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## Core-shell carbon nanosphere-TiO<sub>2</sub> composite and hollow TiO<sub>2</sub> nanospheres prepared by atomic layer deposition

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**Abstract.** Core-shell carbon-TiO<sub>2</sub> composite and hollow TiO<sub>2</sub> nanospheres were prepared using carbon nanospheres as hard-templates, coating them with TiO<sub>2</sub> using atomic layer deposition, and subsequent burning out of the carbon cores. The bare carbon, the composite carbon-TiO<sub>2</sub> and the hollow TiO<sub>2</sub> nanospheres were characterized with TG/DTA-MS, FTIR, XRD and SEM-EDX.

### 1. Introduction

Photocatalysis using solar energy has been acknowledged as an environment friendly approach to address environmental problems, such as pollutant degradation, heavy metal cation reduction and treatment of wastewater [1]. Titanium oxide materials have great potential as photocatalysts in various reactions due to their chemical stability, non-toxicity, and high reactivity [2,3]. However, the fast recombination of photo-excited charge carriers leads to their short lifetime, which interferes with achieving maximum activity of TiO<sub>2</sub> photocatalysts, so it is desirable to use a co-catalyst to synthesize economically feasible TiO<sub>2</sub>-based photocatalysts with improved charge separation and low electron-hole recombination rates. To fulfill this, several carbon materials have been utilized to synthesize carbon-TiO<sub>2</sub> composite photocatalysts [4,5]. Carbon-based nanomaterials are very attractive, due to their high surface area, good thermal and electrical conductivity, mechanical as well as chemical stability, and they provide an ideal support for heterostructure elaboration. Spherically shaped carbon materials have been known for decades and their properties have been exploited in many areas (e.g. tyres, batteries, printer inks) [6,7]. Inorganic hollow spheres, such as ZnS, WO<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>, have special optical, optoelectronic, magnetic, electrical, thermal, electrochemical, photoelectrochemical and catalytic properties, and have been investigated due to their potential application in catalysts, lithium-ion batteries, biomedical materials and gas sensors [8,9].

There are several preparation methods for creating carbon nanospheres as cores for carbon TiO<sub>2</sub> composites, such as laser ablation, chemical vapor deposition and hydrothermal synthesis [7]. Atomic



layer deposition (ALD) allows the coating of surface of nanostructures in a conformal and homogeneous way, with precise control of the thickness of the deposited film at the nanoscale [6,10–14]; hence, it is an outstanding possible tool to coat carbon nanospheres.

In this study, we prepared carbon nanospheres using hydrothermal synthesis, and coated them with TiO<sub>2</sub> layer using ALD to obtain a composite material. In order to get the hollow TiO<sub>2</sub> nanospheres, we burnt out the carbon cores of the composite. We used thermogravimetry and differential thermal analysis coupled with mass spectrometry (TG/DTA-MS), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX) to characterize the as-prepared materials.

## 2. Materials and characterization

### 2.1. Preparation of the carbon nanospheres

To prepare the carbon nanospheres, the hydrothermal method was used [7]. A sucrose solution of 0.15 M concentration was placed into an autoclave with a volume of 275 ml. The pH was set to 12 using 0.194 M NaOH solution. The reaction went for 12 hours at 180 °C under autogenous pressure. Then the resulting product was washed with distilled water three times, suspended in 45 V/V % ethanol-water solution, centrifuged for 20 min at 4000 rpm. After that, the product was filtered, washed with warm distilled water, and placed in drying cabinet at 70 °C for overnight. The resulting product was fine black powder. This method was similar to the one described in [15].

### 2.2. Preparation of the composites

TiO<sub>2</sub> was deposited by atomic layer deposition on the carbon nanosphere powder using TiCl<sub>4</sub> and H<sub>2</sub>O as precursors in a Beneq TFS-200-186 ALD thermal reactor at 1 mbar pressure. The pulse and purge times for one cycle were 0.3 s/3 s and 0.3 s/3 s for the TiCl<sub>4</sub> and H<sub>2</sub>O precursors, respectively. The depositions were carried out at 250 °C, and 700 ALD cycles were used.

### 2.3. Characterization

TG/DTA measurements were conducted on a TA Instruments SDT 2960 simultaneous TG-DTA device in helium or air atmosphere (130 ml/min) using an open platinum crucible and 10 °C/min heating rate. EGA-MS (evolved gas analytical) curves were recorded by a Balzers Instruments ThermoStar GSD 200T quadruple mass spectrometer (MS) coupled on-line to the TG/DTA instrument; the on-line coupling between the two parts was provided through a heated (T=200 °C), 100 % methyl deactivated fused silica capillary tube with inner diameter of 0.15 mm [16].

FTIR measurements were carried out between 4000 and 400 cm<sup>-1</sup> on a Biorad Excalibur Series FTS 3000 infrared spectrometer. 300 mg KBr pellets were used, which contained 1.0 mg sample. 64 measurements were accumulated into one spectrum.

Powder XRD patterns were recorded on a PANalytical X'Pert Pro MPD X-ray diffractometer using Cu K $\alpha$  radiation.

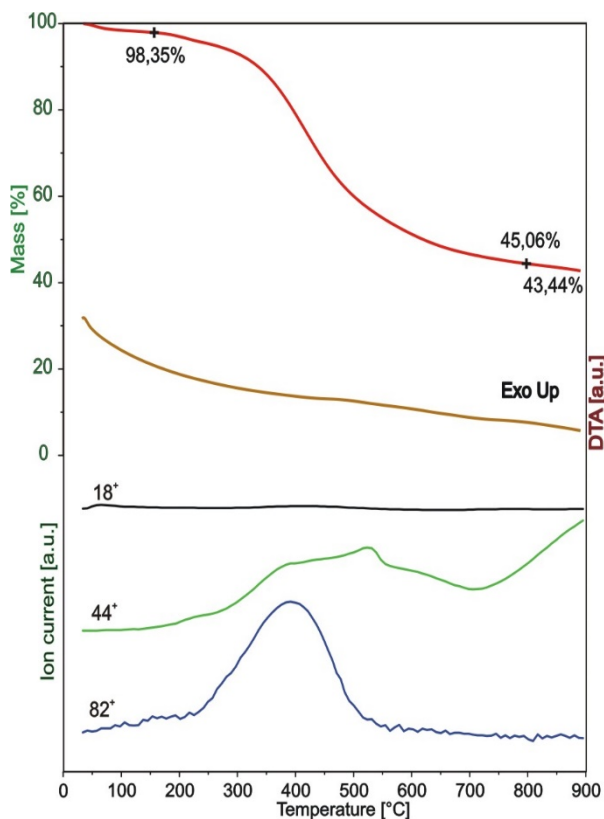
SEM-EDX data were obtained by a JEOL JSM-5500LV scanning electron microscope and the samples were sputtered with an Au/Pd conductive layer for the imaging.

## 3. Results

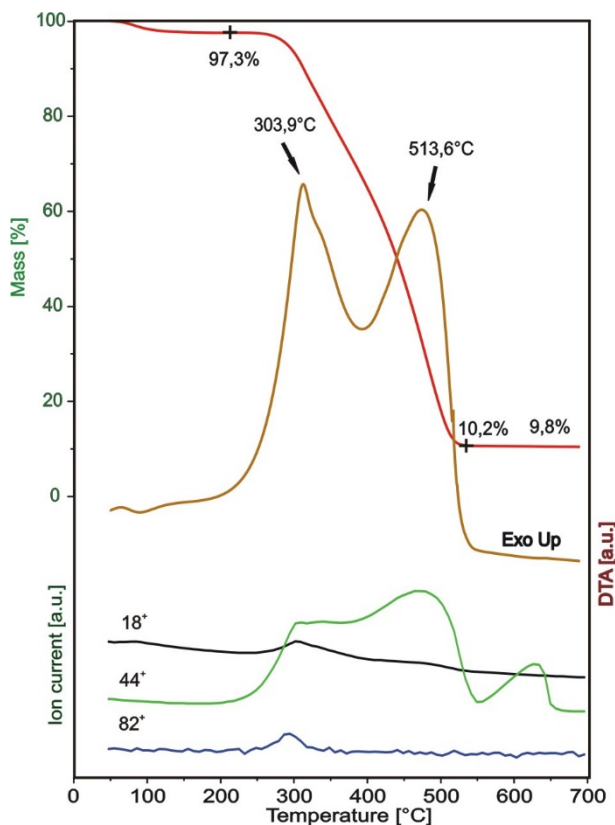
### 3.1. TG/DTA-MS

Figure 1 shows the TG/DTA-MS analysis of pure carbon nanospheres in helium. First, the nanospheres lose a minimal amount of water (m/z=18), then the decomposition begins around 300 °C,

which can be seen from the evolving gases of CO<sub>2</sub> (m/z=44) and cyclohexene (m/z=82). This ensured that the ALD depositions could be done safely at 250 °C without damaging the template.



**Figure 1.** TG/DTA-MS analysis of the carbon nanospheres in helium

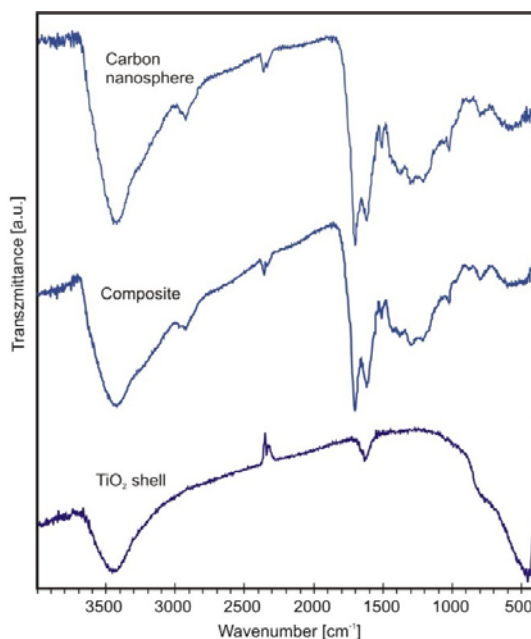


**Figure 2.** TG/DTA-MS analysis of the carbon nanosphere-TiO<sub>2</sub> composite in air

Figure 2 displays the thermal analysis of carbon nanosphere-TiO<sub>2</sub> composite in air. In summary, the carbon core burnt out and only the hollow TiO<sub>2</sub> nanospheres remained in the platinum crucible. The molecule-ion of CO<sub>2</sub> (44<sup>+</sup>) was dominant in the mass spectrum of the evolved gaseous products, and unlike the analysis in helium, the cyclohexene was much less abundant because of its oxidation. In the case of both EGA analyses, the intensity of the ion current curve of the CO<sub>2</sub> increased at higher temperatures (above 600 °C), owing to the decomposition of the polymer coating of capillary between the TG/DTA and the MS [4,9,17,18].

### 3.2. FTIR

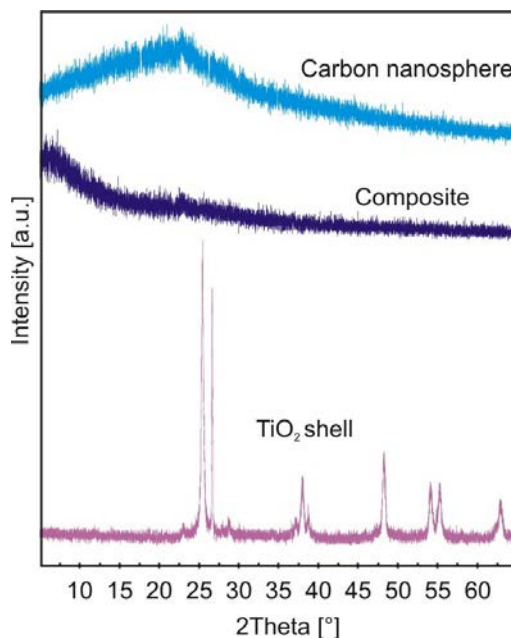
In the FTIR spectra (figure 3) at 1600 cm<sup>-1</sup> the characteristic peak of the carbon-carbon double bond can be seen, and at 2850 cm<sup>-1</sup> the characteristic peak of the carbon-hydrogen bond is visible, both of which disappeared after burning out of the carbon nanosphere template [7]. At 1700 cm<sup>-1</sup> and 3400 cm<sup>-1</sup> the characteristic peaks of the OH-group are present [19]. The lattice vibration bands of the TiO<sub>2</sub> are under 500 cm<sup>-1</sup>, which can only be seen at the spectrum of the hollow TiO<sub>2</sub> shell, because there was only small amount of TiO<sub>2</sub> on the carbon nanosphere-TiO<sub>2</sub> composite [20].



**Figure 3.** FTIR spectra of the samples

### 3.3. XRD

From the powder XRD diffractograms (figure 4) it can be seen that both the carbon nanospheres and the carbon nanosphere-TiO<sub>2</sub> composite are amorphous; in the latter the peaks of TiO<sub>2</sub> are not recognizable due to the low amount of it. The hollow TiO<sub>2</sub> shell is crystalline and is identified as anatase (ICDD 01-075-2546).

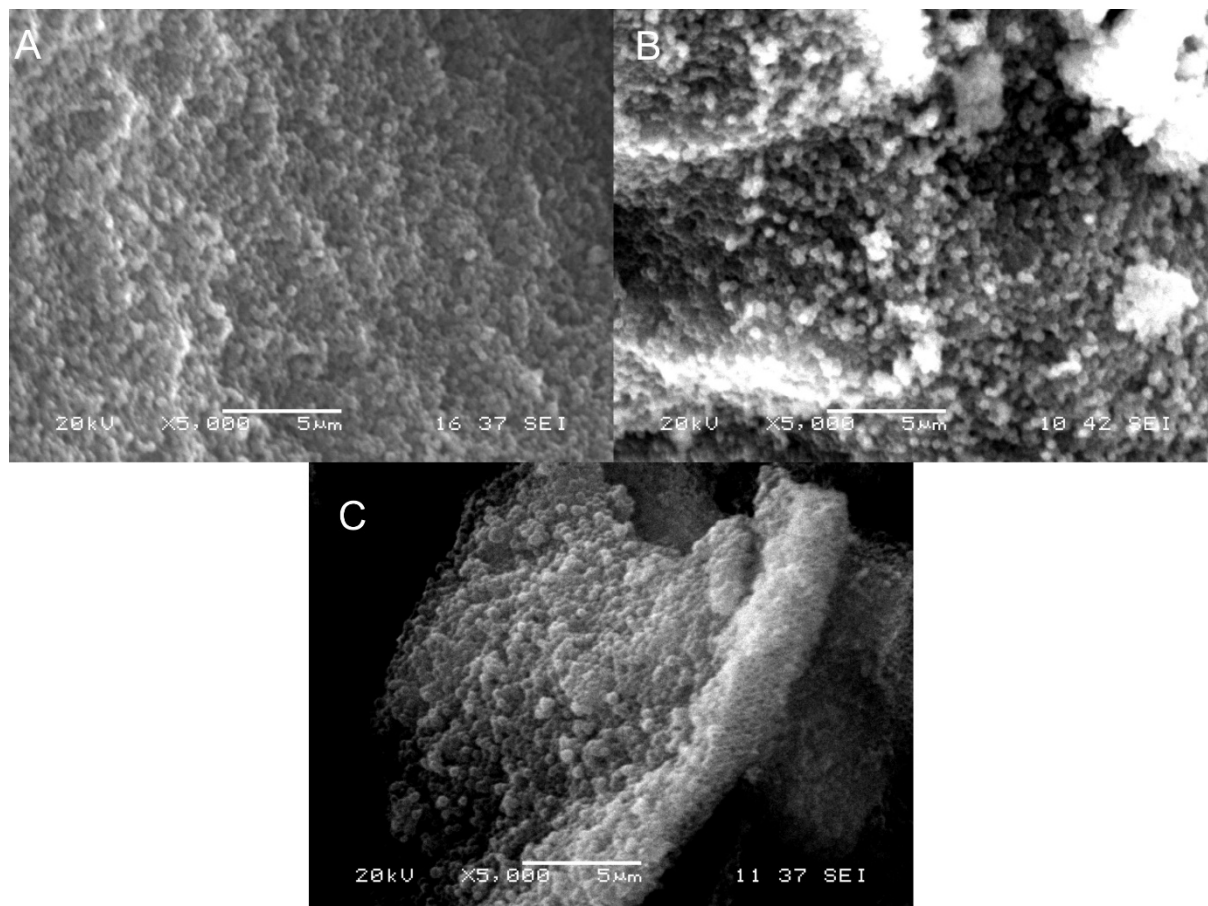


**Figure 4.** Powder XRD patterns of the samples

### 3.4. SEM-EDX

From the SEM images (figure 5) the spherical shape of carbon particles can be seen, which was maintained both after the ALD reaction and the burning out of the carbon core as well. The steps of

the synthesis could be followed by the EDX results as well (table 1). The atomic % of the C decreases after the ALD process, while the O and Ti increases. The burning out of the carbon core was successful, only 12.7 atomic % carbon remained. The Cl is residue from the  $\text{TiCl}_4$  precursor of the ALD deposition.



**Figure 5.** SEM images of (A) the carbon nanospheres; (B) the carbon nanosphere-TiO<sub>2</sub> composite material and (C) the hollow TiO<sub>2</sub> shells

**Table 1.** Composition of the samples from the EDX spectra

	C	O	Ti	Cl
	atomic %			
Carbon nanospheres	77.3	22.7	0.0	0.0
Carbon nanosphere-TiO <sub>2</sub> composite	62.0	27.8	10.1	0.1
Hollow TiO <sub>2</sub> nanospheres	12.7	69.4	17.8	0.1

#### 4. Conclusions

We successfully prepared carbon nanospheres using the hydrothermal method. Consecutively, we deposited TiO<sub>2</sub> film on the carbon nanospheres by atomic layer deposition and then burnt out the

carbon cores to get hollow TiO<sub>2</sub> nanospheres. The ALD deposition and the formation of the hollow TiO<sub>2</sub> shells were followed by TG/DTA-MS, FTIR, XRD and SEM-EDX techniques. The TG/DTA-MS measurement of the carbon nanospheres in helium confirmed that the ALD process could be done at 250 °C without damaging the template. Based on the results of TG/DTA-MS of the carbon/TiO<sub>2</sub> composite in air, the carbon cores burnt out between 200 and 600 °C. The FTIR and EDX measurements proved the presence of the oxide in the composite and the effectiveness of the following annealing. The XRD showed that the hollow TiO<sub>2</sub> nanospheres were crystalline (anatase). The SEM images revealed that the spherical shape was maintained through the whole process. The carbon-nanosphere-TiO<sub>2</sub> composite and the hollow TiO<sub>2</sub> nanospheres can have great potential in the field of photocatalysis using solar energy.

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