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Au(I) complex-titania hybrid photocatalyst for hydrogen production

Elisabet Aguiló,[b] Lluís Soler,[a] Albert Casanovas,[a] Artur J. Moro,[c] João Carlos Lima,[c] Laura Rodríguez,*[b] and Jordi Llorca*[a]

Abstract: Integration of TiO_2 and an Au(I) complex containing a thio-coumarin moiety results in a very efficient photocatalyst for the generation of H_2. The molecular structure of the complex is preserved under photoreaction due to the strong Au(I)-S bond. The Au(I) complex plays 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 an Au(I) complex-semiconductor hybrid photocatalyst. The rate of H_2 generation under dynamic conditions from water-ethanol is about 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 used directly to power fuel cells or may be further converted into CH_4 or fixed into liquid fuels via hydrogenation of CO_2. The most used photocatalytic material is by far TiO_2, which exhibits an outstanding chemical stability, high photoactivity, availability and affordability. Irradiation of TiO_2 with photons of energy higher than its band gap produces 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 the photogenerated electrons and originate H_2. However, rapid recombination of electron-hole pairs and 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 or carbon nanomaterials to accomplish effective photoinduced electron transfer to enhance H_2

photoproduction.[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 used are limited to Fe, Co, Ni and Pt.[5–7] A remarkable TON>10^5 for the photocatalytic hydrogen evolution using a hybrid system comprised of CdSe quantum dots and Ni or Co complexes in aqueous solutions has been reported, and several bioinspired molecular diiron photocatalysts supported on CdSe and CdTe quantum dots have achieved TON>10^4 of H_2 evolution.[6] Here we report for the first time the use of an Au(I) 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.
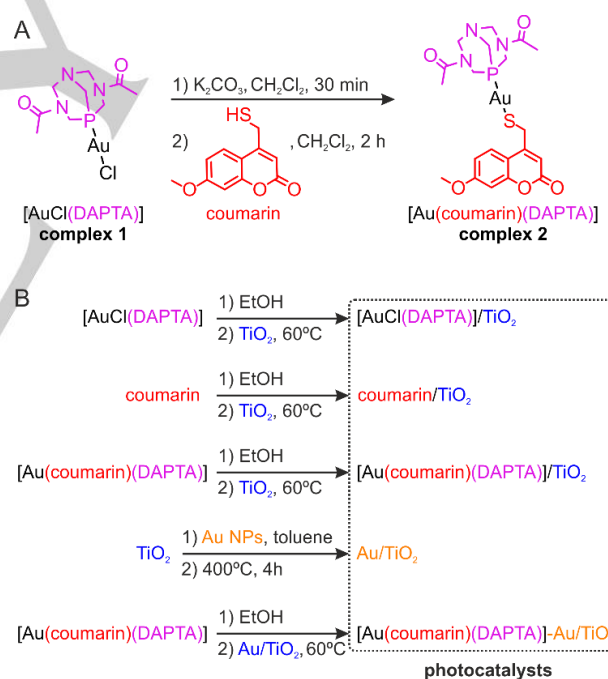
Scheme 1. (A) Synthesis of [Au(coumarin)(DAPTA)] complex 2. (B) Preparation of photocatalysts.

Three photocatalysts with an Au(I) loading of 0.5 wt.% were prepared (Scheme 1). [AuCl(DAPTA)] (DAPTA=3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) complex **1** was synthesized as reported elsewhere[8] and impregnated over commercial titania (Degussa P90) from an ethanol solution. The resulting solid, **[AuCl(DAPTA)]/TiO₂**, was dried at 60°C. [Au(coumarin)(DAPTA)] organometallic complex **2** was prepared by reaction between complex **1** and deprotonated thio-coumarin,

[a]   Dr. L. Soler, Dr. A. Casanovas, Prof. J. Llorca
        Institut de Tècniques Energètiques and Barcelona Research Center
        for Multiscale Science and Engineering
        Universitat Politècnica de Catalunya
        EEBE, Eduard Maristany 10-14, 08019 Barcelona, Spain
        E-mail: jordi.llorca@upc.edu
[b]   E. Aguiló, Prof. L. Rodríguez
        Departament de Química Inorgànica i Orgànica, Secció de Química
        Inorgànica
        Universitat de Barcelona
        Martí i Franquès 1-11, E-08028 Barcelona, Spain
        E-mail: laura.rodriguez@qi.ub.es
[c]   Dr. A. J. Moro, Prof. J. C. Lima
        LAQV-REQUIMTE, Departamento de Química, CQFB
        Universidade Nova de Lisboa
        Monte de Caparica, Portugal

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        the document.

4-mercaptomethylchromen-2-one, in a K_2CO_3 dichloromethane solution (see Scheme 1A and SI). The corresponding 1H-NMR spectrum showed the disappearance of the terminal thiol proton (observed as a triplet in the free ligand, due to the coupling with the CH_2) upon coordination with the Au(I) atom as a clear indication of the successful formation of the complex. Moreover, the methylene proton (S-CH2) became a singlet instead of a doublet due to the lack of coupling with the terminal thiol proton (see Figure S1 and S2). DAPTA phosphine protons[9,10] were observed together with the coumarin signals.[11] $^{31}P\{1H\}$ spectrum carried out in $CDCl_3$ shows one signal at -29.8 ppm, ca. 45 ppm downfield shifted in comparison with the free phosphine (Figure S3). ESI mass spectrum (Figure S4) showed the molecular peak of complex **2** and IR spectrum (Figure S5) displayed the typical C=O bands both from the phosphine and the coumarin as the main vibration bands. Absorption spectra of both coumarin ligand and complex **2** displayed a band centred at ca. 325 nm due to the π-π* transition of the coumarin moiety (Figure S6). Excitation of the samples at 325 nm rendered the corresponding emission band at ca. 400 nm (Figure S7 and S8 and Table S1). As observed in other gold(I) phosphine coumarin complexes, the fluorescence emission was lower with respect to the emission of the free ligand due to heavy atom effect.[11] Complex **2** was dissolved in EtOH and impregnated over TiO_2 and the resulting solid, **[Au(coumarin)(DAPTA)]/TiO₂**, was dried at 60°C. The IR spectra recorded for the photocatalyst is shown in Figure 1.
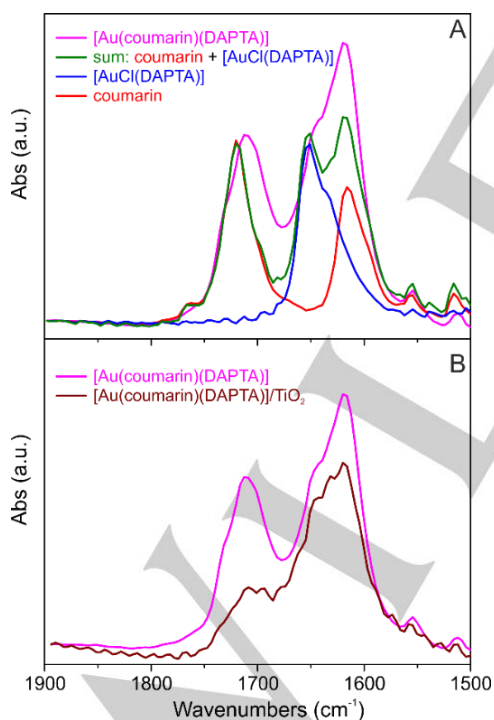
Figure 1A shows the IR peaks in the carbonyl region for [AuCl(DAPTA)], coumarin ligand and [Au(coumarin)(DAPTA)] (complex **2**). Despite the small shifts in frequency responsible for the differences observed between the experimental spectrum of [Au(coumarin)(DAPTA)] and the sum of [AuCl(DAPTA)] and coumarin spectra, it is safe to claim that the higher energy peak is due to the coumarin moiety while the lower energy peak has contributions of both coumarin and DAPTA carbonyls. Figure 1B superimposes the spectra of [Au(coumarin)(DAPTA)] and **[Au(coumarin)(DAPTA)]/TiO₂** where a significant decrease in intensity of the higher energy peak with respect to the lower energy peak is observed, *i.e.*, the binding affects more significantly the coumarin carbonyl. Therefore, the anchoring of the photocatalyst on TiO_2 is likely occurring through the coumarin moiety, specifically through the coumarin carbonyl group. This is corroborated through the impact of the binding to TiO_2 in the UV-Vis absorption spectrum of the photocatalyst (Figure S9), where a new band at ca. 290 nm is an indication of the decrease in conjugation of the coumarin moiety upon coordination of the carbonyl.

Finally, complex **2** was also impregnated over TiO_2 previously loaded with preformed Au metal nanoparticles (3 wt.% Au) of ca. 4 nm in diameter[12] to obtain photocatalyst **[Au(coumarin)(DAPTA)]-Au/TiO₂** with aurophilic interactions between complex **2** and the Au metal nanoparticles in Au/TiO_2.[13]

The three photocatalysts were tested in the photoproduction of H_2 at room temperature under dynamic conditions from a gaseous water-ethanol mixture using Ar as carrier gas and UV radiation (365 ± 5 nm LEDs, 81.7 mW·cm⁻² measured directly on the sample). Ethanol was chosen as sacrificial agent due to its renewable character and 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, $GHSV\sim80000\ h^{-1}$). The outlet of the photoreactor was monitored continuously by GC. The evolution of the hydrogen yield for each photocatalyst is shown in Figure 2.
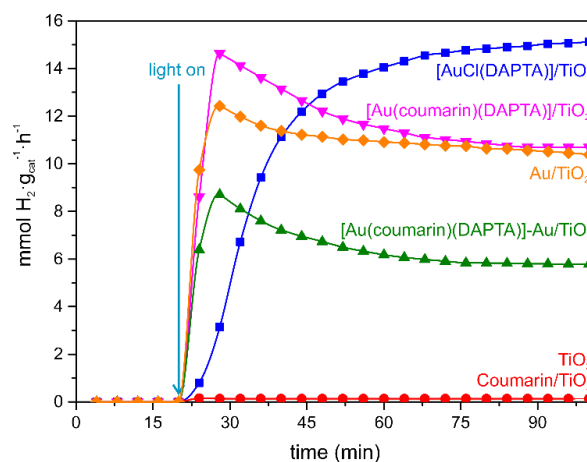

Figure 1. (A) Superimposition of the IR peaks in the carbonyl region for [AuCl(DAPTA)], coumarin ligand and [Au(coumarin)(DAPTA)], together with sum of [AuCl(DAPTA)] and coumarin spectra. (B) superimposition of the IR spectra of [Au(coumarin)(DAPTA)] and photocatalyst [Au(coumarin)(DAPTA)]/TiO₂.

**Figure 2.** Photoproduction rates of H_2.

The anchoring of the molecular complexes **1** and **2** to the TiO_2 semiconductor strongly improved the efficiency of photocatalytic H_2 evolution with respect to the bare TiO_2 support. Noticeably, no H_2 was photogenerated with the complexes in the absence of TiO_2 under otherwise identical conditions. The results indicate that TiO_2 served 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 the H_2 photoproduction in **[AuCl(DAPTA)]/TiO₂** and **[Au(coumarin)(DAPTA)]/TiO₂** was completely different. Over **[Au(coumarin)(DAPTA)]/TiO₂** the photogeneration of H_2 was immediate upon light exposure and reached 14.6 mmol $H_2 \cdot g_{cat}^{-1} \cdot h^{-1}$ (TOF=0.16 s^{-1} on Au atom basis) after ca. 8 min, and then decreased smoothly reaching a constant value of about 10.7 mmol $H_2 \cdot g_{cat}^{-1} \cdot h^{-1}$ at steady state. A similar behaviour 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 $H_2 \cdot g_{cat}^{-1} \cdot h^{-1}$ after ca. 8 min, and then it also decreased smoothly until steady state. In contrast, over **[AuCl(DAPTA)]/TiO₂** a strong induction period exceeding 1 h was necessary to reach a constant photogeneration rate of H_2, which was maintained at about 15.1 mmol $H_2 \cdot g_{cat}^{-1} \cdot h^{-1}$. A detailed study by STEM (Figure 3) and XPS (Figures S10 and S11) was carried out 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)]/TiO₂** after photoreaction showed the existence of Au metal nanoparticles of about 0.8-1.5 nm in size dispersed over TiO_2 (Figure 3B) and the corresponding XP spectrum showed Au 4f photoelectrons at 83.9 and 87.4 eV, characteristic of metallic Au (Figure S11). Importantly, no metallic Au nanoparticles were seen in the **[Au(coumarin)(DAPTA)]/TiO₂** after photoreaction, nor were they seen in the fresh photocatalysts. Therefore, progressive photodeposition of Au nanoparticles occurred when **[AuCl(DAPTA)]/TiO₂** was exposed to UV-light, which was responsible for the long induction period observed. The electrons photogenerated in TiO_2 by light irradiation reduced complex 1 to Au metal due to the labile character of the Au-Cl bond; in fact, photodeposition from Au(I,III) salts is a well-established method for preparing Au/TiO_2 catalysts with ultradisperse Au metal nanoparticles.[14,15] Thus, photoproduction of H_2 by **[Au(coumarin)(DAPTA)]/TiO₂**, where photodecomposition of Au(I) species was not observed, merits to be highlighted and represents the first example of an Au complex-semiconductor hybrid system for the photogeneration of H_2. The presence of a strongly bonded ligand to Au(I), like the thio-coumarin employed in our work, is an essential requirement for preserving the molecular nature of the Au(I) complex. Importantly, the H_2 photogeneration initial rate on an Au basis over **[Au(coumarin)(DAPTA)]/TiO₂**, 2.9 mol $H_2 \cdot g_{Au}^{-1} \cdot h^{-1}$, is much higher than that obtained over the Au/TiO_2 photocatalyst under the same operational conditions, 0.41 mol $H_2 \cdot g_{Au}^{-1} \cdot h^{-1}$, which represents a remarkable increase in photoactivity for the Au(I) complex-TiO_2 hybrid system.
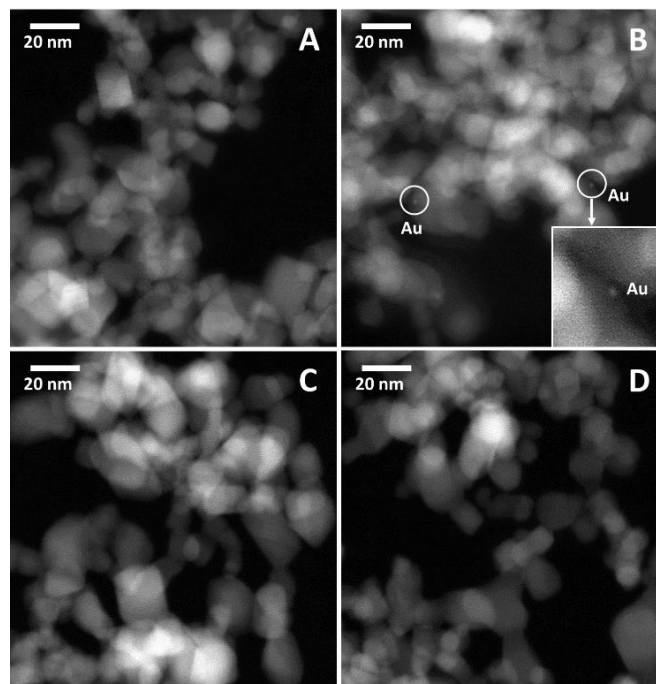
Figure 3. STEM images of photocatalysts **[AuCl(DAPTA)]/TiO₂** as prepared (A) and after photoreaction (B) and photocatalyst **[Au(coumarin)(DAPTA)]/TiO₂** as prepared (C) and after photo-reaction (D).

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 originated in the semiconductor upon UV-light exposure, which are later transferred to protons to form molecular H_2 (Scheme 2). A sample prepared by impregnating the thio-coumarin ligand directly onto TiO_2 was almost inactive in the photoproduction of H_2 (Figure 2) ruling out the possibility that coumarin accepted the photoinduced electrons and highlighting the role of Au(I) species. The photocatalyst containing aurophilic interactions, **[Au(coumarin)(DAPTA)]-Au/TiO₂**, where complex **2** is preferably in contact with preformed Au metal nanoparticles rather than TiO_2, yielded lower H_2 photoproduction rates than **[Au(coumarin)(DAPTA)]/TiO₂** and Au/TiO_2 photocatalysts (Figure 2). Thus, both the presence of Au(I) species and the direct electron coupling between complex **2** and the semiconductor play a determinant role in the photogeneration of H_2 in **[Au(coumarin)(DAPTA)]/TiO₂**.
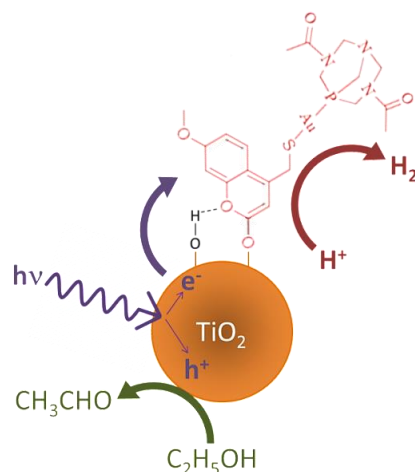
Scheme 2. Schematic diagram of the H_2 generation photocatalyzed by the **[Au(coumarin)(DAPTA)]/TiO₂** hybrid system.

Here we have shown that Au(I) species is intrinsically active for the photogeneration of H_2 when hybridized with TiO_2. The selection of the thio-coumarin ligand is crucial; a strong bond between Au(I) and the ligand is required to avoid photodecomposition into metallic Au nanoparticles upon UV exposure and, in addition, the ligand should anchor directly and covalently to the TiO_2 surface for an effective electron transfer from the conduction band of TiO_2 to the complex. Future work is in progress to tune the absorption characteristics of the thio-coumarin ligand to use the visible spectrum for an efficient production of H_2 from direct sunlight.

Experimental Section

Details of experimental procedures, syntheses of compounds, additional figures and spectral data are given in the Supporting Information.

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COMMUNICATION

Integration of TiO$_2$ and an Au(I) complex containing a thio-coumarin moiety is intrinsically active for the photogeneration of H$_2$

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