A new polythiophene-driven coating method on inorganic INT/IF-WS₂ nanomaterial surface

D. Raichman*, R. Ben-Shabat Binyamini* and J.-P. Lellouche

Department of Chemistry, Nanomaterials Research Center, Institute of Nanotechnology & Advanced Materials, Bar-Ilan University, Ramat Gan 5290002, Israel

Jean-Paul.M.Lellouche@biu.ac.il

* These authors contributed equally to the paper

The chemical stability of the organic layer present onto the WS₂ nanomaterial surface was examined in the following manner. The functional INT-WS₂ bithiophene linker nanomaterial was incubated for 1 hour (room temperature) within a 0.01M HCl (pH 4.0) acidic aqueous solution, in order to mimic acidic thiophene monomer oxidative liquid phase polymerization conditions. The corresponding TGA graphs (Figure SI-1) showed a quite minor difference in weight losses measured before and after such an aqueous acidic treatment.

Corresponding TGA graphs (Figure SI-1, non-oxidant N₂ flow)) of the HCl-treated composite vs. the starting functional polyCOOH one disclose a very little difference in weight losses for the indicated 350-650°C temperature range of measurements, i.e., ~1.06% (7.08-6.02 = 1.06%). It clearly means that, during the 2nd step polythiophene polymerization/polymer growth from the INT surface, such an organic shell is significantly stable.
Figure SI-1: TGA analysis of INTs WS$_2$-bithiophene before and after acidic 0.01M aqueous HCl treatment (measured weight losses in a 350-650°C temperature range)
In addition and in order to more deeply address this functional layer thermodynamic stability issue for differently functionalized INT-bithiophene-Si-NPs, corresponding nanomaterials have been treated with a basic aqueous 0.01M NH₄OH (pH = 8.5) solution overnight (room temperature) mimicking the inorganic polymerization conditions described for INT nanotube functionalization. As shown in figure SI-2 above (TGA graphs), there is also less than 1.0% differential weight loss of functional coating. Thus, such basic conditions that fit 2nd step inorganic polymerization conditions did not cause any significant exfoliation of the attached organic adlayer.
Polymer-decorated nanomaterials have been washed several times (x 3) using analytical grade EtOH. Thus, all the obtained composite washing solutions have been UV-tested (measurement scale: 200-800 nm, detection of conjugated Th and/or polyTh chromophore/species) to detect the presence of (i) thiophene acetic acid monomer and of (ii) any short polymerized polythiophene molecules/components. As clearly deduced from Figure SI-3 data, the 3rd wash step already disclosed no UV-based evidence at all for the presence of any further free UV-absorbing TAA or/or free polythiophene polymeric chains/species in the bulk solution (3rd wash UV graph).