.4/932.5/933.7.\textsuperscript{39}
surface to Cu$^2$/Cu$^+$ states (e.g., Cu$_2$O or CuCl), which is consistent with related work on copper-coated titania.$^{24,39}$ As noted above, Cu is more readily photodeposited onto P25-TiO$_2$ than Co or Ni, and XPS compositional analysis supports the idea that the ease of Cu$^{2+}$ reduction leads to higher surface deposition. The Co(1%)/Ni(1%):TiO$_2$ sample has a nickel peak position similar to those of comparable Ni$^{2+}$ peaks observed in the Ni:TiO$_2$ samples, but the cobalt peak appeared at a slightly higher energy near a Co$^{3+}$ state. The mixed-metal samples show that Cu is still in a Cu$^2$/Cu$^+$ state, though the Ni/(1%)/Cu(1%):TiO$_2$ sample may have some Cu$^{2+}$ character. In related studies, chemically precipitated Cu(OH)$_2$ or Ni(OH)$_2$ clusters onto the P25-TiO$_2$ surface show similar 2p$_{3/2}$ shifts from 935 to 933 eV as surface Cu$^{2+}$ transforms to metallic Cu and a Ni peak at 856 eV is attributed to surface Ni$^{2+}$. Chlorine is also present on the titania surface after photoreaction with metal chloride solutions, and higher surface chlorine is detected for Co and Ni cations versus partially reduced Cu on the titania surface requires less chloride anion charge balance.

Optical Properties of M:TiO$_2$. UV–vis diffuse reflectance spectroscopy (DRS) spectra for the M:TiO$_2$ samples relative to P25-TiO$_2$ show that the 3d metal surface modification leads to visible colors and apparent new absorption events in the red or orange regions as well as a slightly lower energy band gap absorption energy ($E_g$). Figure 3 shows the raw reflectance data and Tauc plot for P25-TiO$_2$ along with M(2%):TiO$_2$ products. Each of the M:TiO$_2$ samples shows a band gap absorption shift to lower $E_g$ near 2.9 eV from 3.2 eV for P25-TiO$_2$. Cu:TiO$_2$ samples show a decrease in reflectance at wavelengths above 600 nm, correlating with its light blue color. For comparison, a blue CuCl$_2$ solution has an absorbance maximum at 800 nm corresponding to d–d electronic transitions. Similar absorption near 700–800 nm are observed for Cu(OH)$_2$ deposited onto TiO$_2$.$^{21,41}$ The Co:TiO$_2$ samples show decreased reflectance from 520 to 680 nm, similar to CoCl$_2$ solutions with an absorbance maximum near 500 nm. The light gray-colored Ni:TiO$_2$ samples exhibit a broad decrease in total reflectance across the visible spectrum relative to P25-TiO$_2$. The spectra for M(1%):TiO$_2$ and M(1%)/M(1%):TiO$_2$ samples show similar absorption events and trends (see Figures S3 and S4). The increase in visible absorptions and band gap decrease may be due to nanoscale surface plasmon resonance effects,$^{33,42}$ whereas others have ascribed these optical transitions to charge transfer between TiO$_2$ bands and the surface-deposited metal species.$^{40,41}$

Photocatalytic Hydrogen Evolution with M:TiO$_2$. Photocatalytic hydrogen gas evolution from aqueous methanol solutions was quantified in real time using RGA–MS for different M:TiO$_2$ samples under UV irradiation with methanol serving as a sacrificial oxidant. Calibration curves for the H$_2$/Ar headspace mass analysis data allowed direct conversion to molar quantities of evolved hydrogen (Figures S5 and S6). The use of direct mass quantification by RGA–MS allowed continuous measurement of rates of H$_2$ produced, and it yielded similar evolution rates for Pt(1%):TiO$_2$, reported by gas chromatography analysis.$^{43}$ For comparison, photocatalytic hydrogen gas evolution was determined for highly active platinum-coated titania, Pt(1%):TiO$_2$, and unmodified P25-TiO$_2$, which yielded average H$_2$ evolution rates of 200 and 5 μmol/h, respectively (for our 10 mg samples: 20,000 and 500 μmol h$^{-1}$ g$^{-1}$). Each M:TiO$_2$ sample showed considerably higher H$_2$ evolution rates than the P25-TiO$_2$ starting material, and multiple cycle data for M(1%):TiO$_2$ samples are shown in Figure 4. Similar cycling data for M(2%):TiO$_2$ and mixed-metal systems are shown in Figure S7.

Each M:TiO$_2$ catalyst was tested in several 1 hour cycles of UV exposure in the same aqueous methanol solution, and the average hourly hydrogen evolution data are summarized in Table 2. The hourly H$_2$ evolution rates for most samples across the multiple cycles showed small deviation. The samples with the least stability were Co(1%):TiO$_2$ and Ni(2%):TiO$_2$, where
H2 evolution dropped by 30–50% after the third cycle. The Cu(1%):TiO2 sample had the highest hydrogen evolution rate of 85 μmol/h (8500 μmol h−1 g−1), which is comparable to or greater than prior studies of copper deposition on porous or nanoscale titania with H2 evolution in range from 1500 to 3400 μmol h−1 g−1.34,40,41 Apart from H2 evolution, though at lower activity than the initial cycling tests.

Table 3 compares several Ni- and Cu-modified titania for hydrogen evolution photocatalysis. Some cases note the ideal amount of metal that could be deposited onto TiO2 from solution where bulk chemical analysis was not available. The metal salt solutions vary from using nonoxidizing chloride anions to potentially reducible sulfate and nitrates anions. As P25-TiO2 alone only yields ∼500 μmol h−1 g−1 of H2 in aqueous UV photocatalytic reactions with a methanol sacrificial oxidant, the wide range of surface deposition strategies in Table 3 all show enhanced H2 evolution abilities with various illumination strategies and oxidants. Recycling tests were performed after recovering M(1%):TiO2 photocatalysts, though this may be due to the higher amount of Cu deposition based on the ICP results. Scaling hydrogen evolution activity to the amount of metal cocatalyst present indicates that Co(1%):TiO2 is the most active at 8400 μmol h−1 mg−1 Co, whereas Cu(1%):TiO2 has an activity of 2400 μmol h−1 mg−1 Cu. The calculated quantum yields (QYs) from the broad spectrum UV illumination are generally similar (∼1–20% range) to those reported in other Cu or Ni surface-modified titanias.34,40,41

There was no synergistic photocatalyst effect observed for the titania surface-modified with both Ni and Co as the activity for the mixed-metal sample was similar to or lower than that of the individual M(1%):TiO2 products. Although the addition of a second photodeposited metal (Co or Ni) species onto TiO2 does enhance copper photodeposition, this may lead to higher surface metal coatings that inhibit hydrogen evolution activity by favoring redox reactions of the surface metal species (e.g., Cu+/Cu) or blocking the illumination of the titania core. On the basis of the results in Table 2 for M(1%)/Cu(1%):TiO2, addition of Ni2+ to the Cu+/Cu-photodeposited coating has less negative impact on hydrogen production versus the Co2+ addition. There are many variables that prevent direct comparisons with other related metal-coated heterojunction titanias, but Table 3 compares several other studies with the current work.

In the results in Table 3, some cases note the ideal amount of metal that could be deposited onto TiO2 from solution where bulk chemical analysis was not available. The metal salt solutions vary from using nonoxidizing chloride anions to potentially reducible sulfate and nitrates anions. As P25-TiO2 alone only yields ∼500 μmol h−1 g−1 of H2 in aqueous UV photocatalytic reactions with a methanol sacrificial oxidant, the wide range of surface deposition strategies in Table 3 all show enhanced H2 evolution abilities with various illumination strategies and oxidants.

Recycling tests were performed after recovering M(1%):TiO2 samples and testing the activity in new aqueous methanol solutions. All M:TiO2 samples retained enhanced hydrogen evolution, though at lower activity than the initial cycling tests. As an example, Cu(1%):TiO2 had an average rate of 62 μmol/h during a recycle test, roughly 73% of the average activity of the initial cycles. During several catalyst recycle runs, the individual cycles were fairly consistent (see Table S4, Supporting Information). Postreaction XPS analysis was used to check for changes in the catalyst surface composition (Table S3). Cu(2%):TiO2 showed an ∼70% decrease in the Cu:Ti atomic ratio to 1.1:98.9, but no change in the Cu 2p3/2 peak position. The Co(2%) and Ni(2%) samples did not show clearly identifiable surface metal peaks in the postreaction analysis, thought the solids retained some of their initial color. This loss
of surface metal may be related to the decrease in activity over the initial cycles as well as the drop in activity during the recycle tests for these catalysts. In related CuO/TiO₂ photocatalytic systems, it was determined that photocorrosion of chemically deposited copper occurs during UV hydrogen evolution photocatalysis along with possible competing reverse deposition of some dissolved copper.\(^3\)

In the Ti 2p\(_{3/2}\) spectrum of Ni(1%)/Cu(1%):TiO₂, a small peak appeared at 454.9 eV, which is consistent with the presence of reduced Ti\(^{3+}\) on the surface of this sample.\(^3\) The presence of Ti\(^{3+}\) sites on TiO₂ has been associated with enhanced photooxidation abilities.\(^4\) As noted earlier, the copper photooxidation preference may be due to its ease in reduction relative to Co\(^{3+}\), Ni\(^{2+}\), or H\(^+\). The Ti\(^{4+}\)/Ti\(^{3+}\) reduction is slightly less favored than H\(^+\), and control experiments with P25-TiO₂ alone under UV illumination in methanol solution show no visible change in color or enhanced hydrogen evolution activity (see the P25-TiO₂ sample in Figure 4).\(^3\)

Thus, if present, Ti\(^{3+}\) is not generated in the absence of other metals under the conditions of this work. Given that chloride ions are present on the surface after photodeposition reactions in metal halide solutions, another control experiment with P25-TiO₂ was performed in the presence of NaCl(aq) under the same aqueous methanol/UV conditions. No detectable changes in H₂ evolution were observed for P25-TiO₂, indicating that the presence of chloride is not a determining feature of enhanced H₂ evolution from the M:TiO₂ materials.

**In Situ Photodeposition and Hydrogen Evolution Studies.** Several in situ photocatalytic hydrogen evolution experiments were run with P25-TiO₂ in the presence of MCl₂ in 50% methanol, equivalent to the 1% photodeposition experiments. Cycling data are presented in Figure 5 for these single-step deposition/hydrogen evolution experiments. These tests showed that even without the metal previously deposited onto the TiO₂ surface, hydrogen gas is produced very quickly, once some metal surface photodeposition occurs. After the first in situ cycle for CuCl₂, the titania catalyst developed its characteristic blue color. The in situ copper photodegradable test showed an average hydrogen evolution rate of 29 \(\mu\)mol/h (2900 \(\mu\)mol h\(^{-1}\) g\(^{-1}\)), 5 times higher than that of P25-TiO₂ alone, which is higher than those observed in other in situ Cu:TiO₂ studies (\~1500 \(\mu\)mol h\(^{-1}\) g\(^{-1}\)).\(^4\) But about one-third of that observed for the isolated Cu(1%):TiO₂ material described above. Related titania experiments have shown that the addition of copper sulfate to a titania suspension also improves the rate of hydrogen evolution to 2200 \(\mu\)mol h\(^{-1}\) g\(^{-1}\).\(^3\) The initial rates for the in situ Co and Ni tests were comparable to the values for the isolated Co(1%) and Ni(1%):TiO₂ materials but dropped in activity over four cycles. This loss of activity is comparable to that observed for the isolated Co(1%):TiO₂ sample, but the activity of the isolated Ni(1%):TiO₂ catalyst was more stable under UV photocatalytic cycling than that shown by the in situ test.

An in situ Cu(1%):TiO₂ experiment was also performed in 18 MΩ water to verify the importance of methanol as a sacrificial oxidant in this photochemical reaction. Two UV illumination cycles (P25-TiO₂, 1 wt % CuCl₂, pure water) were run without methanol, and there were no visible titania color change and no detectable H₂ production by RGA–MS analysis (Figure 6). After the second illumination cycle, methanol was spiked into solution and this produced detectable H₂ evolution and a titania color change observed during the third UV illumination cycle. This test confirmed the importance of a sacrificial oxidant for both photoassisted copper surface deposition/reduction and hydrogen generation processes.

**Photocatalytic Considerations.** The CB energy for anatase TiO₂ is energetically well-suited for the solution reduction of H\(^+\) to H₂. One of the primary limitations on its activity is the fast charge recombination of photoexcited electrons in the CB with holes in the VB before they are utilized in external redox reactions. The addition of metal or metal oxide to the TiO₂ surface provides a pathway to transfer photogenerated electrons from the TiO₂ CB to the surface-bound metal (or metal ion) cocatalyst that facilitates hydrogen reduction. In the absence of a photocatalyst, the overall reaction of CH₃OH with water to produce CO₂ and H₂ is a thermochromically uphill process with a calculated \(\Delta H_{\text{rxn}}\) of +53 kJ/mol using standard enthalpy of formation values. One study estimated an endothermic free energy of +16 kJ/mol for this reaction in the absence of a catalyst.\(^5\) On the basis of the relatively low energy redox processes for Co, Ni, and Cu ions in solution and metals on titania particles, the enhanced photocatalytic activity of these heterojunction semiconductor composites is usually attributed to the 3d metal engaging in surface redox reactions that lead to H\(^+\) to H₂ reduction. During

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**Figure 5.** In situ metal deposition and hydrogen evolution data; average rates for all four cycles (\(\mu\)mol/h) are Co 12.2, Ni 15.8, and Cu 28.3. H₂ production was measured during 1 h illumination cycles followed by a 10 min argon flush. Each illumination cycle began at the 30, 100, 170, and 240 min marks.

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**Figure 6.** In situ copper UV photodeposition and hydrogen evolution in 18 MΩ water. First UV lamp cycle begins near 30 min and ends at 90 min. Reactor headspace was flushed with argon between UV illumination runs. Second UV lamp cycle begins at 100 min and ends at 160 min. Methanol is spiked into solution during the argon flush prior to the third cycle.
UV illumination, there is a continuous flow of CB electrons from TiO2 to the surface metal cocatalyst, enabling reduction processes, which could transiently involve the metal (e.g., metal oxide to metal particles) as well as the H+/H2 reduction. Given the different reduction potentials for Co and Ni versus Cu, there may be different surface reactions occurring, for example, H2 from Ni or Co systems via transient production of nanoscale metals that reoxidize during H2 production versus H2 production from metallic copper particle surfaces. These general heterojunction photocatalyses have been proposed in several related previous systems.40,41 The general reaction steps described for these photocatalytic redox reactions are

\[
\text{TiO}_2 + h\nu (>E_g) \rightarrow e^{-}(\text{TiO}_2 \text{ CB}) + h^+(\text{TiO}_2 \text{ VB})
\]

(1)

\[
e^{-}(\text{TiO}_2 \text{ CB}) + \text{surface}(M^{+}/M^{2+}) \rightarrow \text{TiO}_2/(M\text{reduced})
\]

(2)

\[
2e^{-}(\text{TiO}_2 \text{ CB}) + \text{TiO}_2/(M\text{reduced}) + 2H^+
\rightarrow H_2 + \text{TiO}_2/(M\text{reduced})
\]

(3)

\[
2h^+(\text{TiO}_2 \text{ VB}) + \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + 2H^+
\]

(4)

In this work, the lower activity of our photodeposited M:TiO2 samples for Co or Ni versus Cu can be attributed to the (a) differing amounts of metal species on the TiO2 surface and (b) differences in metal ion redox activity versus hydrogen reduction. In this photocatalytic metal species deposition, there appears to be an upper limit for metal deposition that competes with hydrogen gas formation. Other studies have also shown that catalytic activity of surface-deposited metals or metal oxides/hydroxides peaks at a low metal content (~0.2–0.5 mol % M) and then drops in activity overlap of reactive surface sites, such as with Ni(OH)2 and Cu(OH)2 cluster depositions on TiO2.

As demonstrated in the in situ test, the presence of methanol plays a crucial supporting role in the overall photocatalytic reaction. While hydrogen is reduced, methanol is oxidized stepwise to formaldehyde and formic acid by holes in the VB of TiO2, eventually forming CO2.40,41 This occurs in preference to the oxidation of water, which would limit overall hydrogen production because of the back reaction between hydrogen and oxygen.

**CONCLUSIONS**

This paper describes a facile method of modifying commercial P25-TiO2 to improve its activity for photocatalytic hydrogen production. The photodeposition of Co, Ni, or Cu onto the surface of TiO2 led to visible optical absorption properties. Compositional analysis showed that low metal contents (~0.04–1 at. % of bulk material, highest for copper) are photodeposited onto the TiO2 surface, but this surface modification is sufficient to show beneficial effects on the utilization of titania CB electrons for photocatalytic hydrogen reduction using methanol as a sacrificial oxidant. The rate of UV photocatalytic hydrogen production was improved to as high as 8500 μmol h−1 g−1 (7% QY) for Cu(1%):TiO2 versus 500 μmol h−1 g−1 (0.4% QY) for P25-TiO2. Direct atmospheric-pressure headspace gas sampling by portable mass spectrometry was demonstrated as a useful portable tool for real-time monitoring of reactor headspaces and quantification of hydrogen gas production.

**EXPERIMENTAL SECTION**

**Materials.** TiO2 (Degussa P25, ~50 nm size and 45 m2/g), CoCl2·6H2O (Aldrich, reagent grade), NiCl2·6H2O (Aldrich, ReagentPlus), CuCl2·2H2O (Aldrich, 99+%), H2PtCl6·6H2O (99.9%, Strem), methanol (ACS certified, Fisher), deionized water (18 MΩ).

**Single-Metal-Modified TiO2.** In a 50 mL Erlenmeyer flask, 4 mg (0.017 mmol) of MCl2·6H2O (M = Co or Ni) or 3 mg (0.017 mmol) of CuCl2·2H2O was dissolved in 30 mL of 50 vol % aqueous methanol. TiO2 (100 mg, 1.25 mmol) was added to the solution. The flask was covered with a septum, and the solution was degassed with argon while stirring. The flask was exposed to a water-jacketed UV light (450 W Hg lamp, Ace-Hanovia) for 90 min under an argon blanket. Solids were isolated by centrifugation (3000 rpm), rinsed once with methanol, centrifuged again, and then dried in air. The product from nominal 1 wt % metal relative to TiO2 was denoted as M(1%):TiO2. The photodeposition reaction was also run with twice the initial amount of MCl2, and the products are denoted as M(2%):TiO2.

**Mixed-Metal-Modified TiO2.** In a 50 mL Erlenmeyer flask, a combination using two of the metals (6 mg (0.035 mmol) of CuCl2·2H2O, 8 mg (0.034 mmol) of CoCl2·6H2O, or 8 mg (0.034 mmol) of NiCl2·6H2O) was dissolved in 30 mL of 50 vol % aqueous methanol. TiO2 (200 mg, 2.5 mmol) was added to the solution. The flask was exposed to UV light for 90 min under an argon blanket. Solids were isolated by centrifugation (3000 rpm), rinsed once with methanol, centrifuged again, and then dried in air. These mixed-metal products each had nominal 1 wt % metal relative to TiO2 and are denoted M(1%)/M(1%):TiO2.

**Platinum-Modified TiO2.** In a 50 mL Erlenmeyer flask, 2.4 mg (0.006 mmol) of H2PtCl6 was dissolved in 30 mL of 50 vol % aqueous methanol. TiO2 (100 mg, 1.25 mmol) was added to the solution. The flask was covered with a septum, and the solution was degassed with argon while stirring. The flask was exposed to UV light (450 W Hg) for 90 min under an argon blanket. Solids were isolated by centrifugation (3000 rpm), rinsed with methanol, and dried in air. This platinum loading is nominal 1 wt % Pt relative to TiO2 and is denoted Pt(1%):TiO2.

**Product Characterization.** A Bruker D8 DaVinci powder X-ray diffractometer was used for analysis of powders uniformly placed on glass slides (Cu Kα, 0.0504/n step). XPS was performed on a Kratos Axis Ultra XPS (Al Kα) with samples mounted on carbon tape. XPS peak analysis was performed using CasaXPS software (www.casaxps.com). ICP–OES (PerkinElmer Optima DV 7000) was used for bulk elemental analysis. Samples were dissolved in a heated 5:1 mixture of concentrated H2SO4:HNO3 and diluted with 5% HNO3. Calibration standards were prepared from 1000 ppm commercial ICP standards for Ti, Co, Cu (Alfa Aesar), and Ni (Fluka). UV–vis DRS spectra were collected on a Cary 5000 Series spectrophotometer (300–800 nm, 10 nm/s). Raw reflectance data were converted to Kubelka–Munk units [F(R)], and band gaps were calculated using [F(R) × E]1/2 extrapolations of linear regions of the curve. SEM images were collected on a Hitachi S-4800 FE-SEM with an accelerating voltage of 1.3 kV. Samples were mounted on aluminum stubs using carbon tape and were not coated prior to analysis. BET
surface area measurements were collected on a Quantachrome NOVA 1200 using approximately 50 mg of solid sample.

**Photocatalytic Hydrogen Evolution.** Reactions were carried out in a 50 mL Schlenk flask containing 10 mg (0.125 mmol) of the titania catalyst suspended in 10 mL of 50 vol % aqueous methanol solution. The reactor was purged with argon and connected to the capillary of a Stanford Research Systems quadrupole mass spectrometer 300 series residual gas analyzer via the flask side arm. Masses corresponding to N₂ (28), Ar (40), H₂ (2), O₂ (32), and H₂O (18) were monitored as a function of time. The flask remained under a constant blanket of argon for the entire experiment, supplied from a Schlenk line with an oil bubbler. Following a period of 30 min for instrument and background stabilization, the flask was illuminated with a UV lamp in 60 min cycles with an approximate photon flux of 4.0 × 10¹⁷ photon s⁻¹. Details on photon flux calculations and QY estimations are shown in the Supporting Information. Between each cycle, the reactor was briefly opened and its headspace was flushed with argon. Pressure signals were converted to molar amounts of evolved H₂ based on a calibration curve created using known-concentration H₂/Ar mixtures (Figure S5). The H₂/Ar ratio was used to minimize errors from variation in absolute hydrogen pressure signal values from reaction to reaction. Micromoles of H₂ present were calculated for actual headspace volume in the reactor.

**In Situ Metal Photodeposition and Hydrogen Evolution.** This experiment used the same reactor/analysis setup as described above. Here, 10 mg (0.125 mmol) of Degussa P25-TiO₂ was suspended in 10 mL of 50 vol % of aqueous methanol containing 4 mg (0.017 mmol) of MCl₂·6H₂O (M = Co, Ni) or 3 mg (0.017 mmol) of CuCl₂·2H₂O. The reactor was purged with argon and connected to the residual gas analyzer as described above. Following a period of 30 min for instrument and background stabilization, the flask was illuminated with a UV lamp in 60 min cycles. The reactor headspace was flushed with argon between each cycle. To verify the critical nature of the methanol sacrificial oxidant in metal deposition and hydrogen evolution, 10 mg (0.125 mmol) of Degussa P25-TiO₂ was suspended in a 10 mL solution of 18 MΩ H₂O with 3 mg (0.017 mmol) of CuCl₂·2H₂O and was UV-irradiated for two cycles and then 2 mL of methanol was added for the third UV cycle onward.

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