Investigations on new carbon-based nanohybrids combining carbon nanotubes, HfO₂ and ZnO nanoparticles

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Abstract: In this work, we present two types of hybrid materials. The first hybrid material is a combination of carbon nanotubes (CNT) with HfO₂ nanoparticles. The latter constituent on its own exhibits unusual visible photoluminescence, which is in stark contrast to non-luminescent HfO₂ in the bulk form. The small size of HfO₂ nanoparticles, 2.6 nm in average, suggests surface-defect related origin of the observed photoluminescence. The other hybrid material is CNT-ZnO with the embedded ZnO nanoparticles ranging from 50nm to 100nm in size. ZnO represents a direct bandgap semiconductor renowned as highly-luminescent in a broad spectral range. The visible region is attributed to luminescence involving deep-level defects, and hence depends on the synthesis conditions. In this study we compare the morphology of the two hybrid materials with transmission electron microscopy. We further compare the photoluminescence properties and the influence of the CNT coupling on enhancing or suppressing defect related emissions. Finally, we present a novel hybrid material CNT-HfO₂ capable of producing a photocurrent under zero bias.

1. Introduction
Hybrid materials are gaining interest as they combine different classes of materials, commonly involving both inorganic and organic components. By combining these two materials, it is possible to obtain a composite material that displays properties of the individual constituents as well as entirely new ones as a result of hybridizing. At present, carbon based materials have gained momentum owing to their superior electrical, mechanical, physical and optical properties [1]. Moreover, carbon based materials are abundant and are known to be non-toxic and bio-compatible thereby enlarging their sphere of application [2]. HfO₂ is a dielectric material and produces no visible luminescence once in the bulk form [3], however, ultrasmall HfO₂ nanoparticles were recently demonstrated to display strong photoluminescence originating from surface defects viz., Hf and O vacancies [4, 5]; the signature of these defects is an emission in the blue-green part of the visible spectrum. On the other hand, ZnO is a semiconductor material with a direct bandgap of 3.2eV. The spectral range of highly-luminescent ZnO covers the UV and visible regions, the latter strongly dependent on the morphology, synthesis route and size [6]. For instance, the characteristic green luminescence dominates in oxygen deficient ZnO, whereas hydrothermal or sol gel methods produce ZnO emitting in the yellow-orange region [7]. Although ZnO has shown photovoltaic activity on its own, more efficient charge transfer to an external load can be obtained by hybridizing them with carbon nanotubes [8]. Moreover, from an industrial point of view, ZnO is already used in sun screens and water purification owing to its non-
toxic character.

In our previous study, we have demonstrated that photocurrent generation is possible at zero bias in the hybrid CNT-HfO$_2$ structure [9]. In the present work, we compare the photoluminescence properties of these two hybrid structures viz., CNT-HfO$_2$ and CNT-ZnO, and demonstrate how the size, morphology and synthesis routes affect the optical properties of the material. We also present proof-of-concept results on photocurrent generation of a novel, non-conventional optical material such as CNT-HfO$_2$ hybrid.

2. Experimental

2.1 Synthesis

2.1.1 Synthesis of CNT-ZnO hybrid: The procedure for synthesizing ZnO NPs was carried out under air. In a typical synthesis, zinc acetate (3.41 mmol) (99.99%, Aldrich) was added to 20 mL (183 mmol) benzyl amine (>99.0%, Aldrich). The reaction mixture was transferred into a stainless steel autoclave and carefully sealed and heated in a furnace at temperature ranging from 200°C to 300°C for 2 days. The resulting milky suspensions were centrifuged, the precipitates thoroughly washed with ethanol and dichloromethane and subsequently dried in air at 60°C. In the case of the carbon nanohybrid synthesis, NANOCYL™ NC7000 MWCNT with an average diameter and length of 10 nm and 1.5 μm, respectively were used in the synthesis. For the synthesis of carbon based ZnO nanocomposite, the MWCNTs were directly homogeneously dispersed into the solution of zinc acetate and benzylamine before transferring the solution into autoclave for the reaction synthesis.

2.1.2 Synthesis of HfO$_2$-CNT hybrid: The procedure for synthesizing cubic HfO$_2$ NPs was carried out in a glove box (O$_2$ and H$_2$O, <1 ppm). In a typical synthesis, hafnium tert-butoxide ((Hf(Ot-Bu)$_4$) precursor (STREM 99.9%) (0.87 mmol) was added to 20 mL (183 mmol) of benzylamine (purified by redistillation (99.5%), Aldrich). The reaction mixture was transferred into a stainless steel autoclave and carefully sealed. Thereafter, the autoclave was taken out of the glove box and heated in a furnace at 300°C for 2 days. The resulting milky suspensions were centrifuged; the precipitates were thoroughly washed with ethanol and dichloromethane and subsequently dried in air at 60°C [5]. NANOCYL NC7000 MWCNTs with an average diameter and length of 10 nm and 1.5 μm, respectively, were used in the synthesis. The nanoparticles were then dispersed in pure ethanol along with the CNT and sonicated for a total of 2h.

2.2 Characterization:

Transmission electron microscopy studies were carried out on a Titan G2 80-200 working in TEM mode at 200kV. PL was investigated at a room temperature by employing a 325 nm wavelength CW He-Cd laser with an output power of 6 mW as an excitation source. The emission was collected by a microscope and directed to a fiber optic spectrometer (Ocean Optics, USB4000) with a spectral resolution of 2 nm. The electrical measurements were carried out using a source measure unit (Agilent 4156). The sample was illuminated by a 125 W Hg lamp emanating a wavelength of 365 nm.

3. Results and discussions:

3.1 Morphological characterizations

TEM images of CNT decorated with HfO$_2$ and ZnO are presented in Figures 1(a) and (b) respectively. In Figure 1(a) the HfO$_2$ nanoparticles with average sizes of 2.6 nm appear to be agglomerated. It was previously shown that they attach themselves to topological defect sites of the CNT which were already present or were created after sonication [9]. In the case of CNT decorated with ZnO nanoparticles in Figure 1(b), ZnO nanoparticles are larger with sizes ranging from 50-100 nm. Moreover, they decorate the CNT randomly as compared to HfO$_2$. In Figure 1(c) a HRTEM image of the CNT-HfO$_2$ hybrid structure is presented clearly showing the atomic resolution of HfO$_2$ and its high crystalline quality along with the CNT walls where the outermost walls on one hand appear to be
damaged but on the other hand facilitate the decoration of the HfO$_2$ nanoparticles on them and create a strong contact at the interface of CNT and HfO$_2$. The HRTEM image in Figure 1(d) of CNT used with ZnO not only show wall damage but also amorphous carbon on the side walls due to the synthesis and sonication processes. The damaged side walls contain dangling bonds which are either functional groups or carbon and act as anchorage points for ZnO.

3.2 Photoluminescence characterization
The room-temperature PL spectra of the two hybrid materials, i.e. CNT decorated with HfO$_2$ and ZnO, are represented in Figure 2(a) and (b), respectively. The PL spectrum of the HfO$_2$ decorated hybrid material consists of several components which can be clearly discriminated using Gaussian deconvolution algorithm. The emission components centered at photon energies of 2.2 eV, 2.5 eV, 2.8 eV and 3.1 eV emerge as a result of the synthesis method applied as well as particle size reduction to nanoscale, which accordingly yield extrinsic luminescent centers and enhance the role of surface defects. The emission around 2.5 eV is attributed to luminescent surface-defects associated with oxygen vacancy, while the emission component at 3.1 eV corresponds to Hf$^{3+}$ centers on the surface of the HfO$_2$ linked to oxygen deficiency [4]. In a recent report comparing PL of the hybrid CNT-HfO$_2$
nanocomposites dispersed in colloidal suspension in ethanol and of the free-standing HfO$_2$ nanoparticles [9], the observed stronger emission at 3.1 eV in nanocomposites is attributed to an enhancement of Hf$^{3+}$ defects at CNT-HfO$_2$ interface, which in turn indicates an increase in oxygen vacancies. The CNT-ZnO hybrid material also presents several emission components at room temperature. The emission at 3.2 eV corresponds to the near band edge emission of ZnO or its band gap and its intensity is negligible compared to the intensity of the visible emissions located at 2.5 eV, 2.2 eV and 2.1 eV corresponding to the green-orange emission in the visible spectrum. The enhanced deep level defect at 2.5 eV indicates an increase in the oxygen vacancy related defects at the interface of CNT-ZnO viz., O$_{2n}$ or neutral Oi. The latter is all the more pronounced considering the surface to volume ratio increase in the nanostructured material.

![Figure 2: Room-temperature PL spectra of CNT decorated with (a) HfO$_2$ and (b) ZnO](image)

![Figure 3. Photocurrent generation in CNT-HfO$_2$ hybrid materials](image)
3.3 Photocurrent generation

For the electrical characterization, the nanocomposite is deposited on a glass slide and contacted using a micromanipulator manual probe station. The dark current-voltage characteristic illustrated by the black graph is linear, indicating an ohmic type conduction via the CNTs. On illumination, the I-V curve is shifted to a higher current value. This extra current is not depending on the voltage and is maintained at 0V, indicating the generation of a photocurrent.

4. Conclusion

Here we present a novel hybrid material CNT-HfO$_2$ as a possible candidate for photocurrent generation. We have compared its morphology and photoluminescence to CNT-ZnO hybrid. In terms of morphology, the HfO$_2$ nanoparticles have an average size of 2.6 nm. Moreover, TEM observations illustrate that these nanoparticles are decorated on defect sites of the CNT and are usually in the form of agglomerates. ZnO on the other hand are much larger in the range of 50-100nm. Both materials show similarities with orange-yellow emissions originating from synthesis via sol-gel methods. Also, on hybridizing, at the interface of the hybrid and the oxide nanoparticle, the oxygen vacancies increase whereby an intense emission in both cases is observed at 2.5eV. In the case of HfO$_2$, these oxygen vacancies at the interface are also responsible for the increase in Hf$^{3+}$ vacancies thereby emanating light in the UV-blue region of the spectrum. A similar but a less intense emission is observed for ZnO however, the origin is completely different. The emission at 3.1eV for ZnO is the near band edge due to the band gap of the material and indicates the purity of ZnO when compared to the defect emission in the visible region. In both cases, we observe an increase in defect related emission. We have also studied photocurrent generation in the CNT- HfO$_2$ material. Considering the large amount of defects which act as traps and accumulate charges in the free-standing HfO$_2$, the dissipation of these charges on contacting them with CNTs seems to be the most probable explanation for photocurrent generation. The photocurrent generation in CNT-ZnO hybrid structure is being presently studied to understand explicitly the origin of photocurrent generation in the two hybrid materials

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