

Effect of an external applied potential on the photocatalytic properties of manganese-doped titanium dioxide

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To cite this article:

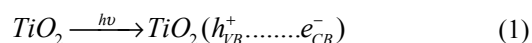
Gracien Bakambo Ekoko, Joseph Kanza-Kanza Lobo, Omer Muamba Mvele, Jérémié Lunguya Muswema, Jean-Félix Senga Yamambe. Effect of an External Applied Potential on the Photocatalytic Properties of Manganese-Doped Titanium Dioxide. *American Journal of Physical Chemistry*. Vol. 3, No. 4, 2014, pp. 41-46. doi: 10.11648/j.ajpc.20140304.11

Abstract: The electrochemical anodic oxidation method was used to prepare thin films of titanium dioxide (TiO₂) semiconductors (undoped and doped with Mn). These films were used to test the oxidation of methanol (CH₃OH), the degree of which was quantified by measuring the current density produced as a function of an applied potential between 0.5 V and 5.0 V. The value of the potential to be applied in order to prevent fast electron-hole recombination was determined. The observed phenomenon is explained by considering the wave nature of the electron.

Keywords: Anodic Oxidation, TiO₂, Mn-Doped TiO₂, Applied Bias, Tunnelling Process

1. Introduction

The remarkable photocatalytic properties of nanosized TiO₂ semiconductor particles have, in the recent past years, prompted an intense research work which still continues with unabated interest [1,2]. It is well known that TiO₂ (anatase) has a band gap of 3.2 eV. It can, therefore, be excited upon irradiation with ultraviolet light (UV) at 365 nm. This excitation leads to the promotion of electrons (e^-) from the valence band (VB) to the conduction band (CB) leaving behind holes (h^+) in the VB as shown in Eq. 1:



The produced charge carriers (h^+ and e^-) can recombine within 10^{-9} s, generating heat. This recombination substantially reduces the photocatalytic ability of TiO₂ to oxidize organic pollutants. It has been reported that the probability of charge carriers' recombination diminishes as the grain size of TiO₂ decreases, what should result in an improvement of the photocatalytic properties [2].

Fujishima and Honda [3] were the first ones to use a single crystalline TiO₂ photoanode for electrocatalytic decomposition of water under the influence of an external applied anodic potential. The application of such an anodic

bias was found to increase the photocatalytic efficiency of TiO₂ for degrading undesirable pollutants in aqueous solution.

The electron transport in nano-crystalline TiO₂ electrode occurs via diffusion and is not potential dependent, while the Fermi energy level of such a semiconductor is potential dependent [2]. Therefore, the application of a positive potential could be expected to lower the Fermi energy level of the semiconductor. This would increase the efficiency of electron removal from the illuminated semiconductor film and consequently improve quantum efficiencies by limiting recombination of charge carriers. The role of an external potential is then to drive away the photogenerated electrons and so reduce the electron-hole recombination. The photogenerated hole acts as an oxidizing species of the organic pollutants present in the aqueous solution [4].

Some researchers had studied the synergic effect on the oxidation of organic pollutants under higher-potential applied bias (up to 30 V). Their results showed that the oxidation was due both to the electrochemical and the photocatalytic oxidation in the presence of TiO₂ [5-9].

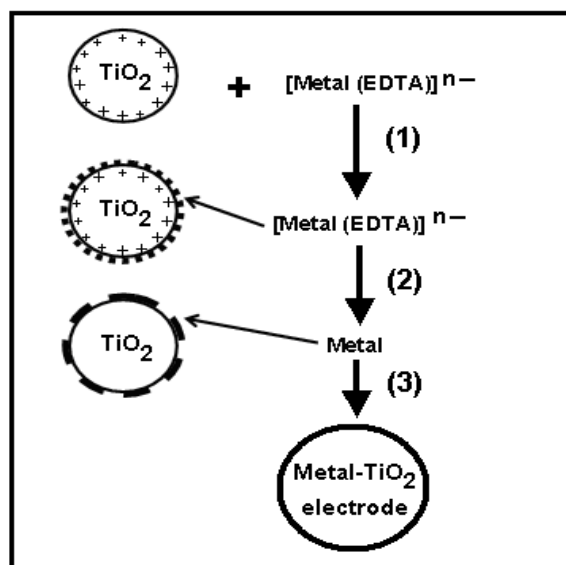
It is now known that incorporation of a transition metal

into the lattice of TiO_2 inhibits the recombination of charge carriers in the semiconductor. The enhancement in activity that results from it can be explained in terms of a photoelectrochemical mechanism in which the electrons generated upon illumination of TiO_2 by UV light are drawn to the loaded metal cations (M^{n+}), while holes remain in the VB of the semiconductor [10-12].

The aim of the present work was to determine, experimentally, the value of the external applied bias that, by preventing electron-hole recombination, would positively affect the photocatalytic properties of TiO_2 in the oxidation of organics. The efficiency of the method is tested with CH_3OH which is chosen as pollutant model.

2. Experimental

As illustrated in Scheme 1, an electrochemical method comprising three steps was designed to prepare multinanoporous particles of titanium dioxide, in anatase structure, doped with manganese atoms. The titanium sheet was the starting material while the anodic oxidation and the electrodeposition were the starting point for all the synthetic methods.



Scheme 1. The three-step electrochemical method used for the production of transition metals doped- TiO_2 electrodes.

Step 1: The first step consisted of anodization, at ambient temperature, of the titanium film in oxalic acid solution (0.8 mol.dm^{-3}), at high current density ($90\text{--}100 \text{ mA.cm}^{-2}$) and low voltage (60 V) for 3 min. This process leads to the formation of a conductive porous coating layer of TiO_2 over the entire surface of the titanium film. This film is the pre-anodized TiO_2 [13-17].

Step 2: In the second step, atoms of manganese (Mn) were incorporated into the conductive pores of the pre-anodized TiO_2 through electrodeposition, using MnSO_4 (12 g.dm^{-3}) to provide a metal-doping agent in ionic form [1-5]. The electrodeposition was carried out under a high current

density of about 75 mA.cm^{-2} to 90 mA.cm^{-2} . For this purpose, an output voltage statically controlled alternative electric power source and a thermostatically controlled water bath were used. During the electrodeposition process, the bath was kept at 40°C and the pH at 2.0.

The high current was applied to enhance the adhesion of manganese atoms into the coating layer [18-20]. The pH was set at 2.0 because at higher values, the stability of the bath decreased and this could cause precipitation or incorporation of non-adherent manganese hydroxides in the metal coating. Boric acid (10 g.dm^{-3}) was also added to the solution to increase its conductivity (i.e. to lessen high current density burning) and thus to prevent precipitation of the manganese hydroxides. Not using boric acid may cause inefficient and poor adhesion of manganese atoms on the pre-anodized TiO_2 . $\text{Na}_2(\text{EDTA})$ (0.02 mol.dm^{-3}) was added as a chelating agent to increase the solubility of the metal through anionic complex formation with Mn(II) ions. The anionic complexes formed were electrostatically bound to the positive surface of TiO_2 . The electrodeposition time varied from 4.0 min to 30 min.

Step 3: At this stage, re-anodizing was performed at room temperature for 5 min, by direct current (dc) in sulfuric acid solution (1.0 mol.dm^{-3}), at high voltage (130 V), with a current density of about 15 mA.cm^{-2} to 20 mA.cm^{-2} . The cathode was made of graphite. Nanoporous films consisting of TiO_2 particles doped with atoms of manganese were then produced. The films were immediately rinsed with distilled water to remove byproducts, then dried in air and finally characterized. Energy Dispersive X-ray Spectroscopy (EDS) was used to investigate the elementary chemical composition of the films obtained.

A Raman scattering spectrum was recorded at room temperature using a Spex 1403 Laser Raman scattering spectrometer with the aim of determining the TiO_2 structure in our study. The laser power was kept low in order to avoid undesired heating effects of the samples.

The effect of a potential bias on the oxidation of CH_3OH in aqueous solution was investigated using TiO_2 and manganese-doped TiO_2 electrodes. The oxidation of CH_3OH was quantified via current density measurements using TiO_2 as working electrode and a circular electrode (made of graphite) as a counter electrode. For this purpose, the oxidation under UV light (at 365 nm) of CH_3OH 0.2 mol.dm^{-3} in aqueous solutions was investigated. Sodium sulphate (Na_2SO_4 0.3 mol.dm^{-3}) was used as supporting electrolyte because Na_2SO_4 has high conductivity, which can be translated into little or no ohmic resistance between the reference electrode and the working electrode, so that the measured current is limited by CH_3OH solution diffusion at the TiO_2 surface [19,20]. The photoanode TiO_2 (surface area 95 cm^2) and the circular electrode were immersed in the photoreactor containing the CH_3OH solution. The applied voltage was varied from 0.5 V to 5.0 V, and the changes in current density were recorded as a function of the applied potential.

3. Results and Discussion

Table 1. Manganese contents (in atom percent) of the TiO_2 electrodes as a function of the electrodeposition time.

Electrodeposition time (min)	Mn contents in Mn-doped TiO_2 electrodes (at.%)
4.0	0.31 ± 0.02
6.0	0.50 ± 0.01
8.0	1.03 ± 0.01
10.0	1.12 ± 0.03
13.0	1.71 ± 0.02
20.0	1.93 ± 0.02
30.0	2.40 ± 0.03

The results on the elementary chemical composition of the films are presented in Table 1. Each value of the manganese contents given in the table is an average of three measurements of manganese contents made at three different points of the electrode under study.

Fig. 1 shows the X-ray diffraction patterns of Mn- TiO_2 (with 1.03 at.% and 2.40 at.% of Mn as dopant), and of undoped TiO_2 . From Fig. 1, it can be seen that an increase in Mn contents up to 2.40 at.% leads to the formation of MnO_2 while at 1.03 at.% only one phase of TiO_2 (anatase) is observed. No dopant related peaks were observed by X-ray diffraction analysis. This suggests that there is no metal aggregation in amounts large enough to be detected by X-ray diffraction [1].

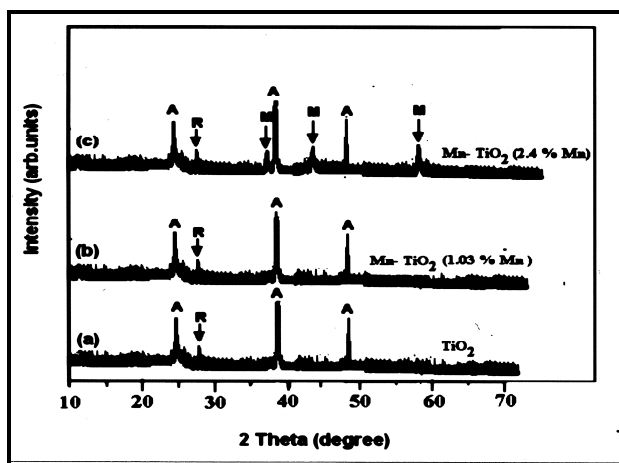


Fig 1. X-ray patterns of (a) undoped TiO_2 , (b) Mn-doped TiO_2 (Mn: 1.03 at.%), and (c): Mn-doped TiO_2 (Mn: 2.40 at. %). The various Bragg peaks are followed by A: anatase, R: rutile, M: MnO_2 . The results were obtained using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$).

Fig. 2 presents the Raman scattering spectrum of the prepared undoped TiO_2 and Mn-doped TiO_2 . The Raman peaks are located around 408.71 cm^{-1} , 511.9 cm^{-1} , and 642.1 cm^{-1} , corresponding to B_{1g} , A_{1g} or B_{2g} , and E_g modes of TiO_2 anatase structure, respectively [21, 22].

The additional peak at 448.612 cm^{-1} is attributable to the rutile phase of TiO_2 . This result is consistent with the analysis from X-ray diffraction spectrum of the prepared TiO_2 and Mn-doped TiO_2 (Mn: 1.03 at.%).

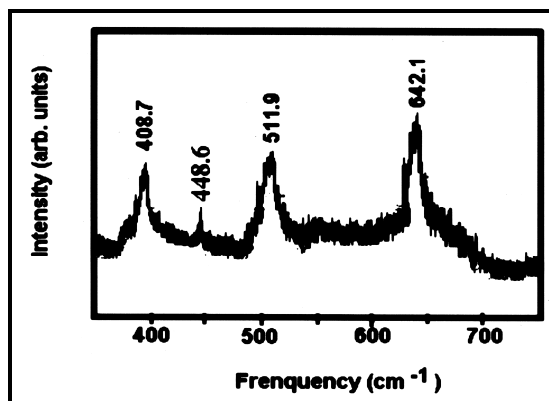


Fig 2. Raman spectrum of undoped TiO_2 and Mn-doped TiO_2 (Mn: 1.03 at.%).

Measurements of the photocurrent densities were made, first in dark and then under UV illumination. Fig. 3 displays the current densities obtained for the different working electrodes tested as a function of applied bias.

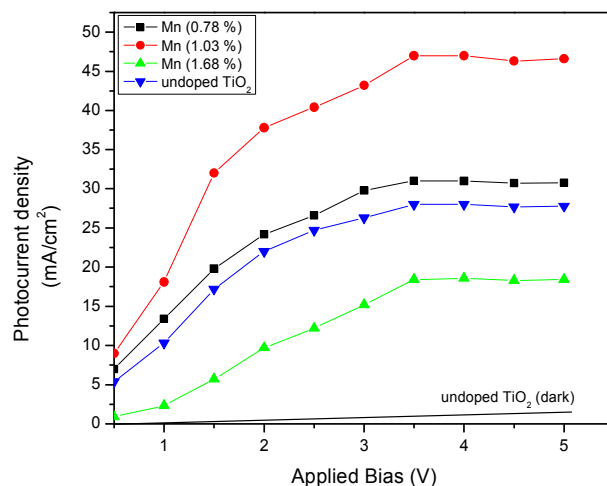


Fig 3. The current-potential curves of undoped TiO_2 and Mn-doped TiO_2 electrodes (the film area: 95 cm^2 illuminated by the side).

On the one hand, it can be seen from Fig. 3 that the current density increases with the applied voltage, indicating that the current density rate is much faster at high potential. Thus, it can be inferred that the $h^+ - e^-$ recombination is related to the applied voltage. On the other hand, by applying the potential, electrons escape from the potential well, very likely through tunnelling. Regardless of the type of working electrode, a plateau is reached from 3.5 V and no significant changes in the slope of the produced photocurrent are observed. This would suggest that at this potential value, the electron tunnelling through the potential well was completed. The value of 3.5 V was therefore selected as the most appropriate potential bias to be applied for improving the photocatalytic properties of undoped TiO_2 and of Mn-doped TiO_2 semiconductors.

From Fig. 3, it can also be observed that when a potential is applied even in the presence of TiO_2 , yet in the dark, the electrochemical oxidation of CH_3OH was not noticeable:

the current density measured was too low, thus indicating that the oxidation of CH_3OH is rather photoinduced. Consequently, it can be assumed that the complete oxidation of CH_3OH that is observed was achieved essentially through photocatalysis rather than through a sole electrochemical oxidation.

The undoped TiO_2 film exhibited lower current density compared to that from Mn-doped TiO_2 electrodes. This suggests that the photogenerated electron-hole pairs were separated even more efficiently in Mn-doped TiO_2 film by applying an external bias. The highest photocatalytic oxidation efficiency of CH_3OH was achieved with metal doping of about 1.03 % contents. This result can be rationalized by assuming that the metal in TiO_2 lattice serves as shallow trapping sites and greatly enhances the activity of TiO_2 . It was also observed that an increase in the metal contents in TiO_2 above 1.03 % leads to a deterioration of the photoactivity of TiO_2 .

The curves in Fig.3 display the same profile as in previous works [23,24]. Interestingly, in our present work as well as in the latter ones, the photocurrent density reaches its highest value for a doping of around 1.00 at %, regardless of the transition metal used for the doping process.

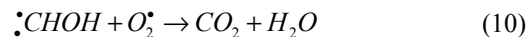
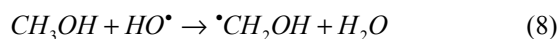
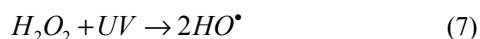
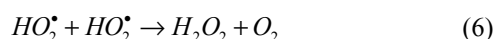
At higher manganese dopant contents, there is a sequence of decreasing average distance between the trap sites, favouring the electron-hole recombination [25,26]. The main role assigned to the metal in this process is shown in Eqs. 2 and 3 [27,28].

For small manganese contents and optimum number of clusters, the following sequence can be postulated:



Manganese atoms interact with excited TiO_2 to produce Mn^- anions. The manganese atom $\text{Mn}:[\text{Ar}].4s^2.3d^5$ can form a transient anion $\text{Mn}^-:[\text{Ar}]4s^2.3d^6$ on addition of one electron to its electronic configuration. In the presence of dissolved oxygen, O_2^\bullet radicals are formed.

After production of the O_2^\bullet radicals, the following steps are postulated which would lead to complete photodegradation of CH_3OH into CO_2 and H_2O :



As can be seen, apart from the O_2^\bullet radicals, a chain of other radicals (e.g. $\bullet\text{CH}_2\text{OH}$, $\text{H}_2\text{O}^\bullet$ and HO^\bullet) and the hydroxycarbenes are successively produced and then involved in the oxidation of CH_3OH .

Additionally, from Fig. 1, it can be seen that an increase in *Mn* contents up to 2.40 at.% leads to the formation of MnO_2 , while at 1.03 at.%, only one phase of anatase TiO_2 could be observed. This suggests that the decrease in the photocatalytic activity of TiO_2 doped with higher metal concentration could be due to the formation of the second phase, which is rather inhibiting for the TiO_2 photocatalytic activity.

From the current density measured against the applied bias as shown in Figure 3, one can suspect that the observed improvement of the TiO_2 photocatalytic activity may be related to the holes generated on the surface of TiO_2 , which could act as potential wells. The wave nature of the electron may allow it to penetrate, by tunnelling, a thin barrier even if the electron energy is less than the height of the well.

The recombination and the reflection of an electron through a thin potential well barrier with height V_o and width d can be calculated using the corresponding Schrödinger equation in one dimension [29]. The square of the transmission coefficient T_0 is then equal to the square of the ratio of the transmitted wave E to the incident wave A:

$$T_0^2 = \left| \frac{E}{A} \right|^2 = \frac{(4k\alpha)^2}{(\alpha^2 + k^2)^2} e^{-2\alpha d} \quad (11)$$

$$T_0^2 = 16 \frac{E}{V_o} \left(1 - \frac{E}{V_o} \right) e^{-2\alpha d}, \text{ for } e^{2\alpha d} \gg 1 \quad (12)$$

The transmission (T_0) could be referred to as the probability of the electron to escape the hole recombination. This leads to:

$$T_0^2 = \left| \frac{E}{A} \right|^2 = \frac{(4k\alpha)^2}{(\alpha^2 + k^2)^2} e^{-2\alpha d} = 16 \frac{E}{V_o} \quad (13)$$

$$T_0 = 4 \sqrt{\frac{E}{V_o}} \quad \text{where } E \ll V_o \quad (14)$$

E being the energy of the electron (in eV), V_o the height of the potential well (in eV), and T_0 the transmission coefficient.

Moreover, the energy E of the electron can be expressed by the following equation:

$$E = F.d = \phi.e.d = \frac{U.e.d}{S} \quad (15)$$

F is the force which makes the electron to act, ϕ is the electric field intensity, e is the quantity of electricity, U is the external potential bias expressed in volt (V), d is the distance separating the electron and the hole, and finally, S is the distance between the anode (TiO₂) and the cathode (graphite).

By inserting Eq. 15 into Eq. 14, a parabolic Eq. 16 is obtained:

$$T_o = 4 \sqrt{\frac{U \cdot e \cdot d}{S \cdot V_o}} \quad (16)$$

From equation (16), one can see that the probability of the electron escaping from hole recombination increases with the potential bias that is applied. The photocurrent density which expresses the probability of reducing the recombination of the electron and the hole would then increase with the applied potential bias. The measured current densities in Fig. 3 show the same variation as that predicted by equation (16). By applying a potential of 3.5 V, the electron can be assumed to escape by tunnelling from the well. This means that at this potential, the electron-hole recombination is best prevented, and the oxidation efficiency is consequently improved.

4. Conclusion

Doping with manganese improves the intrinsic photocatalytic ability of titanium dioxide as it makes possible the production of radicals which are subsequently involved in the photodegradation process. The higher photocurrent density that is observed could be the cause of the higher efficiency of CH₃OH oxidation on the surface of TiO₂ where the hole is acting as the oxidizing agent. The approach based on the electron tunnelling model from a well when a potential bias is applied is found to explain the experimental results in a satisfactory manner.

Acknowledgements

The authors express their thanks to Dr. Xin Lihui of the National Center of Shanghai Institute of Measurement and Testing Technology for helping with SEM, TEM, Raman and X-ray analyses.

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