Applied Catalysis B: Environmental 224 (2018) 912–918

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research Paper

Influence of surface density on the CO_2 photoreduction activity of a DC magnetron sputtered TiO_2 catalyst

F. Fresno[a,**], P. Reñones[a], E. Alfonso[a], C. Guillén[b], J.F. Trigo[b], J. Herrero[b], L. Collado[a], V.A. de la Peña O'Shea[a,*]

[a] Photoactivated Processes Unit, IMDEA Energy Institute, Parque Tecnológico de Móstoles, Avda. Ramón de la Sagra, 3, 28935 Móstoles, Madrid, Spain
[b] Department of Energy, CIEMAT, Avda. Complutense 40, 28040 Madrid, Spain

ARTICLE INFO

Keywords:
CO2 photoreduction
TiO2
DC-magnetron sputtering
Reaction mechanism
Peroxocarbonates

ABSTRACT

Advancing in the photocatalyst scale-up is crucial for the development of highly efficient solar fuels production at industrial scale. Here, we report DC-magnetron sputtering as a suitable technique to produce photocatalytic TiO_2 coatings for CO_2 reduction with a view on process scalability. The crystallinity of the obtained TiO_2 coatings varies with surface density, with amorphous or quasi-amorphous coatings obtained with very low densities, while UV light absorption coefficients show the opposite trend, which has been related to the proportionally higher abundace of surface defects and grain boundaries associated to the small crystal size and/or amorphicity of the lightest coatings. The as-prepared samples lead to the reduction of CO_2 as demonstrated by ^{13}C isotope tracing. An optimum catalyst area density of 1 g/m^2 (by geometric area) is obtained in terms of CO_2 photoreduction production, which is ascribed to a compromise situation between crystallinity and absorption coefficient. Selectivity to the different reaction products also varies with the coating characteristics, with amorphous or quasi-amorphous light coatings favouring methanol formation, in contrast with the preferred CO evolution in heavier, crystalline ones. Raman spectroscopy reveals the formation of peroxo and peroxocarbonate species on the photocatalyst surface as oxidation products during the CO_2 reduction, the accummulation of which is proposed to be related to the observed catalyst deactivation.

1. Introduction

The development of CO_2 valorization strategies has become a crucial goal in order to fulfil the climate pledges that were raised by the Paris Agreement and ratified in Marrakesh in the last Conference of the Parties (COP22). The big challenge lies in the high stability of the CO_2 molecule, which requires a large amount of energy to be activated. Therefore, the key for the promotion of CO_2 transformation technologies is their integration with renewable energy sources. Photocatalytic CO_2 reduction, one of the processes encompassed in the so-called Artificial Photosynthesis, aims at producing sustainable fuels using water as reducing agent, and is mainly based on the use of semiconductor catalysts under mild operation conditions and using sunlight as the driving energy source [1–3]. One of the main bottlenecks for the development of this process resides in the difficulty for establishing comparison criteria for catalytic activities, reaction conditions and irradiation geometries, which redounds to the current lack of optimized parameters with a view on process scalability [4,5]. Therefore, in order to achieve a successful photofuels production it is necessary to tackle the challenge in a holistic manner that identifies and solves the barriers and needs inherent to a large-scale development.

In this sense, it is crucial to advance in the fabrication and scale-up of photocatalytic materials using techniques that provide uniform and pure films with high deposition rates and short processing times. In any case, in order to lead to an efficient scale-up, it would be necessary to use preparation procedures adequate for large areas. In recent years, great advances have been realized in procedures, both chemical and physical, for the large-scale preparation of nanostructured materials, which can be applied to the scale-up of devices for artificial photosynthesis [1–3,6]. In this respect, thin film conformations offer advantages such as an optimal surface conformation and material quantity minimization in comparison with powdered materials. These large-area techniques are especially indicated for CO_2 photoreduction since they do not introduce undesired organic compounds on the catalyst surface. Additionally, the optimization of highly dispersed active sites provided by these methods may lead to an improvement of the photocatalytic

---

* Corresponding author.
** Co-Corresponding author.
E-mail addresses: fernando.fresno@imdea.org (F. Fresno), victor.delapenya@imdea.org (V.A. de la Peña O'Shea).

https://doi.org/10.1016/j.apcatb.2017.11.022
Received 26 August 2017; Received in revised form 8 November 2017; Accepted 9 November 2017

activity.

However, in the scale-up of a process, especially in the specific case of photo-activated processes, an increase of the layer thickness leads to a threshold value above which little or no dependence is found. This threshold depends on the nature of the light and the depth, structure and optical absorption coefficient (α) of the film, which arises from two main factors: 1) at high depth the light intensity becomes so weak that no significant number of electron-hole pairs can be produced [7,8]; and 2) the proportion of the charge carriers produced at high depth that reach the surface before recombination is low due to their limited diffusion length [7]. Therefore, not all thin-film techniques are appropriate for a fruitful integration in pilot and demonstration plants, and currently those based on, e.g., nanolithography, are only adequate for fundamental studies. However, others like reactive DC magnetron sputtering (DC-MS), starting from conductive substoichiometric oxides or pure metal targets, are powerful methods to synthesize oxides over large areas and at high deposition rates by setting the deposition conditions in the metal-oxide transition region. This would enable these techniques to be transferred from the laboratory to larger scales. The DC-MS technique allows the deposition of well adherent, transparent films with a controllable density at high deposition rate, with good reproducibility and control over the chemical, structural, morphological and textural properties of the final materials [8–11]. From the manufacturing point of view, it is also interesting that the technique allows the use of flexible substrates like carbon fibre and polymer foils, among others. The deposition onto flexible supports facilitates the transport and manipulation in shape-adaptable devices [12,13] and enables a low-cost mass production by roll-to-roll based continuous fabrication processes [14,15]. In addition, it allows the preparation of tailor-made photocatalytic coatings with improved reactivity due to the control of the nanostructure from amorphous to even preferentially facet-oriented [16,17].

The aim of the present study is to assess DC magnetron sputtering as a suitable method to prepare photocatalytic coatings for CO_2 reduction with a view on process scalability and to study the effect of the coating conditions on the structure, optoelectronic properties and photoactivity of the catalyst, in order to propose an optimum situation for the pursued reaction. For that purpose, results obtained using coatings with different area densities are reported and related to the coating characteristics. Regarding the photocatalyst choice, TiO_2 still represents the most appropriate material for photocatalysis [18–20]. In the particular case of CO_2 reduction, TiO_2 is clearly preponderant, being employed in more than 50% of the works published to date [21]. Therefore, it appears as the most suitable option for scalability studies.

2. Experimental

2.1. Synthetic procedures

TiO_2 catalysts were prepared at room temperature by reactive DC magnetron sputtering of a metallic target (Ti, 99.6% purity). The deposition processes were performed simultaneously on glass fibre (GF) wafers with 132.7 cm^2 geometrical area and on soda-lime glass (SLG) substrates with $2 \times 2\ cm^2$ area taken as references for characterization purposes only (Table 1). The sputtering chamber was first evacuated to a base pressure of 3.0×10^{-4} Pa, and then raised three orders of magnitude by introducing the working gas (Ar) and the reactive gas (O_2) through separated mass-flow controllers, according to the proportion that was optimized in a previous work for the attainment of anatase TiO_2 layers [11]. The sputtering power density was maintained at 8 W/cm^2 and the sputtering time was varied to obtain film thicknesses ranging from 0.05 to 1.79 µm, as has been verified by profilometric measurements on the SLG substrates. In this way, the mass deposited on the GF substrates has been increased from 3 to 100 mg (geometrical area densities between 0.23 and 7.54 g/m^2). The superficial to geometrical area ratio increases from 1.01 for SLG to 1.35 for GF, as it has been obtained by profilometry on several bare substrates. This has been used to estimate the equivalent film thickness on GF in relation to the thickness value measured on the respective SLG partner, as it is shown in Table 1.

Table 1
Supported TiO_2 samples prepared by DC-MS. Samples numbered the same were obtained simultaneously.

GF samples	SLG samples	TiO_2 area density (gm^{-2})	TiO_2 film thickness on SLG (µm)	Equivalent film thickness on GF (µm)
GF1	SLG1	0.23	0.05	0.04
GF2	SLG2	0.53	0.12	0.09
GF3	SLG3	1.06	0.25	0.19
GF4	SLG4	2.11	0.50	0.37
GF5	SLG5	3.17	0.75	0.56
GF6	SLG6	4.22	1.00	0.75
GF7	SLG7	7.54	1.79	1.34

2.2. Characterization methods

The obtained samples were characterized by X-ray diffraction (XRD) using Cu K_α radiation in a Panalytical EMPYREAN. Diffraction angles were compared with International Centre for Diffraction Data Powder Diffraction Files (PDF) for phase identification. Mean crystallite sizes were calculated by using the Scherrer formula. The surface topography has been examined with a Park XE-100 atomic force microscope (AFM).

Raman spectra were recorded at room temperature using a JASCO NRS-5000/7000 series spectrometer with an excitation wavelength of 532 nm. For Raman shift and band width determination, the most intense band of the anatase spectrum was fitted to an asymmetric variation of the pseudo-Voigt profile [22]. Total transmittance T and reflectance R of the coatings were measured in the wavelength range between 250 and 1800 nm in a Perkin–Elmer Lambda 9 spectrometer equipped with an integrating sphere. Then, the absorptance A(%) was deduced using $A(\%) = 100 - T(\%) - R(\%)$ and the absorption coefficient α has been calculated as $\alpha = (1/t) \ln\{100/(T(\%) + R(\%))\}$ [23], taking t as the film thickness on SLG or GF substrates.

2.3. CO_2 photoreduction procedure

Gas-phase photocatalytic experiments were conducted in a continuous-flow mode. The TiO_2-sputtered GF wafers were introduced in a stainless steel reactor with an effective volume of 280 mL and provided with a borosilicate glass window for irradiation. The reaction conditions were set at 2 bar and 50 °C maintaining a CO_2:H_2O molar ratio of 7.25. In-line gas chromatography analyses (GC Agilent 7890A) were performed to quantify the reaction products every 22 min. The photocatalytic measurements were performed using four UV lamps of 6 W each (λ_{max} = 365 nm), with a total irradiance of 27.95 Wm^{-2} under 400 nm (Fig. S1). Before starting the experiments, the reactor was firstly outgassed at 50 °C and then purged with Ar (100 mL/min) for 1 h to remove any residual compounds weakly adsorbed on the catalyst surface. Then, the reactor was flushed with the CO_2—H_2O mixture for 1 h to establish an adsorption-desorption balance at the reaction temperature. Prior to illumination, the reactor was pressurized and kept at the reaction flow rate. All photocatalytic tests were carried out over an irradiation period of 18 h.

Isotope tracer experiments were carried out in a 15.6 mL stainless steel reactor with a borosilicate glass window operated in batch mode. After outgassing, $^{13}CO_2$ (Cambridge Isotope Laboratories, Inc., 99.2% ^{13}C, < 1% ^{18}O) and H_2O were introduced in the reactor at 50 °C with a total pressure of 2 bar. After 30 min irradiation with a 6 W UV lamp (λ_{max} = 365 nm), the gas was extracted to a quadrupole mass spectrometer (Pfeiffer OMNISTAR) for analysis (Fig. S2).