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Electronic Supplementary Information (ESI)

Simultaneous CO_2 removal from biomass conversion product gas and carbon nanotubes formation *via* catalytic chemical vapour deposition

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Materials characterisation

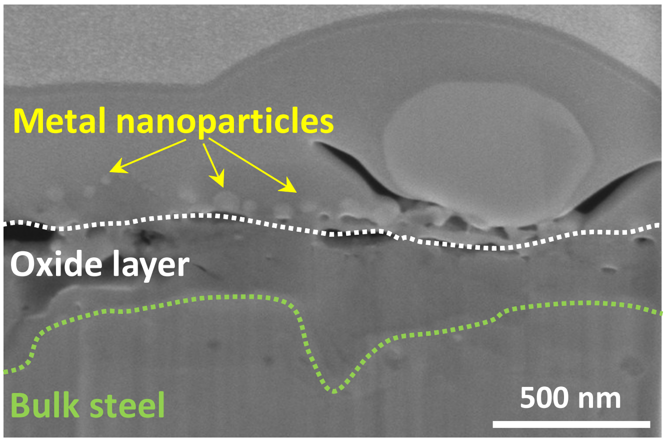

Figure S1. TEM cross section micrograph of the pre-oxidised stainless steel mesh dip-coated in an ethanol-based solution with 5 wt.% surfactant (Ni-ES-SS316L).

Mass balances discussion

Figure S2 shows the carbon mole flow (mol·min^{-1}) in the gas phase at the inlet and outlet of the reactor for the representative samples, 800-SS316L, Ni-ES-SS316L and Ni-Al_2O_3. The carbon moles in the gas phase at the inlet of the reactor were calculated taking into the account the composition of the gas mixture measured by GC at room temperature. The carbon moles in the gas phase at the outlet of the reactor were calculated from the gas compositions measured during the CCVD process at each sampling time (Figure 11). As seen in Figure S2, there is a carbon mole loss in the gas phase when the CCVD process takes place (with respect to the total carbon content of the initial gas mixture). The carbon mole loss in increasing order corresponds to 800-SS316L, Ni-ES-SS316L and Ni-Al_2O_3. This loss in the gas phase is due to the formation of solid carbon. The hydrogen and oxygen balances in the gas phase also showed a loss at the outlet of the reactor when compared to the inlet. The average H/O mole loss ratio was close to 2 for most of the experiments. This is indicative of $H_2O_{(g)}$ formation, which is in agreement with the experimental observations (small amounts of water were collected in the cold trap situated at the outlet of the reactor before the GC). However, it was not possible to quantify the water formed due to the small volumes produced.

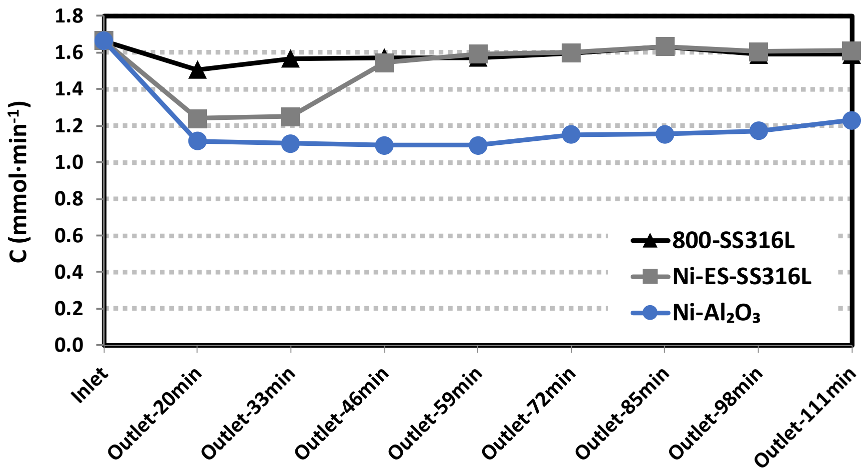

Figure S2. Carbon mole flows in the gas phase at the inlet and outlet of the CCVD reactor for the representative materials, 800-SS316L, Ni-ES-SS316L and Ni-Al_2O_3.

Table S1 shows the solid carbon (in g and mols) measured experimentally by weighing the reactor before and after the CCVD process, together with the theoretical carbon moles produced according to the carbon balance of the gas phase presented in Figure S2. For the experimental carbon mass measured (g), the standard deviation was obtained by weighing the reactor on different days. An error of two standard deviations (2σ) is considered. The percentage errors are between 16 and 60%. These error values are to be expected as the weight change due to carbon deposition is quite small compared to the total weight of the quartz reactor.

The solid carbon mass collected after the CCVD process in increasing order for the reference samples corresponds to 800-SS316L, Ni-ES-SS316L and Ni-Al_2O_3, which is in agreement with the observations from the gas phase balances explained above. Additionally, the results obtained for the other oxidised-reduced (600-SS316L) and dip-coated (Ni-EST-SS316L) stainless steel meshes evaluated as catalysts for the CCVD process are also shown in Table S1. The carbon moles calculated from the gas phase balances are within error of the carbon moles obtained experimentally for 600-SS316L, 800-SS316L and Ni-EST-SS316L; whereas for Ni-Al_2O_3 and Ni-ES-SS316L they are overestimated and underestimated, respectively. For Ni-Al_2O_3, the overestimation is most likely related to an underestimation of the CO_2 concentrations (as values measured were below the limits of quantification of the GC), which would therefore imply that more solid carbon was deposited. For Ni-ES-SS316L, CO values slightly above the GC calibration range contribute to an underestimation of carbon deposition when performing the gas phase balance. The complexity of the gas mixture employed, with many gas species participating in overlapping reactions, makes small variations of a single gas concentration notably affect the estimations of carbon deposition from the gas phase balance.

Table S1. Carbon collected (in g and mols) after CCVD experiments and theoretical moles calculated from the carbon balance in the gas phase.

Code	Exp. carbon mass (g)	Exp. carbon moles (mols)	Theoretical carbon moles (mols)
600-SS316L	0.1765 ± 0.0724	0.0147 ± 0.0060	0.0125
800-SS316L	0.1180 ± 0.0724	0.0098 ± 0.0060	0.0093
Ni-ES-SS316L	0.3323 ± 0.0724	0.0277 ± 0.0060	0.0178
Ni-ETS-SS316L	0.2473 ± 0.0724	0.0206 ± 0.0060	0.0171
Ni-Al_2O_3	0.4335 ± 0.0724	0.0361 ± 0.0060	0.0462