Electronic Supplementary Information (ESI)

Controlled growth of Ni nanocrystals on $SrTiO_3$ and their application in the catalytic synthesis of carbon nanotubes

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(1) Experimental section

CNT synthesis procedure

The CNTs were produced on the $SrTiO_3$ (001) supports with the aid of tailored Ni nanocrystals by ethanol (EtOH)-CVD, toluene (C_7H_8)-CVD, or C_2H_2-CVD over a range of temperatures (600-800 °C) for 30 min. Briefly, samples of Ni/$SrTiO_3$ substrates were placed inside a new quartz tube (2.2 cm inner diameter), which was then positioned in a 50 cm long horizontal furnace. For EtOH-CVD and C_7H_8-CVD, pure ethanol or toluene as carbon feedstock was introduced by an ultrasonic unit (piezo-driven aerosol generator (RBI Pyrosol 7901)) during the growth period, whilst for C_2H_2-CVD, instead of aerosol generator, plastic tubing directly connected to the quartz tube could deliver C_2H_2 (40 sccm). In a typical CVD experiment, a H_2 pretreatment (800 sccm, 5 min) at growth temperature was carried out prior to the introduction of the carbon feedstock. The carbon feedstock was introduced and carried by the Ar/H_2 mixture (400/200 sccm). During heating and cooling the system was flushed with 200 sccm Ar. The as-reacted substrates were collected to be further characterised. No purification procedures were used.

Apparatus and characterisation

A JEOL JSTM-4500xt UHV system, incorporating a treatment chamber, an Ar^+ sputtering source, an *e*-beam evaporation kit, and an STM, enables the fabrication and characterisation of the $SrTiO_3$ supported Ni nanocrystals. The morphology of the bulk samples after CVD reactions was analysed by using a JEOL JSM 840F SEM at 5kV; the detailed structure of grown CNTs was characterised by a JEOL JEM 4000HR TEM operating at an acceleration voltage of 80kV. The quality of CNTs was inspected by a Raman spectroscopy (JY Horiba Labram Aramis imaging confocal Raman microscope with a 532 nm frequency doubled Nd:YAG laser). Elemental analysis on grown samples was performed by using the energy-dispersive X-ray spectroscopy (EDX) equipped within a JEOL JSM 840A.

(2) Elevated-temperature STM studies of Ostwald ripening of Ni nanocrystals

Annealing time effect

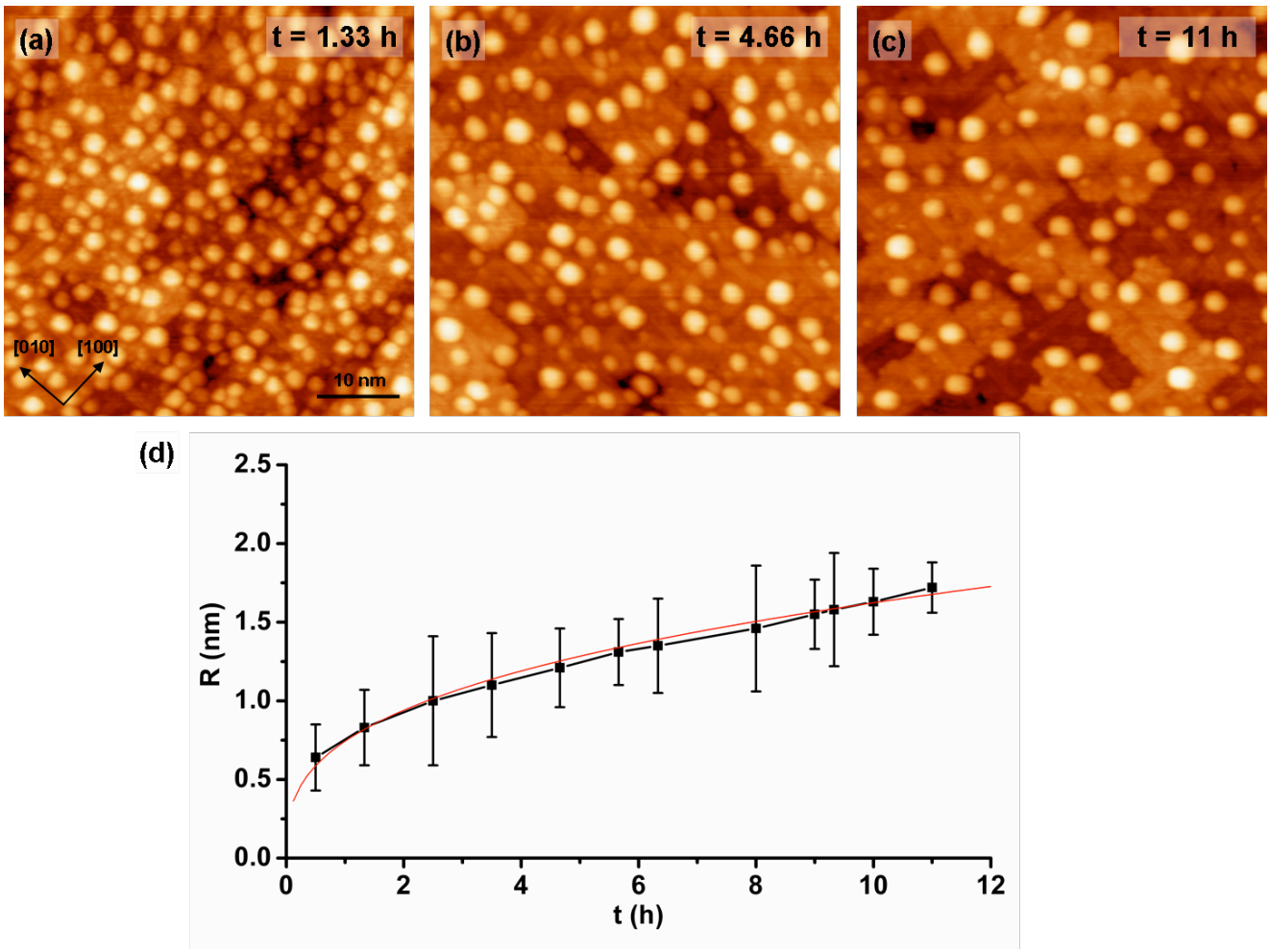

Figure S1. Hot-STM study of $SrTiO_3$ supported Ni nanocrystals at constant annealing temperature (350 ˚C) with increasing annealing time. Ni (1 ML) was deposited onto a room-temperature, $SrTiO_3$ (001)-*c*(4×2) substrate followed by UHV annealing at 350 ˚C. (a-c) Representative STM images taken at different annealing times, as marked on the images. Image conditions: V_s = +1.1 V, I_t = 0.1 nA. (d) Original data plot (black) and fitted curve (red) showing radius of Ni (R) nanocrystals against the annealing duration (t) applied to the sample, where the mathematical expression is: $R = 0.28 + 0.74t^{0.34}$. This study demonstrates that the annealing time plays a leading role in causing the nanocrystals to ripen at a given temperature.

(3) CNT growth experiments performed at low growth temperatures

The growth of CNT/Fs by EtOH-CVD at 650 ˚C

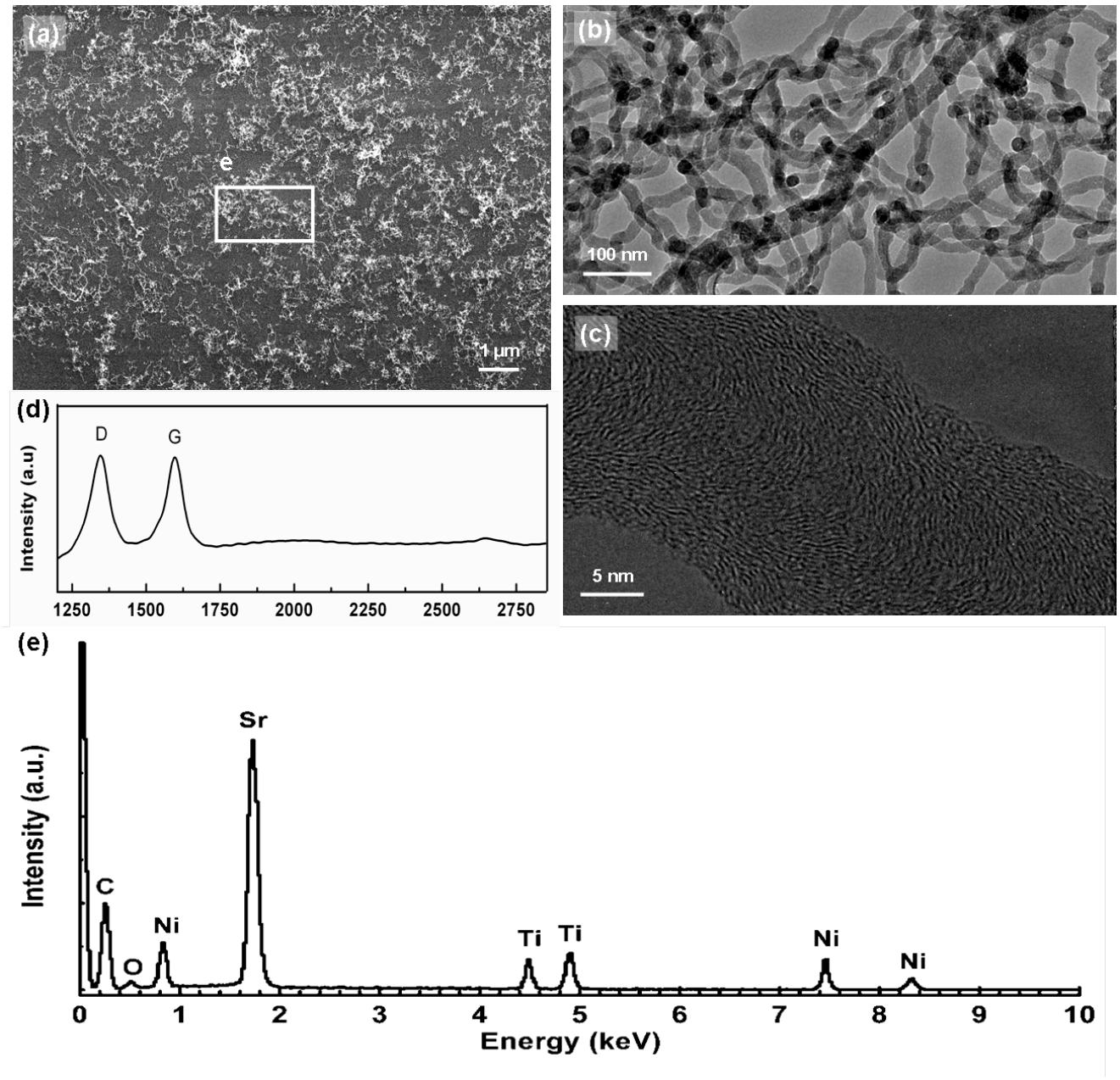

Figure S2. Growth of CNT/Fs on $SrTiO_3$ supported Ni nanocrystals by EtOH-CVD at 650 ˚C. (a) SEM image of grown sample after the CVD reaction. (b) TEM image of grown samples, indicating there are no particles trapped within the tubular structures. (c) HRTEM image of grown samples, showing the grown tubular structures have no clear inner channels thus indicating the formation of CNFs. (d) Representative Raman spectrum confirms the CNF formation on $SrTiO_3$ substrates. (e) EDX pattern (the white box marked in (a)) generated during SEM observations.

The growth of CNTs by EtOH-CVD at 700 ˚C

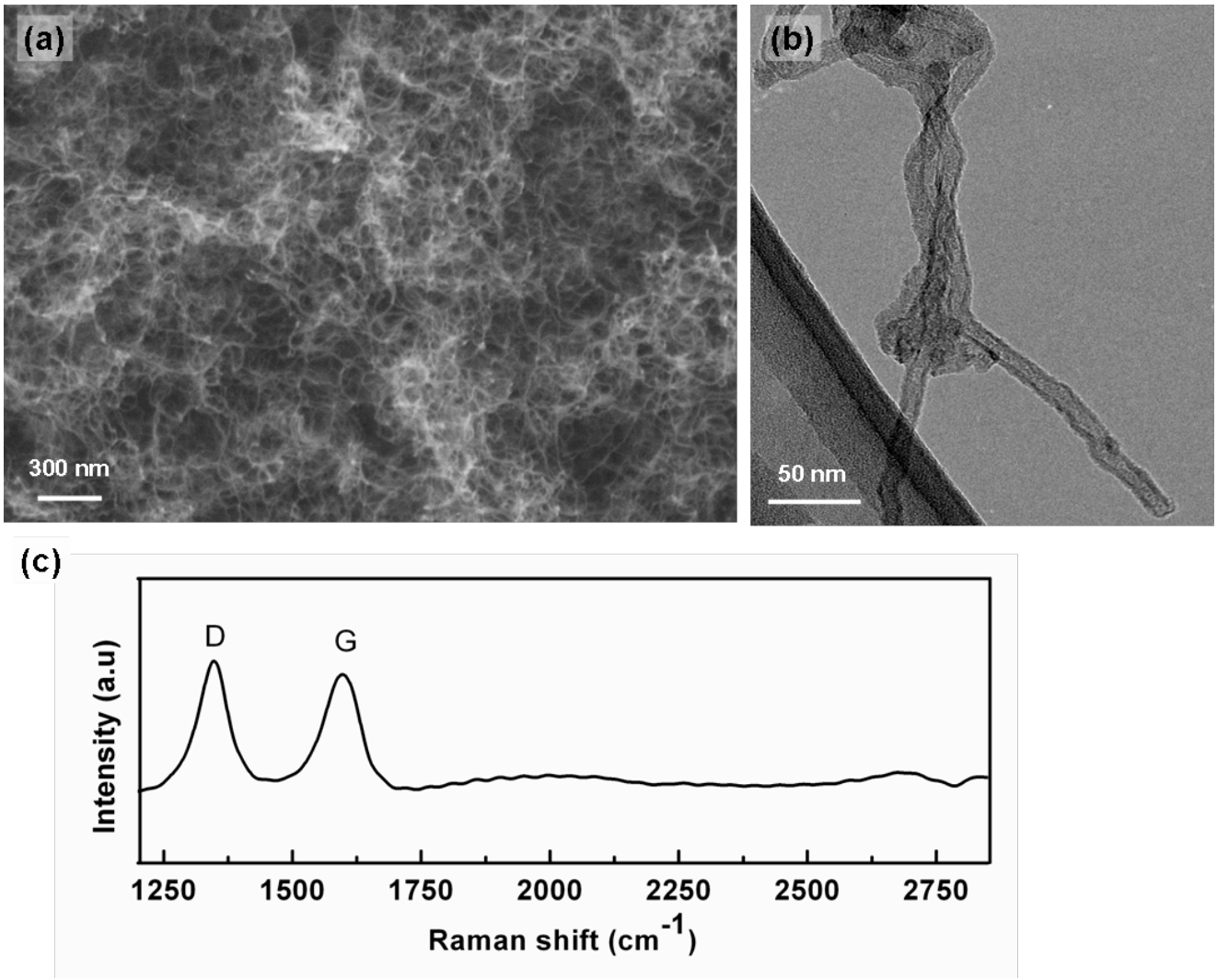

Figure S3. Growth of CNTs on $SrTiO_3$ supported Ni nanocrystals by EtOH-CVD at 700 ˚C. (a) SEM image of grown sample after the CVD reaction. (b) TEM image of grown CNTs, indicating that there are no particles trapped within the tubes. (c) Representative Raman spectrum confirms the CNT formation on $SrTiO_3$ substrates.

(4) CNT growth experiments performed using different carbon feedstocks

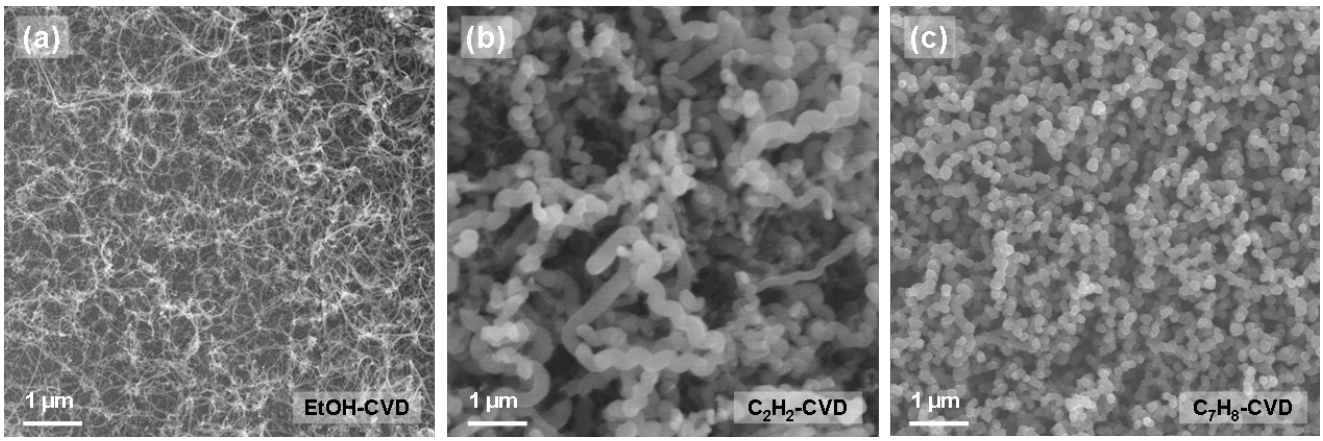

Figure S4. Preliminary CVD growth experiments performed on supported Ni nanocrystals on $SrTiO_3$ (001) substrates by using different types of carbon feedstocks. These CVD reactions were performed at growth temperatures of 600 ˚C, giving rise to distinct morphologies of grown carbons. (a-c) SEM observations of the growth of nanotubes from EtOH-CVD (a), the growth of nanocoils from C_2H_2-CVD (b), and the growth of nanospheres from C_7H_8-CVD. Further investigations are currently under way.