Gold(I)-Complex–Titania Hybrid Photocatalyst for Hydrogen Production

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The integration of TiO$_2$ with a Au complex containing a thiocoumarin moiety resulted in a very efficient photocatalyst for the generation of H$_2$. The molecular structure of the complex was preserved under the photoreaction owing to the strong Au–S bond. The Au complex played a determinant role in the photogeneration of H$_2$ by accepting the photoinduced electrons originated in TiO$_2$ upon light exposure. This is the first example of a Au complex semiconductor hybrid photocatalyst. The rate of H$_2$ generation under dynamic conditions from water/ethanol is approximately one order of magnitude superior on a metal basis to that obtained over conventional TiO$_2$ decorated with Au metal nanoparticles.

Hydrogen is considered as a potential alternative to carbon fossil fuels but only with consideration of an appropriate source.[1] Prominent among the technological challenges to be reached is the development of photochemical mechanisms that lead to the efficient production of H$_2$ from water and sunlight. Once produced, H$_2$ may be further converted into CH$_4$ or fixed into liquid fuels through the hydrogenation of CO$_2$. The most used photocatalytic material by far is TiO$_2$, which exhibits outstanding chemical stability, high photoactivity, availability, and affordability. Irradiation of TiO$_2$ with photons of energy higher than its band gap results in the photogeneration of electrons in the conduction band and holes in the valence band that can react with adsorbed chemical species. In particular, protons can be reduced by photogenerated electrons and originate H$_2$. However, rapid recombination of electron–hole pairs and the inability to utilize the visible range of the solar spectrum still need to be overcome for efficient application. There has been an intense research front in recent years aimed at modifying TiO$_2$ with a variety of dopants, noble-metal nanoparticles (mostly Pt, Au, Pd, and Ag), optical antennas, and carbon nanomaterials to accomplish effective photoinduced electron transfer to enhance the photoproduction of H$_2$.[2-3] Crystal-facet engineering of TiO$_2$ has also been attempted.[4] Another strategy consists in integrating TiO$_2$ with transition-metal complexes. To date, the metal complexes that have been used have been limited to Fe, Co, Ni, and Pt.[5-7] A remarkable turnover number (TON) $>10^5$ for photocatalytic hydrogen evolution by using a hybrid system comprising CdSe quantum dots and Ni or Co complexes in aqueous solutions was reported, and several bio-inspired molecular diiron photocatalysts supported on CdSe and CdTe quantum dots were reported to achieve TONs $>10^4$ for H$_2$ evolution.[6] Herein, we report for the first time the use of a Au-complex–TiO$_2$ hybrid system for the photogeneration of H$_2$. Hybrid systems formed by using semiconductors in conjunction with metal complexes are fully reproducible and represent an attractive way to maximize the cost-effective use of expensive metals.

Three photocatalysts with a Au loading of 0.5 wt% were prepared (Scheme 1). [AuCl(DAPTA)] (DAPTA = 3,7-diacetyl-1,3,7-triaca-5-phosphabicyclo[3.3.1]nonane; 1) was synthesized as reported elsewhere[8] and was impregnated over commercial titania (Degussa P90) from an ethanol solution. The resulting solid, [AuCl(DAPTA)]/TiO$_2$, was dried at 60 °C. The organometallic [Au(coumarin)(DAPTA)] (2) complex was prepared by the reaction of complex 1 with a deprotonated thiocoumarin, 4-mercaptomethylchromen-2-one, in a K$_2$CO$_3$ dichloromethane solution (see Scheme 1 a and the Supporting Information). The corresponding $^1$H NMR spectrum shows the disappearance of the terminal thiol proton (observed as a triplet in the free ligand owing to coupling with the CH$_2$ moiety) upon coordination with the Au atom, which is a clear indication of the successful formation of the complex. Moreover, the methylene proton (S-CH$_2$) becomes a singlet instead of a doublet owing to the lack of coupling with the terminal thiol proton (see Figures S1 and S2 in the Supporting Information). Signals for the phosphine protons[9,10] of DAPTA are observed together with the coumarin signals.[11] The $^{31}$P($^1$H) NMR spectrum obtained in CDCl$_3$ solution shows one signal at $\delta = -29.8$ ppm, and this signal is shifted...
downfield by approximately 45 ppm relative to the signal of the free phosphine (Figure S3). The ESI mass spectrum (Figure S4) shows the molecular peak of complex 2, and the IR spectrum (Figure S5) displays the typical C=O bands from both the phosphine and the coumarin as the main vibration bands. The absorption spectra of both the coumarin ligand and complex 2 display a band centered at approximately \( \lambda = 325 \text{ nm} \), and this band can be attributed to the \( \pi-\pi^* \) transition of the coumarin moiety (Figure S6). Excitation of the samples at \( \lambda = 325 \text{ nm} \) rendered the corresponding emission band at approximately \( \lambda = 400 \text{ nm} \) (Figures S7 and S8 and Table S1). As observed in other gold(I)-phosphine–coumarin complexes, the fluorescence emission was lower than the emission of the free ligand as a result of the heavy atom effect. Complex 2 was dissolved in EtOH and was impregnated over TiO\(_2\), and the resulting solid, [Au(coumarin)(DAPTA)]/TiO\(_2\), was dried at 60 °C. The IR spectrum recorded for this photocatalyst is shown in Figure 1.

Figure 1a shows the IR bands in the carbonyl region for [Au(coumarin)(DAPTA)], the coumarin ligand, and [Au(coumarin)(DAPTA)] together with the sum of the spectra of [AuCl(DAPTA)] and the coumarin. Superimposition of the IR spectra of [Au(coumarin)(DAPTA)] and the [Au(coumarin)(DAPTA)]/TiO\(_2\) photocatalyst.

Finally, complex 2 was also impregnated over TiO\(_2\) previously loaded with preformed Au metal nanoparticles (3 wt % Au) to obtain the [Au(coumarin)(DAPTA)]-Au/TiO\(_2\) photocatalyst with aurophilic interactions between complex 2 and the Au metal nanoparticles in Au/TiO\(_2\). The three photocatalysts were tested in the photoproduction of H\(_2\) at room temperature under dynamic conditions from a gaseous water/ethanol mixture by using argon as the carrier gas and UV radiation \( (\lambda = 365 \pm 5) \text{ nm} \) light-emitting diodes, 81.7 mW cm\(^{-2}\) measured directly on the sample. Ethanol was chosen as sacrificial agent because of its renewable character and its widespread use. Au/TiO\(_2\) (3 wt % Au), bare TiO\(_2\), and coumarin/TiO\(_2\) were also tested as control experiments. The photocatalysts (4 mg) were deposited on cellulose membranes, which were sealed in the photoreactor and exposed to the reactants (water/ethanol = 9:1 molar; gas hourly
space velocity, GHSV \( \approx 80,000 \text{ h}^{-1} \)). The outlet of the photo-reactor was monitored continuously by GC. The evolution of the hydrogen yield for each photocatalyst is shown in Figure 2.

The anchoring of molecular complexes 1 and 2 to the TiO\(_2\) semiconductor strongly improved the efficiency of photocatalytic H\(_2\) evolution relative to that of the bare TiO\(_2\) support. Noticeably, no H\(_2\) was photogenerated with the complexes in the absence of TiO\(_2\) under otherwise identical conditions. These results indicate that TiO\(_2\) serves not only as a carrier of the complexes but also as an electron-transfer relay in the UV-light-driven H\(_2\) generation process. However, the dynamics of H\(_2\) photoproduction on [AuCl(DAPTA)]/TiO\(_2\) and [Au(coumarin)-DAPTA]/TiO\(_2\) were completely different. Over [Au(coumarin)-DAPTA]/TiO\(_2\), the photogeneration of H\(_2\) was immediate upon light exposure and reached 14.6 mmol\(_{\text{H}_2}\) g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\) (turnover frequency, TOF \(= 0.16 \text{ s}^{-1}\) on Au atom basis) after approximately 8 min and then decreased smoothly and reached a constant value of approximately 10.7 mmol\(_{\text{H}_2}\) g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\) at steady state. Similar behavior was observed for TiO\(_2\) loaded with preformed Au metal nanoparticles, Au/TiO\(_2\) (see Figure 2), which attained a H\(_2\) photoproduction rate of 12.4 mmol\(_{\text{H}_2}\) g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\) after approximately 8 min, and then it also decreased smoothly until steady state. In contrast, over [AuCl(DAPTA)]/TiO\(_2\) a strong induction period exceeding 1 h was necessary to reach a constant photogeneration rate of H\(_2\), which was maintained at approximately 15.1 mmol\(_{\text{H}_2}\) g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\). A detailed study by scanning transmission electron microscopy (STEM) (Figure 3) and X-ray photoelectron spectroscopy (XPS) (Figures S10 and S11) was performed over both photocatalysts as prepared and after the photocatalytic test. The C/Ti atomic ratios found before and after reaction by XPS were very similar (0.8–1.0), which confirmed the remaining organic species on the TiO\(_2\) surface (Figure S10). STEM images recorded over [AuCl(DAPTA)]/TiO\(_2\) after photoreaction showed the existence of Au metal nanoparticles, approximately 0.8–1.5 nm in size, dispersed over TiO\(_2\) (Figure 3 b), and the corresponding X-ray photoelectron spectrum showed Au 4f photoelectrons at binding energies of 83.9 and 87.4 eV, which is characteristic of metallic Au (Figure S11). Importantly, no metallic Au nanoparticles were seen in the [Au(coumarin)-DAPTA]/TiO\(_2\) catalyst after photoreaction, nor were they seen in the fresh photocatalyst. Therefore, progressive photodeposition of Au nanoparticles occurred upon exposing [AuCl(DAPTA)]/TiO\(_2\) to UV light, and this was responsible for the observed long induction period. The electrons photogenerated in TiO\(_2\) by light irradiation reduced complex 1 to Au metal owing to the labile character of the Au–Cl bond; photodecomposition of Au\(_{\text{14, 15}}\) salts is a well-established method to prepare Au/TiO\(_2\) catalysts with ultradisperse Au metal nanoparticles.[14, 15] Thus, photoproduction of H\(_2\) by [Au(coumarin)-(DAPTA)]/TiO\(_2\), for which photodecomposition of the Au species was not observed, should be highlighted and represents the first example of a Au-complex–semiconductor hybrid system for the photogeneration of H\(_2\). The presence of a strongly bonded ligand to Au, such as the thiocoumarin employed in our work, is an essential requirement to preserve the molecular nature of the Au' complex. Importantly, the initial rate of H\(_2\) photogeneration on a Au basis over [Au(coumarin)(DAPTA)]/TiO\(_2\), 2.9 mol\(_{\text{H}_2}\) g\(_{\text{Au}}\)\(^{-1}\) h\(^{-1}\), is much higher than that obtained over the Au/TiO\(_2\) photocatalyst under the same operational conditions, 0.41 mol\(_{\text{H}_2}\) g\(_{\text{Au}}\)\(^{-1}\) h\(^{-1}\), which represents a remarkable increase in photoactivity for the Au'-complex–TiO\(_2\) hybrid system.

Although a detailed mechanistic study of the photogeneration of H\(_2\) is beyond the scope of our communication, it is likely related to the ability of complex 2, strongly anchored to the TiO\(_2\) surface, to accept the photoinduced electrons originating in the semiconductor upon UV-light exposure, and these electrons are later transferred to protons to form molecular H\(_2\) (Scheme 2). A sample prepared by impregnating the thiocoumarin ligand directly onto TiO\(_2\) was almost inactive in the photoproduction of H\(_2\) (Figure 2), and this rules out the possibility that the coumarin accepted the photoinduced electrons and also highlights the role of the Au' species. The photo-

**Figure 2.** Photoproduction rates of H\(_2\),

**Figure 3.** STEM images of the [AuCl(DAPTA)]/TiO\(_2\) photocatalyst a) as prepared and b) after photoreaction, and STEM images of the [Au(coumarin)-(DAPTA)]/TiO\(_2\) photocatalyst c) as prepared and d) after photoreaction.
tocatalyst containing aurophilic interactions, [Au(coumarin)(DAPTA)]-Au/TiO\textsubscript{2}, in which complex 2 is preferably in contact with the preformed Au metal nanoparticles rather than TiO\textsubscript{2}, yielded lower H\textsubscript{2} photoproduction rates than the [Au(coumarin)(DAPTA)]/TiO\textsubscript{2} and Au/TiO\textsubscript{2} photocatalysts (Figure 2). Thus, both the presence of Au\textsuperscript{I} species and direct electron coupling between complex 2 and the semiconductor play determinant roles in the photogeneration of H\textsubscript{2} over [Au(coumarin)(DAPTA)]/TiO\textsubscript{2}.

Herein, we showed that Au\textsuperscript{I} species were intrinsically active for the photogeneration of H\textsubscript{2} if hybridized with TiO\textsubscript{2}. The selection of the thiocoumarin ligand was crucial; a strong bond between Au\textsuperscript{I} and the ligand was required to avoid photodecomposition into metallic Au an nanoparticles upon UV exposure, and in addition, the ligand needed to be anchored directly and covalently to the TiO\textsubscript{2} surface for effective electron transfer from the conduction band of TiO\textsubscript{2} to the complex. Future work is in progress to tune the absorption characteristics of the thiocoumarin ligand to use the visible spectrum for efficient production of H\textsubscript{2} from direct sunlight.

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**Conflict of interest**

The authors declare no conflict of interest.

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