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Review

Carbon-nanostructures coated/decorated by atomic layer deposition: Growth and applications

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ABSTRACT

Carbon-based nanomaterials demonstrated to be highly suitable as support for the elaboration of heterostructures. Atomic layer deposition (ALD) proved to be a technique of choice for the coating of nanostructured carbon materials. These heterostructures find applications in various areas such as electronics, sensors and energy storage and conversion. Because the chemical inertness of the graphitic carbon inhibits the initiation of ALD film growth, numerous surface functionalization approaches have been investigated in order to provide the required nucleation sites. The different strategies employed for the ALD onto carbon nanotubes, graphene, graphite and other nanostructured carbon materials (*e.g.* carbon black, fibers) are reviewed. The peculiarity of ALD for tailoring the chemical, structural and morphological properties of the deposited material are discussed. Finally, in order to highlight the importance of this class of materials, possible applications in catalysis and gas sensing devices are also reviewed.

1. Introduction

Carbon-based nanomaterials, such as carbon nanotubes (CNTs), graphene and carbon black, are very attractive, due to their high surface area, good thermal and electrical conductivity, and mechanical as well as chemical stability, and provide an ideal support for heterostructure elaboration. Because of that, they constitute ideal components for the realization of such nanostructures, which find applications in catalysis, gas sensing, energy storage or field effect transistor (FET) [1–8]. Therefore, a well-controlled synthetic approach is required in order to deposit either particles or thin films onto carbon-based materials in accurate manner. Based on the successive gas-surface half-reactions, ALD allows the coating of flat surfaces as well as complex and high surface area nanostructures in a conformal and homogeneous manner, with a precise control of the thickness of the deposited film at the angstrom-scale. ALD appears highly suitable for elaborating nanostructures [9–13]. However, since the initiation of film growth requires the presence

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of functional surface groups and defect sites that act as anchoring and nucleation sites [14,15], the inert nature of high quality graphitic carbon leads to non- or incomplete coating. Functionalization of the surface, prior to the deposition, is required, but can also deteriorate the intrinsic properties of CNTs or graphene, which can be detrimental in the case of heterostructures applied in electronics for instance. Many efforts have been devoted in order to create enough anchoring sites at the surface to initiate the ALD growth, while preserving the graphitized carbon structure [16]. Principally two types of surface functionalization can be distinguished: covalent and non-covalent [6,17–20]. The first one is the most commonly used and involves chemical treatment based on mineral acids, *e.g.* HNO_3, H_2SO_4, or other strong oxidizing agent, such as O_3 or H_2O_2 [18,21–23]. It generates oxygen containing groups at the surface, which pave the way to the endless possibility of further attachment. Moreover, it permits also to purify the CNTs by the removal of catalyst particles and amorphous carbon layer, present after their synthesis. However, such treatments tend to damage the structure of the carbon material and thus to affect their properties [22,24]. On the other hand, non-covalent functionalization is mainly based on Van der Walls, π–π interactions, hydrogen bonding or electrostatic forces [1,17,25]. The principal functionalization approaches used for coating of carbon materials are summarized in Table 1, as well as the thus-formed anchoring sites. Both functionalization approaches impact the electronic properties at a certain level. Indeed, the intrinsic properties of sp^2-hybridized carbon material (*e.g.* CNT, graphene) arise from the π–e^- network [17,26]. For instance, the CNT reactivity is related to the π-orbital mismatch due to the curvature of graphene layer [6]. The properties of graphene layer and thus CNTs will be affected by (i) the hybridization state of carbon atom, (ii) π–π bonding and (iii) formation of dipole moment. Covalent functionalization is known to convert sp^2 into sp^3 carbon, inducing a disruption in the delocalization of π-electron, among others. Non-covalent functionalization even though does not impact the sp^2 hybridization; π–π, Van der Walls, dipole-dipole interactions and/or hydrogen bonding are involved between the carbon material and the functionalizing species leading to molecular orbital hybridization/doping effect [26]. Charge transfer and additional barriers have been observed on functionalized carbon and/or carbon based heterostructures [17]. For a deeper understanding of the functionalization impact on electrical properties, the reader can refer to a very comprehensible recent review for graphene [26] and to the reviews of Tasis [17], Eder [6] and Karousis [18] for CNTs. Finally, the main drawback of ALD is the difficulty to process a large amount of carbon nanostructures. However, this problem can be addressed by making use of fluidized bed or rotary ALD reactors [27–33].

This review will focus on the carbon-based heterostructures elaborated by ALD and on their application in catalysis and gas sensing. The important number of studies about the coating/decoration of CNTs, graphene, graphite and other nanostructured carbon materials justify their reviewing. The reader can also refer to some recent specific reviews on CNT surface modification [34] or on graphene functionalization for ALD growth [35] as well as on ALD applied either to CNTs [36] or to graphene [8,37]. However, no general review has been published so far on the ALD coating of carbon structures focusing on the surface properties for the control of structural and morphological aspects of the final material. Along this paper, the coating/decoration of CNTs and the various functionalization performed in order to obtain a suitable coating will be reported, it is followed by the reviewing of the ALD on graphene and graphite. Afterward, the tuning of the ALD material morphology by tailoring either the surface functionalization of graphitized carbon or the ALD parameters will be discussed. Then, the use of other carbon-based nanostructures as support for ALD will be described as well as the different strategies implemented to coat large quantities of materials. Finally, the application of the obtained carbon heterostructures in catalysis and gas sensing will be discussed.

2. Coating/decoration of carbon nanotubes by ALD

Carbon nanotubes presenting either single- or multi-walls have been coated/decorated with diverse ALD materials. For this purpose, various processes and surface functionalization as well as doping of CNTs have been investigated. An overview limited to article published before the end of December 2012 is given in Table 2.

In 2002, Javey et al. [51] reported the first use of ALD to coat CNTs. In order to realize a CNT-based transistor, 8 nm of ZrO_2 was deposited as gate insulator on the top of a single-wall CNT (SWCNT) supported on SiO_2. A conformal crystalline metal oxide film was observed and no significant damage of the electrical properties or reduction of the apparent carrier mobility of the SWCNT was noticed. Later on, the ALD of conformal HfO_2 insulating gate onto SWCNTs was reported by the same group [45–47]. They observed that no uniform film was obtained on suspended CNT, because of lack of anchoring site to initiate the film growth [45]. The possibility to conformally coat supported SWCNTs was attributed to the presence of OH surface groups of SiO_2 allowing the nucleation of the ALD film. Recently, Moriyama et al. [40] observed a change in carrier type when HfO_2 was deposited onto CNT–FET. This phenomenon was attributed to the positive field charges introduced at the interface between the metal oxide gate and the silica support.

Homogeneous coating of multi-walls CNTs (MWCNTs) with Al_2O_3 from trimethylaluminum (TMA) and water was also reported

Table 1
List of the principal ways to functionalize carbon materials and the surface species formed.

	Functionalization	Surface species/anchoring sites
Non-covalent	NO_2	Adsorbed NO_2 molecules
	NO_2 + TMA	NO_2–TMA complex
	Diazonium compounds	$–NO_2$, aryl ligand
	SDS	SO_4^{2-} head group
	Poly-T-DNA	DNA functional groups: –OH, –NH, C=O, $O=PO^-$...
	Polymer: PTCDA, PTDA, PVA, PVP	Oxygen groups. OH groups can be activated by UV/O_3
Covalent	Acid treatment: HNO_3; H_2SO_4/HNO_3	OH, COOH, phenol, C–O–C=O
	N-doping	N-defects
	Plasma O_2	Defects + oxygenated species: C=O, C–O, O–C=O
	Plasma Ar	Defects (dangling bonds...), few oxygen species and anchors
	Plasma Ar/O_2	Defects + oxygenated species: C=O, C–O, O–C=O
	O_3	COOH, COC, COH, OH, CO
	XeF_2	C–F bonds (more labile)
	HF	CO, O groups
	$NH_4OH + H_2O_2$	–OH, O groups
	$HF + NH_4OH + H_2O_2$	–OH, O groups

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