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Scavenging of photogenerated holes in TiO₂-based catalysts uniquely controls pollutant degradation and hydrogen formation under UVA or visible irradiation

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The use of heterogeneous photocatalysts to degrade hard-to-remove pharmaceuticals from polluted water offers a promising approach for efficient water treatment. These contaminants, commonly found in rivers and lakes, can be traced back to wastewater effluents containing harmful chemical species, including endocrine disruptors. Our research provides valuable insights into the functioning of known TiO₂-based photocatalysts as well as novel materials designed to expand the catalyst's absorption range into the visible region. This includes TiO₂, Pd@TiO₂, Cu@TiO₂, and Au@TiO₂. Among the emerging photocatalysts, black TiO₂ (b-TiO₂) was selected as the starting point, and subsequently decorated with metal nanoparticles to produce Pd@b-TiO₂, Cu@b-TiO₂, and Au@b-TiO₂. Mechanistic findings reveal that hole trapping consistently emerges as the yield-determining step, with electron scavenging following closely behind. Consequently, oxygen or proton trapping of electrons has no significant impact on the overall efficiency of removal of pollutants. Additionally, we present a methodology for screening the capability of newly designed materials to photodegrade pollutants by measuring the output of H₂. This eliminates the need for series of experimental trials specific to each target pollutant; thereby, streamlining conventional processes upheld in this field. Each of these materials was first tested for their hydrogen generating ability under UV and visible light using methanol and formic acid as sacrificial electron donors, as well as estradiol, ibuprofen, and acetaminophen. Following this, ibuprofen was selected for extended studies where it would be photooxidized and/or release H₂ gas as a by-product that is readily detectable using gas chromatography.

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Introduction

The current research landscape is dominated by an intense focus on synthesizing novel heterogeneous catalysts. These catalysts have applications in both the synthesis of organic compounds, particularly pharmaceuticals, and the degradation of organic pollutants, including pharmaceuticals.^{1,2} In the context of environmental remediation, photocatalysts can be utilized through oxidative pathways that lead to mineralization, or under anaerobic conditions that simultaneously degrade pollutants and generate hydrogen.³ In this work, we have developed TiO₂-based photocatalysts that possess the unique ability to perform both functions, utilizing either ultraviolet or visible light.

In recent decades, there has been a growing interest in removing various types of environmental pollutants from

natural bodies of water, or to produce drinking water. Among the chemical species that contaminate waterways, pharmaceuticals have garnered particular attention due to their challenging removal. These pollutants, particularly endocrine disruptors, interfere with the development of species exposed to these hazardous compounds.⁴ Titanium dioxide (TiO₂), a semiconductor that has been extensively studied and modified for degrading contaminants using light-driven heterogeneous catalysis, has a limited absorption range in the ultraviolet region. This is because TiO₂ has a wide band gap, approximately 3.1 eV for anatase. To address this limitation, metal doping and decorating are common methods to extend the photoactivity of TiO₂-based catalysts into the visible region.^{5–7} Additionally, modifying TiO₂ through reductive treatment has emerged as a useful technique to broaden the absorption range of the metal oxide, usually attributed Ti³⁺ and oxygen vacancies as active sites which alter the bulk properties of the catalyst.^{8–10} The reactivity of black-TiO₂ remains a subject of active research and conflicting interpretations.¹¹

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In this work we have decorated TiO₂ with Pd, Cu and Au, as all three have been shown to improve its photocatalytic activity,^{12–14} and their performance in the presence of sacrificial electron donors (SED) usually exceeds by about two orders of magnitude that in the absence of SED (true water splitting).¹⁵

Beyond metal decoration, we have also examined novel decorated black TiO₂ catalysts; these blackened photocatalysts possess reduced TiO₂ sites with a reduced bandgap.¹⁶

The ability of photocatalysts to degrade organic matter has frequently been tested using organic dyes, for example methylene blue.^{17–19} Our choice in recent contributions has usually been crocin, as many of our catalysts contain glass fibers and methylene blue has a tendency to bind to glassy materials.^{9,20} The frequent preference for surrogate materials, rather than actual contaminants, reflects that each contaminant requires the time consuming development and validation of analytical methods and materials for each substrate.

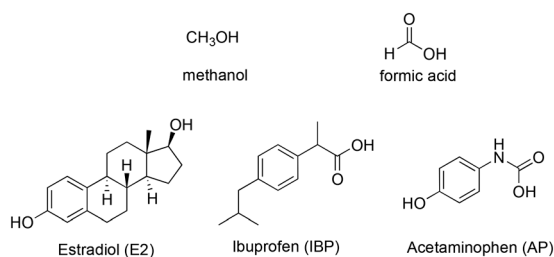
We propose a rapid screening method for potential catalysts and their spectral responses by assessing their ability to generate hydrogen from various contaminants. This approach has been suggested for hydrogen generation from contaminants,³ but has never been evaluated or developed as a tool to test environmentally useful catalysts. While H₂ generation provides no information on the detailed catalytic pathway, it provides compelling proof of the photocatalyst's competence in the oxidation of contaminants. Thus, our proposal involves the use of photocatalytic H₂ generation as a rapid screening strategy that will allow us to select and prioritize those materials where the investment in a full characterization of the catalytic degradation of contaminants is justified.

An important conclusion that emerges from our work is that the photocatalytic activity under oxidative or anaerobic conditions, whether in the visible or ultraviolet region and regardless of the dopant or absence of a dopant, is solely determined by the initial hole trapping event by the organic molecule.

Results and discussion

Materials

Two common SED were utilized in early testing, methanol and formic acid, both well established as easily oxidizable in



Scheme 1 Molecules studied in this work.

previous research.¹⁵ In addition, three common pharmaceuticals were also tested, estradiol, ibuprofen and acetaminophen; their structures are shown in Scheme 1.

All the catalysts are based on P25, a common TiO_2 material, consisting predominantly of anatase (about 84%), with rutile as the balance. Thermal treatments required for the synthesis of the eight catalysts used were limited to temperatures below 400 °C in order to prevent the conversion of anatase to the thermodynamically favored rutile. Table 1 shows the materials used and the corresponding nomenclature; we note that Cu-containing materials will be partially oxidized and contain significant levels of Cu(II) .²¹ Further synthetic details are available in the SI, although we note that some of the catalysts (earlier batches) were included in other publications.^{15,21,22}

Light absorption plays a crucial role in our work, making it essential to understand the spectroscopy of the materials listed in Table 1. The diffuse reflectance of these catalysts is depicted in Fig. 1. The Kubelka–Munk analysis generates a reflectance function, $F(R)$.^{23,24} For instance, once blackened, TiO_2 exhibits values of $F(R)$ exceeding 6, indicating that at least 94% of the light is absorbed within the visible region. Conversely, values exceeding 1.5, achieved with gold and palladium, signify that over 80% of the light is absorbed. For instance, in panel C, blackening of Pd@TiO_2 leads to an increase in light absorption from approximately 85% to over 94%.

While the photodegradation of pollutants typically relies on pathways involving reactive oxygen species, the possibility of utilizing anaerobic pathways that lead to hydrogen evolution presents an intriguing alternative.³ Both processes involve the scavenging of electrons from the TiO₂ conduction band. However, our studies indicate that the entire degradation process is actually controlled by hole scavenging, regardless of the excitation wavelength or the decoration of the semiconductor nanostructure.

Experiments with acetonitrile as co-solvent

The catalysts in Table 1 were tested using UVA light centered at 370 nm and visible light (400–700 nm). Initially, experiments with pharmaceuticals were conducted in a 20% acetonitrile solution in water to address solubility challenges. However, the photogenerated hole in TiO_2 is so highly electrophilic that even acetonitrile can act as a sacrificial electron donor.²⁵ Consequently, a substantial portion of the hydrogen produced in this solvent is attributed to acetonitrile rather than the pharmaceuticals depicted in Scheme 1. Nevertheless, these preliminary findings reveal some intriguing observations, and a comprehensive summary of the results is provided in the SI. Most of the experiments described herein were conducted in water, and the concentrations were adjusted to ensure solubility. In retrospect, while these aqueous concentrations are higher than typical contaminant levels, they are closer to environmental levels compared to those

^a Photographs of some of the materials are available in the SI.

Fig. 2 illustrates that E2 is the least reactive molecule, with 1680 molecules of H₂ generated for every E2 consumed. In contrast, the ratios for IBP and AP are 1070 and 137, respectively. In this solvent, most of the hydrogen is generated from the acetonitrile used as co-solvent. Among

To address the potential for these catalytic materials to be used in a more complex systems, simulating current real-world conditions in bodies of water, experiments were conducted combining the three aforementioned organic pollutants, AP, IBP, and E2 in addition to L-ascorbic acid, AA, (0.1 mM) acting as a potent hole and radical scavenger. Although vitamin C is not a contaminant of concern in lakes and rivers, its ability to scavenge photo-generated holes and

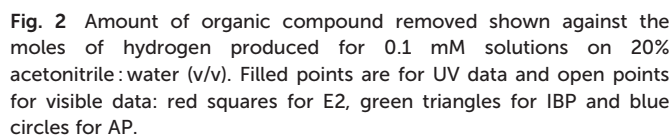
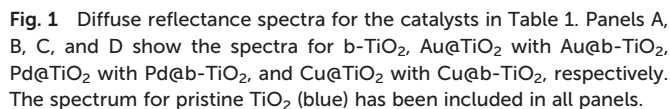


Fig. 3 depicts two radar plots highlighting the performance of all 8 catalysts under UVA (panel A of Fig 3) or visible (Panel B of Fig. 3) irradiation with the target pollutant being IBP. These plots are paired with averages of the consumed amount

In order to perform further detailed studies we selected ibuprofen as the choice material; we note that E2 had been studied at least with pristine and blackened TiO_2 in a recent contribution.⁹

The data for visible light has been divided by 2.44 (*vide supra*) so that UVA and visible data are referred to an irradiance of 177 W m⁻². No hydrogen was detected for exposures under air.

Several features of Fig. 4 are immediately evident. Firstly, the amount of hydrogen produced is significantly higher than the ibuprofen consumed. Secondly, the amount of ibuprofen consumed remains the same regardless of whether it is consumed under air or argon. Catalysts containing Au or

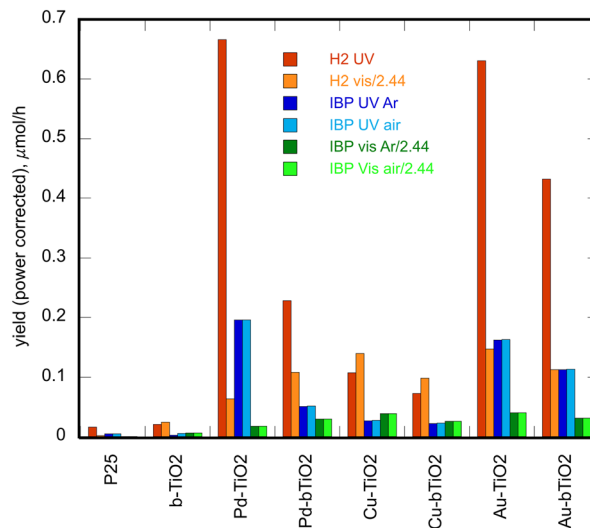


Fig. 4 Yield of hydrogen, or consumption of ibuprofen after 1 hour irradiation of a 0.1 mM solution of ibuprofen in water. The units are μmol per hour and the visible irradiation data have been divided by 2.44 to correct for the stronger visible light source. In this way all results are referred to a nominal irradiance of 177 W m^{-2} .

Pd perform exceptionally well under UVA light; however, under visible light, copper, a more affordable material, performs quite well and could be a suitable choice if the usage or elements at risk of depletion is a concern.

hydrogen are produced regardless of all other experimental parameters and the type of light employed.

As previously mentioned, no hydrogen was produced when the samples were exposed to air. Additionally, we compared the rate of ibuprofen consumption under argon and under air. This comparison yielded an excellent correlation, as evident in Fig. 6, which demonstrates that the atmosphere (air *versus* argon) has no impact on the rate of ibuprofen consumption, irrespective of all other experimental parameters and the type of light used.

The results in Fig. 5 and 6 support the idea that the catalysis observed is solely controlled by the rate of hole scavenging by the organic molecule, ibuprofen in our examples. Further, the fact that ~ 3.6 molecules of hydrogen are produced for each ibuprofen molecule consumed suggests that ibuprofen is well on its way to complete mineralization. Processes that involve trapping the electrons generated in the conduction band do not seem to affect the overall kinetics although they must be part of a cascade of oxidative processes that generate hydrogen or the reactive oxygen species (ROS) that degrade ibuprofen through various effective pathways. Moreover, the observation that 3.6 molecules of hydrogen are produced while a significant portion of IBP remains in the sample, suggests that the initial degradation products are more readily oxidized compared to IBP itself.

The mechanism of reaction proposed is shown in Scheme 2, where A shows the UVA mechanism with the classic hole scavenging by the substrate followed by oxidation of the radical accompanied by H_2 evolution under anaerobic conditions. The mechanism in B starts with excitation of the metal decoration followed by the same processes as in A, but with no direct involvement of the valence band of TiO_2 . The

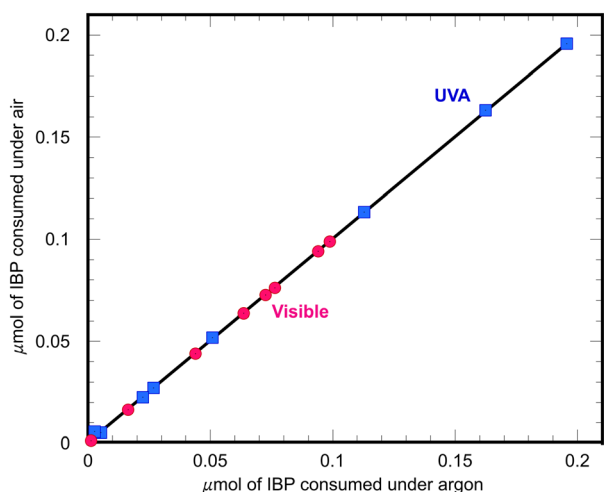
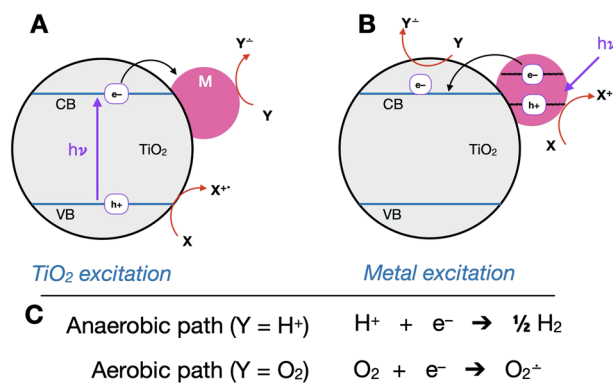


Fig. 6 Ibuprofen consumed after 1 hour irradiation of aqueous 0.1 mM IBP with UVA (177 W m⁻²) or visible light (432 W m⁻²). Data under air plotted against data under argon. All eight catalysts in Table 1 were tested.



Scheme 2 Schematic representation pathways following $M@TiO_2$ excitation. In A UV excitation leads to predominant absorption by TiO_2 followed by electron transfer to M, while on B visible excitation is largely absorbed by M, following electron transfer that populates the conduction band of TiO_2 . For black TiO_2 , both M and the color centres in TiO_2 can be active chromophores. In both cases hole scavenging can involve an SED or a pharmaceutical, while electron scavenging is different under aerobic or anaerobic conditions (C).

mechanism has been proposed by Gomes Silva *et al.* for reaction of Au@TiO₂ with EDTA as SED,³¹ and has also been described as hot electron injection.³² The interaction of the hole in the metal with the TiO₂ band structure is intricate and still a subject of ongoing research. The intense plasmon fields near the plasmonic nanoparticles can induce charge shifts within the host structure, which may actively participate in hole scavenging reactions. Regardless, it is evident that TiO₂ goes beyond being a mere support; it actively contributes to the overall process when visible light excites the metal nanoparticle.^{32,33}

Conclusions

Our findings indicate that the yield of pollutant photodegradation is solely determined by the efficiency of hole scavenging. The effectiveness of hole scavenging varies across different materials, and the wavelength of the excitation light also plays a crucial role in this process. It's not surprising that Pd@TiO₂ (Fig. 3) performs exceptionally well under UV irradiation. A material of particular interest is Cu@TiO₂, which exhibits excellent performance under visible light. Moreover, it is an inexpensive material, relatively abundant, and poses minimal health risks. Once hole scavenging is achieved, conduction band electrons simply follow, leading to the production of hydrogen or reactive oxygen species depending on the availability of oxygen in the medium. Typically, hydrogen yields are 3.6 molecules per ibuprofen degraded, and require that the initial degradation of IBP be followed by products that facilitate additional oxidative degradation. The complex mixture of products resulting from IBP photooxidation has been reported in earlier studies.^{34,35}

The recyclability of the photocatalysts examined in this study is crucial when considering their practical use. Fig. S11–S14 illustrate the removal of the target pharmaceutical using our catalysts after three photodegradation cycles. Notably, blackened and decorated TiO₂ analogs exhibit excellent recyclability for removing pharmaceuticals. It is noteworthy that Cu-decorated photocatalysts maintain their performance throughout the three cycles, making them suitable greener materials for remediation applications compared to Au or Pd-decorated photocatalysts. Additionally, as depicted in Fig. 3, Cu@TiO₂ demonstrates exceptional performance under visible light irradiation.

Experimental

The light-driven hydrogen generation trials were conducted by suspending 10 mg of catalyst in 4 mL of an aqueous solution containing 1% of a sacrificial donor (methanol or formic acid) or a 0.1 mM concentration of a pharmaceutical pollutant (estradiol, acetaminophen, or ibuprofen). These solutions were prepared in 10 mL borosilicate crimp vials that were purged and sealed under nitrogen. Irradiation was performed with continuous stirring for 60 minutes.

Following irradiation, a 1 mL sample of the headspace was collected using a lock syringe and manually injected into the gas chromatograph with a thermal conductivity detector (GC-TCD). The H₂ gas was detected at a retention time of 3.9 min (see SI Fig. S7) and quantified using an established calibration curve. In the case of the pharmaceutical solutions, the liquid phase after irradiation was used for HPLC analysis. A 80:20 gradient (water/acetonitrile) was used as the mobile phase while maintaining a constant flow rate of 2.5 mL min⁻¹. Changes in absorbance were recorded at 280 nm for estradiol and acetaminophen and at 265 nm for ibuprofen experiments.

Additional details, including material characterization are included in the SI.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information is available. See DOI: <https://doi.org/10.1039/D5CY00720H>.

The data supporting this article have been included as part of the SI.

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