[Supplementary Information]

Biomimetic mineralization of Vertical N-doped Carbon Nanotubes

Won Jun Lee, Duck Hyun Lee, Tae Hee Han, Sun Hwa Lee, Hyoung-Seok Moon, Jin Ah Lee, and Sang Ouk Kim*

Department of Materials Science and Engineering, KAIST, Daejeon, 305-701, Republic of Korea.

Corresponding author. E-mail: sangouk.kim@kaist.ac.kr

Experimental Details:

Preparation of Vertical NCNTs by Plasma Enhanced Chemical Vapor Deposition (PECVD)

Thin Fe catalyst film (thickness: 2 nm) was deposited on a silicon substrate by E-beam evaporation. The substrate was heated to 750 °C in a mixture of H_2 and NH_3 gas flow (chamber pressure: 0.4 torr). The NH_3 content varied between 20 and 40 vol%. The thermal annealing (usually for less than 3 min) transformed the Fe film into agglomerated Fe nanoparticles. The chamber pressure was increased to 4.5 torr, and DC plasma was activated with an anode DC voltage of 540 V relative to the grounded substrate. Slow streaming of acetylene source gas at a flow rate of 5 sccm for 1 min fostered dense vertical NCNTs from the catalyst particles.

Preparation of Vertical undoped CNTs by PECVD

Thin Fe catalyst film (thickness: 2 nm) was deposited on a silicon substrate by E-beam evaporation. The substrate was heated to 750 °C in a mixture of H_2 and Ar gas flow (chamber pressure: 0.4 torr). The Ar content maintained 40 vol%. The thermal annealing (usually for less than 3 min) transformed the Fe film into agglomerated Fe nanoparticles. The chamber pressure was increased to 4.5 torr, and DC plasma was activated with an anode DC voltage of 480 V relative to the grounded substrate. Slow streaming of acetylene source gas at a flow rate of 5 sccm for 1 min fostered dense vertical pristine CNTs from the catalyst particles.

Preparation of hydrophilic oxygenated CNTs

The preparation of hydrophilic CNTs was carried out by sonicating pristine CNTs in the mixture of sulfuric acid and nitric acid (volume ratio of 3:1) for 10h. The temperature of acid solution was maintained about 60°C. Upon sonication, Fe catalysts were removed and a limited amount of carboxyl functional groups were formed at the edges and sidewalls of the CNTs.

SiO_2 mineralization procedure

Prior to mineralization, All CNTs (vertical NCNTs, pristine CNTs and CNT-COOHs) were dipped in ethanol for 1 min. SiO_2 mineralization was performed by dipping the CNTs in a Tris·HCl buffer solution (6 mL, 0.5 M) with 60 mg of sodium silicate solution (26.5 wt% SiO_2, obtained from Sigma-Aldrich) for 4 hrs at room temperature. pH value is maintained 6 during the mineralization process.

$CaCO_3$ mineralization procedure

Supersaturated calcium bicarbonate solution was prepared by bubbling CO_2 gas into Mili-Q deionized water in the presence of $CaCO_3$ (obtained from Sigma-Aldrich) (2 g/ 4 L) for 4 hours. Initial pH value was 9.2 when calcium carbonate powder was immersed in deionized water. After bubbling CO_2 gas, pH value was changed to 5.5 and calcium carbonate solution became transparent. Excess solid $CaCO_3$ was removed by filtering, and the filtrate was purged with CO_2 for another 30 min. Prior to mineralization, All CNTs (vertical NCNTs, pristine CNTs and CNT-COOHs) were dipped in ethanol for 1 min. $CaCO_3$ mineralization was performed by dipping the CNTs into 3 mL of pH 8.5 NH_3 solution (titrated by 1M HCl) with 3 ml supersaturated calcium bicarbonate solution. After complete addition of pH 8.5 NH_3 Solution, the pH of solution was changed to 7.9 and kept for 4 hours at room temperature to allow for crystals growth on the surface of CNTs.

Calcination of mineralized CNTs

The mineralized CNTs were calcined at 500 °C for 30 min. This thermal treatment removed the residual water maintaining the vertical alignment of mineralized CNTs.

Characterization

The morphologies of the NCNTs before and after mineralization were characterized with field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800 SEM, Japan) and high-resolution TEM (HRTEM; JEOL JEM-2100F). TEM / Energy Dispersive Spectroscopy (EDX) and the ESCA2000 X-ray Photoelectron Spectroscopy (XPS) was used for the chemical analysis of the NCNTs before and after biomineralization. A Rigaku D/MAX-2500 diffractometer with CuKa irradiation (λ = 1.5418 Å). was used for the X-ray diffraction measurements. The difference of wetting for different CNTs measured using a contact angle analyzer at a static mode (Phoenix 150, SEO). The Raman spectra were recorded on Bruker FT-Raman spectrometer (RFS 100/S) with excitation wavelength of 1064 nm and 20 mW laser power.

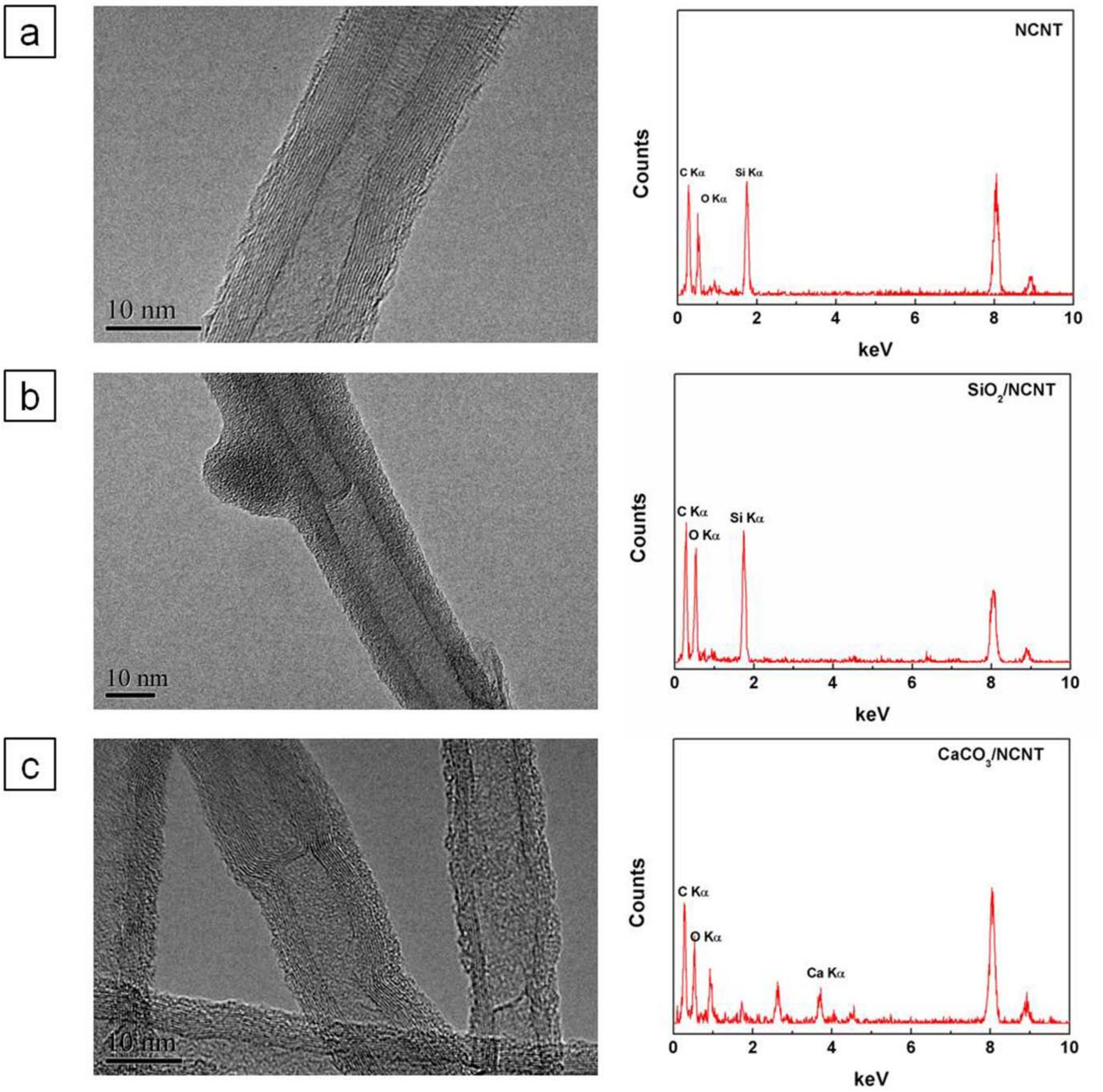


Fig. S1 TEM images and EDX chemical analyses of (a) bare NCNTs, (b) SiO_2 coated NCNTs, and (c) $CaCO_3$ coated NCNTs.

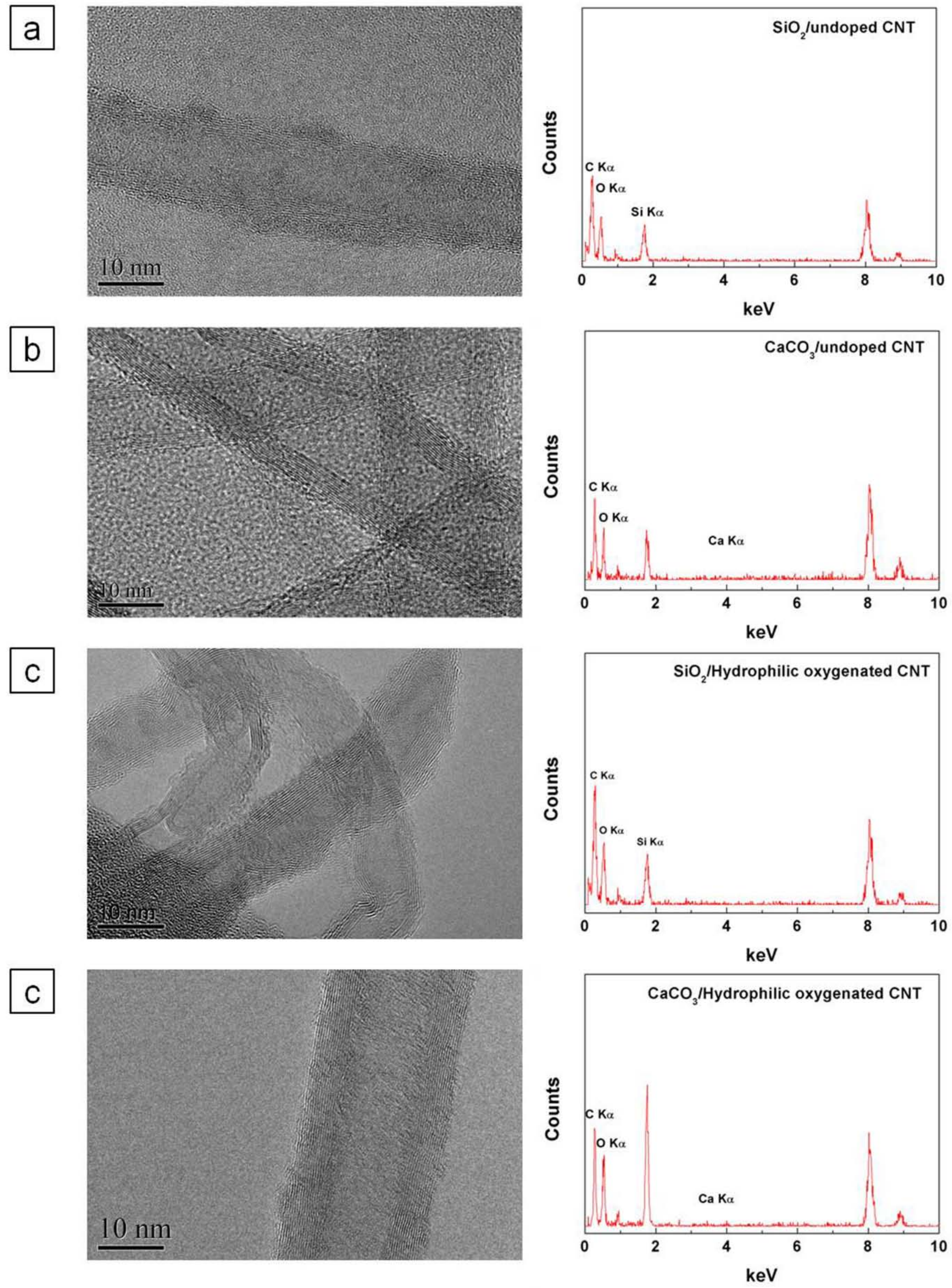


Fig. S2 TEM images and EDX chemical analyses of (a) SiO_2/undoped CNT, (b) $CaCO_3$/undoped CNT, (c) SiO_2/Hydrophilic oxygenated CNT, and (d) $CaCO_3$ / Hydrophilic oxygenated CNT.

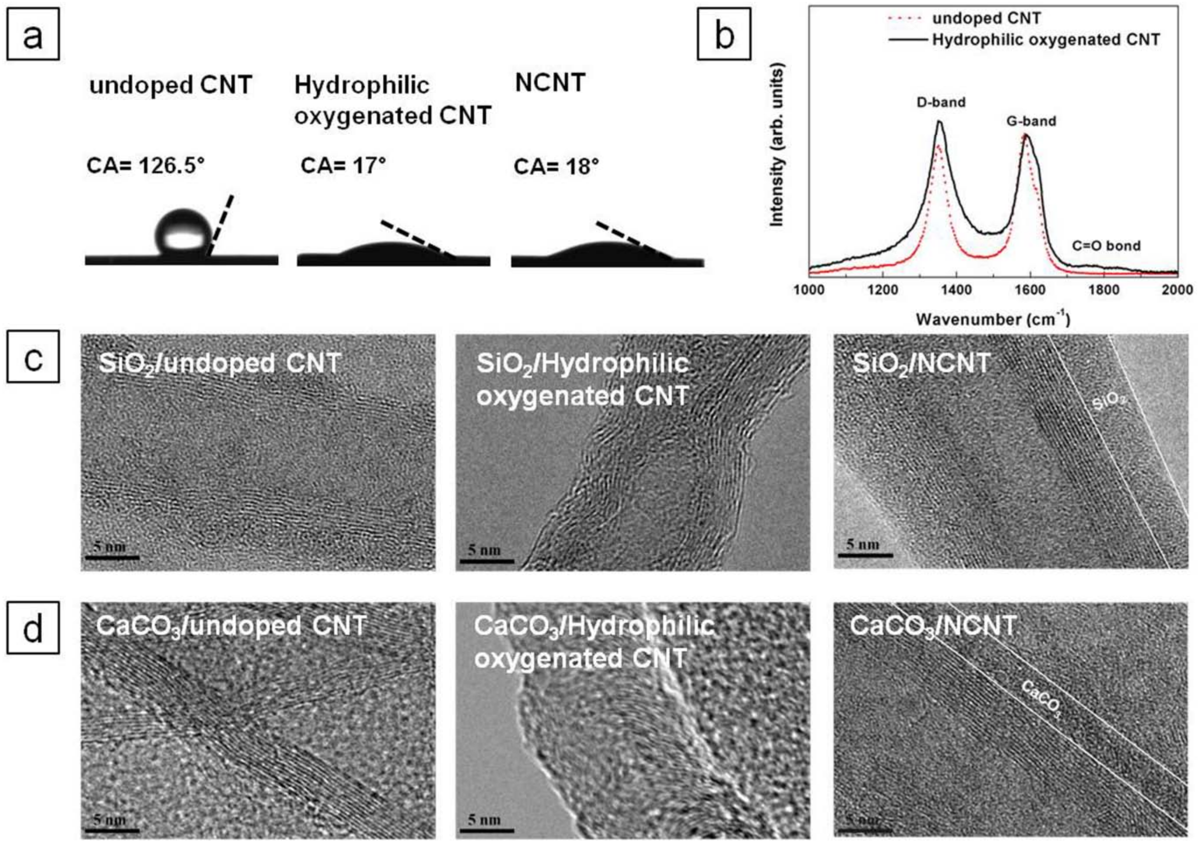
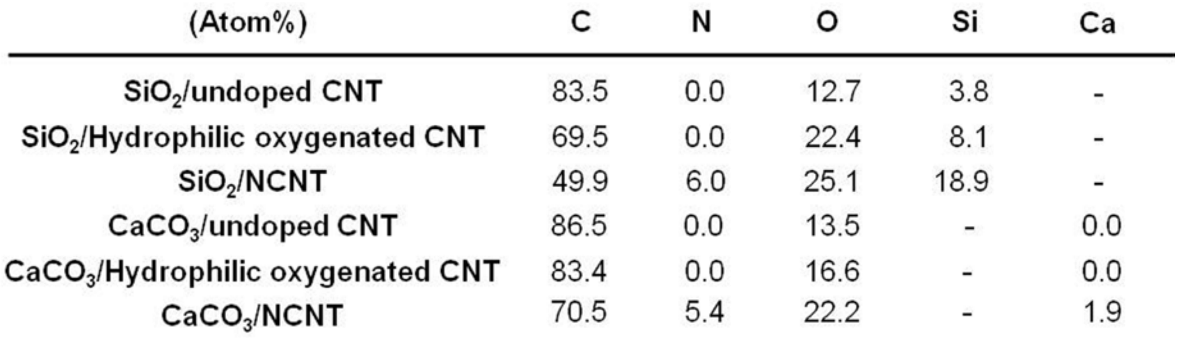


Fig. S3 (a) Static water contact angles (CA) of undoped CNT, hydrophilic oxygenated CNT, and NCNT, (b) FT-Raman spectrum of undoped CNT and hydrophilic oxygenated CNT, TEM images of (c) SiO_2/undoped CNT (left), SiO_2/hydrophilic oxygenated CNT (middle), and SiO_2/NCNT (right), (d) $CaCO_3$/undoped CNT (left), $CaCO_3$/hydrophilic oxygenated CNT (middle), and $CaCO_3$/NCNT (right).



(Atom%)	C	N	O	Si	Ca
SiO_2/undoped CNT	83.5	0.0	12.7	3.8	-
SiO_2/Hydrophilic oxygenated CNT	69.5	0.0	22.4	8.1	-
SiO_2/NCNT	49.9	6.0	25.1	18.9	-
$CaCO_3$/undoped CNT	86.5	0.0	13.5	-	0.0
$CaCO_3$/Hydrophilic oxygenated CNT	83.4	0.0	16.6	-	0.0
$CaCO_3$/NCNT	70.5	5.4	22.2	-	1.9

Table S1 Elemental Analyses (Atom%) using EDX

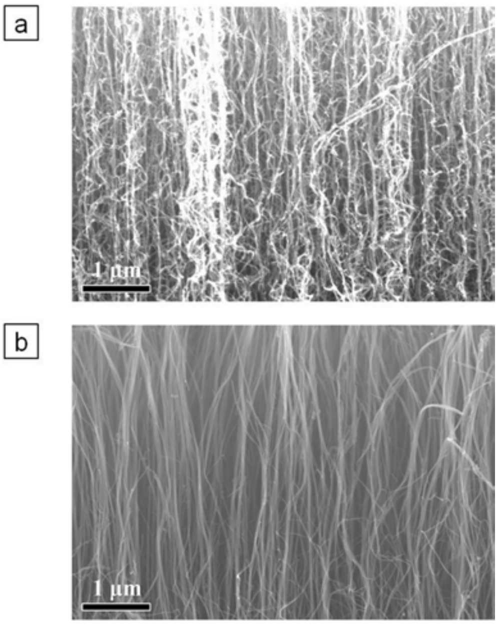


Fig. S4 Individually separated (a) SiO_2 coated NCNTs and (b) $CaCO_3$ coated NCNTs.

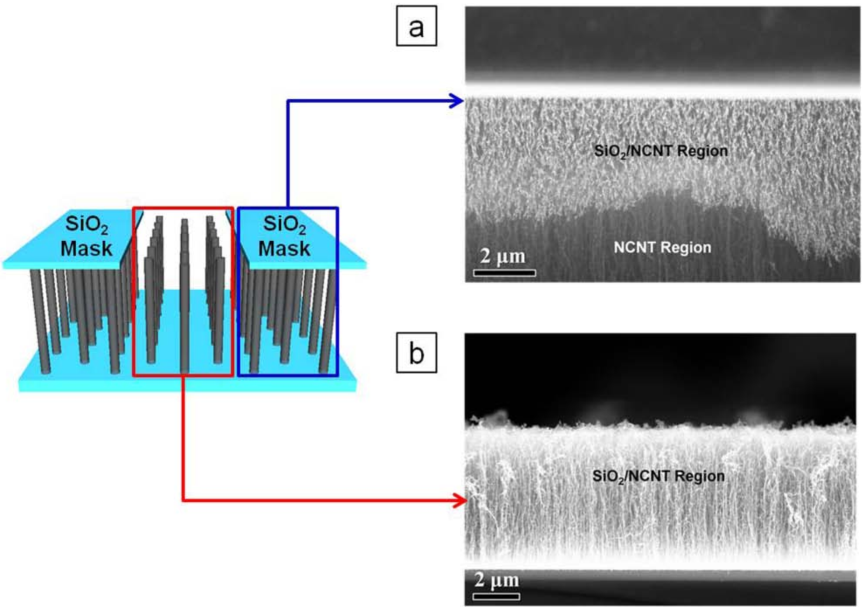


Fig. S5 Comparison between (a) SiO_2 half coated NCNTs and (b) SiO_2 fully coated NCNTs.

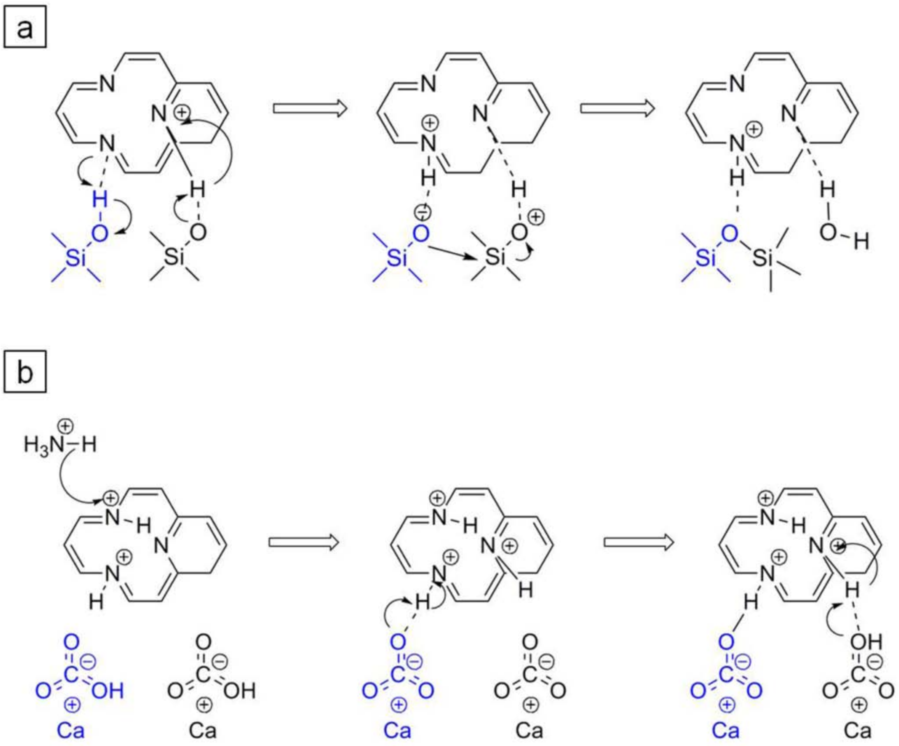


Fig. S6 Proposed biomimetic mineralization mechanisms for (a) SiO_2 coated NCNTs, and (b) $CaCO_3$ coated NCNTs at pyridinic nitrogen nucleation sites.