Supporting Information

Selective Decoration of isolated Carbon Nanotubes by Potassium Evaporation: Scanning Photoemission Microscopy and Density functional theory

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Random distributed carbon nanotubes

For TEM and SPEM analysis the non-aligned CNT samples were supported on conventional TEM grids. The MWCNTs were sonicated in pure ethanol for ten minutes; a drop of the suspension was placed on a lacey carbon film supported on a copper grid, allowing the analysis to be performed on nanostructures that were overhanging a void. TEM images were acquired using a FEI Tecnai G2 microscope operated at 200 kV. The evaporation of potassium atoms was performed in UHV condition on the random spatially distributed carbon nanotubes placed on the copper TEM grid. **Figure S1** shows TEM image recorded on the sample with 16% of relative amount of potassium, the thickness of alkali overlayer has been estimated around 2nm. From the higher resolution images we can identify the different orientation between the walls of the nanotube (depicted by red dotted lines) and the potassium overlayer (yellow dotted lines). Furthermore these images emphasize the spatial inhomogeneity of the K film covering the CNT surface. This inhomogeneity can be associated to the presence of defects and/or impurities at the CNT surface acting as potassium nucleation sites. In addition shadow effects due to the geometry of the preparation chamber promote covering uniformities.

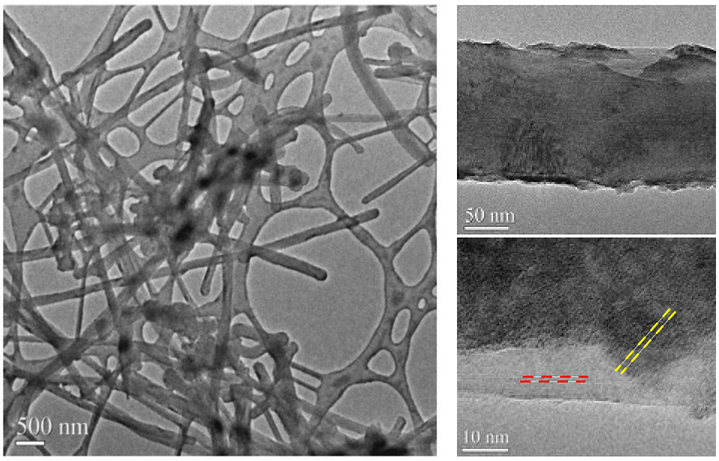

Figure S1: TEM images of MWCNTs covered with a thick K overlayer (2nm) deposited after prolonged K thermal evaporation on carbon nanotubes.

In order to understand the effect evaporation on non-aligned CNTs, we performed 4 potassium evaporations onto CNTs supported on a TEM grid. After each alkali deposition, we acquired the XPS spectra at the same point of the referential nanotube bundle. The C_{1s} spectra recorded after each K deposition were normalized to the maximum and stacked for appropriately follow the increasing amount of K at the CNT surface, **Figure S2a)**. We can observe that the asymmetric contribution to the C_{1s} spectrum increases for increasing amounts K at the CNT surface while the line shape broadens and shifts towards higher binding energy in accordance with the picture of potassium donor and consequent modification of the chemical environment for the photoelectron emitted from the carbon core levels.

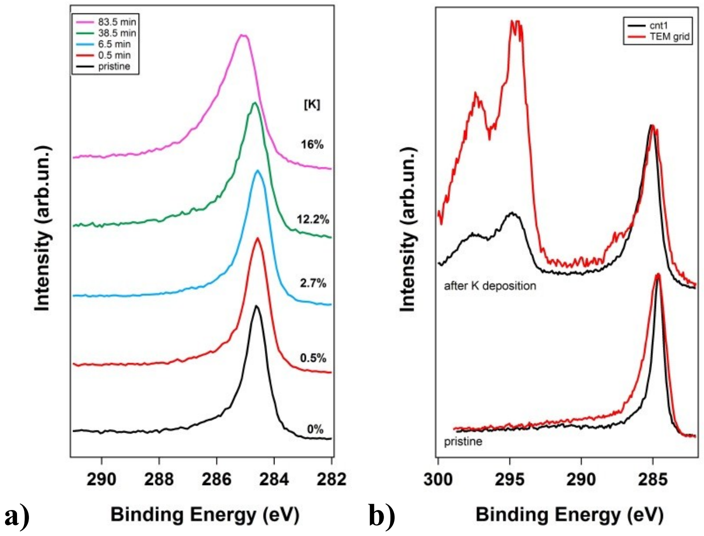

Figure S2 a) Stacked C_{1s} core level spectra acquired on the same point of the CNT exposed to the K evaporation steps expressed in minutes in the legend. K atomic concentration is reported nearby the relative spectrum. **b)** XPS spectra acquired on the nanotube bundle (black solid line) and on the carbon film of TEM grid (red solid line). At the bottom spectra recorded before the evaporation (pristine sample), while at the top after the final deposition of potassium ([K]=16% for the nanotube, and [K]=39% on the grid). All spectra were normalized to C1s intensity to highlight the different amount of potassium on amorphous carbon net.

The carbon film of the TEM grid that is reported to be a thin amorphous carbon membrane was also analysed for comparing the evaporation of K onto amorphous carbon and to exclude misalignment of the microscope during the spectra acquisition (**Figure S2b)).** We observed a much higher relative amount of K at the amorphous surface ([K]=39 at.%) than on the CNT surface ([K]=16 at.%) indicating that lateral diffusion maybe different and that diffusion inside the layered structure of the CNTs may occur. The fitting procedure was performed using the same peak assignment as described in the main text of the paper, an example is reported in **Figure S3** for the case of [K]=16 at.%. The relative contribution of the additional component (green solid line), needed to obtain the best fit of the C_{1s} peak, increased up to 11% when the relative K amount was 16%.

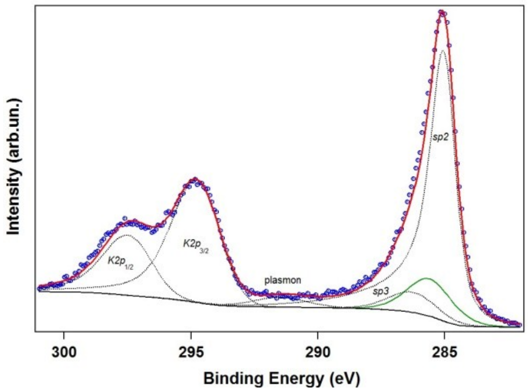

Figure S3 Goodness of the fitting procedure, described in the text, for the case of [K]=16% on CNTs.

The correlation between α (asymmetry), FWHM and the alkali concentration is shown in **Figure S4** where the variation of the parameters follows a square root power low trend starting from the pristine case. The maximal shift of C_{1s} peak obtained by the fit is 0.5 eV for the highest amount of K.

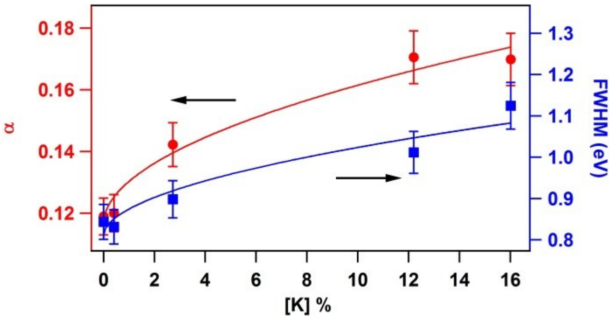

Figure S4 Variations of two fitting parameters (asymmetry α and FWHM) as function of potassium relative amount on the random carbon nanotubes, with respect to the pristine case (point 0 on the graph).

By selecting the carbon energy region we have acquired the SPEM image of a pristine nanotube before K evaporation (**Figure S5 a**) and, after the final potassium deposition by selecting the potassium energy region (**Figure S5 b**). We can observe regions in the image with higher intensity indicating that the deposition was not homogeneous all along the sample; the high intensity in the potassium image corresponds to higher potassium concentration and does not appear to cover uniformly the carbon walls in accordance with the TEM image (**Figure S1**), this was also confirmed by the 6% of difference in the relative amount of potassium evaluated using the XPS spectra acquired at 1 μm away from the referential point in the centre of the nanotube bundle.

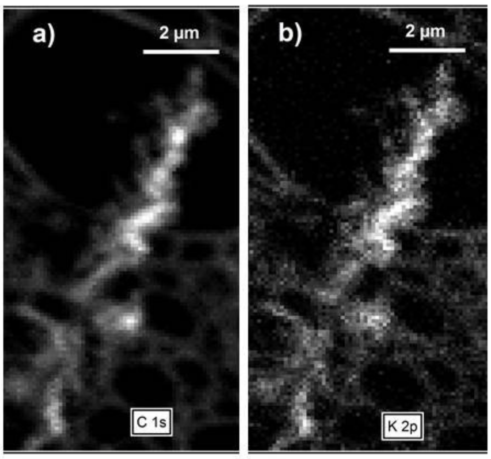

Figure S5 a) SPEM image acquired on random pristine carbon nanotube on TEM grid, by centering the energy window on C_{1s} signal. b) SPEM image acquired on the same carbon nanotube at the potassium deposition (16% of potassium), by centering the energy window on K_{2p} signal. Images are 12.8x12.8 μm^2 in size.

The direct comparison of the concentration achieved on v-CNTs and random distributed, for similar evaporation time and parameters, suggests partial intercalation in vCNTs : the amount of alkali on the walls of randomly dispersed CNTs is higher, as it is shown in **Figure S6** where the full black circle are related to the random distributes nanotube, while the empty red symbol is describing the evolution of potassium concentration on v-CNT described in the main text of the paper.

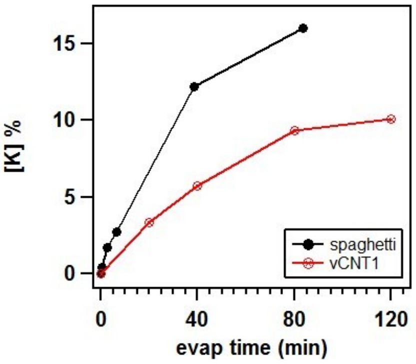

Figure S6 Relative amount of potassium calculated by XPS for vertically aligned carbon nanotube (red open circles) and not aligned carbon nanotube (black full symbol) as a function of evaporation time.