

Titania-based heterogeneous photocatalysis. Materials, mechanistic issues, and implications for environmental remediation*

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Abstract: Using hexavalent chromium [Cr(VI)] and methylene blue (MB) as model substrates, we discuss three aspects of TiO₂-based heterogeneous photocatalysis. We show first that a given TiO₂ sample may not be simultaneously optimal for photocatalytically driving the reduction of Cr(VI) and the oxidation of MB. We further show that a TiO₂ sample that strongly adsorbs either of these substrates in the dark is not optimal as a photocatalyst. The other two aspects concern circumventing the rather poor surface catalytic properties and visible light photoresponse of TiO₂, respectively. Strategies revolving around the visible light photoexcitation of the substrate itself and metal-modification of the TiO₂ surface, are described as possible solutions.

INTRODUCTION

Heterogeneous photocatalysis has been intensely examined from both fundamental and practical perspectives (especially in environmental remediation scenarios) in recent years [1–3]. In spite of this vigorous activity and the search for the “ideal” photocatalyst (Table 1), for more than two decades, titania (TiO₂) in its anatase modification, has remained as a benchmark against which any emerging material candidate will be measured.

In this paper, we examine some outstanding issues with respect to the photocatalyst attributes and mechanistic aspects as they relate to TiO₂-based photocatalysis. The ensuing discussion may have relevance to environmental remediation scenarios, given that the process is amenable to both pollutant oxidation and reduction depending on the tendency of the latter to either give up or accept electrons respectively [4]. Thus, we choose hexavalent chromium and methylene blue as model pollutants for this study. The toxicity and environmental mobility of Cr(VI) are well documented [5]. Dye effluents, espe-

Table 1 Attributes of an ideal photocatalyst in a heterogeneous photocatalysis system for solar applications.

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- Stability and sustained photocatalytic activity
 - Good overlap of absorption cross-section with solar spectrum
 - High conversion efficiency and quantum yield
 - Compatibility with a variety of substrates and reaction environments
 - Low cost
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cially from the textile industry, impart not only an undesirable color to the wastewater stream, but many of these organic compounds are either very toxic themselves or generate harmful byproducts *in situ*. Methylene blue (MB) was chosen as representative of this class of environmental pollutants [3].

EXPERIMENTAL

Materials

Methylene blue was from Allied Chemical Corporation and was used without further purification. Potassium dichromate was reagent grade from Baker and was used as received. Silver sulfate, copper sulfate, and tetrachloroauric acid were from Alfa, Baker, and Aldrich respectively and were used without further purification. All solutions were made from deionized, distilled water.

The TiO₂ photocatalyst samples were obtained from commercial sources. Unless otherwise mentioned in what follows, the photocatalyst was Degussa P-25 titania in predominantly anatase form [6,7]. For some experiments, this material was subjected to thermal treatment. Associated details, as well as the other TiO₂ samples included in this study for comparison, are compiled in Table 2.

Titania gels were prepared by mixing TiO₂, water, and polyethylene glycol (MW: 400, Aldrich) in 2:4:1 ratio by mass. The resultant paste (0.1 g) was evenly spread on glass plates and dried at room temperature for 24 h. The nominal TiO₂ loading of these films was ~5 mg/cm².

Table 2 Designation of the various commercial TiO₂ samples, their properties and details of thermal pretreatment of Degussa P-25 sample.

List of symbols	Make	Surface area, m ² /g	Average particle size	P	Remarks
D	Degussa P-25	60–70 ^a	20 nm	A (80%), R (20%) ^a	Used as received
ST-01	Ishihara Sangyo Kaisha Ltd.	320 ^a	7 nm	A (~100%) ^a	"
A-100	"	11 ^a	0.15 μm	A (~100%) ^a	"
M1	Millennium Inorganic Chemicals	20 ^a	1.2 μm	A (~100%) ^a	"
M2	"	80–100 ^a	"	A (~100%) ^a	"
D-500	Degussa P-25	~55 ^b	ND	A (68%), R (32%) ^b	D heated at 500 °C in air for 24 h
D-600	"	50 ^b	ND	A (65%), R (35%) ^b	As above at 600 °C
D-800	"	10 ^b	ND	A (90%), R (10%) ^b	As above at 800 °C

^aManufacturer-supplied values

^bTaken from: A. Mills and S. Morris. *J. Photochem. Photobiol. A: Chem.* **71**, 285 (1993)

P = catalyst phase; A = anatase; R = rutile; ND = not determined

Procedures

Photocatalysis experiments were performed mostly on TiO₂-loaded aqueous suspensions dosed with requisite amounts of the pollutant substrate. The reactor has been described elsewhere [8]. The purge gas was either O₂ (for experiments with MB) or N₂ [for experiments with Cr(VI)]. For the adsorption experiments, the pollutant-loaded solutions were equilibrated with the TiO₂ photocatalyst (dose: 2 g/L) for 30 min in the dark. The suspension pH was close to neutral (pH 7) unless otherwise mentioned. Aliquots were withdrawn for analysis (see below) at the end of this period using procedures detailed

elsewhere [9]. The difference between the initial concentration of the substrate and that measured at the end of the equilibration period was taken as the amount adsorbed on the TiO₂ surface.

A few experiments were also performed on the TiO₂ gel films prepared as described earlier. For this purpose, 0.5 mL of MB solutions of known concentrations were pipetted onto the TiO₂ film surface followed by air drying in the dark for 24 h. Particular care was exercised to not expose these samples to ambient light as the (blue-colored) dye-loaded films undergo very gradual bleaching under these conditions.

Photocatalytic modification of the TiO₂ particle surfaces with Ag and Au was performed in N₂-purged suspensions (TiO₂ dose: 2 g/L) containing either 300 μM Ag₂SO₄ or 600 μM HAuCl₄ respectively. The deposition of either metal was completed within ~6 min (as assessed by flame atomic absorption spectrometry, FAAS) and the suspensions turned either deep purple (Au) or red (Ag) as a result (see Table 3).

Table 3 Metal-modified TiO₂ samples and the resultant color (see also Fig. 7).

Metal	TiO ₂ color
Unmodified	White
TiO ₂ /Pt	Bluish gray
TiO ₂ /Cu	Grayish brown
TiO ₂ /Ag	Red
TiO ₂ /Au	Purple
TiO ₂ /Cr(III)	Light green
TiO ₂ /Cu/Cr(III)	Green
TiO ₂ /Ag/Cr(III)	Light brown
TiO ₂ /Au/Cr(III)	Purple

Assays

Hexavalent chromium and MB were determined by UV–vis spectrophotometry at 350 nm [8,9] and 660 nm [10] respectively. The MB concentration changes on the gel film surface were probed by UV–vis reflectance spectroscopy. The silver, gold, and copper levels in solution were determined by FAAS at 328.1 nm, 242.8 nm, and 324.8 nm respectively.

Instrumentation

Solution analyses by UV–vis spectrophotometry were done on a Hewlett-Packard Model HP 8452 diode-array spectrometer. Reflectance spectra were taken on a Perkin-Elmer Model Lambda 6 Series instrument with BaSO₄ as reference. A Perkin-Elmer Model 237 instrument was used for FAAS.

For the photocatalysis experiments involving TiO₂ suspensions, the full output of a 400 W Hg lamp was used. The visible light source for experiments with the MB-loaded TiO₂ gel films consisted of a 400 W Philips tungsten-halogen lamp.

RESULTS AND DISCUSSION

Elusive role of substrate adsorption on the photocatalysis behavior of titania

Recent attempts both in this laboratory [8,11,12], as well as elsewhere [13–17], have sought to elucidate the role of substrate adsorption in photocatalysis scenarios. In the vein that a consistent and convincing picture has yet to emerge, new data are presented in Figs. 1–5 for the two model substrates, namely Cr(VI) and MB, respectively. The data in Figs. 1–4 are presented in companion format of both

the photocatalytic conversion profiles (in the ‘a’ frames) and the *dark* adsorption data (in the ‘b’ frames).

Our choice of Cr(VI) and MB as the model substrates for this study was mainly prompted (apart from environmental considerations, see above) by the fact that Cr(VI) is reducible and MB is oxidizable by the photogenerated electrons and holes in TiO₂ respectively [4]. Thus, the following questions are pertinent with respect to the material/mechanism focus of this study:

- How do various commercial samples of TiO₂ compare in terms of their ability to photocatalytically convert Cr(VI) and MB?
- How do these samples compare in terms of their proclivity to adsorb Cr(VI) and MB in the dark?
- Is there a correlation between the two processes addressed above in (a) and (b)?
- For a given TiO₂ photocatalyst (e.g., Degussa P-25), what effects does prior thermal treatment have on photocatalytic conversion and dark adsorption of Cr(VI) and MB?
- Is a given photocatalyst material optimal for driving *both* oxidation and reduction? Or stated differently, is a photocatalyst sample that is found to be optimal for MB equally good for the Cr(VI) substrate as well?

Referring to Fig. 1, it is seen that the two “best” TiO₂ samples for Cr(VI) reduction, namely M2 and D (Fig. 1a), show only moderate tendency to adsorb the substrate in the dark (Fig. 1b). Specifically,

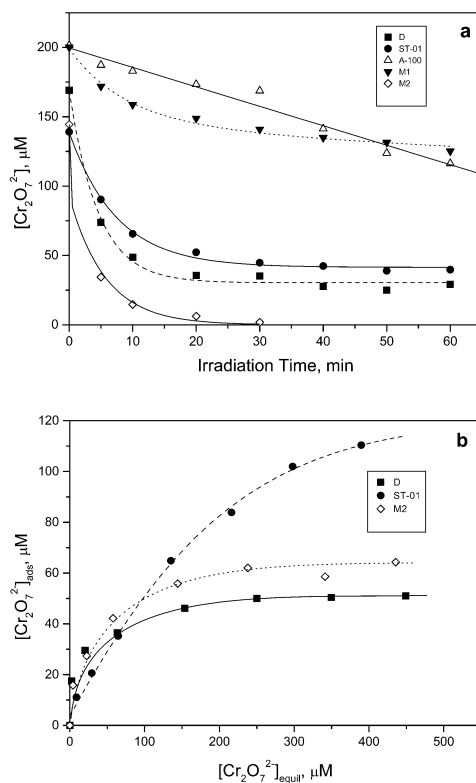


Fig. 1 Photocatalytic conversion profiles for Cr(VI) for the various commercial TiO₂ samples (Table 2) (a) and adsorption profiles on these samples in the dark (b). Data for A-100 and M1 are not included in Fig. 1b because they showed negligible tendency toward adsorption of Cr(VI). The initial concentration of Cr(VI) for the experiments in Fig. 1a was 400 μM (i.e., 200 μM in $\text{Cr}_2\text{O}_7^{2-}$ species).

the sample that exhibits the maximal tendency to adsorb Cr(VI), namely ST-01, is clearly inferior to both M2 and D, in terms of photocatalytic conversion. Interestingly, both A-100 and M1 show negligible tendency to adsorb Cr(VI) in the dark. Thus, these samples are not considered in the plots in Fig. 1b. Their photocatalytic efficiency toward Cr(VI) is also poor (Fig. 1a).

Two further points with respect to the data in Fig. 1a (and in Figs. 2a, 3a, and 4a) must be noted. All these plots could be fit in terms of kinetics models of either first-order or zero-order in substrate concentration. Second, the incomplete conversion noted for Cr(VI) in some cases in Figs. 1a and 3a, can be rationalized in terms of the proton starvation phenomenon discussed by us elsewhere [8].

Turning to the MB data in Fig. 2, it is seen that D (and to a somewhat lesser extent, A-100) are the most optimal for photocatalytic conversion (Fig. 2a). However, as in the Cr(VI) case in Fig. 1b, the Degussa sample (D) adsorbs the dye the least. The “best” sample for MB adsorption, M1, turns out to be the worst for oxidative photoconversion of the dye! The other samples exhibit variable behavior between the extremes outlined above.

Thus, one conclusion that immediately emerges from these rather complex data trends is that a given photocatalyst sample may *not* be simultaneously optimal for driving both photooxidation and photoreduction processes. Nonetheless, the Degussa P-25 sample offers a reasonable compromise in possessing at least acceptable attributes for both these types of processes. Indeed, it could even be agreed that a tendency to strongly adsorb a given substrate may be deleterious to the photocatalytic effi-

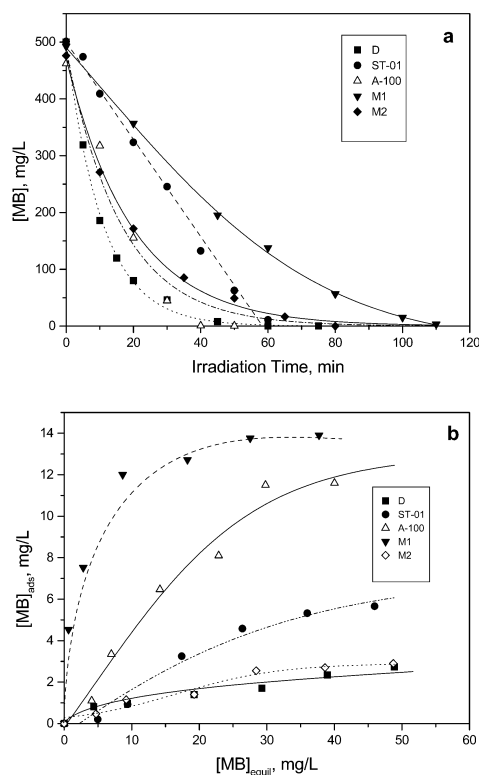


Fig. 2 As in Fig. 1, but for the MB substrate. The initial concentration of MB for the experiments in Fig. 2a was 500 mg/L.

ciency of the TiO_2 surface as exemplified by the ST-01 and M1 samples in Figs. 1 and 2 for Cr(VI) and MB, respectively.

From a mechanistic perspective, it could be argued that very strong binding of a substrate creates surface states that could function as carrier recombination centers. In heterogeneous (thermal) catalysis, it is also well known that persistent binding of a substrate mitigates against its efficient catalytic conversion as manifested in “volcano” plots [18]. Finally, the finding that a given photocatalyst sample may not be optimal for both oxidative and productive substrate conversion processes, is reasonable considering that very different surface (catalytic) sites may be involved in the two cases at relative energies (with respect to the TiO_2 band-edges) that clearly have to be vastly different to mediate hole and electron transfer respectively.

Figures 3 and 4 contain the thermal pretreatment data for Degussa P-25 for the two substrates, Cr(VI) or MB, respectively. In both the cases, thermal treatment (see Table 2 for details) has deleterious consequences for substrate photoconversion, be it reductive or oxidative (Figs. 3a and 4a). Interestingly, the proclivity to adsorb Cr(VI) or MB shows opposite trends as a function of the thermal treatment. Specifically, the Degussa sample adsorbs less Cr(VI) in the dark after it is preheated at temperatures between 500 and 800 °C (Fig. 3b). On the other hand, (and rather surprisingly), progressively more dye is bound on the titania surface after it is subjected to this treatment (Fig. 4b).

We know from previous work (and X-ray/microscopy evidence) in other laboratories [6,19,20] that prior thermal treatment results in particle sintering, and at temperatures higher than ~600–700 °C, to anatase \rightarrow rutile conversion. While some authors [6] attribute the *decrease* in photocatalytic activ-

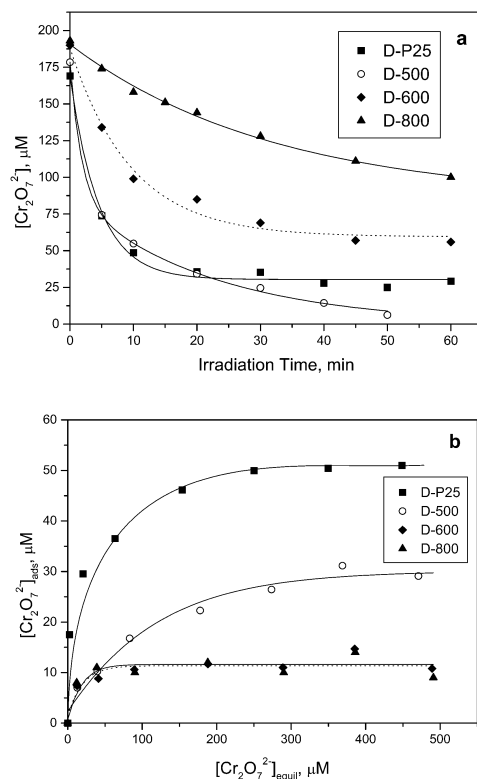


Fig. 3 As in Fig. 1, but for the Degussa P-25 TiO_2 sample showing the influence of thermal pretreatment (see Table 2). Other conditions as in Fig. 1.

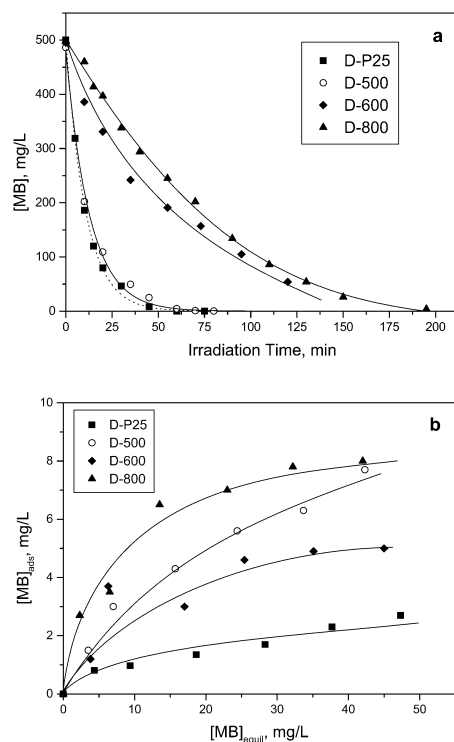


Fig. 4 As in Fig. 3, but for the MB substrate. Other conditions as in Fig. 2.

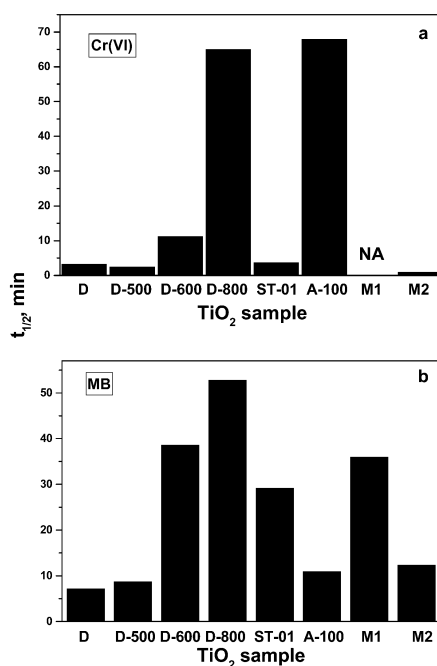


Fig. 5 Reaction half-lives ($t_{1/2}$) for Cr(VI) (a) and MB (b) for all the specimens considered in Figs. 1–4. The $t_{1/2}$ value for the M1 sample in the Cr(VI) case could not be accessed (see Fig. 1a); hence the NA notation.

ity with calcination, to the influence of surface area (rather than the crystal structure transformation), others [20] propose that increased O₂ adsorption on the titania surface may be responsible for the observed *enhancement* in activity up to treatment temperatures in the 400 °C range. Substrates such as acetone [20], 4-chlorophenol [6], or acetic acid, water, or propan-2-ol [19] were deployed in these earlier studies.

Precedence for comparison of the photocatalytic activity of various TiO₂ specimens (both commercial as well as synthesized) can be found in the literature [21–24]. Causal factors in the efficiency variations for anatase vs. rutile crystal forms of TiO₂ have also been examined [7,21,22,25]. This body of data along, with the new results presented above, underline the need for caution, the complexity of the surface behavior of TiO₂ in the dark and under photoirradiation, and the incomplete state of knowledge on the interplay between dark (i.e., adsorption) and light processes involving the substrate and the photocatalyst surface. Finally, Fig. 5 contains a comparison of the reaction half-life ($t_{1/2}$) for both Cr(VI) and MB for all the TiO₂ samples considered in Figs. 1 and 4 above. These $t_{1/2}$ values were culled from the kinetics plots in Figs. 1a–4a.

VISIBLE-LIGHT INDUCED OXIDATION OF MB ON TITANIA GEL FILM

With reference to the attributes of an ideal photocatalyst listed in Table 1, a major handicap of TiO₂ concerns its photoresponse, which is mostly confined to the UV spectral region because of its rather large (3.0–3.2 eV) energy band-gap. On the other hand, if an (adsorbed) substrate itself can absorb visible light, then the resultant photoexcited electrons can be transferred to the underlying TiO₂. The holes thus generated will then photooxidize the substrate [26–28]. Such a sensitization/degradation pathway has been demonstrated for dyes such as Basic Blue 41 [29], X3B [16], and other organic compounds [30]. Even a sensitized *photoreductive* degradation mode has been demonstrated for a Ru-complex modified TiO₂ photocatalyst and CCl₄ as the substrate [31]. However, the vast majority of these studies were performed on TiO₂ suspensions.

Figure 6 contains photographic data on the visible light-induced bleaching of MB confined on a TiO₂ gel film. That this process occurs via the sensitization pathway outlined above (i.e., initial photoexcitation of MB followed by electron transfer to TiO₂) is indirectly shown by the insensitivity of this process to the presence of PEG in the gel film (see Experimental section). By contrast, a UV-irradiated TiO₂ film containing MB on its surface bleaches the dye only very slowly (data not shown) because of the competition for the photogenerated holes in TiO₂ by the two substrates, MB and PEG, respectively. These contrasting data illustrate the fact that the *location of the photogenerated holes, whether in the dye itself or in the underlying photocatalyst*, plays a key role in the dye oxidation pathway.

METAL-MODIFIED TITANIA PHOTOCATALYSTS

Another approach to circumvent the poor visible-light photoresponse of TiO₂ is to modify its surface or bulk with foreign metal ions. Such “doped” TiO₂ samples have been extensively studied even in the early days of photoelectrochemistry/photocatalysis (see refs. 32,33 for reviews), although the reported results have been conflicting. Three main consequences of metal-modification of TiO₂ can be distinguished, however, from this body of work: (a) induction of visible-light photoresponse in the host material; (b) suppression (or in some cases, enhancement) of carrier (electron-hole) recombination as a result of new states introduced in the band-gap of TiO₂ by these dopants; (c) generation of catalytic sites on the TiO₂ surface that serve to store electrons for subsequent transfer to acceptor species in the solution. Examples of the three distinct types of effects are provided by Ag and Pt (effect ‘a’) [29,34–36], Fe (type ‘b’) [32], and noble metals (including Pt) (type ‘c’) [32,33].

We have generated an extensive series of metal-modified TiO₂-specimens in our laboratory; the photograph in Fig. 7 contains a selection of these. In many cases, distinct differences in color alterations (from the basic white pigmentation) can be seen as a result of this surface modification as list-

ed in Table 3. All these specimens were prepared by photocatalytic deposition of the metal onto the TiO_2 surface starting with suitable precursor metal ion carriers [37]. While these results visually suggest a shift of the basic photoresponse of TiO_2 toward the visible range of the electromagnetic spectrum, further work is in progress to quantify this trend [37].

We have focused on the coinage metal series (Cu, Ag, Au) in terms of their influence on the photocatalytic properties of TiO_2 . In a recent communication [38], we reported that Cu exerts a “synergis-



Fig. 6 Progressive irreversible bleaching of a MB-loaded TiO_2 gel film (see Experimental) upon visible light illumination.



Fig. 7 Photograph illustrating the distinctive coloration imparted to the virgin TiO_2 sample by metal modification of its surface (see also Table 3).

tic photocatalytic effect” (SPE) on the ability of TiO_2 to reduce targeted species such as Cr(VI) . That is, not only is the reduction of Cr(VI) accelerated by the presence of Cu on the surface of TiO_2 , but the photoreduction of Cu(II) ions is catalyzed by Cr(VI) as well.

Figure 8 contains new data for the photocatalytic reduction of Cr(VI) by TiO_2 modified with Ag and Au respectively. A control plot for the unmodified TiO_2 sample is included for comparison. The catalytic effect of these two metals is seen to be sizeable, and in some respects, is more dramatic than that of Cu, although the SPE is not seen in these cases (presumably because the reduction potentials for silver and gold lie well positive of that of copper). Thus, the acceleratory effect of the two metals in Fig. 8 is attributed to effect ‘c’ mentioned in an earlier paragraph, namely that these metal sites on the TiO_2 surface serve to store electrons. Such electron storage centers are beneficial for catalytically driving multi-electron processes such as the $\text{Cr(VI)} \rightarrow \text{Cr(III)}$ reduction considered here. Interestingly enough, the proton starvation phenomenon seen for the unmodified TiO_2 sample does not manifest when the overall process itself is very fast, as in the Ag- and Au-modified TiO_2 cases (Fig. 8).

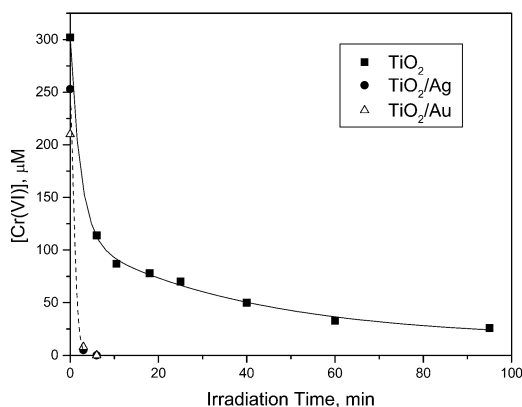


Fig. 8 Photocatalytic conversion profiles for Cr(VI) (initial concentration: $400 \mu\text{M}$) showing the influence of TiO_2 surface modification with Ag and Au respectively. The solution pH was adjusted to ~ 4 with sulfuric acid. Data for the control run were taken from ref. 9.

CONCLUDING REMARKS

In this paper, we have discussed three aspects of TiO_2 -based heterogeneous photocatalysis that, in our estimation, deserve further scrutiny. We have presented new data from our laboratory on these three aspects within the context of emerging results from other laboratories around the world. While clearly the search for new photocatalyst materials must obviously continue, this study hopefully reveals that TiO_2 -based heterogeneous photocatalysis constitutes a fascinating system that itself continues to provide surprising data trends, presenting in turn, new interpretative challenges for the future. The interplay between material (e.g., surface) properties and reaction mechanisms in this system must be better elucidated such that useful, practical applications will ultimately emerge such as in solar environmental remediation.

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