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Preparation and characterization of TiO_2/carbon composite thin films with enhanced photocatalytic activity

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ABSTRACT

Composite TiO_2/carbon thin films prepared by physical vapor deposition techniques on fused silica substrates show enhanced photocatalytic activity towards decomposition of methanol to CO_2 and water, as compared to pure TiO_2 films of similar thickness. Raman and XRD measurements confirm that annealed TiO_2 films exhibit anatase structure while the carbon layer becomes graphitic. Characteristic for the composite films is an enhanced optical absorption in the visible range. The presence of the carbon film causes a shift of the TiO_2 absorption edge and modifies its grain size to be smaller. We hypothesize that the observed enhancement of photocatalytic activity is due to synergy effects at the carbon/TiO_2 interface, resulting in smaller titania crystallite size and anisotropic charge carrier transport, which in turn reduces their recombination probability.

1. Introduction

Titanium dioxide is a well-known and widely studied photocatalyst especially after the pioneering work of Fujishima and Honda on water splitting with light [1]. Ever since it has been of great interest due to potential applications for environmental remedies such as purifying organic waste or cleaning air pollutants [2], for energy conversion technologies such as in solar cells [3], production of "solar" hydrogen [1], etc. TiO_2 is recognized for its characteristic properties such as strong oxidation potential of photogenerated holes, chemical stability, non-toxicity and low cost. TiO_2 crystallizes in three crystal phases; anatase, rutile and brookite, among which the anatase phase typically has a higher photocatalytic activity due to its band position with respect to the hydrogen redox potential [4]. However, it has some practical limitations in absorbing the visible part of the electromagnetic spectrum due to its wide bandgap (~3.2 eV), and it suffers from fast electron-hole recombination [5]. Since the ultraviolet (UV) portion of solar radiation at the earth surface constitutes only 5% of the total, it is highly desirable to extend the light absorption of the photocatalyst in the visible range.

Among the many attempts in this direction, modification with carbon (C) has been an efficient route to alter the photocatalytic properties of TiO_2 [6–8]. Carbon itself plays an important role in a number of heterogeneous catalytic processes acting as adsorbent, catalyst support or active material [9]. In particular, the properties of graphitic carbon films, such as good conductivity and high light absorption in the visible range, are utilized for photocatalytic applications [9].

Carbon as a dopant in TiO_2 improves the optical absorbance in the visible spectral range by introducing localized energy states in the bandgap, but at the same time increases the electron-hole recombination probability [10]. Doping and addition of carbon to TiO_2 catalysts, where the carbon atoms substitute oxygen or titanium atoms or occupy interstitial sites, can be achieved in different ways, and there are several reports on the positive catalytic effect of these procedures [8,11,12]. Despite these observations, it is critically argued that experimental evidence for the enhancement of photocatalytic reactions with visible light for the carbon-doped system is still missing or at least controversial [13]. Several studies also suggest that TiO_2 on an activated carbon matrix simply enhances the surface area and hence more reactants can adsorb on the surface of the catalyst for photocatalytic degradation of pollutants [14,15]. Similarly, recent work describing how carbon nanotubes have been employed as a support for TiO_2 is assigned to improvements of the photo-response due to improved conductivity and dispersion of the system [7,16–18]. With these previous results as a reference, we

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have chosen to introduce carbon as a separate film and investigate its role in a well-defined and simple model system of C/TiO_2 thin composite film. The main investigated parameters are the thickness of the films and the effect of annealing on the morphology and optical properties of TiO_2.

Takahashi et al. [5] have suggested that the efficiency of TiO_2 is decreased due to recombination of the photo-generated carriers at trapping sites both in the bulk and at the surface. Therefore, films with smaller thickness are expected to show reduced (bulk) electron-hole recombination. This is the reason to restrict the thickness of investigated films to no more than 100 nm. It is also expected that interface effects will play an important role, which could be sensed at a certain TiO_2 thickness; meaning for thick TiO_2 films, the underlying carbon film will no longer play a role. Li and Gray [19] have suggested that the interface between solid particles of the same kind or different kinds act as a 'hot-spot' for enhanced photocatalytic activity. Another issue of interest is related to synergy effects at the interface between the films and how they affect the charge transport as well as the photocatalytic activity.

While the primary aim of this work is to understand how a thin, graphitic-like carbon film enhances the optical absorption in the visible range, and what are the structural changes of TiO_2 deposited on carbon, another aim of the study is to provide a base for comparison with core-shell and other self assembled TiO_2/C composites [10,20]. Hitherto, little work has been carried out on graphitic-like carbon material with TiO_2 for photocatalytic and photoelectrochemical applications [10,21,22]. We hope that this work will lead to further improvements in this direction.

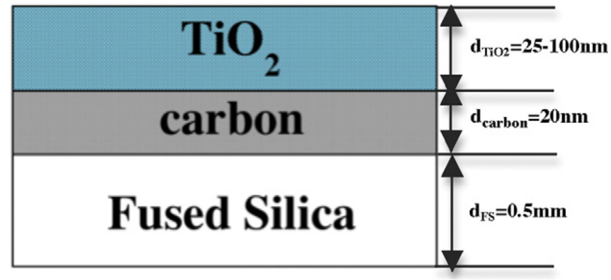

Fig. 1. Schematic structure of the prepared samples with respective thickness of the carbon and titania films.

2. Experimental

2.1. Sample preparation

Fig. 1 shows the schematic structure of the investigated samples. The first fabrication step was the deposition of a carbon film on a fused silica substrate (Double side polished (DSP), University wafer). This was followed by TiO_2 deposition onto the carbon film. Before deposition, the substrates were cleaned by a standard procedure that includes washing in acetone and iso-

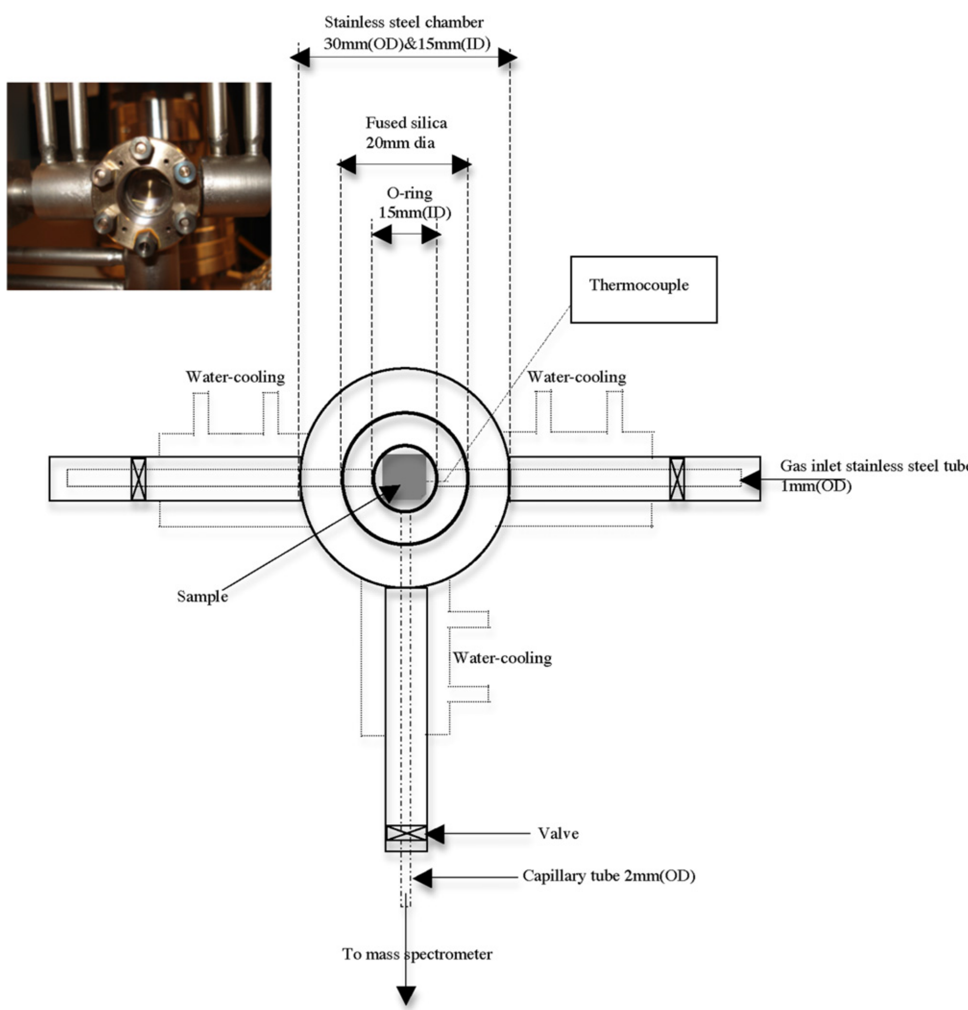

Fig. 2. Schematic of the photocatalytic microreactor setup used in this work; the inset shows a photograph of the reactor chamber.