



Photoformed electron transfer from TiO₂ to metal clusters

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ABSTRACT

Detection of mobile charge carriers consistent with a process involving electron transfer from TiO₂ to metal particle was measured by EPR and FTIR in the presence of a hole scavenger and under UV irradiation. The main role of the metal (Ag, Au or Cu) was to scavenge the photogenerated electrons leading to an improvement in charge separation with respect to unmodified TiO₂ alone. The improvement of charge separation yielded a greater number of holes that were available for surface reaction. A higher rate of reaction on the bleaching of Rhodamine 6G was measured when metal clusters were added to TiO₂. Monitoring of solution pH during the degradation of the dye suggest a range of products were formed, whose nature depended both on the presence of metal and on the particular metal present.

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1. Introduction

Interest in photocatalysis has increased in the past decades due to its potential role in today's environmental and energy-supply related problems. Photocatalysis by definition is the acceleration of a chemical reaction by the presence of a semiconductor photoabsorber. A more in depth approach would include that the solid may accelerate the reaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction [1,2].

TiO₂ is the most widely employed photocatalyst, resulting mainly from its high stability, low cost and widespread availability. There are a growing number of reports relating the various applications of TiO₂, with water and air decontamination being the areas which have attracted most attention [3,4]. However, with the band gap ranging from 3.0 to 3.2 eV, UV light is required to promote an electron from the valence band to the conduction band. A major disadvantage in the employment of any solid in the process is the high degree of recombination between the photogenerated charged species resulting in a decrease of the process quantum yield.

Several groups have focused their efforts in preparing TiO₂-type materials which might exhibit higher efficiency in the visible region of the spectrum [5–9]. Another prominent area of research is concerned with attempts to decrease the rate of charge recombination. It has been observed that the addition of small amounts of noble metals to the TiO₂ can lead to a significant increase in the photocatalytic yields [10–14,15]. The concept of photoformed elec-

trons being transferred from the oxide to the metal particles, decreasing the recombination rate of charged species, has been used to explain the enhancement in activity. Pichat and Anpo et al. [16] were among the first to suggest that an electron transfer process occurs during irradiation from the semiconductor to Pt by following the intensity of the Ti³⁺ signal as a function of irradiation time using ESR and other spectroscopies. Using a clean TiO₂ sample, it was observed that in the presence of a hole scavenger, the signal indicative of the relative concentration of Ti³⁺ grew during irradiation, whereas in the case of Pt/TiO₂ the signal was absent. Lately, the combination of techniques such as infrared, EPR and flash photolysis was able to firmly establish such an electron transfer process [17]. Other studies also pointed out the possible role of noble metals as co-catalyst working independently of the UV-radiation for specific reactions [18]. Studies using TiO₂/noble metal nanocomposites [17,19,20] additionally confirmed the presence of electron transfer process using absorbance spectroscopy. Noble metals led to a negative shift of the absorption edge due to the increase of electron accumulation, resulting in the approximation of the Fermi level and conduction band. In the particular case of Au, this was found to be dependent on the particle size, namely larger shifts were measured on smaller gold particles. Gold was found to store electrons in a quantized manner [21–23].

In respect to electron trapping on TiO₂, the studies [17,24] suggested that it could occur on two sites; shallow traps or conduction band. The shallow traps can be detected by an EPR active Ti³⁺ colour centres, whereas the electrons in the conduction band can be detected by IR absorption due to a shift in the background caused by their presence. They observed a significant difference between trapped holes and trapped electrons on Ti³⁺ centres, which led to the suggestion that only a limited number of photoexcited and

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trapped electrons occupy localized states, i.e., most of the electrons photogenerated are located in the conduction band rather than trapped in the colour centres. Hole trapping can be also observed by EPR as O^- species originating from anion lattice positions or OH surface radicals can be detected with the help of spin trapping molecules [17,25]. The stability of trapped charge species decrease upon increasing the temperature, the shallow trapped electrons being the less stable species. All stable trapped electrons and holes were absent on TiO_2 at 298 K.

The objective of this current work is to bring further insight into the electron transfer process occurring on supported photocatalysts, especially at room temperature. The photocatalysts consisted of a metal (Ag, Cu or Au) supported on TiO_2 P25 were characterized by IR and EPR, and tested in the photocatalytic degradation of Rhodamine 6G.

2. Experimental

2.1. Catalyst preparation

Nanoparticulate Ag and Cu supported on TiO_2 P25 were prepared as described elsewhere [26]. Briefly, 500 mg of support was dispersed (TiO_2 P25) in 110 cm^3 of double distilled water adjusted to pH = 11–12 (with a solution of NaOH concentration 0.01 M) in a sonic bath for 15 min. The suspension obtained was purged with N_2 free oxygen for further 15 min under vigorous stirring. An equimolar amount of desired metal and complexant anion was added to suspension. The anion was added to decrease the solubility of the metal in solution, i.e., to precipitate the metal. The anion selection was based on the solubility product (K_{sp}), which should have a nominal value $<10^{-12}$ [26]. In the present study, Br^- was chosen as Ag^+ complexant ($K_{sp}(AgBr) = 5.0 \times 10^{-13}$) and OH^- for Cu^{2+} ($K_{sp}(Cu(OH)_2) = 2.2 \times 10^{-20}$) [27]. Note, improved and faster homogeneity was achieved if the precursor salts were previously dissolved in no more than 5 cm^3 of double distilled water before added to the suspension. The final volume of solution should be 120 cm^3 . The suspension was stirred and irradiated with UV light (UV – A range with maximum peak at 365 nm) for 7 h. Upon that period the solution containing the catalyst was centrifuged at 4000 rpm for 15 min and rinsed with deionized water. The procedure was repeated 4 times. The catalyst was then dried overnight at 333 K. The loading of Ag and Cu was found to be close to 1 wt% measured by atomic absorption spectroscopy upon digestion in *Aqua regia*. The Au/ TiO_2 P25 catalyst supplied by Autek, contained 1 wt% of metal and had an average particle size of 2.1 nm as measured by TEM, (value provided by supplier).

2.2. Characterization

UV–vis diffuse reflectance spectroscopy was performed on a StellarNet Inc EPP200 using $BaSO_4$ as reference. Atomic absorption spectroscopy (AAS) was performed on Varian Spectro using samples previously digested in *Aqua regia*. This procedure is commonly used to remove the loaded metals from the support.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Escalab X-ray photoelectron spectrometer VGX900 using Al $K\alpha$ radiation. The operating pressure was $<1 \times 10^{-8}$ mbar. The reported binding energies (BE) were corrected for sample charging, by attributing a BE value of 284.6 eV to the C 1s line [28,29]. Software XI-SDP version 4.2, XPS International was used for data analysis.

Electron paramagnetic resonance (EPR) measurements were performed on a Bruker ECS 106 spectrometer in the X band. The EPR sample cells are made of suprasil quartz and were connected to an *ex situ* high vacuum pumping line attached with accessories to perform adsorption experiments with diverse gases. The sam-

ples were evacuated at 423 K for a period of 2 h in order to remove any physisorbed water. The catalysts were exposed to 40 mbar of pure H_2 and UV irradiated with a Xe lamp until saturation of the signal, generally within 20 min, at 77 K.

Fourier Transform Infrared (FTIR) was performed on a Perkin-Elmer Series 1700, with the sample cell connected to a standard high vacuum apparatus. Spectra were collected at 4 cm^{-1} resolution, 32 scans with a TGS detector using ca. 20 mg sample. The samples were evacuated at 423 K for a 2 h to remove the physisorbed water as with the EPR experiments. The catalysts were then exposed to 25 mbar of a hole scavenger (H_2 , CH_3OH or H_2O) and UV irradiated for 20 min using the same lamp as employed for the EPR experiments. The sample was subsequently, exposed to 10 mbar of 5% O_2/He for 5 min.

Degradation of Rhodamine 6G was performed in a 0.2 L batch reactor equipped with a magnetic stirrer. In the case of Cu/ TiO_2 , the sample was reduced *ex situ* for 2 h at 673 K in 100 mL/min H_2 before reaction. All other samples were used as prepared. In a typical run, 20 mg of the catalyst was charged into a reactor containing 80 mL of distilled water and 7 mL of solution of Rhodamine 6G at a concentration of 100 ppm. The initial pH of the reaction mixture was adjusted to ~ 9.0 by the addition of 0.1 M NaOH solution. The reaction was then sonicated for 15 min to decrease the extent of catalyst particles aggregation. The samples were irradiated with a 4 W, UV-TEC lamp throughout the reaction. The degradation of the dye was monitored using the absorption at $\lambda = 578$ nm on a WPA Septrawave S 1000 diode array spectrometer.

3. Results and discussion

The addition of small metal clusters to TiO_2 caused only a minor shift on the absorption cut-off, leading to a slight increase on visible light absorption in comparison to TiO_2 (Fig. 1). The absence of significant plasmon peaks is also apparent from this figure.

Results of XPS analysis of the metal modified TiO_2 catalysts are summarized in Table 1. Cu/ TiO_2 catalyst exhibit two peaks located at 932.1 and 951.8 eV, which are assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The values are typical for Cu in an oxidized state [29,30]. The absence of shake-up satellites suggests that it is Cu (I) however these species are unstable and easily passivated under air, therefore the signal might result from the reduction of CuO by the X-ray beam. As far as silver is concerned, in the photodeposited catalysts, the BE of the $Ag3d_{5/2}$ peak, corrected for the charging effect, is 367.3–367.4 eV, a value typical for silver Ag^{+0} [26,29]. The decision of the most likely oxidation based exclusively on the BE is not easy, however the colour of the catalyst would suggest that silver is mainly in a metallic state. Positive shifts in the range 0.5–2 eV with respect to values for bulk Ag have been previously re-

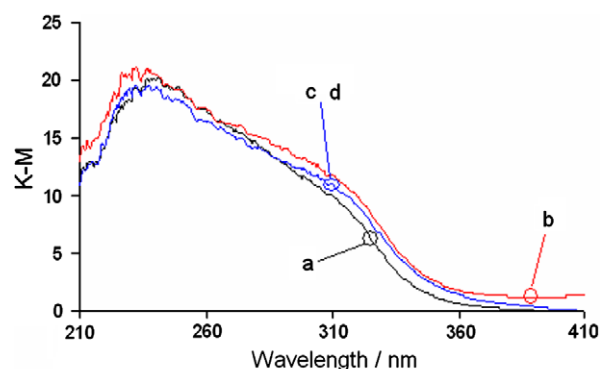


Fig. 1. UV–vis diffuse reflectance spectra of (a) TiO_2 , (b) Ag/ TiO_2 , (c) Cu/ TiO_2 and (d) Au/ TiO_2 .

Table 1
XPS and AAS measurements on the as prepared samples

Catalyst	Metal loading/wt.%	XPS M/Ti	Oxidation state
Cu/TiO ₂	0.82	0.052	2+/1+
Ag/TiO ₂	1.10	0.039	0
Au/TiO ₂	1.00 ^a	0.027	0

^a Value provided by the supplier, M – metal (Ag, Au or Cu).

ported and attributed to particle size effects and support interactions [31,32]. The general trend is that the larger the particle, the less pronounced is the binding energy shift (with respect to the bulk metal) and this becomes negligible for particles larger than 6 nm. The BE values (Table 1) suggests that silver exists in the catalyst in very small nanoparticles, i.e. smaller than 3 nm. The spectrum for Au/TiO₂ shows signals which correspond to binding energies of 83.8 and 87.4 eV, due to Au 4f_{7/2} and Au 4f_{5/2}, respectively, and characteristic of metallic gold [26,29]. XPS data shows an M/Ti trend in the order Cu > Ag > Au. Since the M/Ti atomic ratio values for Cu and Ag are higher than Au and given the particle size measured by TEM for Au is ca 2 nm, it is reasonable to expect similar or slightly smaller average particles size for Cu and Ag.

3.1. Influence of the presence of metal clusters on the shallow trapped electrons (Ti³⁺)

Evidence of the formation of paramagnetic Ti³⁺ centres in TiO₂ as a consequence of exposure to UV irradiation in the presence of H₂ as a hole scavenger was provided by EPR experiments (Fig. 2). Evacuation at 423 K of metal-free titania produced a spectrum with no evidence for any paramagnetic signal, although when H₂ was introduced, a weak, unresolved g signal near 1.98, typical of anatase, was detected (Fig. 2a). Upon irradiation, two characteristic signals appeared in the EPR spectrum (Fig. 2b) and their intensities reached saturation after ca. 20 min. The signal at g_⊥ = 1.993 and unresolved perpendicular component (around 1.96) is related to Ti³⁺ species of anatase whereas the features at 1.970 and 1.951 are ascribed to g_⊥ and g_∥ of Ti³⁺ in rutile. Both signals have been extensively reported in studies of P25 [33–36]. Under these conditions no signal was apparent due to hole trapping species (O⁻) although in agreement with previous studies [17] it is plausible that such species undergo a degree of reduction after being exposed to hydrogen.

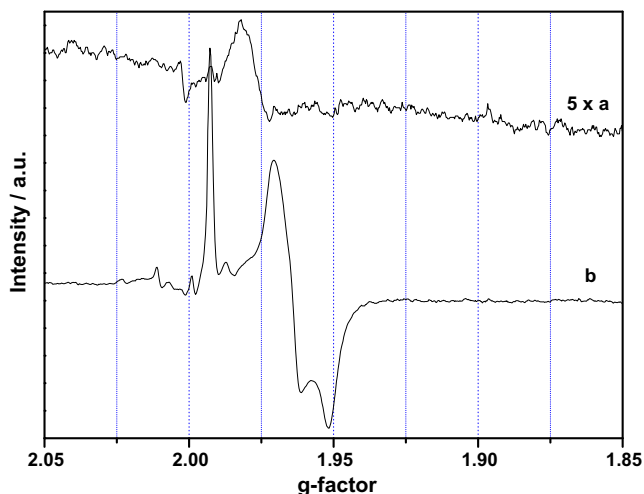


Fig. 2. EPR spectra of TiO₂ after activation at 423 K for 2 h and then (a) exposure to 40 mbar H₂ and (b) subsequent UV irradiation at 77 K for 15 min.

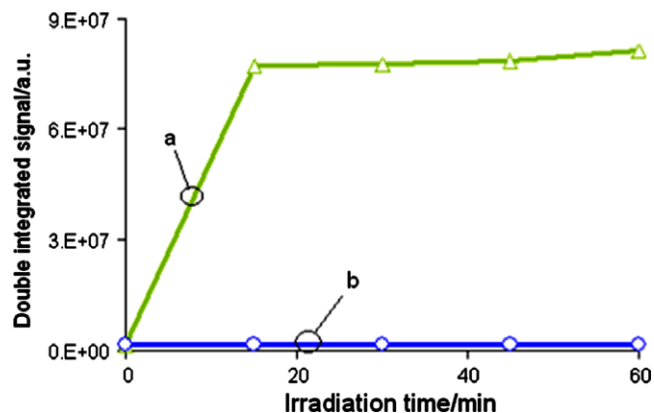


Fig. 3. Relative intensity of Ti³⁺ signal at 77 K as function of irradiation time on (a) TiO₂ and (b) Ag/TiO₂ activated under 40 mbar H₂.

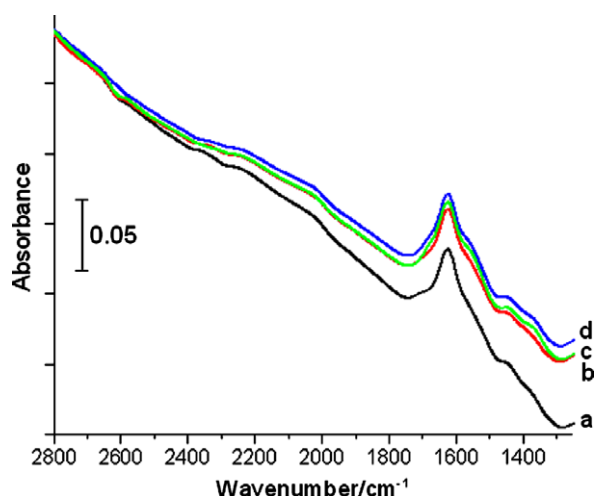


Fig. 4. FTIR of TiO₂ after activation at 423 K for 2 h under UV irradiation. Spectra after (a) exposure to 25 mbar H₂, and UV irradiation for (b) 1, (c) 10 and (d) 20 min.

The intensity of the double integrated peaks of the Ti³⁺ signal was plotted as a function of the irradiation time for TiO₂ (Fig. 3a) and for Ag/TiO₂ (Fig. 3b) as an example of one of the metal doped titania samples. In the case of metal-free TiO₂, the signal increases rapidly upon initiating the irradiation treatment and reached saturation after 20 min (Fig. 3a) whereas in the presence of Ag no signal associated with Ti³⁺ centres either on the anatase or rutile components was observed. Similar results were observed for Au/TiO₂ and Cu/TiO₂. In the latter case, copper was at least partially reduced during evacuation as shown by both the lack of Cu²⁺ EPR signal and the black colour of the sample after pre-treatment. The absence of Ti³⁺ signal following irradiation of the metal containing samples suggests that the electrons otherwise trapped on shallow traps (Ti³⁺) in titania are transferred to the metal clusters. This confirms the presence of a Schottky barrier at the metal–titania interface for the samples where an electron trap may be produced (see Fig. 4).

3.2. Influence of the presence of metal clusters on the conduction band electrons

The use of IR spectroscopy as a tool for monitoring conduction band electrons has been reviewed by Thompson and Yates [17]. The addition of hole scavenger did not change the IR spectrum of TiO₂, whereas application of UV light lead to a shift in the baseline.

An increment of ca. 0.023 absorbance units at 2000 cm^{-1} was measured after 20 min irradiation, consistent with the magnitude of the value reported by Berger et al. [24]. In this case, the measurements were performed at room temperature instead of 140 K in the presence of a hole scavenger and using P25 instead of nanocrystalline TiO_2 anatase. The shift as a function of irradiation time is also similar to observations of Berger et al. [24] namely, a steep increase in absorbance during the first 4 min of irradiation followed by a slower increment until no further shift was observed after 20 min irradiation. Similar results were observed when CH_3OH or H_2O were used as hole scavengers, suggesting that the modifications to the IR signal which are induced by UV irradiation were independent of the nature of the hole scavenger.

To confirm that the shift in the IR background was related to the presence of electrons in the conduction band, O_2 was added to the system after maximum baseline shift had been attained. The effect is summarised in spectra shown in Fig. 5. Treatment in O_2 as an electron scavenger, lead to a decrease in absorbance to values similar to those observed in the spectrum prior to exposure to UV irradiation. This response to the electron scavenger confirms [17,24] that the shift in the IR baseline following UV irradiation is in fact related to delocalized electrons in the conduction band of the photocatalyst.

Having confirmed that electrons can be detected if present in the conduction band of the photocatalyst, the experiment was repeated with the metal loaded catalysts. Fig. 6 illustrates the results of one of these experiments using Au/TiO_2 as an example. As with the pure TiO_2 , introduction of H_2 did not affect the IR absorption spectra. The only change which was apparent during light-on for the metal-loaded catalysts was the increase in intensity of the bands due to the deformation mode of molecular water which resulted from the use of H_2 as hole scavenger. However no changes in respect to background shift, were detected during light-on period, in contrast to the effects observed for pure TiO_2 (Fig. 5). This negative result supports the idea that electrons are transferred from the TiO_2 to the metal. Similar results were obtained for catalysts loaded with Cu or Ag and when either CH_3OH or H_2O were used as hole scavengers.

3.3. Photocatalytic bleaching of Rhodamine 6G

Before presenting the results, it should be noted that the rate of photocatalytic bleaching of Rhodamine 6G was enhanced when the pH was adjusted to ca. 9.0 during the initial stages of reaction. As

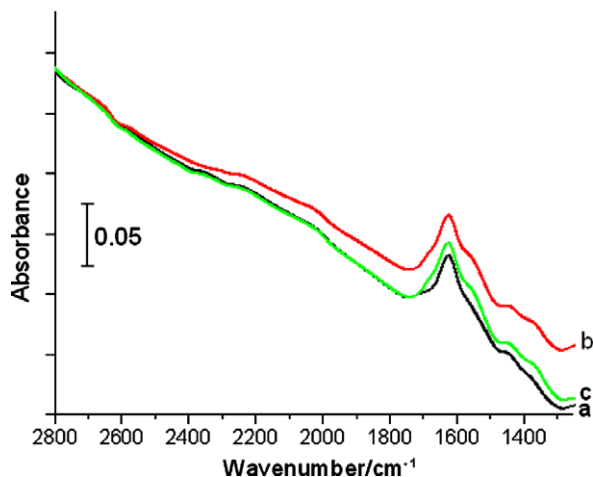


Fig. 5. Influence of the presence of oxygen on the IR spectrum of TiO_2 after UV irradiation under H_2 . Spectra after (a) exposure to 25 mbar H_2 , (b) UV irradiated for 20 min and (c) exposure to 10 mbar of 5% O_2/He .

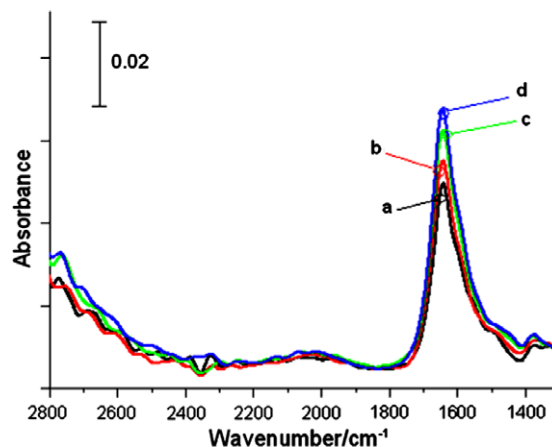


Fig. 6. FTIR spectra of Au/TiO_2 activated under UV irradiation in the presence of H_2 . Difference spectra after (a) exposure to 25 mbar H_2 , and UV irradiation for (b) 3, (c) 10 and (d) 20 min.

Table 2

Summary of reaction rates for the bleaching of Rhodamine 6G and metal electron affinities

Catalyst	Activity/mol (min g cat) ^{-1a}	Metal electron affinity/kJ mol ⁻¹
TiO_2 P25	0.77	–
Cu/TiO_2^b	1.10	118.4
Ag/TiO_2	0.93	125.6
Au/TiO_2	1.19	222.8

^a Average rate during first 10 min of reaction.

^b Reduced before reaction at 673 K in 100 mL/min H_2 for 2 h.

the PZC of P25 lies between 4 and 6, operating at a higher pH would render the surface with a net negative charge which would subsequently facilitate the adsorption of the positively charged reagent molecule. Note however that the PZC may vary following the addition of metal ions to TiO_2 photocatalysts [37]. Reported activities (Table 2) are for systems where the initial pH was adjusted to pH 9 by addition of 0.1 M NaOH.

Fig. 7a shows the decay in colour of the reacting solution as a function of time while continuously exposing the system to UV irradiation. Although pure TiO_2 alone showed good ability to bleach the colour associated with the natural state of Rhodamine 6G, the addition of metal clusters enhanced the rate of reaction. Note that the addition of transition metals to polycrystalline titania is generally believed to be detrimental for the photooxidation of organics from the aqueous phase [15,37]. However, here an increase in the rate of reaction, relative to titania alone was apparent for all metal-containing samples, with activity following the order, $\text{Au} \approx \text{Cu} > \text{Ag} > \text{TiO}_2$ (Table 2). Unlike the other samples, the copper sample was prereduced prior to activity testing in order to render it in a reduced/partially reduced state, more consistent with the nature of the metals in the other samples as judged by the XPS analysis (Table 1) and consequently more appropriate for comparative purposes. However, when starting with the as prepared sample, the initial activity was only slightly less than when the sample had been prereduced in hydrogen. This would suggest that an active form of the metal was rapidly formed on contact with the solution phase independent of any pretreatment conditioning.

Although the profiles for dye degradation were of a similar nature for both metal-free and metal containing titania (Fig. 7a), monitoring of the pH (Fig. 7b) allowed a greater degree of discrimination between the behaviour of titania and the metal containing samples and, to a lesser extent, between the different metals. Given that over the 60 min of reaction the dye was effectively

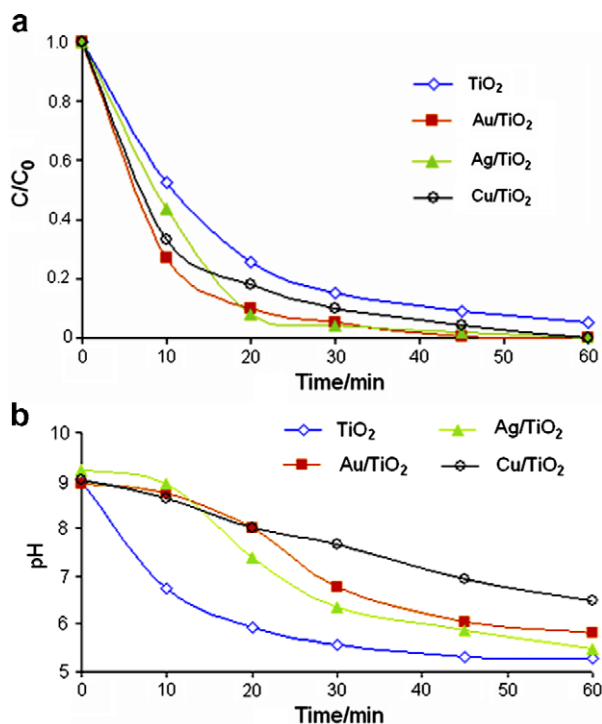


Fig. 7. (a) Depletion of Rhodamine 6G colour as a function of irradiation time for the different samples. Irradiation initiated after adjusting the pH to 9. (b) Evolution of pH as a function of time during photocatalytic reaction of Rhodamine 6G.

totally discoloured for all of the samples with the exception of some residual colour retained by the sample in contact with the metal-free titania (Fig. 7a) then the relatively wide range of pH values exhibited by the solutions after 60 min would indicate the products of reaction were not identical for all photocatalysts. Additionally, although the products of reaction were not monitored, it is clear that the different trends in pH exhibited by the samples over the course of the reaction, and in particular between the metal containing and metal-free titania indicate that the degradation products and pathways are not identical. The titania in particular appears to rapidly release acidic species into solution whereas the metal containing systems, while degrading the dye more rapidly (Fig. 7a) apparently release degradation products which are less acidic. While it is accepted that the addition of transition metal ions to titania may impact on the PZC of the titania and may consequently impact on the observed reaction rates (Fig. 7a as previously observed for certain acidic substrates [37]), the solution pH is unlikely to be affected by sample to sample variation in PZC unless the surface was able to effectively buffer the solution by adsorbing differing amounts of acidic product molecules onto a negatively charged surface. In the absence of data identifying the different product molecules in solution, it is difficult to provide a definitive answer, however, it is more likely that a range of degradation products exist and that the presence of metal clusters and the nature of the metal influence the product formed. Experiments are being performed to further elucidate this aspect of the work.

4. Conclusions

FTIR and EPR characterisation results demonstrated that the addition of metal clusters to titania creates a sink for photogenerated electrons thus decreasing the rate of charge recombination, i.e., improving charge separation. Evidence for electron transfer from TiO₂ to metal cluster was observed, and this process appeared

to occur in all metals tested, and was independent of the nature of the hole scavenger. Furthermore, measurements suggested that shallow trapped or delocalized electrons in the conduction band, are transferred to the metal clusters. The addition of metal clusters to TiO₂ resulted in an improvement of the catalytic performances in the degradation rates of Rhodamine 6G. The improvement seems to be related to improved charge separation resulting in a higher concentration of reacting species on the catalyst surface. The presence of metal cluster appeared to result in different degradation products from the metal-free titania as indicated by a monitoring of the solution pH.

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