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# Methanol photo-reforming with water on pure titania for hydrogen production

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**Abstract.** The behavior of titania for the photo-reforming of methanol with water at ambient temperature has been examined. It is shown that the reactivity is very poor, compared with metal-loaded catalysts at low methanol levels in solution, but the rate becomes much higher at high methanol levels, such that the difference from metal-loaded samples is much less. The optimum yield is with approximately a 1:1 methanol/water solution. The reaction also proceeds well in the gas phase. During all such catalysis the titania becomes blue, due to light absorption increasing across the range 400-800 nm. However, this does not result in visible range activity for the photo-reforming and is due to the reduction of the material in the presence of light and the formation of anion vacancies and $Ti^{3+}$ centres. These anion vacancies are only very slowly re-oxidised in air on P25 titania, taking days to recover the original whiteness of the oxide. The performance of anatase, rutile and the mixed phase are compared.

## Introduction

Titania has traditionally been an important material in terms of its optical properties and has been added as a white pigment to paint (the main use for titania) for a long time. However, it has become of much more modern technological significance since it is now used for a wider variety of applications. Of most importance, and again related to its interaction with light is photocatalysis. Titania is used for cleaning up the environment (e.g. NOx removal) via embedding in, for instance, pavements and roadways[1], for removing aqueous pollution, for cleaning window surfaces when used as a coating.[2] However, another important area for the future is its use in anaerobic conditions for producing hydrogen[3-6].

One of the first papers to suggest this was the much quoted work of Fujishima and Honda[7], although they did actually show the amount of any, if any, hydrogen, just the photocurrent generation in an electrolyte. Such materials have evolved considerably over the years to give much enhanced yields of hydrogen, especially when doped at the surface with metal nanoparticles[3, 8-10], and when used in combination with a hole scavenger, such as methanol[3, 8-10]. There are also many reports of more complex systems which can operate in the visible region of the spectrum, though rates are usually lower than for metal doped titania when applied over the whole solar spectrum at ground level.

Although there has been considerable work on titania itself, it is mostly in aerobic conditions, and mainly for the uses described in the first paragraph. Much less has been done in pure inert or vacuum conditions.

In more recent times titania has become a material of some fascination to the surface science community, largely because it is one of the few bulk oxides which can have enough conductivity in UHV conditions to be imaged at atomic resolution by scanning tunneling microscopy (STM)[11-14]. Here it is seen that reduction has significant effect on the colour of the material, its conductivity and also its surface structure.

In the work here we report results for the photocatalytic reforming of water with methanol in anaerobic conditions, and show that titania alone is capable of carrying out this reaction, but only at high methanol concentrations. There is a very strong dependence of the rate on the methanol concentration, which is very different from the much more often reported rates for metal-doped titania. In concert with this there are changes in the colour of the titania with the material becoming intense blue during the reaction. The relevance of these changes for the photocatalysis is discussed.

## Experimental

All experiments were carried out in a 250ml round bottom Pyrex flask equipped with a rubber septum for sample extraction using a gas-tight syringe (1 ml, Hamilton). The required amount of catalyst, typically 150 mg was placed in the reactor with the desired quantity of methanol and solution made up to 200 ml with MilliQ water. The initial reaction mixture was sonicated for 30 minutes to disperse the catalyst and provide thorough mixing of the components. The solution was then purged with argon for 30 minutes to remove air from the headspace and any dissolved oxygen from the system. Illumination of the reaction mixture was performed by a 150 W Xe arc lamp (LOT-Oriel) with constant stirring using a magnetic bar. Headspace samples were taken periodically (every 30 minutes) by gas tight syringe and were used to calculate hydrogen concentration. Analysis was performed on a Shimadzu GC (mode 2014), containing Haysep-N and molecular sieve (Shimadzu 80-100 mesh) columns arranged in series. The reproducibility of photocatalytic data, over 4 sets for the same system, is a mean deviation of ± 3% of the hydrogen yield.

Pellets of pure titania (P25, anatase and rutile) were made by using a die set to compress 300 mg into a 13 mm diameter disc with ~1.5 tonnes of pressure. These pellets were placed into a 250 ml Pyrex round bottom flask supported on a 3D printed stick, and purged with inert gas ($N_2$, Ar or He) to remove oxygen. Depending on the test the round bottom flask was either empty, containing 20 ml of water or 20 ml of 50% methanol/water solution.

## Results

### 1. *Photocatalytic reforming of methanol.*

The reaction of a high concentration of methanol in water over P25 titania was measured over time and is shown in figure 1. Here we can see that there is an induction time before hydrogen production begins, but which then increases with time and is near linear after around 150 mins. It is clear that a significant amount of hydrogen is produced. We have varied the methanol concentration in solution and the dependence of hydrogen evolution rate on concentration is shown in fig 2 (the time evolution curves are shown in fig S1). Here a maximum in rate is observed somewhere in the region 20-50% methanol. We also compare this with the more usual catalysts used for this reaction in fig. 3 and fig S2 – namely those loaded with precious metals. The major differences are that

i) the rates are always higher when metal is present

ii) the rates show the most difference when the methanol concentration is low, but the difference is reduced significantly at high methanol concentrations as is the case in fig. 3.

iii) there are colour changes in the catalyst under irradiation which are quite different with and without metal loading, as discussed below.

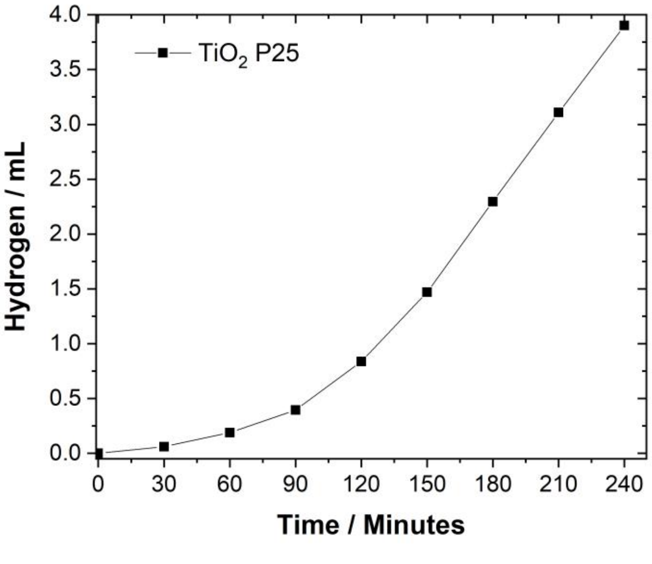

**Figure 1.** Hydrogen production as a function of time from 200 mL of 50 % methanol in water solution and 50 mg of TiO2 (P25).

We have previously shown that rates are very high for metal-loaded catalysts even at very low methanol concentrations, for which rates are immeasurably small without metal. However, for the Pd-loaded catalysts, the rate is near zero order already at very low methanol concentrations (0.02%) and increases relatively little between 0.02% and high levels [15, 16]. Clearly metal loading has a very positive effect on the reaction, which is probably a combination of the extended lifetime of the excited electron by trapping on the metal particle [17, 18] together with direct involvement of the metal in the chemical conversion pathway[3].

We also examined the reaction of two different polymorphs of titania under these high methanol concentrations in fig 3, which shows that P25 is far better than either anatase or rutile individually, though the combination of the two gives significantly higher rates, as reported by others [8, 19, 20]. Thus P25 (a combination of ~80% anatase and 20% rutile made by air pyrolysis of $TiCl_4$) has the highest rate, while anatase and rutile physically mixed shows approximately 4x the rate which could be obtained from the sum of the individual components. Clearly, then, there is the synergistic effect of the combination which has been reported by others.

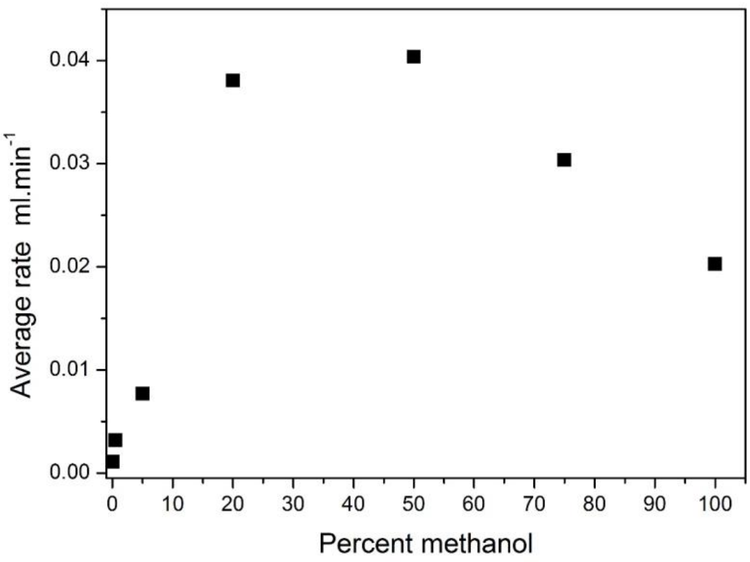

**Figure 2.** Rate of hydrogen produced from 150 mg of TiO2 (P25) and 200 mL of various volume concentrations of methanol in water.

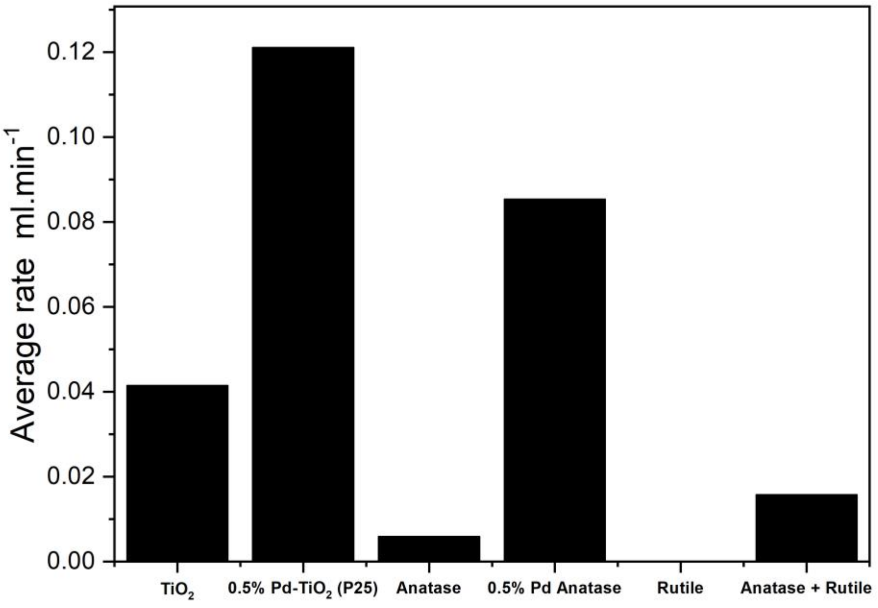

**Figure 3.** Average hydrogen production rates in ml.min$^{-1}$ from 200 mL of 50 % methanol in water solution. For 150 mg of catalysts $TiO_2$ (P25), 0.5%Pd-$TiO_2$ (P25), $TiO_2$-anatase, 0.5%Pd-anatase and a mixture of anatase + rutile (0.075 mg of each).

### *2. Reaction of related molecules*

A number of publications refer to various intermediates involved in methanol photoreactions on TiO2 – such as formaldehyde and formic acid for instance. So, to determine whether these were end points for the reaction, we examined the reactions of these two molecules. The results are shown in fig. 3 and what this makes clear is that the reaction rate of these molecules is significantly higher than for methanol, showing that they cannot be end points, but may perhaps be short-lived intermediates in solution.

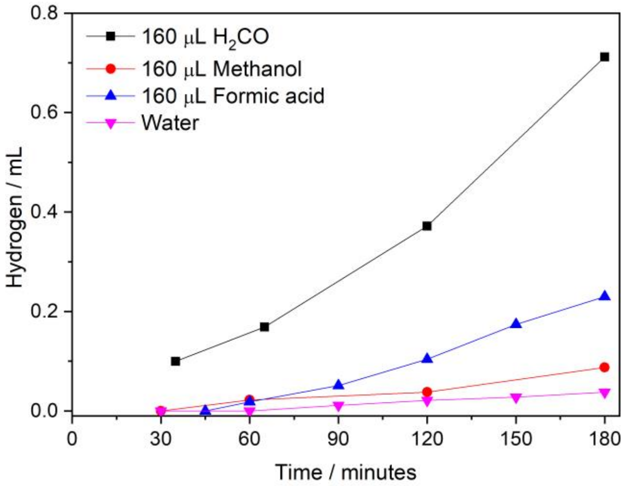

**Figure 4.** Hydrogen production as a function of time. 150 mg of $TiO_2$ (P25) and 200 mL of MilliQ water with 160 μL of formaldehyde, methanol or formic acid added.

### 3. *Blue titania and UV-vis spectra*

As often reported, titania can become blue in the presence of reducing agents such as methanol and other alcohols[21-28], and this is indeed the case here during photocatalytic reactions with pure $TiO_2$ (P25) with 50 % methanol in water (figure S3). It is important to note here that metal-loaded titania does not attain this blue colur during photocatalysis. To investigate this further, the blue $TiO_2$ powder was recovered (by filtering and drying) at the end of a photo reaction and analysed by UV/Vis spectroscopy. Figure S4 shows the UV/Vis analysis of $TiO_2$ (P25) before reaction, after reaction, one month later (after being exposed to air) and one month later and calcined in air (400 C for 3 hours).

We have also carried out experiments with the disc form of P25, as described in the experimental section. Figure 5 shows the absorption spectrum of the disc after removal from the reactor. The initial colour is shown in the inset and it is, of course, much more intense here since the titania is not diluted by solution (as it is in fig S4). The pelleted material is an intense blue, and the UV-vis spectrum reflects this with absorption increasing in the region between 400 nm and 800nm. However, it is not only in the presence of a reductant that this blue colour is observed, it also occurs after exposure to the lamp in an inert gas – He or N2, as is the case in fig 5 (exposure for 1 hour in N2). As can be seen this absorption diminishes over time after removal from the reactor into air, but very slowly, having much higher absorption at 800nm than the initial white P25 even after 120 hours exposure. Note that exposure of the titania in air to the lamp did not produce the blue colour.

Of course, it may be possible that there are very small amounts of a reductant present, and it is this which reduces the titania. We can estimate how much this might be. It is known that pure titania changes colour upon reduction [1-4] Both Diebold[11] and ourselves[12-14] have associated this colour change with the presence of $Ti^{3+}$ interstitials and reduction of the material, and have also associated it with changes of colour during reduction/re-oxidation. The blue colour is thought to be due to the presence of these interstitials at very low levels ($TiO_{2-x}$, where <0.001), with higher levels resulting in the darkening of titania and the formation of black titania, at which point Magneli phases/shear planes are formed. Aona and Hasiguti[29] carried out detailed measurements by EPR and estimate that these phases appear above ~ $x=3x10^{-4}$. Note that the blue colour seen in figs 5, S5, S7, S8 seems to be the limit of reduction in these experiments; the sample never goes grey or black.

So, on this basis we can give a rough estimate of how little of a reductant is required to form a level of vacancies with, say, $x=10^{-4}$, which seems to be associated with the level we would expect for the blue colour to be present. The pellets weigh approximately 0.3g representing 0.004 mol of titanium and $O_2$, and twice that number of O atoms. Thus, at $x=10^{-4}$, we have ~ $8 \times 10^{-7}$ vacancies, which is the same as the amount of reductant required, if we assume 100% efficiency of reaction and removal of one oxygen atom per reductant (and it may of course be more oxygen than that per reductant, depending on the nature of the reaction). So that represents $8 \times 10^{-7}$ mol of the reductant, or approximately 0.01% in the 250 ml flask. We cannot be certain that that kind of level of reductant was not present in the flask.

In that sense Fig S5 also shows the result from exposure of the disc form of the pellet to a gas phase methanol/water mix, and the same kind of blue colour is formed, and very quickly.

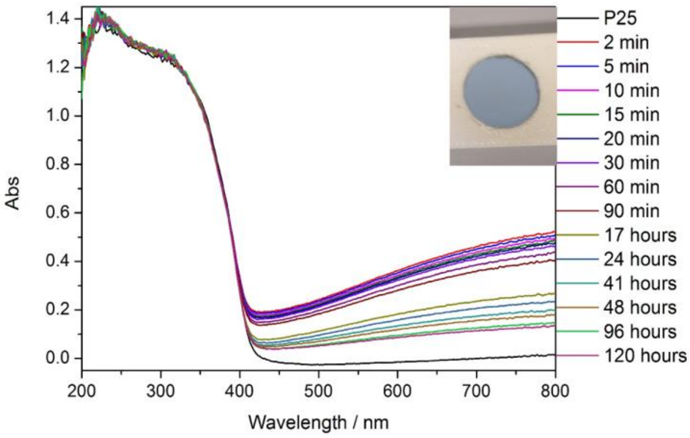

**Figure 5.** UV/Vis spectra of a 13 mm TiO2 (P25) pellet after irradiation for one hour in an atmosphere of N2. Scanned at various time intervals after being exposed to air, as indicated.

## Discussion

In previous publications [3, 15, 16, 30-33] we have noted how much better metal loaded titania is than the unloaded material for hydrogen production by photoreforming at ambient temperature. The significance of the metal was its importance in activating methanol (and other similar molecules [10, 20, 32]), especially its ability to perform dehydrogenation/decarbonylation of the alcohol [33, 34]. However, most of that work was carried out at very low methanol concentrations in solution and it is clear from the data here that titania becomes much better at the reaction at high alcohol concentrations. Thus at a methanol concentration of 160 microlitres (0.08%) in there is a factor of 50 difference between titania and 0.5 wt% Pd/TiO2, whereas at 50% methanol in solution the rate difference has reduced to a factor of 3, fig. 3.

Obviously then the titania is itself capable of decomposing and photoreforming the methanol at these high concentrations, though at the highest concentrations it becomes negative order (fig 2). It is likely from the IR work of Arana et al [35], that the major intermediate present at the surface is the formate under these circumstances. It is also likely that the adsorption constant on titania alone is such that the surface does not compete well with water at low solution concentrations and that the coverage increases at higher concentrations, as suggested in other work [28].

However, the observation that a blue colour is seen after a short time of irradaiation begs the question – is it only blue titania which can carry out the reaction? This is supported by the observed induction time for the blue colour during irradiation. Maybe the defects induced by the irradiation are important for the reaction. However, at low methanol, the samples still go blue after a short time of irradiation, but the rate does not increase significantly at this point. It is our feeling that the blue colour is not required for hydrogen production, as described below, and is due to very much minority species which may anyway reside in the bulk of the sample [14].

What is the nature of this blue colour? Well, it is most likely to be due to the formation of electron-hole pairs, but these are normally associated with a very short lifetime before recombination, with a half life in inert of the order of nanoseconds [17], or a hundred nanoseconds or so [18] for very thin colloidal films. As shown in figure 6 below, the lifetime of these states on P25 here is very long when formed in inert gas; it does not go blue in air or oxygen. Clearly, then, this is a different process than that reported by Tang et al [18] . The loss appears to be in two stages, one in the first hour or so, which is rapid compared with the second which takes place over days. Even after 5 days, the colour has not returned to the white colour of the original P25. Fig S6 is a plot of ln(absorbance) against time (as log scale to clarify the short time change) and clearly shows the two different orders associated with this process of decolourisation. The half lives are around 200 mins for the fast process and around 4000 mins for the slower one.

It is likely that the longevity of the blue colour is due to the loss of holes ($O^-$) to the gas phase as oxygen (see below), leaving anion vacancies and (probably localised electrons), as described for single crystals of titania [12, 14].

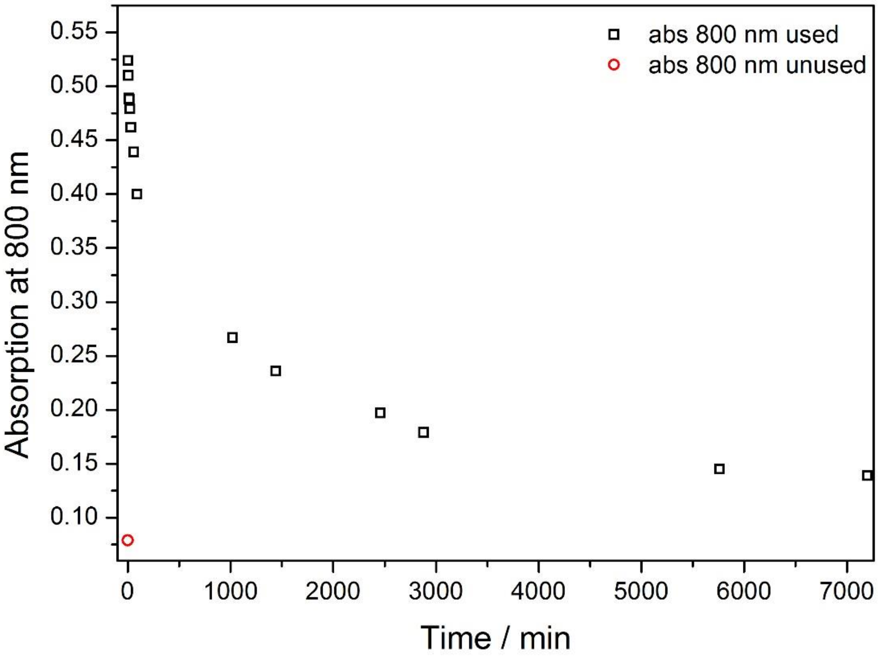

**Figure 6.** The decay of absorption in the visible as a function of exposure time to air, from the data of fig 5.

The very slow nature of this second process indicates that it is not due to normal e-h recombination since it is so slow. Our only explanation for this occurring in the presence of inert gas is that a process occurs by the electron (effectively $Ti^{3+}$) remaining trapped in the solid and the hole (effectively $O^-$) is somehow lost perhaps as follows. However, as described above, we also cannot discount a very small amount of a reductant being present during the experiment, as the cause of oxygen loss from the material.

$Ti^{4+}O^{2-} + hv \rightarrow Ti^{3+} + O^-$

$O^- \dashrightarrow 1/2O_2 + e^-$

It is likely that the latter also results in $Ti^{3+}$ formation. Work on single crystals of titania [11] has shown that high temperature treatment in vacuum results in reduction and the production of interstitial $Ti^{3+}$, and variations of colour from transparent pale blue to deep blue to black, depending on the extent of reduction. Although the colour can be deep, and the effect on electrical conductivity high [11, 13, 14], nevertheless this all occurs with very low levels of non-stoichiometry, with x in $TiO_{2-x}$ being very low, typically $< 0.001$ [13, 29] Such defects are induced by high temperature treatment, whereas here they are produced by photo-excitation at ambient temperatures. Under these conditions it is most likely that the colour centres are simply a combination of $Ti^{3+}$ sites, and oxygen vacancies with itinerant 3d electron states of some considerable mobility in the conduction band. That they have considerable mobility is evident from investigating the discs above after irradiation. The disc is around 1 mm thick, so the rear of the disc is well outside the penetration depth of the light and yet it becomes blue relatively quickly (within 5 minutes) on the front and within 30 minutes at the back. Fig S7 shows that the middle of the disc can still be white if irradiation is stopped after 5 minutes.

Clearly then the material has to re-oxidise, presumably by the reverse of the equations above, and this is apparently very difficult on P25, hence the slow loss of colour shown in fig 5. Note however, that when the irradiation is carried out in air the sample remains white, so presumably the loss mechanism is countered by re-ad/absorption of oxygen in the sample before it can penentrate the material to any significant degree. It is interesting to note that it is only P25 which shows this behaviour: both anatase and rutile titania also go blue (and indeed rutile is a more intense blue, see figure S8, but when exposed to air go white extremely quickly. Like P25 they do not go blue in air.

The nature of the two different rates of re-oxidation on P25 probably relates to two different processes taking place. The faster process is re-oxidation of the surface region, followed by a slower bulk process, perhsaps limited by inter-grain and inter-nanoparticle transport, especially between nanoparticles of anatase and rutile in the sample.

But does this blue colour have any significant influence of the reaction rate? For instance, can the photons absorbed in the visible region induce photocatalysis? The answer appears to be no, because measuring the rates with various filters in place (figure S9 shows the absorbance profiles of the filters) shows hydrogen production only in the range <~ 400nm, figure 7, in other words it is still the normal band gap excitation of the titania which is the important energy storage mechanism for driving the catalysis, even though the sample absorbs light in the visible region.

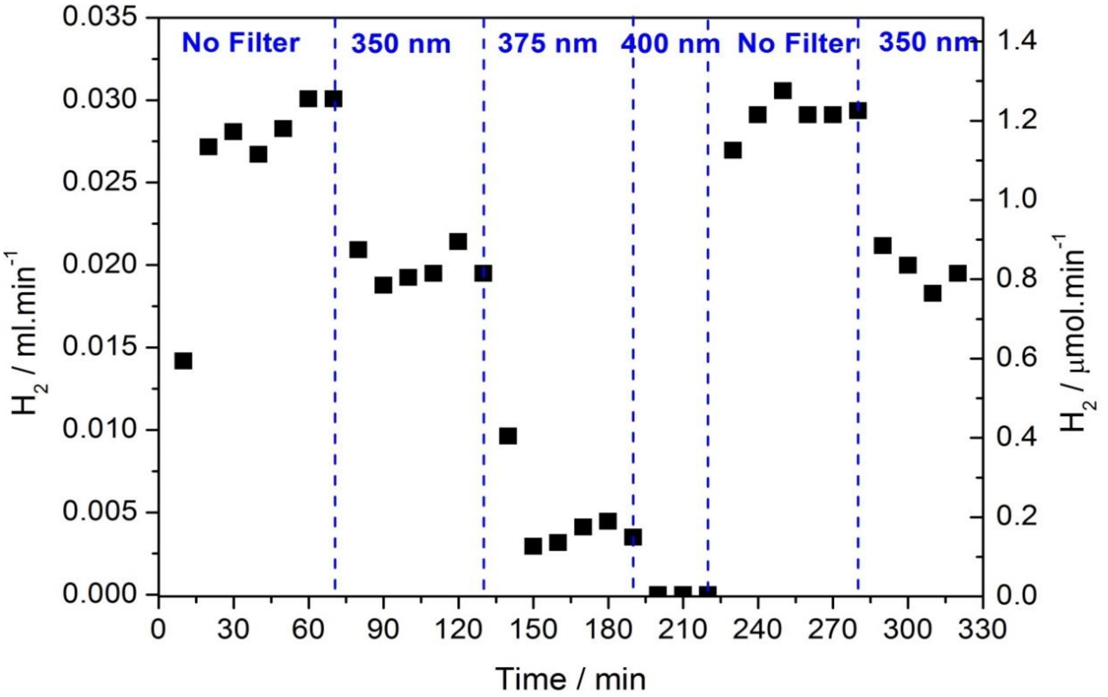

**Figure 7.** Rate of photocatalytic $H_2$ evolution from a 0.5% Pd-$TiO_2$ catalyst made by incipient wetness with a series of long band pass filters. Reactions was performed under continuous flow operation, 30 ml.min$^{-1}$ $N_2$ flow, 150 mg catalyst, 1 ml of methanol and 200 ml water.

In conclusion it appears that P25 titania is active for methanol phot-reforming in water, but only at relatively high levels of methanol. Metal loading in the catalyst results in much higher rates when methanol concentration is low, but the gain is much less at high methanol concentrations, though metals do still promote photo-reforming even then. The samples go blue when metal is absent, but this blue colouration does not result in visible light activity for the materials. The blue colouration is likely to be due to the formation of anion vacancies within the material.

**Data accessibility.** There is supplementary information on the journal webpage. There are seven figures there. Fig. S1 shows the time dependence of hydrogen evolution for different mixes of methanol/water while fig S2 shows the same, but for several different materials. Fig. S3 shows the change in colour of the catalyst during irradiation in the liquid phase. Fig S4 shows the UVvis spectra of P25 titania before and after use in the liquid phase and fig. S5 shows the colour change of a titania disc during irradiation. Fig. S6 gives the time dependence of air re-oxidation of a disk, while S7 shows the cross-section of a disc to show only partial reduction during irradiation at short times and S8 displays a deep blue colour for irradiated rutile. Fig. S9 presents the absorption characteristics of the filters used in the study.

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