Full Length Article

Preparation of graphene oxide/semiconductor oxide composites by using atomic layer deposition

Nóra Justh[a], Barbara Berke[b], Krisztina László[b], László Péter Bakos[a], Anna Szabó[c], Klára Hernádi[c], Imre Miklós Szilágyi[a,*]

[a] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4, Hungary
[b] Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, P.O. Box 92, H–1521 Budapest, Hungary
[c] Department of Applied and Environmental Chemistry, University of Szeged, Szeged 6720, Rerrich B. ter 1, Hungary

ABSTRACT

TiO$_2$, Al$_2$O$_3$ and ZnO are grown by atomic layer deposition (ALD) at 80 °C on graphene oxide (GO), synthesized by the improved Hummers' method. The preparation steps and the products are followed by FTIR, Raman, TG/DTA-MS, SEM-EDX, XRD and TEM-ED. Both Al$_2$O$_3$ and TiO$_2$ grown with ALD are amorphous, while ZnO is crystalline. Through decomposing methylene orange by UV irradiation it is revealed that the GO itself is an active photocatalyst. The photocatalytic activity of the amorphous TiO$_2$, deposited by low temperature ALD, is comparable to the crystalline ZnO layer, which is the best photocatalyst among the studied oxides. Al$_2$O$_3$ used as reference suppresses the photocatalytic performance of the GO by blocking its active surface sites.

1. Introduction

Photocatalytic composites have great potential in the field of environmental remediation, water splitting and self-cleaning surfaces [1,2]. Among the various semiconductor oxide photocatalysts, TiO$_2$ being stable and non-toxic is the most widely studied due to its ideal band gap width for both half reactions of water splitting [3–5]. However, its use still faces the difficulty of its narrow light response range limited to UV [2,6,7]. Among others, its composites with semiconductor-oxides or other nanomaterials, such as carbon nanostructures, may enhance the photocatalytic activity. The inhibition of recombination by promoting the charge separation, the widening of the wavelength response range and the modifying the photocatalytic selectivity are three advantages of TiO$_2$ composites [8–11].

Carbon-based nanomaterials, such as fullerene, carbon nanotubes (CNTs), carbon nanospheres, graphene, graphene oxide (GO) or carbon aerogels are very attractive substrates for TiO$_2$ composites, due to their high surface area, good thermal and electrical properties, and mechanical as well as chemical stability [12]. There are several ways how TiO$_2$ and other semiconductor oxides can be deposited on carbon substrates (e.g. sol-gel synthesis, CVD, sputtering) [13–18]. Atomic layer deposition (ALD) is an outstanding tool as it allows the coating of complex and high surface area nanostructures in a conformal and homogeneous manner, with a precise control of the grown film thickness at nanometer scale [19–21]. There have been several ALD

depositions on carbon substrates previously. The majority of them were done on CNTs [19]; however, there have been also attempts on graphene and graphene oxide. These latter studies involved depositing oxides (e.g. A$_2$O$_3$ [22]; TiO$_2$ [23–30]) and metals (e.g. Pt [31]). The application of these composites included electrocatalysis [24], ion detection [31], Li battery electrodes [25,29], transistors [26]. Photocatalytic properties were only scarcely studied, and in this case TiO$_2$ was grown in crystalline (anatase) form onto GO [24]. The photocatalytic performance of ALD grown amorphous TiO$_2$/GO composites were not studied; however, recently it was shown that an amorphous ALD TiO$_2$/fullerene composite had remarkable photocatalytic activity [32].

As substrates for ALD growth, the main disadvantage of the carbon substrates is that the direct deposition of oxide layers is challenging due to the chemical inertness of the surface. The films can typically nucleate only at defect sites or at functional groups. In the case of graphene, this can be overcome by using an NO$_2$ layer first, which binds to the graphene as a Lewis base, and it serves as nucleation center for further ALD growth of other materials [24]. On the other hand, the GO exhibits a rich surface chemistry, as the graphene sheet is functionalized with chemically reactive carboxyl, hydroxyl and epoxy groups, which makes ALD growth much easier on GO than on graphene [33]. Due to these, GO also has attractive tunable electronic, magnetic and optoelectronic properties. Introduction of functional groups into the graphene lattice partially disrupts the in-plane symmetry of the carbon π-network and

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induces an optoelectronic bandgap in the electronic structure resulting in semiconducting GO [34,35]. This semiconductor behavior of GO might mean that GO in itself has photocatalytic activity; however, this is still a subject of debates [11,34,35]. The reason for the controversy can be that the exact composition and hence the electric properties of GO strongly depend on the way of preparation. Therefore, the previously studied GO samples might have had small differences in their properties, and thus they could show diverse activities. This underlines the importance of a detailed characterization of GO prior to its application [16,36–38]. Hence, this study reports the synthesis of GO by the improved Hummers' method, and the ALD growth of TiO_2, ZnO and Al_2O_3 layers on the GO substrate at low temperature (80 °C). The as-prepared materials are studied by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, simultaneous thermogravimetry and differential thermal analysis coupled on-line with mass spectrometry (TG/DTA-MS), scanning electron microscopy (SEM) with energy dispersive X-Ray analysis (EDX), X-ray powder diffraction (XRD) and transmission electron microscopy with electron diffraction (TEM-ED). The photocatalytic activity of bare GO and GO/oxide composites are also tested, which allows to determine whether GO has photocatalytic effect on its own and to compare the interaction of GO with the ALD deposited photocatalytically active and non-active oxides. The low temperature ALD growth resulted in amorphous TiO_2, which enabled to investigate the possible photocatalytic effect of GO/amorphous TiO_2 composite. As reference, ALD ZnO is selected as photocatalytically active crystalline semiconductor oxide, while Al_2O_3 as an inactive oxide photocatalyst.

2. Results and discussion

According to the SEM images, both the GO and the GO/oxide composites are present in micrometer scale flakes (Fig. S1). EDX measurements show that the ALD doped GO composites contain only C, O and S atoms and the corresponding metals from the ALD grown oxides (Table 1 and Table S1). The graphite starting material had 0.01 at.% S; therefore, the great majority of sulfur present in GO is the result of the exfoliation reaction. The Al and Zn content of the composites is 11.9 and 10.1 at.%, respectively, meaning that the amount of ZnO is ca. 25% larger than the Al_2O_3 content; nevertheless, they are in the same order of magnitude. In contrast, even though we raised the number of the ALD cycles from 100 to 250 when depositing TiO_2, much less Ti is detected (0.75 at.%) on the GO, because the TiO_2 growth rate is lower [39].

The vibration bands (Fig. 1) belonging to the carbon GO support are at 3030 cm^{-1} (aromatic −CH), 3080 cm^{-1} (=CH), 1650 cm^{-1} (C=C), 1400 cm^{-1} (=C−H) and 900 cm^{-1} (−CH deformation) (Fig. 2) [40,41]. The bands of the functional groups of GO are also visible in the FTIR spectra. The main stretching bands of the carboxyl and epoxy groups in the GO are at 1725 cm^{-1} (C=O) and 1050 cm^{-1} (C−O). The band at 1250 cm^{-1} (−C−O−C) are assigned to the epoxy mode of the lactone group. The wide stretching hydroxyl band appears at 3400 cm^{-1} and the OH deformation band is also present at 1400 cm^{-1}. As the GO sample contains sulfonyl functional groups [42], the corresponding stretching vibration bands are also visible at 1250 cm^{-1} (SO_2 asymmetric) and 1100 cm^{-1} (SO_2 symmetric).

Table 1
EDX data of GO as well as GO/TiO_2, GO/ZnO and GO/Al_2O_3 composites.

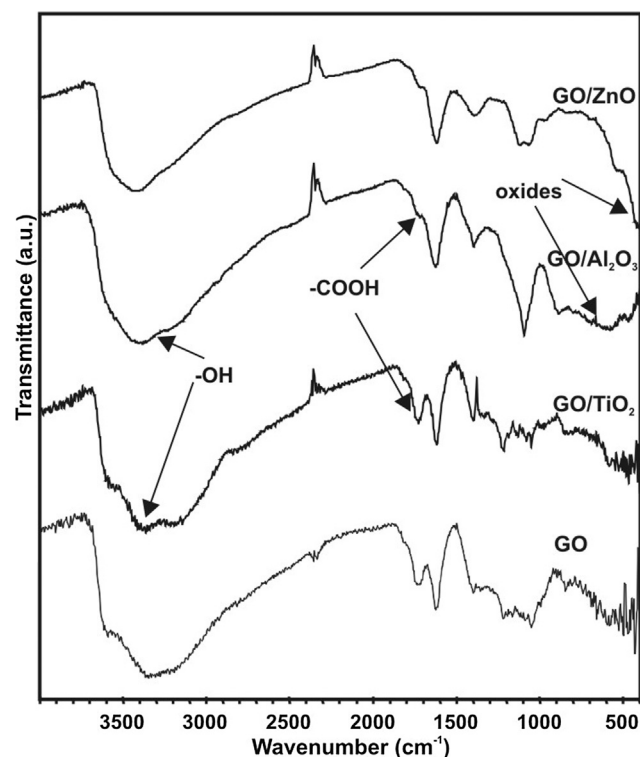| Element (at.%)						
Sample	C	O	S	Ti	Al	Zn
GO	64.95	34.25	0.69			
GO/TiO_2	63.97	34.91	0.34	0.75		
GO/Al_2O_3	59.94	30.34	0.86		11.85	
GO/ZnO	59.10	29.34	0.58			10.06

Fig. 1. FTIR spectra of GO, GO/TiO_2, GO/ZnO and GO/Al_2O_3.

When oxides are grown on the GO by ALD, they can be associated with the lattice vibration bands under 1000 cm^{-1} [43–45]. Al−O stretching bands are between 900 and 400 cm^{-1}, i.e. the 900–700 cm^{-1} region is assigned to tetrahedral AlO_4, and the proposed characteristic frequencies of octahedral AlO_6 are between 750 and 400 cm^{-1} [46–48]. The Zn−O stretching vibration is at around 400 cm^{-1} [49,50]. In the TiO_2 composite spectra, due to the low amount of TiO_2, only smaller peaks are visible around 600 cm^{-1} [9,51,52]. Hence, FTIR spectra also confirm that the ALD process was successful with all the oxides on GO. The intensity of the bands belonging to the carbon functional groups decreases after the ALD; e.g. it is clearly visible in the case of the 1725 cm^{-1} (−C=O) band. However, the OH vibration bands are exceptions: after the ALD deposition these bands are as intensive as before. On the one hand, the ALD process uses up the OH functional groups; on the other hand, new hydroxyl groups appear on the surface of the new oxide layers.

Fig. 2a shows the TEM image of the GO sheets. In the case of the GO/TiO_2 composite (Fig. 2b), because of the island type growth mechanism, only discrete particles form on the surface instead of a continuous TiO_2 film [53]. In the case of the other oxides (Fig. 2c and d), the ALD nucleation is easier, and the deposited oxides form continuous films on the GO sheets [19].

Fig. 3 demonstrates the powder XRD data. The peaks at 2Θ = 10,9° (0 0 1), 43° (1 0 0), 23° and 27° are associated with the GO [54–56]. The long amorphous like baseline between 2Θ = 10–20° shows that the graphene sheets did not reassemble. The diffractograms of the TiO_2 and Al_2O_3 composites do not differ from the GO, i.e., both oxides are in amorphous phase. In contrast, ZnO is grown in crystalline form; the additional peaks, e.g. the characteristic triple peak at 2Θ = 35° and the large peak at 2Θ = 57° in the GO/ZnO composite are identified as wurtzite ZnO phase (ICDD 00-036-1451) [50,57,58]. The crystalline structure of ZnO as-grown by ALD is further confirmed by HRTEM and ED images recorded about the GO/ZnO sample (Fig. S2).

It is well known that the TG curve of GO has a main mass loss step around 200 °C, showing that the functional groups are leaving from the surface [43,59,60]. This step is well visible on the TG/DTA curves