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Effect of covalent and non-covalent linking of zinc(II) phthalocyanine functionalised carbon nanomaterials on the sensor response to ammonia

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ABSTRACT

In this work, a comparative study of the sensor response of single walled carbon nanotubes (SWCNTs) and reduced graphene oxide (rGO) covalently and non-covalently functionalised with1-[N-(2-ethoxyethyl)-4-pentynamide]-8(11),15(18),22(25)-tris-{2-[2-(2-ethoxyethoxy) ethoxy]-1-[2-((2-ethoxy ethoxy)-ethoxy)methyl]ethyloxy}zinc(II) phthalocyanine (ZnPc) to ammonia is carried out. It was shown that in the case of SWCNT-based materials both covalent and non-covalent functionalisation with zinc(II) phthalocyanine leads to the increase of the sensor response toward NH_3, while functionalisation of reduced graphene oxide causes a decrease in the response. At the same time both covalent and non-covalent linking of zinc(II) phthalocyanine leads to twofold decrease of the sensor recovery times. The sensor response of the carbon nanomaterial (single walled carbon nanotubes or reduced graphene oxide) hybrids covalently functionalised with zinc(II) phthalocyanine is several times higher than in the case of non-covalent linking of zinc(II) phthalocyanine to these nanomaterials, which is in good correlation with the number of zinc(II) phthalocyanine molecules adsorbed onto the SWCNT and rGO walls.

1. Introduction

Carbon materials such as carbon nanotube, graphene, graphene oxide or reduced graphene oxide (rGO) are widely investigated as promising materials for chemical sensing applications [1,2]. This is mainly due to the large surface to volume ratio in these materials, which can provide significant adsorption sites of various gaseous as well as chemical analytes. Furthermore, the most of carbon nanomaterials exhibit comparatively high conductivity in addition to their high mechanical stiffness and chemical stability.

Defect sites and different oxygen contained groups could enhance adsorption of gases onto the carbon materials surface and make them viable candidates as active materials in chemical detection. For instance, rGO contains such functional groups as epoxide, alcohol and carboxylic acid which do not repair upon hydrazine reduction. This makes rGO a material that has both high electrical conductivity and chemically active defect sites, making it a promising candidate for gas detection. The sensitivity of rGO to some gases, such as NO [1,2], NO_2, NH_3 [3], Cl_2 [4,5], H_2 [6], and volatile organic compounds [5,7] is revealed in several published articles and reviews [8,9]. Carbon nanotubes (CNT) have also been investigated as chemical sensors toward gases and vapors such as NH_3, NO_2 [10], H_2, CH_4, CO, SO_2, H_2S, H_2O_2 and O_2 [11,12]. However, the selectivity of chemical sensors based on rGO and CNT usually is not good enough. One of the ways to improve their selectivity is controlled functionalisation of the surface of carbon nanomaterials with different molecules in order to define the chemically active sites. The other challenges of the development of rGO- or SWCNT-based hybrid materials are the poor solubility, non-uniform film surface and as a consequence non-reproduced sensor response of non-modified carbon nanomaterials.

Carbon nanomaterials (SWCNT and graphene) are favorable for functionalisation with different classes of molecules as well as nanoparticles of metals [13], metal oxides [14,15] and polymers

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[16,17]. For instance, rGO modified by SnO_2 nanoparticles has been investigated for improved detection of NO_2 gas [18]. rGO/SnO_2 hybrid demonstrates a higher sensor response toward NO_2 than the pristine rGO, providing twice as good synergetic effect between graphene and nanoparticles. Quantum effects dominate the sensing mechanism of metal oxide/carbon nanomaterial sensors; and the nature of metal oxide and the manner of preparation of the composite material make it more selective to one or another analyte [19–23].

Another route for graphene and CNT modification is preparation of composites with polymers and organic molecules [17]. A double-layer consisted of rGO and polyethylenimine (PEI) has been exhibited better sensor response toward CO_2 and shorter recovery time than the pristine rGO and rGO/PEI mixed layers. It has already been shown elsewhere [24–26] that functionalisation with metal phthalocyanines (MPc) may improve the solubility and sensor properties of these carbon materials. Actually, phthalocyanines are known to exhibit high electron charge transfer due to their π-conjugated system [27]. On the other hand, the phthalocyanine derivatives are organic semiconductors that have been applied as chemiresistive sensors [28,29]. The extended π-electronic system of CNTs and graphene makes them very attractive for manipulating charge transfer by combining with such electrophiles as porphyrins and phthalocyanines [30]. A wide variety of functional groups in MPc molecule is used to attach them either covalently or non-covalently to the surface of rGO [31–33] and CNTs [34–38] to obtain hybrid materials with improved sensor performance. The enhanced sensing properties are attributed to the synergistic effect of MPc and carbon materials in the hybrids due to the strong electron transfer interaction, superior electrical conductivity and gas adsorption activity [36].

In our previous works [39–41], we have directed our research to study the influence of phthalocyanines containing different central metals, symmetric or asymmetric substitution, and type of

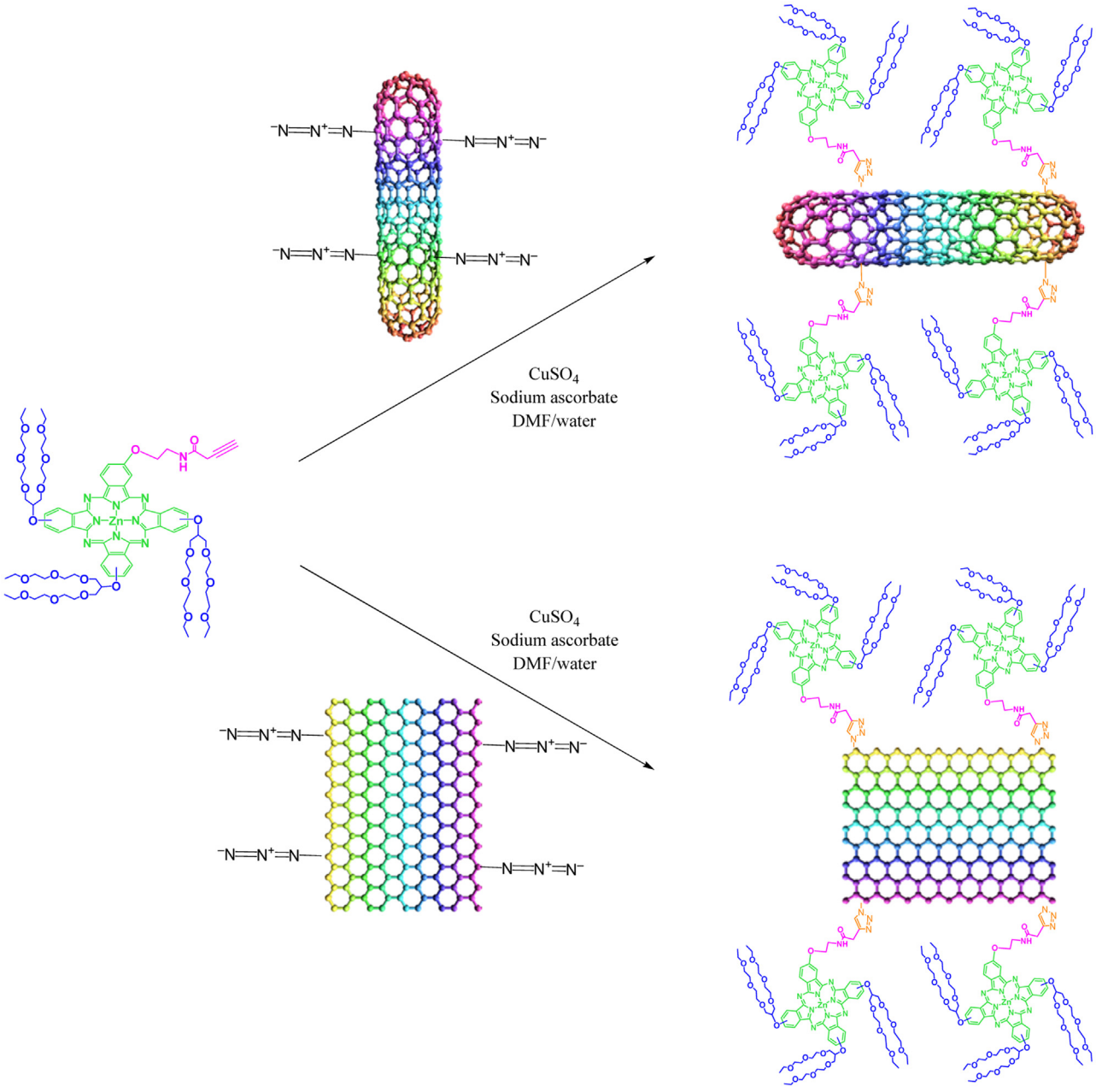

Fig. 1. Scheme of ZnPc and covalently bonded ZnPc:SWCNT-co and ZnPc:rGO-co hybrid materials.