Investigation of the photocatalytic activity of TiO_2–polyoxometalate systems for the oxidation of methanol

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Abstract

We have developed a TiO_2–POM co-catalyst system for use in a hybrid photo-electrochemical cell to oxidize methanol. We employed a simple α-Keggin-type polyoxometalate ($PW_{12}O_{40}{}^{3-}$) that is known to adsorb to the surface of positively charged TiO_2 particles at low pH. The use of a co-catalyst dramatically improves the separation of photogenerated electron–hole pairs in suspended TiO_2 nanoparticles, leading to a 50-fold increase in the observed photocurrent compared to the use of TiO_2 alone. The photocurrent densities we observed exceeded those recently reported by Kamat and co-workers [K. Drew, G. Girishkumar, K. Vinodgopal, P.V. Kamat, J. Phys. Chem. B 109 (2005) 11851]. Due to the improved charge separation offered by the co-catalyst system, electron transfer from the reduced polyoxometalate to the anode now appears to be the kinetic limitation. In addition, we find that the polyoxometalate itself can oxidize methanol efficiently in the absence of TiO_2. However, photogenerated holes in the POM are unable to oxidize either formic acid or acetic acid, in contrast to the behavior of TiO_2. The dependence of the photocurrent on $[PW_{12}O_{40}{}^{3-}]$ was also investigated. We find that the optimum $[PW_{12}O_{40}{}^{3-}]$ is approximately 2 mM.
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1. Introduction

Fuel cells are environmentally benign and versatile alternative power sources that are currently under active development. Direct methanol fuel cells (DMFCs) are a relatively new fuel cell technology, and are promising candidates to supply power to mobile phones, laptop computers and other low power-density applications. In a DMFC, methanol is oxidized in the presence of water to produce CO_2 and protons at the anode. Electrons flow through the external circuit while hydrogen ions cross a proton exchange membrane (PEM) to combine with oxygen at the cathode to form water. Existing DMFC technology is limited by several factors, including the use of precious metals such as platinum in both the anode and cathode, poisoning of the catalyst by CO adsorption, thermal management issues, and lower efficiencies than other types of fuel cells.

Several strategies have been explored in an attempt to improve the overall efficiency of DMFCs. For example, efforts have been made to minimize the use of Pt in the catalyst either by increasing the electrode surface area or by exploring alternative catalyst materials [1]. More recently, several groups have looked into ways of incorporating photocatalysts such as TiO_2 on the anode side of the DMFC to further improve device performance and reduce the amount of precious metals in the catalyst. The use of photons to boost DMFC performance may be practical in applications where the fuel cell is operated outdoors under ambient illumination. In such a hybrid device, UV photons absorbed by the TiO_2 would generate electron–hole pairs by promotion of an electron from the valence band to the conduction band of the TiO_2 [2]. If the electrons can be collected efficiently, thereby minimizing the rate of electron–hole recombination, the holes can be used to carry out oxidative chemistry. This basic approach has been used successfully for many years to oxidize methanol at wide band gap semiconductors using UV irradiation [3–9], for CO_2 fixation [10], and for the remediation of environmental pollutants [11].

Electron–hole recombination is always a critical issue in the efficiency of TiO_2 photocatalyst systems, regardless of the application. The solution to this problem has typically been to use a sacrificial oxidant, such as dioxygen, to scavenge the photogenerated conduction band electrons, but this is not always an efficient process [12]. Another approach is to adsorb the TiO_2 photocatalyst directly onto the surface of an electrode where the

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electrons can be collected by applying a suitable voltage. Kamat and co-workers recently have shown that such an approach is workable in principle in a hybrid DMFC [13]. These workers deposited TiO_2 particles onto an anode formed from carbon fibers and showed that photocurrents arising from the photo-oxidation of methanol could indeed be collected. Interestingly, improved performance in the dark was also observed, which might be due to the mitigation of poisoning effects by adsorbed TiO_2. A possible drawback to this approach, however, is that there must be a robust electrical contact between the anode and the photocatalyst. For example, if any kinetic barrier exists at the junction between the anode and the TiO_2, the electron collection efficiency will be reduced and device performance will suffer due to increased electron–hole recombination rates in the semiconductor.

An alternative approach would be to employ an electron scavenger such as a polyoxometalate (POM) to transport electrons from suspended TiO_2 particles in the supporting electrolyte to the anode. This would offer the additional advantage of being able to turn over a larger fraction of the incident photons by using more TiO_2 than could be directly adsorbed onto the surface of the anode. The ability of polyoxometalates to accept electrons readily has been known for many years. Upon chemical or electrochemical reduction, many polyoxometalates form stable, highly colored mixed-valence species generically termed 'heteropoly blues' [14,15]. Ozer and Ferry have investigated the use of POMs such as $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $W_{10}O_{32}^{4-}$ to facilitate the transfer of photogenerated TiO_2 conduction band electrons to dioxygen as a means of increasing the efficiency of the photodegradation of 1,2-dichlorobenzene [16]. Using TiO_2–POM mixed systems, these workers observed an eight-fold increase in the apparent degradation rate of 1,2-dichlorobenzene compared to TiO_2 alone. Zhao and coworkers have reported similar findings, but also discovered that different product distributions can result when using TiO_2 alone or in tandem with POMs [17]. POM systems have also been shown to be viable in fuel cell applications. For instance, Dumesic and co-workers have demonstrated that it is possible to use POMs such as $PMo_{12}O_{40}^{3-}$ to drive a fuel cell by oxidizing CO to CO_2, thus bypassing the water gas shift reaction [18]. Electrons were stored in the form of $PMo_{12}O_{40}^{5-}$ and later collected at a gold electrode.

With these results in mind, we decided to investigate the possibility of using POMs to catalyze the transfer of photogenerated electrons in TiO_2 to a Pt anode in an electrochemical cell. The operation of these 'soluble photoanodes' as a component of a DMFC is illustrated in Scheme 1. In this study, we employed a simple α-Keggin-type polyoxometalate ($Na_3PW_{12}O_{40}$) to scavenge electrons from photoexcited TiO_2 particles suspended in solution. The reduced polyoxotungstates were subsequently oxidized back to the parent Keggin complex at the Pt anode, resulting in a photocurrent. Using a POM to collect and store photogenerated electrons from TiO_2, we have observed a 50-fold increase in the methanol oxidation photocurrent as compared to the use of TiO_2 alone. Indeed, the photocurrent densities we measured were higher than those reported by Kamat and co-workers [13].
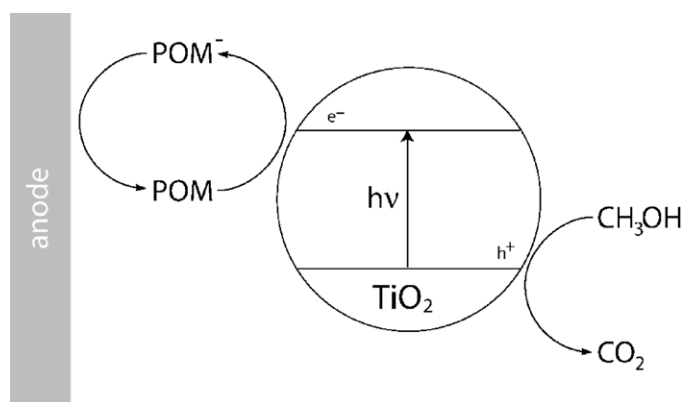
Scheme 1. POM-mediated electron transfer from the conduction band of TiO_2 to a Pt anode.

2. Experimental section

2.1. Materials and reagents

TiO_2 powder (Degussa P-25), with an anatase to rutile ratio of 8:2, a surface area of $50\,m^2/g$ and average particle diameter of 30 nm, was used as received. Methanol (99.9%, Fisher Chemical), perchloric acid (Fisher Chemical) with a nominal composition of 69–72% $HClO_4$, acetic acid (Fisher Chemical), formic acid (Fisher Chemical), and $Na_3PW_{12}O_{40}$ (>99.9%, Sigma–Aldrich) were used as received. Millipore-Q purified distilled water (18 MΩ/cm) was used to make up all solutions.

2.2. Electrode preparation

Pt electrodes were cleaned by rinsing sequentially with distilled water, absolute ethanol, piranha solution (1:3 (v/v) 30% H_2O_2, 18 M H_2SO_4), distilled water, and absolute ethanol. After being dried in a stream of flowing nitrogen, the clean Pt was annealed in a H_2 flame for several minutes. The cleanliness of the Pt electrodes was verified by cyclic voltammetry prior to making measurements.

2.3. Photoelectrochemistry

Photoelectrochemical measurements were carried out in a Rayonet Photochemical reactor (RPR-100, Southern New England Ultraviolet Company) equipped with RPR 3500 lamps (ca. $500\,\mu W/cm^2$ for $\lambda = 350\,nm$). The temperature inside the reactor was maintained at $35\,^\circ C$ with a cooling fan in operation. A 20 mL vessel made of Pyrex glass was used as the photoelectrochemical cell. The pH of the reaction suspension/solution was adjusted to 1.0 before reaction (after the addition of $Na_3PW_{12}O_{40}$). A platinum flag electrode (approximately $0.77\,cm^2$), a Ag|AgCl(sat) electrode and a platinum gauze electrode were used as the working, reference, and counter electrodes, respectively. Nitrogen gas (>99.9%) was used to purge the suspension during the experiment. The Pt anode was held at a potential of +0.60 V versus Ag|AgCl(sat) to measured the generated photocurrent. The potential of the working electrode was controlled using a

potentiostat (Pine Instruments, AFRDE-4) connected to a computer. Data was acquired using Lab View.

3. Results and discussion

Representative photocurrent–time data for a series of four experiments are presented in Fig. 1. In all cases, the concentration of methanol was fixed at 0.2 M and the pH was adjusted to a value of 1.0 using perchloric acid, which also served as the supporting electrolyte. The solutions were rigorously purged with N_2 prior to all experiments and N_2 was flowed continuously through the photoelectrochemical cell during data acquisition to prevent reaction of the reduced POMs with dioxygen. The anode (Pt, 0.077 cm^2 geometrical surface area) was poised at a potential of 0.6 V versus Ag|AgCl(sat) to ensure efficient collection of the reduced POM. In the first experiment, Fig. 1D, a solution containing 1 mM POM and 0.05 mg/mL TiO_2 was held at a potential of 0.6 V in the dark. The data clearly indicate that no significant electrochemical oxidation of any of the solution components occurs under these experimental conditions.

We then performed an experiment in which a 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution containing 0.05 mg/mL TiO_2 but no POM was irradiated at 350 nm. This concentration of TiO_2 was chosen to ensure that there was no significant settling of particles during the course of the experiment. Typical data are shown in Fig. 1C and are characterized by a very slow increase of current as a function of time over the course of many hours. We estimated the steady state photocurrent to be about 0.81 mA cm^{-2} for this experiment. The low photocurrents measured under these experimental conditions are a result of the poor efficiency of photo-oxidation processes in the absence of an electron scavenger.
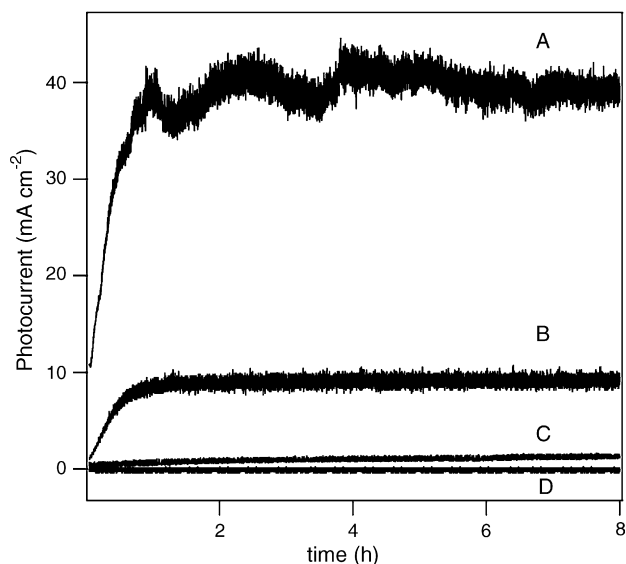

Fig. 1. Photocurrent vs. time plots for samples irradiated at 350 nm. (A) 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution with 0.05 mg/mL TiO_2 and 1 mM $PW_{12}O_{40}^{3-}$. (B) 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution with 1 mM $PW_{12}O_{40}^{3-}$ (no TiO_2). (C) 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution with 0.05 mg/mL TiO_2 (no POM). (D) 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution with 0.05 mg/mL TiO_2 and 1 mM $PW_{12}O_{40}^{3-}$ in the dark.

Next, we carried out an experiment in which a 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution was irradiated in the presence of 1 mM $PW_{12}O_{40}^{3-}$, Fig. 1B. In this experiment, the photocurrent increased rapidly and monotonically over the course of the first hour or so of irradiation at 350 nm, finally reaching a steady state value of 9.0 mA cm^{-2} after about 2 h. Interestingly, the steady state photocurrent we observed in this experiment is significantly larger than in the case of TiO_2 alone. This result provides clear experimental evidence that the $PW_{12}O_{40}^{3-}$ anion itself displays significant photocatalytic activity toward methanol oxidation, consistent with previous research on the photooxidation of alcohols by POMs [19]. Furthermore, our observation that $PW_{12}O_{40}^{3-}$ is a better photocatalyst than TiO_2 in the absence of O_2 parallels the results reported by Hill and Chambers, who compared the ability of semiconductor- and POM-based photocatalysts to photodegrade a series thioethers [20]. In addition, the solution was observed to turn blue upon irradiation, indicating the formation of a significant concentration of reduced POM. Finally, when methanol was replaced with either acetic acid or formic acid, no color change was observed and no significant photocurrents were detected at the Pt anode.

The reason that a photocurrent is observed when methanol is used as the substrate but not in the other cases is that while the oxidized form of the POM can oxidize methanol, it is not able to oxidize either formic acid or acetic acid under our experimental conditions. There is some debate in the literature about the exact nature of the POM that facilitates electron transfer to the anode. On the one hand, Park and Choi claim that both ground state and excited state POM can serve as effective electron acceptors [21]. In their view, photoexcited POMs can accept an electron from a donor species in solution to produce POM^-, which can then be oxidized back to POM at the anode. Photocurrent data obtained by these workers from solutions containing POM alone and compared to data from solutions containing mixtures of POM and TiO_2 appear to bear this out. On the other hand, Ozer and Ferry assert that the electron mediator is exclusively ground state POM, presumably on the basis of the weak absorption of the POM at the narrower band of wavelengths used in their experiments [16]. Our results clearly show the ability of the photoexcited state of the POM to oxidize methanol, although the oxidizing power of the POM excited state holes does not match that of the photogenerated holes in TiO_2.

Finally, we irradiated a 0.2 M $CH_3OH + 0.1$ M $HClO_4$ solution that also contained 0.05 mg/mL TiO_2 and 1 mM $PW_{12}O_{40}^{3-}$, Fig. 1A. As in the previous experiments, the photocurrent increases almost linearly over the course of about two hours and then reaches a plateau value. In the case of the mixed TiO_2–POM system, however, the rate of increase of the photocurrent with respect to time appears to be somewhat greater than in the previous measurements. In this experiment, a steady state current of about 40 mA cm^{-2} was observed. This is about 50 times greater than the steady state photocurrent we observed for TiO_2 alone and about a factor of four greater than in the case of POM alone. As before, the solution turned blue upon irradiation, demonstrating that reduced polyoxomtalates are formed.

When methanol is replaced with either acetic acid or formic acid, photocurrents similar to those previously reported by Park and Choi were observed [21]. These findings confirm our earlier assertions about the oxidizing power of the photoexcited POM as compared to TiO_2. The formation of CO_2 as a reaction product was qualitatively confirmed by headspace analysis using FTIR spectroscopy. The characteristic vibrational modes of CO_2 are clearly observed as intense bands in the spectra. Taken together, our observations are consistent with a mechanism whereby methanol is oxidized by the TiO_2 excited state as shown in Scheme 1. Of course, we cannot rule out the existence of other, parallel reaction pathways, such as the formation of formaldehyde [22]. Similarly, Fox et al. showed that, in the presence of dioxygen, methanol is oxidized to formaldehyde using phosphotungstate photocatalysts [23].

Perhaps most importantly, however, the blue color of the solution persists for several minutes after the light is turned off. This observation is an unambiguous demonstration of the fact that the conduction band electrons from photoexcited TiO_2 are scavenged so efficiently by the POM that the rate of oxidation of POM^- at the anode now represents the kinetic bottleneck in the system. The highly efficient electron transfer from the conduction band of TiO_2 to POM is in great part due to the fact that POMs such as $PW_{12}O_{40}^{3-}$ adsorb strongly to the surface of TiO_2 particles, which are positively charged at pH 1. As noted earlier, Ozer and Ferry compared a series of POMs to dioxygen as electron scavengers in the photodegradation of 1,2-dichlorobenzene (DCB) using TiO_2 suspensions under UV irradiation [16]. The binding constants between the electron acceptor (either dioxygen or POM) and TiO_2 correlated reasonably well with the Langmuir–Hinshelwood kinetic data they measured for DCB decomposition. Specifically, the binding constants for $PW_{12}O_{40}^{3-}$ and O_2 adsorption on TiO_2 at pH 1 were found to be 467 and 84.6 M^{-1}, respectively, a ratio of 5.5:1. The apparent rate constants for DCB degradation were reported to be 0.638 and 0.0818 min^{-1}, a ratio of 7.8:1. More recently, Zhao and coworkers have carried out a detailed mechanistic study of the TiO_2 $PW_{12}O_{40}^{3-}$ system as it pertains to the photodegradation of organic compounds [17]. These workers measured the adsorption of $PW_{12}O_{40}^{3-}$ onto TiO_2 under conditions similar to those of Ferry et al. using similar experimental methods. However, the binding constant reported by these workers is two orders of magnitude greater than that reported by Ferry and co-workers. It should be noted that accurate measurement of Langmuir adsorption parameters can be notoriously difficult, especially in cases where the kinetics of adsorption and/or desorption are slow, owing to the fact that the measurement system may not be at thermodynamic equilibrium. In addition, other factors, particularly ion pairing interactions, are expected to play a critical role in the adsorption of POM on the TiO_2 surface, and these effects will be strongly dependent on the nature of the supporting electrolyte [24]. Another useful predictor of electron acceptor activity is the free energy change for the one electron reduction of the electron acceptor by TiO_2 conduction band electrons. The redox potential of $PW_{12}O_{40}^{3-}$ and the flatband potential of the TiO_2 (particle) conduction band are +0.218 and –0.189 V versus NHE, respectively [25,26]. Thus, electron transfer between
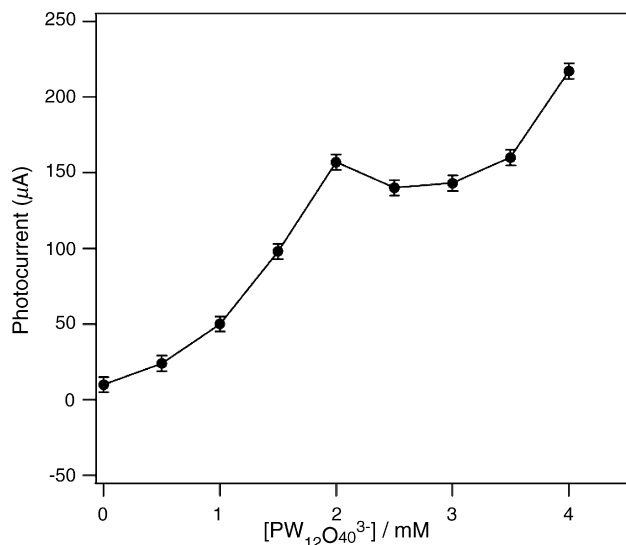

Fig. 2. Dependence of the steady state photocurrent on $[PW_{12}O_{40}^{3-}]$. The filled circles are experimental data points, while the line is a guide to the eye.

the conduction band of TiO_2 and $PW_{12}O_{40}^{3-}$ is thermodynamically favored by about 39 kJ/mol. It should be noted, however, that such arguments do not take into account many complicating factors that may be important in POM systems, including the diversity of electron acceptor states, the possibility that more than one electron may be transferred simultaneously and the fact that the acceptor and donor energy levels may be perturbed upon adsorption of POM to TiO_2.

To further investigate the scavenging of electrons from photoexcited TiO_2 by $PW_{12}O_{40}^{3-}$, we performed concentration dependent studies in which $[PW_{12}O_{40}^{3-}]$ was varied at a constant TiO_2 concentration of 0.05 mg/mL. As seen in Fig. 2, the steady state photocurrent increases with increasing POM concentration, reaching a maximum when $[PW_{12}O_{40}^{3-}]$ is about 2 mM. At higher $[PW_{12}O_{40}^{3-}]$, the steady state photocurrent decreases slightly, and then begins to increase again above ca. 3 mM. The observation of a local maximum suggests that interactions between the POM electron scavenger and the surface of the TiO_2 nanoparticles are important. Previous researchers have suggested that such behavior is due to competition between $PW_{12}O_{40}^{3-}$ and methanol for the finite number of surface sites on TiO_2 [16]. Assuming a Langmuir adsorption isotherm, and using Ferry's previously reported binding constants, a POM concentration of 2 mM corresponds to roughly 50% surface coverage. Zhao and coworkers have reported behavior similar to what we have observed; however, they offer a different interpretation [17]. These workers suggest that at elevated [POM], POMs in solution act as an 'inner filter', absorbing a significant fraction of the incident UV, and effectively blocking that radiation from being absorbed by the TiO_2 particles. This model predicts that if TiO_2 particles become encapsulated by POM, the adsorbed POM would essentially behave as a local UV 'filter', resulting in a lower absorbance by the TiO_2. This is not an entirely unreasonable possibility; for instance, it is well known that POMs readily adsorb to metal surfaces [27]. Nevertheless, such a fil-

ter effect seems not to be important in the case of methanol photooxidation, as evidenced by the increase of in steady state photocurrent when $[PW_{12}O_{40}{}^{3-}] > 3\,mM$. This increase may be due to increased absorption of UV by the POM relative to the TiO_2 at these concentrations, leading to direct oxidation of methanol by the POM excited state.

4. Conclusions

We have developed a TiO_2–POM co-catalyst system for use in a hybrid photo-electrochemical cell for the oxidation of methanol. Although the photocatalytic behavior of POM and TiO_2 photocatalysts are nominally quite similar [28], the use of a co-catalyst dramatically improves the separation of photo-generated electron–hole pairs in suspended TiO_2 nanoparticles, leading to a 50-fold increase in the photocurrent compared to the use of TiO_2 alone. Thus, the problem of efficient electron transfer out of the conduction band of the semiconductor appears to have been solved in our co-catalyst system. The use of Pt(0) clusters to improve the rate of electron transfer to and from POMs has been explored by several groups [19]. Such a strategy might lead to improved electron transfer between the reduced POMs and the anode in our photoelectrochemical system and will be explored in future studies. There also appears to be an optimum concentration of POM, above which direct oxidation of methanol by the photoexcited state of the POM competes with the oxidation of methanol by TiO_2.

Acknowledgements

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