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Highly dispersed PTFE/Co_3O_4 flexible films as photocatalyst showing fast kinetic performance for the discoloration of azo-dyes under solar irradiation

P. Raja [a], M. Bensimon [b], U. Klehm [c], P. Albers [c], D. Laub [d], L. Kiwi-Minsker [a], A. Renken [a], J. Kiwi [a,*]

[a] *Institute of Chemical Sciences and Engineering, LGRC, Laboratory of Photonics and Interface, Station 6, 1015 Lausanne, Switzerland*
[b] *EPFL, ENAC, ICARE, GEOLEP, Station 18, 1015 Lausanne, Switzerland*
[c] *AQura GmbH, Wolfgang, Rodenbacher Chaussee 4, D-63457 Hanau, Germany*
[d] *Interdepartamental Institute of Electron Microscopy (CIME), Station 12, EPFL, 1015 Lausanne, Switzerland*

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Abstract

Small nanosized clusters of Co_3O_4 coated on PTFE (polytetrafluoroethylene) flexible film is reported as a novel supported photocatalyst effective in the fast discoloration of the azo-dye Orange II under simulated solar radiation in the presence of oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$). The photocatalytic discoloration of Orange II on the PTFE/Co_3O_4 films proceeds within minutes and the process could be repeated many times without a loss in photocatalyst stability. The photodiscoloration proceeds with a photonic efficiency of ∼1. The PTFE seems to act as a structure forming matrix for the colloidal Co_3O_4 coated on it surface leading to nanosized clusters of Co_3O_4. Monitoring the amount of Co^{2+}-ions shows the Co^{2+}-ions from the PTFE/Co_3O_4 during the photocatalysis enter the solution and at a later are stage re-adsorbed the Co_3O_4 crystallographic network (∼8 min). By elemental analysis (EA) the loading of Co-loading per cm^2 PTFE film was found to vary between 1% and 2%. Transmission electron microscopy (TEM) shows the size of the Co_3O_4 clusters to vary between 3 and 10 nm. Electron dispersive spectrometry (EDS) confirms the presence of Co on the PTFE. X-ray photoelectron spectroscopy (XPS) of the PTFE/Co_3O_4 films reveal a partial reduction of the Co_3O_4 after Orange II discoloration leading to a substantial increase of the amount of Co(II) species in the Co_3O_4. Physical insight is provided into the catalyst film surface by carrying out Ar-sputtering of the PTFE/Co_3O_4 surface to remove the catalyst overlayers up to ∼20 nm.

Keywords: Photocatalyst; PTFE–Co-oxide; XPS; Azo-dye

1. Introduction

The abatement of organic pollutants and dyes in water bodies, industrial sites and furtive emissions by Advanced Oxidation Technologies has become a topic of growing interest and concern during the last 15 years [1,2]. Oxone is an oxidant widely used in the degradation of pollutants in the dark and under light radiation [3]. The redox potential of the oxosulfo-radicals generated by oxone ($HSO_5{}^{\bullet -}$ in net sense) of 1.82 eV [4–7] is higher than the potential of the $OH^{\bullet}$ radicals generated by H_2O_2 of 1.76 eV [8]. The accelerated decomposition of oxone in homogeneous solution in the presence of Fe, Cu and Mn-ions has been recently reported [9,10]. More recently, the kinetics of azo-dye decomposition was shown to be drastically accelerated when Co^{2+}-ions was used instead of Fe, Cu and Mn to mediate oxone decomposition under light irradiation [11,12].

Oxone/Co^{2+}-ions systems to degrade organic pollutants in the dark or under light have revealed to be effective but present the drawbacks of homogeneous systems. A separation of the catalyst from the solution is required at the end of the treatment. This is why we focus the present work on supported photocatalysts.

In the present study, we show that the discoloration of Orange II proceeds in the minute range on PTFE/Co_3O_4 films under visible light irradiation. In the last few years we have reported

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* Corresponding author.
E-mail address: john.kiwi@epfl.ch (J. Kiwi).

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several TiO_2 supported photocatalysts fixed on inert supports able to discolor and degrade azo-dyes. These supported catalysts were: Nafion/TiO_2 [13], glass-fibers/TiO_2 [14], Fussabond/TiO_2 films [15] and the discoloration proceeded only within several hours under light irradiation.

A fast dye discoloration kinetics is an important parameter to address in the field of Advanced Oxidation and since reaction kinetics limits the practical application of most processes in this area. A slow kinetics processes precludes the practical utilization of photocatalysis when it comes to treat sizable amount of industrial effluents. Slow reaction kinetics implies long treating times with the ensuing high amount of costly photons (energy) and increased labor costs.

2. Experimental section

2.1. Reagents and materials

Reagents like acid and bases, organic solvents, the dye (Orange II) and H_2O_2 were pro-analysis (p.a.) from Fluka AG Buchs, Switzerland and used without further purification. Millipore-Q tri-distilled H_2O was used throughout this study. The oxone is potassium peroxymonosulfate [CAS-RN 10058-23-8] which is one component of the triple salt as noted in the Aldrich Cat No. 22803-6. The poly-tetra-fluoro-ethylene (PTFE) was obtained from Longfellow, UK is a polymer film 100 μm thick showing in its structure a recurring monomer unit $[CF_2–CF_2]_n$. The thermal resistance shows a PTFE film with a fusion point at 327 °C, 2 min stability at 320 °C and long-term heat resistance up to 260 °C. Other properties of PTFE are: density 2.2 g/cm^3, excellent resistance to UV-light and against acids, bases and organic solvents.

2.2. Catalyst preparation

The films of spinel Co_3O_4 were prepared from Co(II) sulfate hepta-hydrate solution 3 M (842.91 g/l) precipitating the oxide out with a solution KOH 3 M (56.10 g/l). The precipitate was washed with deionized water and re-dispersed (peptized) with concentrated acetic acid. The Co-colloid was deposited on the PTFE film by dip coating and was kept at 4 °C (fridge) for subsequent use [16]. The PTFE film was rinsed with deionized water and then dried at 60 °C. The dried film was dipped into the Co_3O_4 sol. Then, the films were dried at room temperature before heating them at 280 °C for 2 h to form the spinel crystallographic structure and concomitantly diffusing the oxide into the PTFE film. The PTFE/Co_3O_4 film was then let cool to room temperature. The fact that 280 °C was employed a temperature above the fluid temperature limit of PTFE was requires for the adhesion process of the Co_3O_4 to the PTFE surface.

2.3. Irradiation procedures and analyses of the irradiated solutions

The photodegradation of Orange II was carried out in small batch cylindrical photochemical reactors made from Pyrex glass (cut-off λ = 290 nm) of 70 ml capacity containing 50 ml aqueous solution. The strips 48 cm^2 films of LDPE-TiO_2 were positioned immediately behind the reactor wall. Irradiation of the samples was carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air cooled at 35 °C. The light intensity in the cavity of the Suntest simulator at tuned at 90 mW/cm^2 (AM 1) was 2×10^{16} photons/s cm^2. The Suntest Xe-lamp emitted 7% of the photons in the 290–400 spectral range. The integral radiant flux in the reactor cavity was monitored with a power-meter from YSI Corp., CO, USA. The absorption of the Orange II solutions was followed in a Hewlett-Packard 38620 N-diode array spectrophotometer by the disappearance of the Orange II peak at λ = 486 nm. Figs. 1–5 report the results for the discoloration runs of Orange II withdrawing a certain portion of the solution (aliquot) at the intervals shown in the *x*-ordinates (time) in these figures.

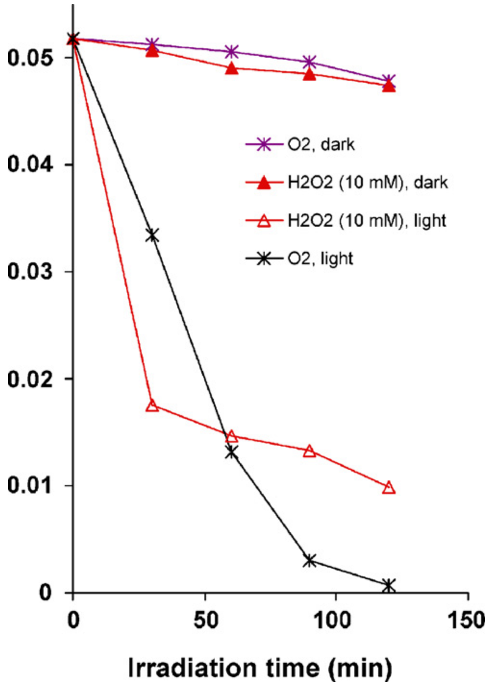

Fig. 1. Dark discoloration and photodiscoloration of diluted Orange II (0.05 mM) in homogeneous solution. Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2) at initial pH 7.

2.4. Elemental analysis of the Teflon/Co_3O_4 films

The elemental analysis of the content of Co on the PTFE films before and after the Orange II photocatalytic degradation was carried out by atomic absorption spectrometry using a Perkin-Elmer 300S unit.

2.5. Transmission electron microscopy (TEM)

A field emission TEM microscope Philips EM 430 (300 kV, source LaB_6, resolution 2 Å) was used to measure the particle size of the nanocrystalline Co_3O_4 particles surface. Energy dispersive X-ray spectroscopy (EDS) was used to identify the deposition of Co on the PTFE film. The PTFE film was coated

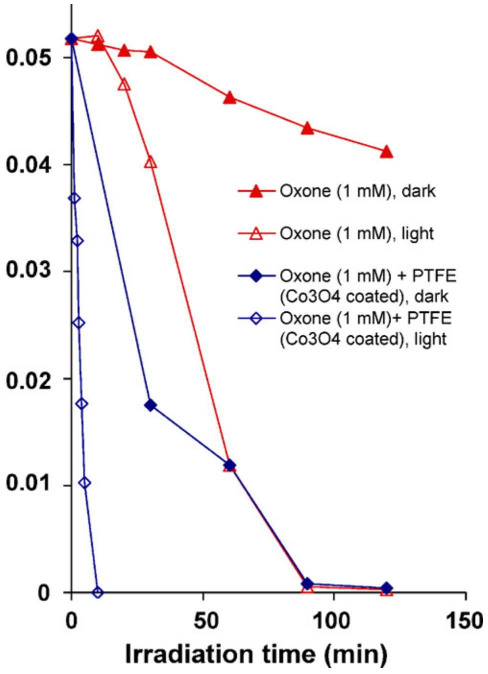

Fig. 2. Dark discoloration and photodiscoloration of Orange II solutions (0.05 mM) in homogeneous and heterogeneous mediated PTFE/Co_3O_4 film in the presence of oxone (1 mM). Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2) at initial pH 7.

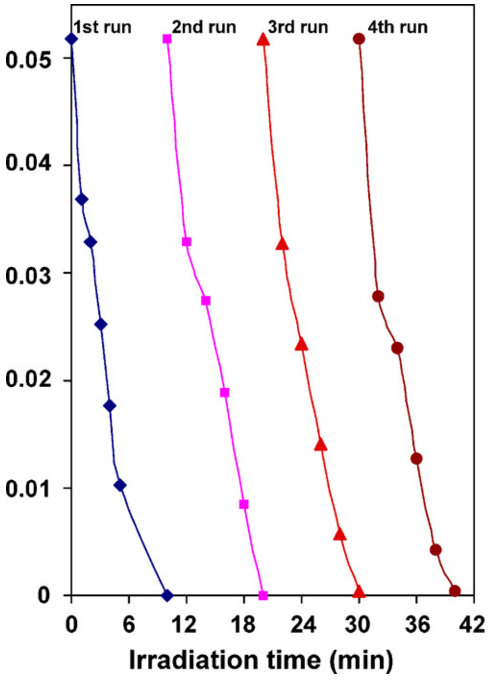

Fig. 4. Repetitive photocatalytic discoloration of Orange II (0.05 mM) mediated by PTFE/Co_3O_4 in the presence of oxone (1 mM). Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2). Initial pH 7.

with EPON 812 epoxy resin polymerized at 60 °C and then cut with a microtome at room temperature to a thin layer of ∼200 nm thickness. Magnification of 10,000× up to 450,000× were used to characterize the samples. The resolution attained was ∼0.5 nm.

2.6. *X-ray photoelectron spectroscopy (XPS)*

The XPS was performed using Mg Kα radiation of 150 W. The electron energy analyzer (Leybold EA200) was operated with a band pass energy of 75 eV in the pre-selected transmission mode. The binding energy of the spectrometer was referenced

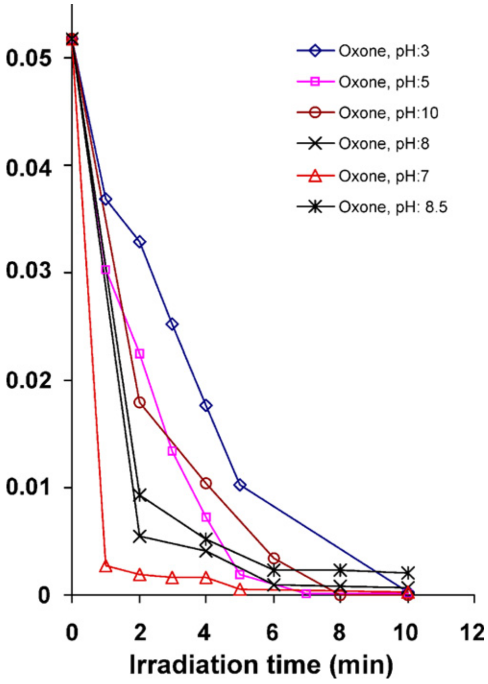

Fig. 3. Photocatalytic discoloration of Orange II (0.05 mM) as a function of the initial pH mediated by PTFE/Co_3O_4 in the presence of oxone (1 mM). Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2).

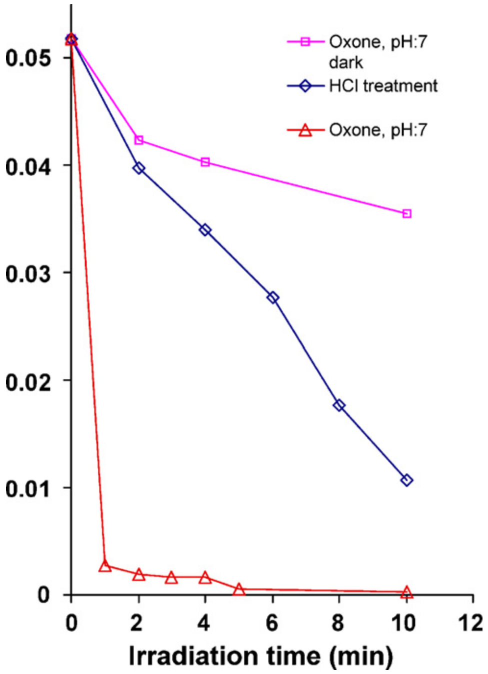

Fig. 5. Dark and photocatalytic discoloration of Orange II (0.05 mM) mediated by PTFE/Co_3O_4 in the presence of oxone (1 mM). Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2). The HCl treatment refers to PTFE/Co_3O_4 films pretreated with 1 M HCl for 1 h.

to 84.0 eV for the Au $4f_{7/2}$ signal according to the SCA A83 standard of the National Physics Laboratory [17]. The evaluation of the binding energies of the embedded Co-clusters was carried out following the standard procedures. A reproducibility of ±5% was attained in the XPS measurements. The ADS100 set was utilized to evaluate the XPS data by subtraction of X-ray satellites applying the background correction according to Shirley [18]. The presence of electrostatic charging effects was followed by measurements including charge compensation by changing the electrostatic potential at the aperture site of the electron energy analyzer.

2.7. Analysis of the Co^{2+}-ions during the photodiscoloration process

The Co^{2+}-ions in solution were quantified by high-resolution inductively coupled plasma spectrometry (ICPS). The samples were acidified with nitric acid and diluted with ultra-pure water. The ion-beam in the plasma unit was directed through the sampling interface and then accelerated into the mass analyzer. The collector system was provided with a Faraday cup for high beam current coupled with an electron-multiplier amplifier for the low intensity signals.

3. Results and discussion

3.1. Homogeneous photocatalytic discoloration of Orange II in homogeneous solution

Fig. 1 shows the dark and light activated photodiscoloration of Orange II. The dark discoloration in the presence of O_2 and H_2O_2 is seen to be negligible. Under solar simulated Suntest light the addition of H_2O_2 (10 mM) leads to a considerable reduction of Orange II, and full discoloration is attained in the case of O_2 purged solutions within 120 min. The O_2 purged solutions seem to produce highly oxidative radicals in solution more effective than H_2O_2. Recently, the details of the oxidation of Orange II in O_2 purged solutions have been investigated [19]. It was reported that H_2O_2 is produced in Orange II/O_2 solutions under light during the decomposition of Orange II. This, in addition to the highly oxidative radicals produced by the O_2 may account for the results obtained in the presence of O_2 in Fig. 1.

Fig. 2 presents the homogeneous photodiscoloration in the dark and under solar simulated irradiation of Orange II diluted solutions and also the photodiscoloration in both cases mediated by PTFE/Co_3O_4 films. The concentration of oxone to be used of 1 mM was estimated form the stoichiometric relation for the degradation of Orange II reported previously using other photocatalysts [9,11,12]:

$$C_{16}H_{11}N_2NaO_4S + (37/2)(2KSO_5\cdot KHSO_4\cdot K_2SO_4) \rightarrow 16CO_2 + 5H_2O + N_2 + NaHSO_4 + 3KHSO_4 + K_2SO_4 \quad (1)$$

The dark decomposition of oxone by Co^{2+}-ions in Fig. 2 was accelerated with respect to the case when oxone was added alone in the dark and/or under light as previously reported [11,12]. Accelerated photodiscoloration in less than 10 min was observed for Orange II under simulated solar light mediated by PTFE/Co_3O_4 films. The long-lived intermediates of within 10 min of reaction were identified as: oxalic acid, 4-hydroxybenzenosulfonic acid and acetic acid. Within this period, also small amounts of formic and glyoxalic acid were also observed. The measurements of the CO_2 production within 10 min concomitant to the discoloration in Figs. 3–5 indicated a mineralization <20%. No attempt to determine the total mineralization time of Orange II beyond the 10 min reaction was carried out in this study since we focused on the details involving the rapid photodiscoloration process.

3.2. Effect of pH on the photodiscoloration of Orange II homogeneous/heterogeneous reactions and repetitive photodiscoloration of Orange II

Fig. 3 presents the kinetics of Orange II photodiscoloration under solar simulated light mediated by PTFE/Co_3O_4 as function of solution pH. Fig. 3 shows that the photodiscoloration kinetics increases as a function of pH in the sequence $7 > 8 > 8.5 > 5 > 10 > 3$. These results suggest a homogeneous–heterogeneous mediated catalysis involving the Co_3O_4 and Co-ions in solution since the Co-ions were observed to precipitate in solution between pH 6.8 and 8.5. Co^{2+}-ions available in solution at $pH < 6.8$ contribute to the oxone decomposition via homogeneous reactions. The competing reactions (2) and (3) are considered to estimate the extend of the homogeneous and heterogeneous reactions:

$$\text{Orange II} + \text{oxone} + Co_3O_4/Co^{2+} \rightarrow \text{oxidation products} \quad k_{\text{hetero}} \quad (2)$$

$$\text{Orange II} + \text{oxone} + Co^{2+} \rightarrow \text{oxidation products} \quad k_{\text{homo}} \quad (3)$$

Since the fastest kinetics in Fig. 3 was observed at initial pH 7, information was sought by induced coupled plasma spectrometry (ICPS) for the amounts of Co^{2+}-ions available in solution as a function of time at this pH. The amounts of Co^{2+}-ions in solution were: $t = 0$, 0.05 ppm; $t = 2$ min, 0.6 ppm; $t = 4$ min, 0.4 ppm; $t = 6$ min, 0.1 ppm; $t = 8$ min, 0.05 ppm. The amounts of Co^{+2}-ions were observed to increase up to 2 min and decreases afterwards. The Co^{2+} seems therefore to be re-oxidized in solution by the oxone and return to the PTFE/Co_3O_4 film due to two reasons: (a) the overwhelming predominance of the photocatalyst mass present in the solution driving the equilibrium during the photocatalytic process and (b) the predominant crystallographic structure of Co^{3+} in the initial Co_3O_4 that assimilates the Co^{2+} in solution in oxidative media as Co-oxide. This mechanism of ion-release and absorption onto a surface is one of the common routes by which nature mineralize bio-refractory organic contaminants in the natural cycle leading to soil and ground water remediation [20,21]. The amounts found in solution for the Co^{2+}-ions suggest a mechanism implying that after Orange II photodiscoloration, these Co-ions go back to the catalyst surface and would subsequently participate in a new degradation cycle.

Fig. 4 shows the stable nature of the PTFE/Co_3O_4 film during repetitive photodiscoloration runs of Orange II. The release in time of the Co^{2+}-ions in solution and subsequent re-adsorption of these ions on the PTFE/Co_3O_4 film explains the stable catalyst performance in Fig. 4. The relative photonic efficiency relates the reactant disappearance (Orange II) to the incident photon flux on the reactor cell walls in a defined time interval. This number allows the standardization of photochemical processes when using different experimental conditions in different laboratories. In Fig. 4, the photonic efficiency (PE) for the photobleaching of Orange II is calculated from the relation:

$$\text{photonic efficiency} = \frac{\text{molecules of Orange II reacted}}{\text{quanta reaching reactor wall}} \tag{4}$$

Taking the Suntest light flux as 1.6 photons/s cm^2, the solution volume in the reactor as ~50 ml and a cell wall surface of 48.8 cm^2, the photobleaching of Orange II (0.05 mM) within 10 min proceeds with a photonic efficiency ~1.

Further evidence for the participation of PTFE/Co_3O_4 film Co-clusters during the photodiscoloration of Orange II is presented in Fig. 5. Photodiscoloration runs of Orange II mediated by oxone 1 mM in the dark an under light are shown in the upper and lower traces of Fig. 5. The middle trace shows the photodiscoloration for a solution of Orange where the catalytic process was mediated by a PTFE/Co_3O_4 film pre-equilibrated during 1 h in 1 M HCl. It is readily seen that the PTFE/Co_3O_4 leached film has a considerably lower catalytic activity compared to the non-leached PTFE/Co_3O_4 film under light. This is due to the solubilization of some of the Co_3O_4 attached clusters.

3.3. Transmission electron microscopy (TEM) of the Co-clusters on PTFE

Fig. 6 presents the TEM clusters of Co_3O_4 with sizes between 3 and 10 nm on the PTFE surface. The distribution of these clusters is seen to be non-uniform and the formation of agglomerates seems to be widespread. The Co_3O_4 attaches on the two sides of the PTFE film. No difference was found in the amount and distribution of the Co_3O_4 clusters in the non-used PTFE/Co_3O_4 film and the same film after the photocatalysis. The cut of the PTFE by cryo ultra-microtomy at temperatures −100 °C does not lead to good results. The PTFE is one of the few plastic films able to conserve some of its ductility at a temperature close to the absolute zero (−269 °C). The compression–expansion during the cutting process induces some movements in the Co_3O_4 particles and the TEM does not allow the accurate determination of the thickness of the Co_3O_4 agglomerates on the PTFE film.

Fig. 7 presents the Co_3O_4 particles and agglomerates on the surface of PTFE close to the epoxy resin coating polymerized at the surface of the PTFE/Co_3O_4 catalyst. This epoxy region is shown in the lower left-hand side of Fig. 7. The epoxy coating is necessary when cutting with the microtome a slice of 200 nm of the PTFE/Co_3O_4 sample.

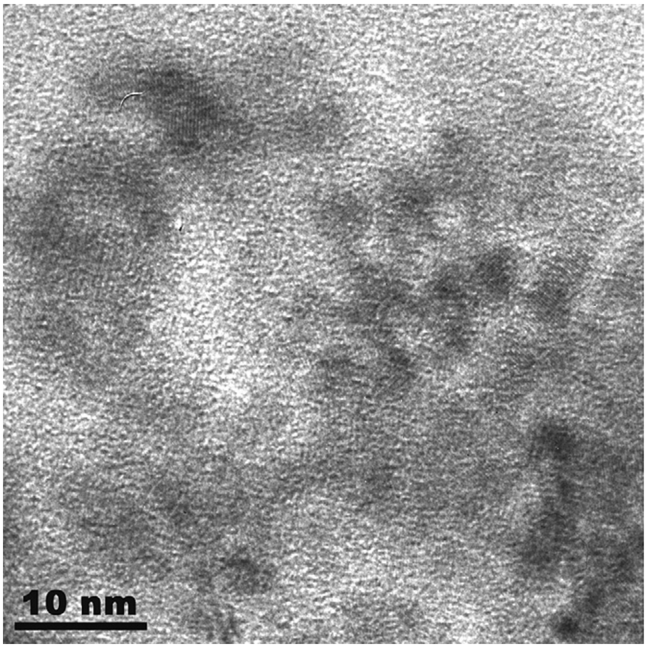

Fig. 6. Transmission electron microscopy (TEM) of the Co_3O_4 particles on the PTFE film showing the Co-oxide agglomerates on the PTFE film.

3.4. X-ray photoelectron spectroscopy (XPS) of PTFE/Co_3O_4 films. Mechanistic considerations

The XPS spectroscopy allows the determination the surface composition of the 2 nm topmost layer and the following composition was found for the surface area occupied by the main elements of the PTFE/Co_3O_4 catalyst: C 1s 15%; O 1s 51.5%; F

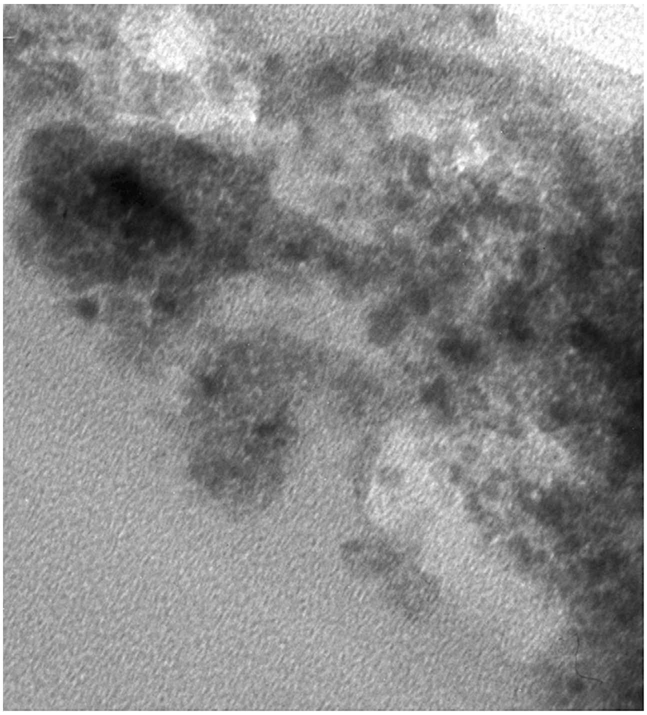

Fig. 7. Co_3O_4 particles on the PTFE film close to the epoxy region after the PTFE film cut by the ultra-microtome.

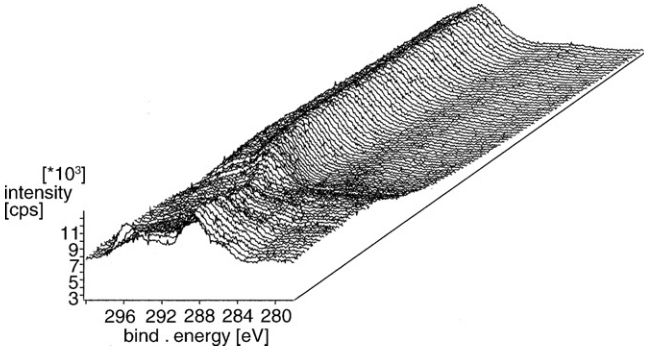

Fig. 8. Depth profile of an Ar sputtered film showing the C-layer distribution in the sub-surface layers.

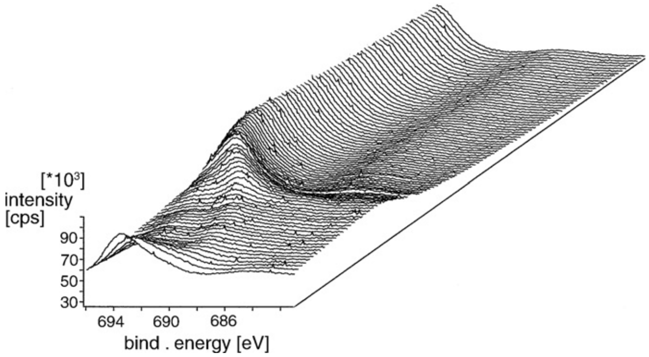

Fig. 9. Depth profile of an Ar sputtered film showing the F-layer distribution in the sub-surface layers.

1s 21.7%; C 11.5%. The composition for the surface area occupied by the main elements of the PTFE alone were: C 1s 21.5%; O 1s 0.25%; F 1s 78.3%.

Fig. 8 shows the PTFE/Co_3O_4 film after erosion of the 100 topmost layers due to the sputtering with 5 keV Ar^+-ions. Figs. 8–11 show the results of XPS depth profile experiments for the C, F, Co and O atomic layers of the PTFE/Co_3O_4 film. About 100 layers with thickness of ~2 Å each were eroded for each of the elements investigated. The value of 2 Å for the layer thickness is an approximate value since: (a) due to preferential sputtering effects [18] and (b) the layer thickness for each of the elements investigated depends on its particular sensitivity factor [17]. Fig. 8 shows that the C 1s peaks begin to decrease in the topmost 15 layers close to the catalyst surface due to the Co_3O_4 loading on the PTFE. A small increase of the C 1s peak is noticed in the 5–6 topmost layers due to the atmospheric CO_2 contaminating the catalyst surface.

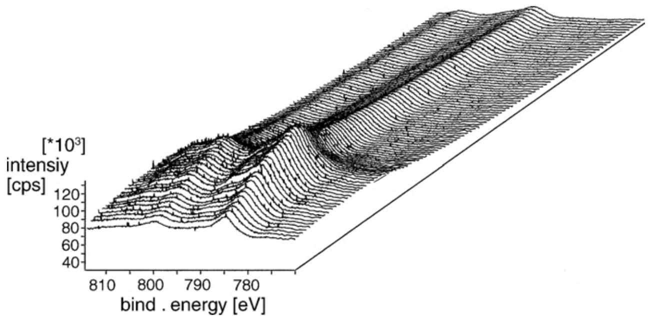

Fig. 10. Depth profile of an Ar sputtered film showing the Co-layer distribution in the sub-surface layers.

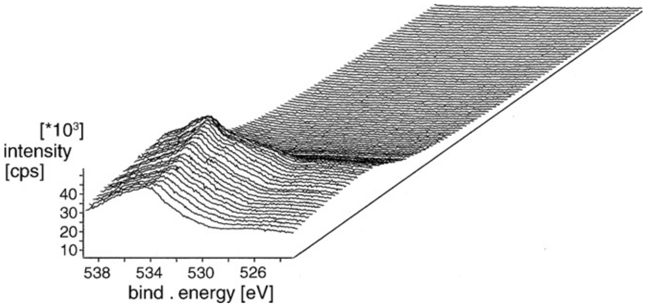

Fig. 11. Depth profile of an Ar sputtered film showing the O-layer distribution in the sub-surface layers.

Fig. 9 shows the depth profile of the F topmost layers of PTFE/Co_3O_4 film. The F atomic layers comprising the $(CF_2–CF_2)_n$ units of PTFE begin to decrease about 40 layers or 80 Å below the topmost layer. This is an indication that the Co_3O_4 reaches this depth in the PTFE film. Fig. 10 shows the growth of Co_3O_4 in the topmost 40 layers of the PTFE/Co_3O_4 film as shown by the increase in the doublet Co $2p_{3/2}$ at 782.3 eV and Co $2p_{3/2ox}$ at 784.2 eV. Fig. 11 shows the depth profile of the O 1s doublet showing the rich content of the O-atomic layers in the 21–22 topmost catalyst layers. This O 1s signals are associated with the Co_3O_4 deposited in the PTFE film. At the end of the dye photodiscoloration process no S- or N-atoms were detected on the PTFE/Co_3O_4 film. This is indicative of the efficient catalytic nature of the photocatalyst employed that decomposes the Orange II without accumulating decomposition products on its surface.

At time zero the Co in the photocatalyst shows a doublet with Co $2p_{3/2}$ BE of 782.3 eV (64.2%) and Co $2p_{3/2ox}$ at 784.2 (45.8%). After the photocatalysis the doublet shows a notable increase for the Co $2p_{3/2}$ peak shifted to a BE of 781.8 eV. This is the evidence for the increase in the reduced form of Co^{2+}-ions after Orange II discoloration. The origin of the of the reduced form of Co^{2+}-ions is due to the photosensitization by Orange II of the PTFE/Co_3O_4 film leading to the formation of an azo-dye radical cation [19,22]. A concomitant charge transfer of the electron to the Co_3O_4 layer of the PTFE film occurs as shown in Eq. (7) followed by reactions leading to the dye decomposition in Eqs. (8) and (9) as previously reported in Refs. [11,12]:

$$\begin{aligned}&\text{Orange II} + \text{PTFE/Co}_3\text{O}_4 + h\nu\\&\quad\rightarrow [\text{Orange II}* + \text{PTFE/Co}_3\text{O}_4]\\&\quad\rightarrow \text{Orange II}^{\bullet+} + \text{PTFE/Co}_3\text{O}_4\text{e-}_{\text{cb}}\ (\text{or Co}^{2+})\end{aligned}\tag{5}$$

$$\text{Orange II}* + \text{HSO}_5{}^- \rightarrow \text{Orange II}^{\bullet+} + (\text{HO}^- + \text{SO}_4{}^{\bullet-})\tag{6}$$

$$\begin{aligned}&\text{PTFE/Co}_3\text{O}_4\text{e-}_{\text{cb}}\ (\text{or Co}^{2+}) + \text{HSO}_5{}^-\\&\quad\rightarrow \text{Co}^{3+} + \text{SO}_4{}^{2-} + \text{HO}^-\end{aligned}\tag{7}$$

$$\text{Orange II}^{\bullet +} + \text{HSO}_5^{\,-}\ (\text{oxone in net sense}) \rightarrow \text{organics/radicals}\,(\text{R}^{\bullet}) + (\text{HO}^- + \text{SO}_4^{\,\bullet -}) \quad (8)$$

$$\text{organic/R}^{\bullet} + \text{Co}^{3+}/\text{Co}^{2+}/\text{HO}^-/\text{SO}_4^{\,\bullet -} \rightarrow \text{long-lived intermediates} \quad (9)$$

$$\text{R}^{\bullet} + \text{HSO}_5^{\,-}/\text{O}_2 \rightarrow \text{organics} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{\,\bullet -} \quad (10)$$

With the possible side reactions:

$$\text{HSO}_5^{\,-} + (\text{OH or SO}_4^{\,\bullet}) \rightarrow \text{SO}_5^{\,\bullet -} + (\text{HO}^- \text{ or SO}_4^{\,2-}) + \text{H}^+ \quad (11)$$

$$\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet} \quad (12)$$

4. Conclusions

An innovative way has been presented to prepare PTFE/Co_3O_4 supported catalyst by a suitable thermal treatment of the PTFE film in contact with the Co_3O_4 colloid. This catalyst allows the accelerated discoloration of Orange II. The nanosized Co_3O_4 clusters observed on PTFE suggests that this inert film is a structure forming agent leading to highly divided clusters of Co_3O_4. The absence of S- and N-atoms on the PTFE/Co_3O_4 film shows the efficient intervention of the photocatalyst in the discoloration process. By XPS Ar-sputtering it is possible to obtain the profile of the C-, O-, Co- and F-components of the 100 topmost PTFE/Co_3O_4 film. The nature of the homogeneous/heterogeneous nature of the photocatalysis is described and a mechanism is suggested for the dye photodiscoloration. The reaction mechanism suggested is consistent with the observed long-range performance of the PTFE/Co_3O_4 catalyst.

Acknowledgment

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