

PHOTOELECTROCATALYTIC REMOVAL OF COLOR FROM WATER USING TiO₂ AND TiO₂/Cu₂O THIN FILM ELECTRODES UNDER LOW LIGHT INTENSITY

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ABSTRACT. This work describes, photoelectrocatalytic degradation of organic pollutants by using methyl orange (an azo dye) as a model compound. The TiO₂ thin film and TiO₂/Cu₂O composite electrodes were used as semiconductor photo electrodes. Photo catalysis by UV light corresponding to the light intensity range of the solar light was employed with the aim of using renewable and pollution-free energy. Result showed that the rate of removal of color was enhanced when potential bias of 1.5 V was applied. The degradation rate was also increased either in acidic (pH 2) or alkaline (pH 10) conditions. The application of a positive potential higher than the flat-band potential on the TiO₂ electrode decreases the rapid charge recombination process, and enhanced the degradation of organic compound. When the TiO₂/Cu₂O thin film electrode was used, more efficient electron and hole separation was observed in the composite system under very low potential. It is considered that the photo-generated holes migrate towards the interface while the electrons migrate towards TiO₂ and then to the back contact transparent fluorine doped tin-oxide-coated glass (TCO), making the behavior of the composite film analogous to that of an n-type semiconductor. In all cases, the kinetics of the photo catalytic oxidation of methyl orange followed a pseudo first order model and the apparent rate constant may depend on several factors such as, the nature and concentration of the organic compound, radiant flux, the solution pH and the presence of other organic substances.

KEY WORDS: Photoelectrocatalysis, Titanium dioxide, Cuprous oxide, Composite thin film, Photo electrode

INTRODUCTION

Photo catalytic processes to degrade organic pollutants in water by oxidation utilizing TiO₂ as a catalyst in the form of suspended TiO₂ powder have been the subjects of extensive research recently [1-4]. In practice, the rapid unfavourable electron-hole recombination reaction in TiO₂ compared with the relatively slow redox reactions of organic compounds resulted in low quantum yield [5, 6].

Modifications of semiconductor surfaces such as addition of metals as dopant or combinations with other semiconductors have been considered to decrease the electron and hole recombination rate and thereby increase the quantum yield of photocatalytic process [7-9]. Coupling of two semiconductor particles with different band gap energy levels has also been considered either to minimize electron-hole recombination or to modify the catalyst so as to absorb light from the sun in the visible region. A variety of semiconductor heterojunctions such as CdS/TiO₂, CdS/PbS, CdS/ZnO, CdS/AgI, Cd₃P₂/TiO₂ and Cd₃P₂/ZnO and AgI/Ag₂S have been investigated [10-16]. Further improvements have been reported by employing photoelectrochemical approach [17]. However, most of the semiconductor materials with relatively shorter band gap have very low stability for the purpose of water purification.

Among the numerous transition metal semiconductor oxides, cuprous oxide (Cu₂O) is of intense interests and has been extensively investigated for its distinctive properties. Cu₂O is a reddish p-type semiconductor with a direct band gap of 2.0-2.2 eV [18, 19]. Cu₂O has been

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tested as photo electrode in electrochemical cells and water-splitting materials [20-22] and photocatalytic degradation of cyanide in water using titanium dioxide/copper oxide composite catalyst system in powder form. Vigil *et al.* [23] Studied the incorporation of copper oxide to nanoporous TiO₂ from an aqueous solution of copper formate with the purpose of sensitizing the TiO₂ to wavelengths in the visible range for the application of heterojunctions in solar energy. Based on the direction and wavelength dependence of photocurrent they show that photons are absorbed by the copper oxide and electrons injected to the TiO₂. Most of the studies reported in the literature use high intensity UV lamp, which makes it difficult for wide applications.

In the present work, photoelectrocatalytic approach was considered using both TiO₂ thin film electrode and TiO₂/Cu₂O composite electrode. The objectives of the study were to investigate the photoelectrocatalytic activity of titanium dioxide (TiO₂) thin film and titanium oxide (TiO₂)/cuprous oxide (Cu₂O) composite thin film electrode for the destruction of organic contaminants in water under low light intensity by using methyl orange as a model organic compound. We have focused our attention on the low-intensity range of UV illumination, from 1 mWcm⁻² to 2 mWcm⁻² in our studies, since the ultraviolet light in direct sunlight is generally 2-4 mWcm⁻² depending on the geographical location.

EXPERIMENTAL

Preparation of Cu₂O thin film

Cu₂O was electrodeposited on a transparent conducting substrate TCO from alkaline Cu(II) lactate aqueous solution [24, 25] in a conventional two-electrode cell. Prior to electrodeposition, the TCO was sonicated in ethanol solution and dried in air. Copper wire was glued to the conducting side using aqueous based graphite conductive adhesive. The pH of the solution was adjusted between 9 and 12 by the addition of sodium hydroxide. The solution temperature was kept constant during deposition by a thermostat (IKA. ETS-D4 fuzzy, The Netherlands). Deposition temperature was varied in the range from 25 to 60 °C. The deposition potential was maintained at -0.4 V and the current density varied from 0.1 mA/cm² to 0.8 mA/cm². The duration of deposition ranging from 2 min to 30 min was used to obtain films of various thicknesses. All the potentials are reported versus the SCE reference electrode. Electrochemical deposition was controlled by an EG and G 283 potentiostat. Cuprous oxide films were annealed in air at 300 °C for 1 h or used without annealing. The structure of the films was identified by X-ray diffraction (XRD) under θ -2 θ mode (AXS D8 Advance, Bruker, England).

Preparation of TiO₂ and TiO₂/Cu₂O composite thin film electrodes

TiO₂ films were prepared from pure Anatase Paste (ECN, The Netherlands). Two types of paste were used to prepare the TiO₂ electrode with different particle size 9 nm and 100 nm. The electrodes are represented as E1 (9 nm) and E2 (100 nm). Then, the films were annealed in air at 450 °C for 3 h in a furnace equipped with temperature control unit. The TiO₂/Cu₂O composite film was prepared by electrodepositing the Cu₂O on to the TiO₂ film from alkaline copper lactate solution at bath temperature of 60 °C. To vary the amount of deposited Cu₂O, the time of deposition was varied from 2 min to 30 min.

Measurement of photoelectrochemical response

The photoelectrochemical measurements were performed in a single compartment Teflon cell having 1 cm diameter circular quartz three-electrode system. The light source was a light

emitting diode (LED) with maximum emission of 375 nm (FWHM ~ 15 nm, Roithner) array that was aligned for proper sample illumination. The potential was controlled with the potentiostat (EG and G 283, The Netherlands). Current-time and current-voltage measurements were made in 0.5 M K₂SO₄ solution. For quantitative photoelectrochemical characterization at different wavelength, white light from a halogen lamp (200W, Osram, The Netherlands) in an Oriol housing was passed through a monochromator (Spectropro150, Acton). The light intensity was measured with a UV photodiode (PD300, Ophir, Germany). The spectral photo response was measured with a potentiostat (EG and G 283, The Netherlands) equipped with shutter (UNIBLITZ, Model T132, France). The photo response was measured with and without oxygen bubbling.

Photo catalysis and photoelectrocatalysis experiments

The photocatalytic activity of the TiO₂ thin film electrodes and the Cu₂O/TiO₂ composite thin film electrode was evaluated using [4-(dimethylamino)phenylazo]benzenesulfonic acid, sodium salt (methyl orange) as a model compound (Figure 1). Screening photo catalysis experiments were carried out using rectangular 3 mL capacity quartz cell. The light source was a deuterium lamp with light intensity of 2 mW/cm² (Model C4545, Germany). Further photocatalytic (PC) and photoelectrocatalytic (PEC) degradation experiments were performed in a single-compartment Teflon cell (40 mL) reactor having a circular quartz window of 20 mm diameter (Figure 2). A circular opening in the cell opposite to the quartz window allowed exposure of 3.14 cm² of the working electrode (TiO₂ or TiO₂/Cu₂O) to UV illumination. The platinum coil counter electrode was placed just in front of the working electrode. A saturated calomel electrode (SCE), used as a reference, was placed close to the working electrode. The experiments were carried out in the pH range from 2 to 10 in 0.1 M K₂SO₄ or 0.1 M KCl electrolyte solutions. A potentiostat model EG and G 243 was used to bias the working electrode. Unless noted otherwise, the concentration of dye used was 20 mg/L.

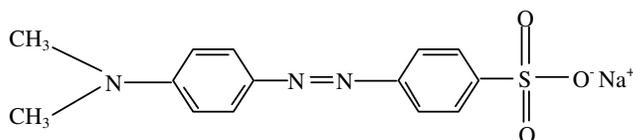


Figure 1. [4-(Dimethylamino)phenylazo]benzenesulfonic acid, sodium salt (methyl orange).

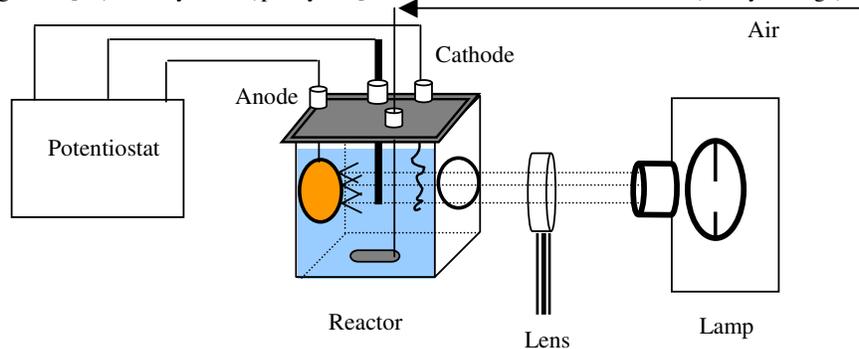


Figure 2. Schematic diagram of photocatalysis and photoelectrocatalysis reactor system.

Aqueous solution of methyl orange (40 mL) was photolysed under various operating conditions. The pH of the solution was adjusted to desired value with sodium hydroxide and sulfuric acid solution. The potential was controlled with the potentiostat (EG and G 243). The photo degradation of methyl orange was monitored with UV-Vis spectrophotometer (Varian) at its wavelength of maximum absorption (464 nm).

RESULTS AND DISCUSSION

Film compositions and structure

The XRD spectrum of film sample, deposited on tin oxide conducting glass (TCO) substrate from lactate solution under alkaline medium is shown in Figure 3. The film deposited is polycrystalline and chemically pure Cu_2O with no traces of CuO . The XRD spectrum indicates a strong Cu_2O peak with (200) preferential orientation. This is in good agreement with the results of other studies [24, 26, 27].

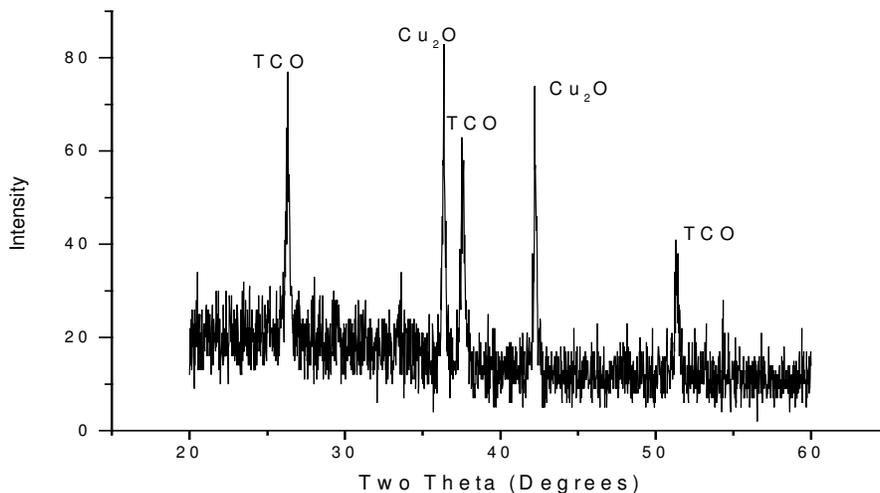


Figure 3. X-ray diffraction patterns of copper oxides deposited at -0.4 V on TCO from alkaline lactate solution pH 10.

Photo response

The dark and photocurrent of the Cu_2O electrode at -0.4 V vs. Ag/AgCl is represented in Figure 4. A typical p-type photocurrent versus time behavior is observed. In addition, photocurrent was stable over longer time range. The photo response was not changed after repeated use of the electrode and similar photo response was obtained for films deposited for 2, 5, 10, 20, and 30 min (data not shown). This indicates that the overall process of light absorption by the semiconductor, generation and separation of electron hole pairs, and transfer of electrons, is efficient even for thick films.

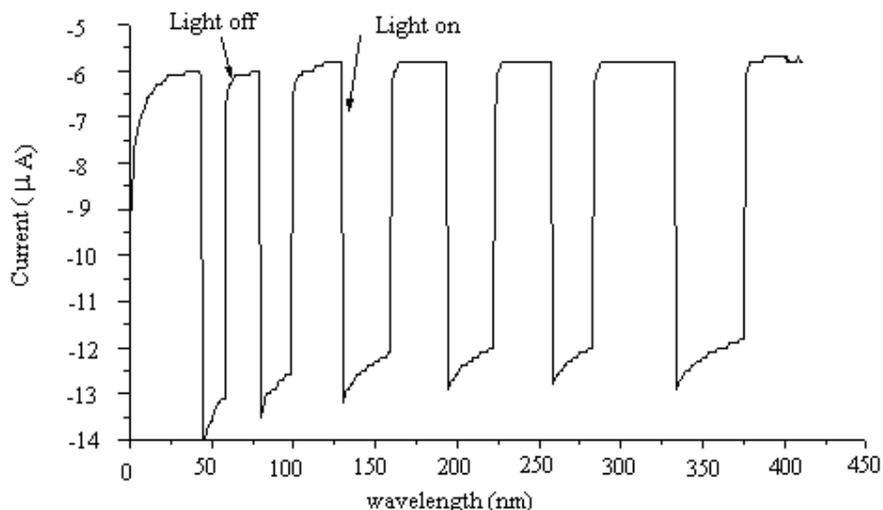


Figure 4. Photo response Cu₂O electrodeposited from alkaline lactate solution on TCO conduction substrate under oxygen bubbling (0.5 M K₂SO₄, 0.2 mA/cm², -0.4 V).

The cyclic voltammogram of the Cu₂O thin film electrode in 0.5 M K₂SO₄ solution in the dark and under illumination (375 nm) is shown in Figure 5. The sweep starts at open-circuit potential and is scanned cathodically at 10 mV/s. At potential more negative than -0.8 V vs. SCE, a fast increasing cathodic current was observed due to the reduction of Cu₂O to Cu, which is also reported by other researchers [25]. The deposition currents are in a potential window between -0.3 and -0.7 V, which is about 400 mV window. The potential range corresponds to the Pourbaix diagram for the stability of Cu, Cu₂O, and CuO system [28]. Other studies on the electrochemical deposition of Cu₂O oxide films showed that the potential window is between -0.35 V and -0.55 V [24]. The deposition current in Figure 5 is very stable indicating that the p-type electrode containing Cu₂O as main component is resistant against photo corrosion.

Figure 6 shows the spectral photo response of the electrodes prepared from alkaline lactate solution at pH 10. The photoresponse region of Cu₂O lies in the UV and visible region (300-600 nm) with absorption maximum around 450 nm. The maximum instantaneous photocurrent efficiency (IPCE) calculated from Equation (1) at 375 nm is 7 %. This value is comparable to the value reported by Jongh *et al.* [25] for absorption in the visible region, but lower for absorption in the UV region. The photocurrent measurement in this study was carried out without air bubbling. The spectral photo response of the TiO₂/Cu₂O composite film is shifted to a maximum around 400 nm (Figure 6). The pattern of photo response is similar to that of an n-type semiconductor photo catalyst. It is interesting to note that the maximum IPCE calculated using Equation (1) is 6 % at wavelength around 375 nm. The relatively high photo response property of cuprous oxide might be useful for photo catalytic decontamination of water under low light intensity if it is combined with titanium oxide (TiO₂).

$$\text{IPCE} = \frac{i}{P \times F} \times 100 \quad (1)$$

where i = photocurrent density, F = Faraday constant, P = light intensity (E s⁻¹ cm⁻²).

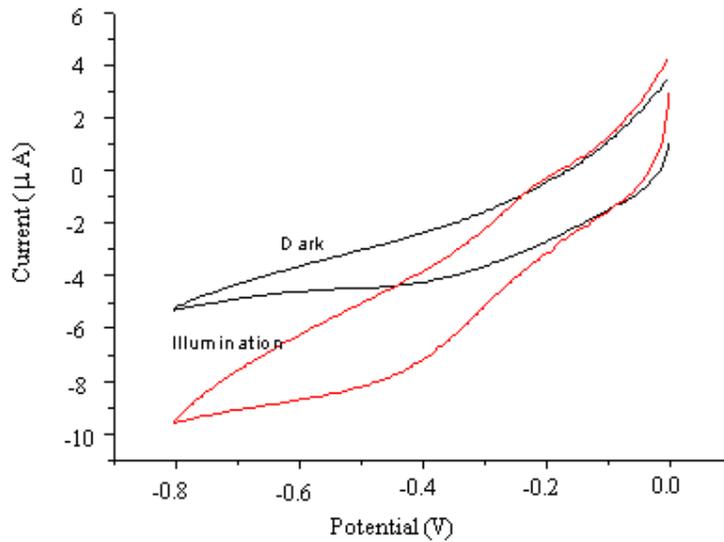


Figure 5. Cyclic voltammogram of Cu_2O thin film deposited at -0.4 V on TCO from alkaline lactate solution pH 10 (scan rate 10 mV/s., 0.5 M K_2SO_4 electrolyte).

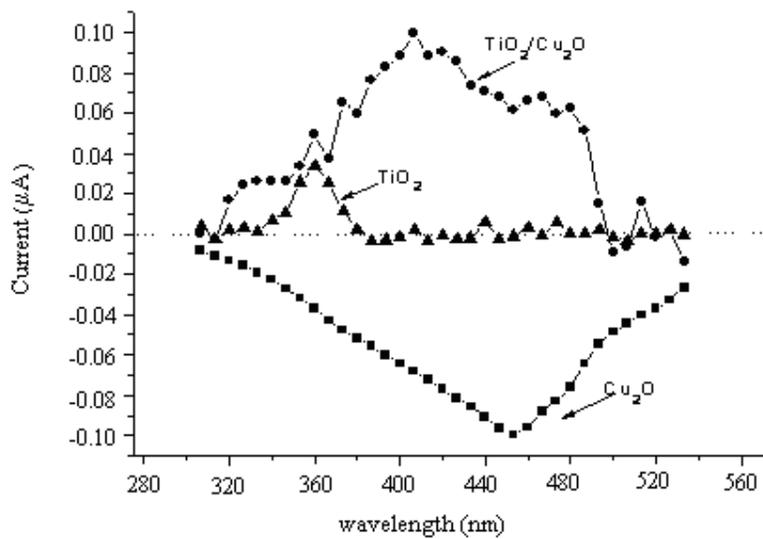


Figure 6. Spectral photo response of the electrodes prepared from alkaline lactate solution at pH 10.

Photo catalysis and photoelectrocatalysis with TiO₂ thin film

Figure 7 shows the removal of color by photolysis (P), photo catalysis (PC), electrolysis (EC), and photoelectrocatalysis (PEC) using TiO₂ electrode as a function of time. No apparent change in methyl orange absorbance was observed by electrolysis alone. Whereas about 10 % decrease was observed under photo catalysis and 40 % decrease was observed under photo catalysis in 24 h reaction time. However, by applying a potential bias of +1.0 V, 100 % decrease in absorbance was achieved for the same duration of reaction time. The results obtained at pH 6.5 illustrate that under applied potential there is an improvement of the photocatalytic decomposition of the dye. It has been reported that by applying an anodic bias potential higher than the flat-band potential of the semiconductor, the competitive reactions of charge recombination (e^-/h^+) can be minimized [17, 29-32]. A potential gradient within the photo catalyst film is provided at potentiostatic conditions to efficiently force the electrons to reach the counter electrode. Therefore photo-generated holes can be trapped in the surface by H₂O/OH⁻ species to give rise to OH[•] radicals, which are essential for promoting the efficient degradation of dyes. It has been reported that the photoelectrocatalytic reaction may depend on applied potential, solution pH, and the type of electrolyte used [31-33].

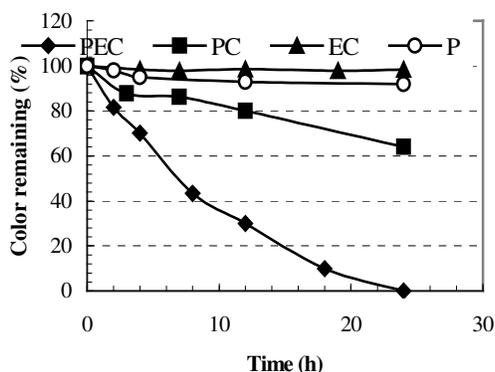


Figure 7. Removal of color by photolysis, photo catalysis, electrolysis, and photoelectrocatalysis (+1.0 V) using TiO₂ electrode in photoelectrochemical reactor.

Effect of pH on photoelectrocatalytic degradation rate

The investigation on the kinetics of methyl orange degradation in aqueous solution under light irradiation was performed and absorbance reduction rate was assumed to follow a pseudo first-order model according to the following equation [4]:

$$\left(\ln \frac{A_t}{A_o} \right) = -Kkt = -k_{app}t \quad (2)$$

where A_o is the initial absorbance, A_t is absorbance at time t , k is the reaction rate constant, and K a constant associated with light intensity, adsorption behaviour of methyl orange, and the electric field.

The absorbance had an exponential relationship to reaction time and the apparent first-order rate constant k_{app} could be calculated from Equation (2). A plot of $\ln(A_t/A_o)$ versus time represents a straight line as shown in Figure 8, the slope of which upon linear regression equals the apparent first-order rate constant k_{app} , which is a function of light intensity, adsorption

behaviour of methyl orange, and the electric field. The degradation rate was also increased either in acidic (pH 2) or alkaline (pH 10) conditions compared to the neutral (pH 6.5) solution. The reaction rate was decreased when the initial concentration of methyl orange increased at a given pH.

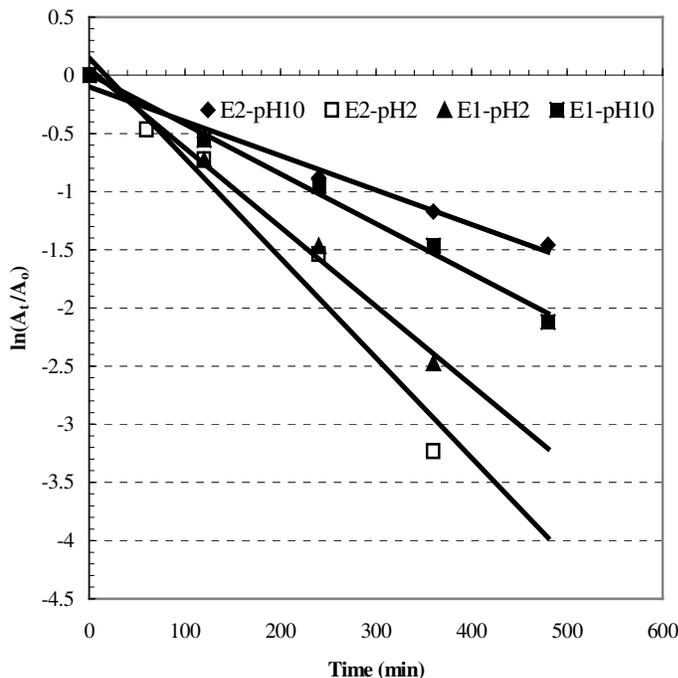


Figure 8. Effect of pH on photoelectrocatalytic color removal at bias potential of +1.5 V using TiO₂ thin film electrodes.

The pH is related to the ionization state of the surface as well as to that of reactants, and to the change of flat band potential of the semiconductor electrode. As illustrated in Figure 9, both the acidic and alkaline conditions favored color removal and almost complete removal of color was realized in electrochemically assisted photocatalytic degradation process at 6 h in acidic media. In neutral and alkaline media, the powerful electron-donating dimethylamino group generates a $\pi - \pi^*$ transition which lies in the visible region of the spectrum ($\lambda_{\text{max}} = 464 \text{ nm}$) with typical orange color. The molar extinction coefficient of this charge transfer transition is low ($\epsilon_{\text{max}}(464) = 267 \text{ M}^{-1} \text{ cm}^{-1}$). The wavelength of maximum absorption shifts to a higher value when the pH is decreased due to protonation of the azo group to form the azonium ion [34]. It is known that pH values can influence the adsorption of dye molecules onto the catalyst surfaces [31, 33, 35]. The flat band potential E_{fb} is a well-known function of the electrode characteristics and the pH of the solution ($E_{\text{fb}} = E_{\text{fb}}^0 + 0.05915 \text{ pH}$) and follows Nernstian behaviour with a slope of -59 mV. The applied potential is positive to the flat band potential (-0.808 V). Therefore, there is always a potential gradient over the titania film, resulting in an electric field, which keeps photogenerated charges apart.

Under alkaline condition, the color removal rate may be affected by an increase in the density of TiO⁻ groups on the semiconductor electrode surface. Due to the coulombic repulsion, no direct electrostatic interaction between methyl orange and TiO₂ particles can occur. However,

since the anode is a positively charged electrode, the influence of electric field becomes predominant on the electrode surface. As a consequence, the interaction of the methyl orange with the electrode surface is both potential and pH-dependent.

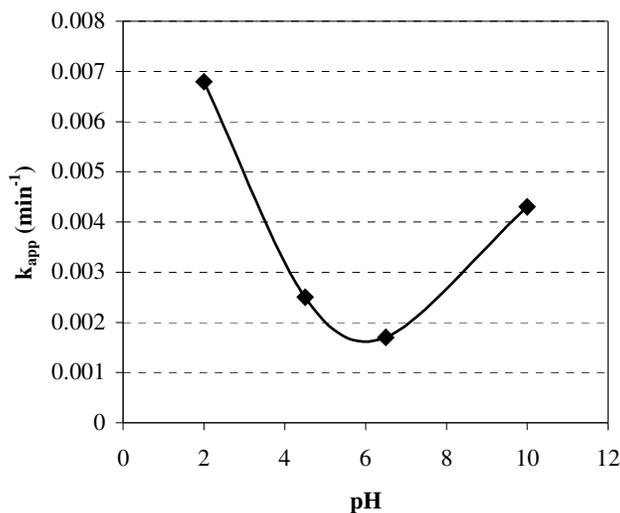


Figure 9. Variation of apparent reaction rate constant as a function of pH at bias potential of +1.5 V using TiO₂ thin film electrode.

As illustrated in Figure 9, the apparent rate constant dramatically increases at higher pH values. This might suggest that different mechanisms take place. It is assumed that the electric field due to applied potential control the interaction of methyl orange and TiO₂ electrode.

In high alkaline solutions (pH > 10), since hydroxyl radicals are easier to be generated by oxidizing more hydroxide ions available on TiO₂ surface according to reactions (3-4), the efficiency of the process is logically enhanced. The minority charge carriers photo generated upon illumination on the photo anode can oxidize the H₂O/OH⁻ producing OH[•] radicals that adsorb on the photo electrode surface with the release of H⁺ ions to the solution.



On the other hand, the drastic increase in the discoloration rate at lower pH may follow a different mechanism. Methyl orange is an anion in aqueous solution, whose absorption spectrum remains invariant in the pH range 4-14, but changes below pH 4, as expected for protonation of the nitrogen atom of the azo linkage. Whereas the unprotonated compounds is an electron donor, the protonated species has electron-withdrawing character. At the same time, the TiO₂ particles are positively charged at low pH values and the semiconductor electrode is also positively charged. The improved photocurrent behavior in the presence of oxygen suggests that the oxygen may pick up the conduction band electron in TiO₂ particles, leading to the production of peroxy radical according to the reactions (6-7) (data not shown).



Indeed experiments conducted without oxygen supply at low pH indicated lower reaction rate. Peroxide radicals are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates such as dyes [36]. Further, since methyl orange has a sulfonic group in its molecular structure, which is negatively charged, the acidic solution favors adsorption of dye onto the photo catalyst surface, leading to the improvement of the degradation efficiency to some extent. More investigation is required in this regard to elucidate the predominant reaction mechanisms.

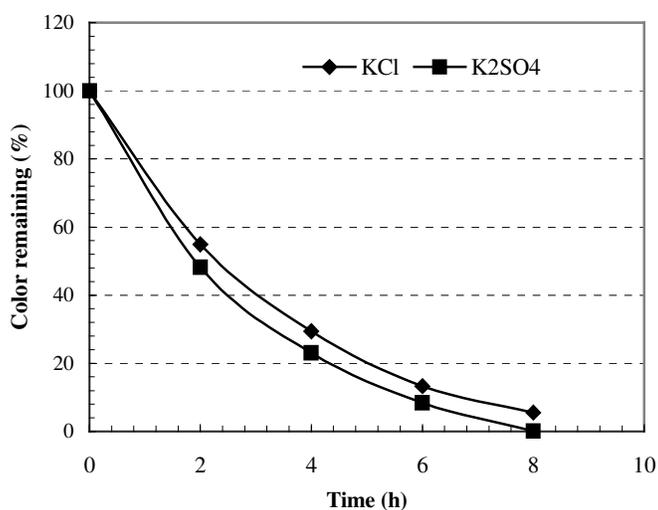


Figure 10. Color removal as a function of irradiation time at pH 2 with TiO_2 thin film electrodes (E1) at bias potential of 1.5 V in KCl and K_2SO_4 supporting electrolytes.

Investigation of the influence of the type of electrolyte on the removal of color with 20 mg/L of methyl orange in 0.1 M K_2SO_4 and KCl solutions (Figure 10) showed that there is no significant difference of color removal under the two supporting electrolyte conditions. This indicates that the photo catalytic oxidation reaction of chloride and sulfate or electrochemical oxidation of chloride ion to chlorine at potentials around +1.3 V versus Ag/AgCl is not significant under the experimental conditions used in this study, as shown previously by others [37, 38].

Effect of applied potential

The effect of applied potential on the photoelectrocatalytic degradation rate of methyl orange was investigated by comparing the color removal during oxidation of 20 mg/L dye in 0.1 M K_2SO_4 at pH 10 in order to check for the importance of selecting the best potential for this process. Potentials ranged between -0.6 and +2.5 V was applied and the decrease in absorbance at 464 nm was monitored. The results in Figure 11 show that the apparent rate constant for the removal of color increases progressively with increase in bias potential. On the other hand, the

current produced was increased as the applied potential increased (data not shown). This indicates the influence of the applied potential to force the transport of photoelectrons across TiO₂ film and also the photo generated electrons are the charge carriers. As anodic potential increased, a large amount of current carrier (photoelectrons) passed through the TiO₂ film. Additionally, photogenerated holes were consumed by methyl orange in the solution, which is reflected in the decrease of absorbance.

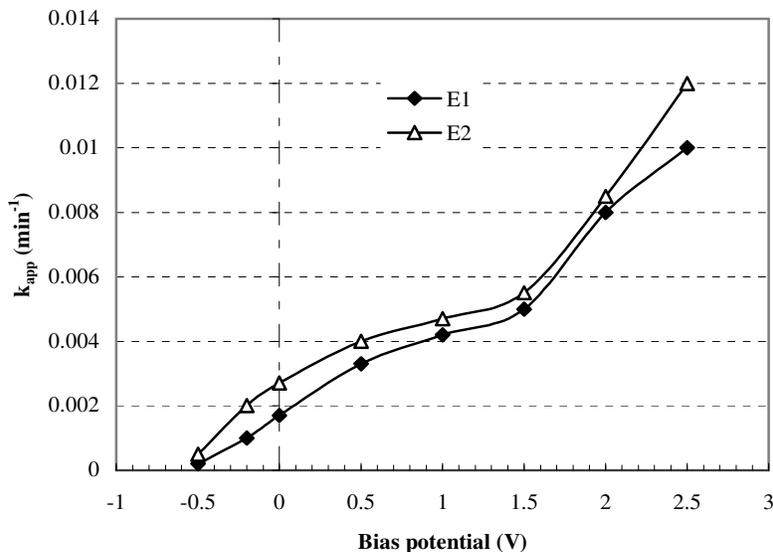


Figure 11. Dependence of the apparent reaction rate constant (min⁻¹) as function of time at different potential in K₂SO₄ at pH 10 using TiO₂ thin film electrodes.

The standard electrode potential values for the couple OH[•], H⁺/H₂O and O₃, 2H⁺/O₂, H₂O are +2.7 V and 2.076 V, respectively [38]. The potential applied across the electrodes was 1.5 V in this study and OH[•] radicals could not be formed by anodic oxidation under the conditions examined. The result shows that color removal was mainly attributed to photocatalytic degradation in the experiments involved.

When the potential exceed 1.5 V, the reaction rate become faster and deviation from linearity was observed. The deviation from linearity at higher potential is associated with the combined effect of the generation of more oxidants at the anode. Overall, the application of a positive potential higher than the flat-band potential on the TiO₂ electrode decreases the charge recombination process shown by reaction (8).



It is interesting to note that the apparent rate constant approach zero as the applied potential approach the flat band potential of TiO₂ semiconductor (pure anatase) at pH 10 for the two electrodes. This indicates that charge recombination reaction become predominant if the applied potential is not sufficient for the separation of charge carriers. A slightly higher reaction rate was observed for the electrode made of 100 nm particles (E2).

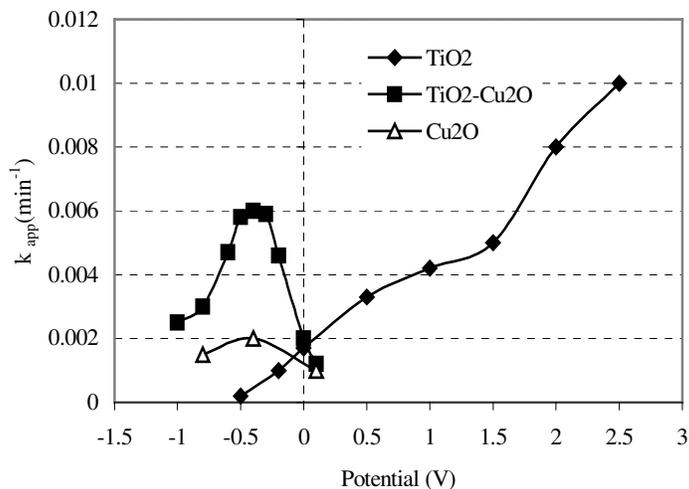


Figure 12. Dependence of the apparent reaction rate constant (min^{-1}) as function of time at different potential in K_2SO_4 at pH 10 using Cu_2O , TiO_2 , and $\text{TiO}_2/\text{Cu}_2\text{O}$ composite thin-film electrodes.

TiO₂/Cu₂O composite electrode system

The apparent rate constant for the removal of color by $\text{TiO}_2/\text{Cu}_2\text{O}$ thin film electrode as a function of bias potential is shown in Figure 12. Preliminary screening tests (data not shown) indicated that the Cu_2O electrodeposited for 5 min at galvanostatic condition (0.2 mA/cm^2) showed better catalytic activity. Good removal efficiency was observed in the potential range -0.6 V to -0.2 V vs. SCE. This potential range corresponds to the stability range of the Cu_2O [28].

At potential below -0.6 V , formation of reduction to Cu was observed and the electrode surface was gradually changed to black color. The color removal continued at reduced rate, possibly due to the catalytic activity of TiO_2/Cu system. On the other hand, the reduction in catalytic activity was more pronounced at positive bias potential. This indicates that only Cu_2O has strong contribution to the removal of color and further oxidation to other copper oxide species may inhibit the catalytic activity of TiO_2 . It is interesting to note that apparent rate constant obtained at -0.4 V for the composite thin film (Figure 12) is comparable to that of pure TiO_2 film at bias potential of $+1.5 \text{ V}$.

The enhanced catalytic effect by Cu_2O at this low potential value is possibly due to more efficient electron and hole separation in the composite system. The potential gradient at the interface promotes the electrons and holes to flow in opposite directions, and the photo generated holes migrate towards the interface while the electrons migrate towards TiO_2 and then to TCO, making the behavior of the composite film analogous to that of an n-type semiconductor as shown schematically in Figure 13. It can be concluded that the composite semiconductor electrode may have better harvesting efficiency of light due to observed shift in absorption spectrum as compared to that of pure TiO_2 .

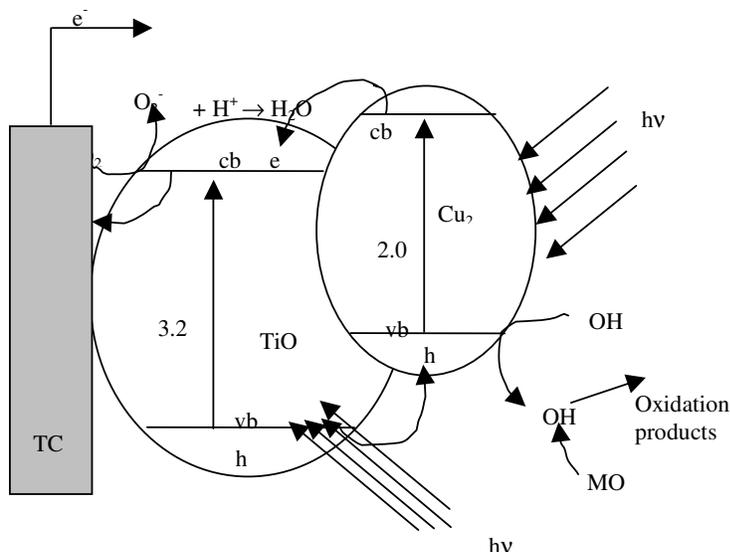


Figure 13. Schematic representation of proposed reaction mechanism TiO₂/Cu₂O composite thin-film electrode.

Based on the above explanation, Cu₂O in the composite thin films have a beneficial role in improving charge separation and may also extend the light absorption spectrum of TiO₂.

CONCLUSIONS

The p-type semiconductor Cu₂O electrode prepared from the cupric lactate solution under alkaline condition showed a stable photocurrent over longer time range. The photo response was not changed after repeated use of the electrode. The rate of removal of color by TiO₂ thin film electrode was enhanced when potential bias of 1.5 V was applied. The TiO₂/Cu₂O composite thin film electrode showed an n-type semiconductor photocurrent characteristic. When the TiO₂/Cu₂O thin film electrode was used, the color removal rate reach maximum, at potential bias of -0.4 V. Further increase or decrease of bias potential caused decreased reaction rate. It is considered that the photo-generated holes migrate towards the interface while the electrons migrate towards TiO₂ and then to the back contact (TCO), making the behavior of the composite film analogous to that of an n-type semiconductor. Cu₂O in the composite thin films have a beneficial role in improving charge separation and may also extend the light absorption spectrum of TiO₂ to the visible region of the electromagnetic spectrum. In all cases, the kinetics of the photocatalytic oxidation of methyl orange followed a pseudo first order model and the apparent rate constant may depend on several factors such as, the nature and concentration of the organic compound, radiant flux, the solution pH and the presence of other organic substances.

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