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Full Length Article

Photocatalytic C_{60}-amorphous TiO_2 composites prepared by atomic layer deposition

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ABSTRACT

Nanocomposites of TiO_2 and single fullerene (C_{60}) molecule are prepared by atomic layer deposition (ALD). To create nucleation sites for the ALD reaction, the bare fullerene is functionalized by H_2SO_4/HNO_3 treatment, which results in C_{60}-SO_3H. After a NaOH washing step the intermediate hydrolyzes into C_{60}—OH. This process and the consecutive ALD growth of TiO_2 are monitored with FTIR, TG/DTA-MS, EDX, Raman, FTIR, XRD, and TEM measurements. Although the TiO_2 grown by ALD at 80 and 160 °C onto fullerol is amorphous it enhances the decomposition of methyl orange under UV exposure. This study proves that amorphous TiO_2 grown by low temperature ALD has photocatalytic activity, and it can be used e.g. as self-cleaning coatings also on heat sensitive substrates.

1. Introduction

Photocatalytic materials using solar energy have important applications both in green chemical synthesis of e.g. organic compounds or H_2 and also in the treatment and decomposition of environmental pollutants [1–5]. Semiconductor oxides are widespread photocatalysts, and among them TiO_2 is the most researched and used one, because it is an n-type semiconductor with ideal band gap and energy levels for both half reactions of water splitting. In addition, it is stable and non-toxic. However, its application still faces some difficulties, mostly owing to its narrow light response range, i.e. the band gap of TiO_2 (3.2 eV) limits its absorption to the UV spectrum [5–7]. In order to increase the photocatalytic activity of TiO_2, various strategies have been tried. To shift the absorption to the visible range, TiO_2 can be doped with heteroatoms to introduce new energy levels in the bandgap. Also composites of TiO_2 with Vis active organic molecules or other semiconductors may show similar effect. Another strategy is to reduce recombination of the photo-generated electrons and holes. This can be achieved by using electron scavenger compounds during the photocatalysis or applying composites of TiO_2 with semiconductors and other nanomaterials, like carbon nanostructures [8].

The C_{60}, as an electrophilic acceptor, due to its conjugated π electron system, may facilitate the TiO_2 in the separation of the light induced electron-hole pairs [5,9,10]. Several methods have been reported to prepare C_{60}-TiO_2 composites, e.g. sol-gel synthesis, oxidation or wet impregnation [4,5,10,11]. These composites showed enhanced photocatalytic activity compared to TiO_2. In most cases the charge transfer between C_{60} and TiO_2 was emphasized in the photocatalytic mechanism [5,6,10,12,13].

To make TiO_2 composite with a single C_{60} molecule required a method which can deposit TiO_2 in very low and programmable amount. Since C_{60} is very small with ca. 0.6 nm diameter, we decided to grow TiO_2 onto C_{60} by atomic layer deposition (ALD), which is a surface controlled, gas phase technique capable of controlling the thickness of the film with sub-nm precision [14–25]. ALD films were already successfully grown on various carbon nanostructures like carbon nanotubes (CNTs), carbon aerogels, graphene oxide and graphene [26,27]. However, direct deposition of ALD layers onto a single fullerene molecule has not been reported yet. There was only one attempt, where thermally evaporated C_{60} porous films were covered with ZnO using ALD, but no composites of single C_{60} and ZnO were reported [28].

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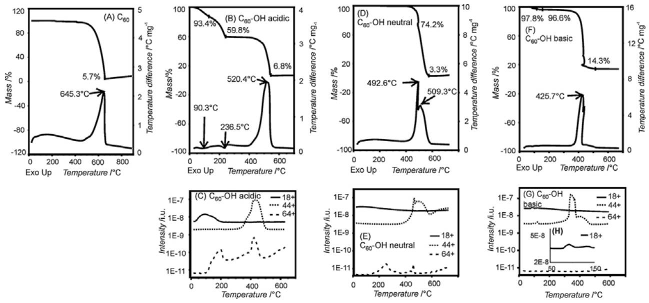

Fig. 1. TG/DTA-MS curves of (A) bare C_{60}; (B-C) C_{60}—OH after functionalization with acidic pH; (D–E) C_{60}—OH after washing with H_2O to neutral pH, (F–G) C_{60}—OH after washing with NaOH to basic pH. The inset in the MS image shows the magnified ion current curve of the $m/z = 18^+$ fragment. Molecular fragments $m/Z = 18$, 44 and 64 are associated with water, CO_2 and SO_2 respectively.

Hence, this study presents the first ALD onto an individual fullerene molecule. At first C_{60} was functionalized by OH groups to generate nucleation sites for ALD. This was achieved by treating C_{60} with a HNO_3/H_2SO_4 mixture, followed by washing with H_2O and NaOH solution. The formation of fullerol (C_{60}—OH) was monitored by TG/DTA-MS and FTIR. Consecutively, TiO_2 was successfully deposited onto fullerol by ALD at both 80 and 160 °C, as proven by SEM-EDX, Raman, FTIR, XRD and TEM. At such low ALD temperatures the TiO_2 grown is amorphous; but the C_{60}/TiO_2 composites did exhibit photocatalytic activity. We suggest that ALD deposited amorphous TiO_2 seems to be unique as it is photocatalytically active, unlike other TiO_2 materials.

2. Results and discussion

2.1. Functionalization of C_{60} with OH groups

TG/DTA-MS measurements in air were carried out after each preparation step to check the success of functionalization (Fig. 1). Hence, intermediate samples were taken from the bare fullerene, from the HNO_3/H_2SO_4 acidic suspension of C_{60}, from the suspension washed with water to neutral pH and from the final basic suspension treated with NaOH, respectively. These intermediate samples were studied in dry state. The bare fullerene decomposed and burnt at around 600 °C in an exothermic process (Fig. 1A). The TG and DTG curves of the as-prepared acidic sample showed that its decomposition occurs in three steps (Fig. 1B). Based on the evolved gas analytical (EGA) curves, H_2O (identified as $m/z = 18^+$) was released up to 200 °C, and SO_2 ($m/z = 64^+$) between 150 and 250 °C (Fig. 1C). Finally the sample decomposed between 400 and 550 °C accompanied with the release of SO_2 and CO_2 ($m/z = 44^+$), 100 °C lower than the bare fullerene. The parallel evolution of H_2O and SO_2 indicated the presence of H_2SO_4 in the acidic sample. Thus, the H_2O released does not exclusively come from the expectedly introduced surface OH groups of C_{60}, but mostly from the decomposition of H_2SO_4. After washing the acid treated sample to neutral pH there was no sign of H_2O evolution, however, SO_2 still evolved (Fig. 1D–E). Finally after the NaOH treatment there was only a small weight loss step at 100 °C on the TG curve before the final decomposition around 500 °C (Fig. 1F). At 100 °C only H_2O was released. This H_2O can be originated from the surface OH groups of C_{60}, because there is no parallel SO_2 evolution (Fig. 1G). This finding means that oxidation process resulting in C_{60}—OH goes through the formation and consecutive hydrolysis of a C_{60}-SO_3H intermediate [29], rather than through the previously expected C_{60}-NO_2 intermediate [30]. Based on the 1.2% mass loss between 80 and 160 °C (excluding adsorbed water), after the functionalization reaction each C_{60} molecule has two OH groups in average.

The functionalization process was also followed by FTIR measurements (Fig. 2A). In the spectrum of bare fullerene there is no peak above 3400 cm^{-1} showing the absence of OH groups; only the four characteristic FTIR peaks of C_{60} are visible. These peaks have been assigned to the four dipole-active vibrational modes of a C_{60} skeleton with icosahedral symmetry. The 527 and 576 cm^{-1} modes are associated with radial motion, while the 1182 and 1427 cm^{-1} modes belong to tangential motion of the carbon atoms, respectively. Among them, the most characteristic vibrational mode is the pentagonal 'pinch' mode at 1427 cm^{-1} [31–33]. The final NaOH treated fullerene, i.e. fullerol (C_{60}—OH), has a peak at 3400 cm^{-1} proving the successful functionalization. The 1429 cm^{-1} peak gets wider, and further peaks at 1619, 1385 and 1051 cm^{-1} belonging to the υ C=C, δ C—O and υ C—O vibrations are observable (Fig. 2a) [34].

2.2. Deposition of TiO_2 on C_{60}—OH by ALD

After the ALD reaction the SEM images show only aggregated blocks (Fig. S1), because the C_{60}—OH molecules and TiO_2 particles are too small to be seen at this resolution. The presence of Ti on the fullerol was confirmed by EDX (Fig. S2). The amounts of Ti, O and C are listed in Table 1 (Au and Pd from the as-sputtered conductive Au/Pd layer are only shown in Fig. S2, but not in Table 1). The atomic% of Ti in the sample prepared at 160 °C was the half of the one obtained at 80 °C. Due to their heat sensitivity, less OH groups remain on C_{60}—OH at the higher temperature, and thus there are less nucleation sites for the ALD reaction at 160 °C.

The powder XRD analysis confirmed the purity of bare fullerene (ICDD 01-081-2220 and ICDD 00-044-0558); however, in the case of C_{60}-TiO_2 composites there were no peaks corresponding to TiO_2 in the diffractograms (Fig. S3), as the TiO_2 deposited by ALD below 200 °C is amorphous[5,11,35]

The Raman spectrum of the bare C_{60} (I_h point group) showed the characteristic peaks of fullerene [36], i.e. $H_g(1)$ (270 cm^{-1}); $H_g(2)$ (432 cm^{-1}); $A_g(1)$ (494 cm^{-1}); $H_g(3)$ (707 cm^{-1}); $H_g(4)$ (770 cm^{-1}); $H_g(7)$ (1420 cm^{-1}); $A_g(2)$ (1464 cm^{-1}) (Fig. 2.B). Among these the A_g ones are the most intensive ones (494 cm^{-1} and 1464 cm^{-1}). The TiO_2 has characteristic Raman vibrations at e.g. 144, 403, 520, and 642 cm^{-1} [22]; however, in the case of the as-prepared C_{60}-TiO_2 samples these TiO_2 peaks were not observed, since the deposited TiO_2 was amorphous. Nevertheless, the presence of TiO_2 on C_{60} and the bond formed between them can be indirectly concluded from the Raman spectra [37]. Due to the charge transfer between the fullerene and TiO_2, the 1464 cm^{-1} peak shifted to higher wavenumbers and the base of the bands got wider, i.e. C_{60} (1461 cm^{-1}), C_{60}—OH (1462 cm^{-1}), C_{60}-TiO_2–80 °C (1465 cm^{-1}), C_{60}-TiO_2–160 °C (1465 cm^{-1}), as seen in Fig. 2C.

The FTIR spectra also showed the successful bond formation between C_{60} and TiO_2 in an indirect way, similarly to the Raman results. The 1428 cm^{-1} peak of the C_{60} is sensitive to losing or gaining an electron [37]. After the ALD of TiO_2 onto fullerol, this peak splitted into several peaks and the base of the peak got wider (Fig. 2A), showing the interaction between TiO_2 and C_{60}. The change in the intensity of the OH peak over 3200 cm^{-1} also confirmed indirectly the formation of C_{60}-TiO_2 composites (Fig. 2A). While on the one hand, the ALD reaction consumes the surface OH groups of fullerol; on the other hand, new OH groups appeared on the surface of the as-formed TiO_2 particles. Their amount was in fact larger than that of the surface OH groups of C_{60}—OH. This phenomenon was more notable on the C_{60}-TiO_2 sample prepared at 160 °C, because the surface structure of this sample is probably better organized due to the higher ALD temperature.

Direct evidence about the existence of the C_{60}-TiO_2 composites was obtained by TEM. Since the Formvar film on the Cu grid was ca. 10 nm thick, the bare 0.6 nm large fullerene molecules could