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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

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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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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.

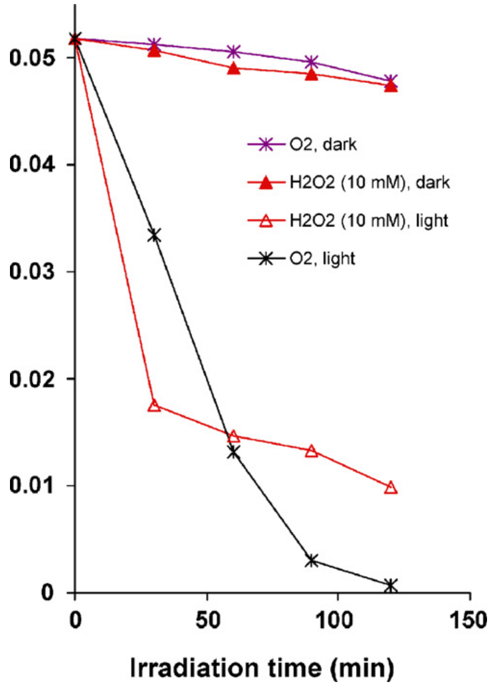

Fig. 1. Dark discoloration and photodiscoloration of diluted Orange II (0.05 mM) in homogeneous solution. Solutions were irradiated in a Suntest solar light simulator (90 mW/cm^2) at initial pH 7.

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