Electronic Supplementary Information

Carbon Nanotube-Amorphous $FePO_4$ Core-Shell Nanowires as Superior Cathode Material for Li-Ion Batteries

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Experimental details

Materials: Multi-walled CNT was purchased from Hanhwa Nanotech (Korea). $FeCl_3$ (99.99 %), NaH_2PO_4(99 %), and $FePO_4{\cdot}2H_2O$ (98%) were purchased from Sigma-Aldrich (USA). HNO_3 (60-62 %) and H_2SO_4 (98 %) were purchased from Junsei (Japan).

Fabrication of CNT-Amorphous $FePO_4$ Core-Shell Nanowires: CNT (1 mg mL^{-1}) was immersed into a 1:3 (v/v) mixture of HNO_3 and H_2SO_4, and sonicated for 12 h to functionalize the surface with carboxyl group. The sonicated solution was diluted and rinsed with deionized water until the pH of the solution achieved 7. Then, the solution was filtrated and dried to obtain functionalized CNT powder. Mineralization process was composed of two steps: (i) Fe^{3+} ion adsorption step and (ii) mineralization step by $(PO_4)^{3-}$ ion. At the step (i), CNTs were dispersed in aqueous solution of 5 mM $FeCl_3$, stored in refrigerator for 5 h to adsorb Fe^{3+} ions on the carboxyl groups, and then filtrated. At the step (ii), CNTs were re-dispersed in 5 mM NaH_2PO_4 solution in 50 mM Tris (pH 7.0), stored in the refrigerator for 5 h to mineralize the adsorbed Fe^{3+} ions into $FePO_4$, and then filtrated. These steps were sequentially repeated 10 times to cover the whole surface of CNT with $FePO_4$. After the final filtration, the obtained powder was dried and annealed at 350 °C for 5 h to remove residual H_2O in hydrated $FePO_4{\cdot}2H_2O$. To prove the superiority of the core-shell nanowire, simple mixture of CNT-amorphous $FePO_4$ was also prepared. CNT and commercial $FePO_4{\cdot}2H_2O$ was mechanically mixed by ball mill (Fritsch, PULVERISSETTE 23) for 5 h and then annealed at the same condition.

Characterization of CNT-Amorphous $FePO_4$ Core-Shell Nanowires: The morphology of the core-shell nanowire was observed using field emission high resolution transmission electron microscopy (JEOL, JEM-2100F). Bonding nature of the CNT before and after the mineralization was analyzed using Fourier transformation infrared spectroscopy, (Bruker Optics, Hyperion 3000) and high resolution dispersive Raman spectroscopy (Horiba Jobin Yvon, LabRAM HR UV/Vis/NIR). Crystallinity was identified using

X-ray diffraction with Cu Kα radiation (Rigaku, D/MAX 2500). Weight fraction of CNT was measured using Carbon/Sulfur determinator (ELTRA, CS800).

Electrochemical Analysis: The obtained CNT-amorphous $FePO_4$ core-shell nanowire or simple mixture was mixed with carbon black (Super-p), and polyvinyledene fluoride binder with 8:1:1 ratio in N-methyl-2pyrrolidone solvent (Aldrich, 99.5%) until homogeneously mixed slurry was obtained. The slurry was dried in a vacuum oven after casting onto aluminum foil, and then punched to be used as a test electrode. CR2016-type coin cell was assembled in an Air-filled glove box (Mbarun) with the test electrode, a Li metal counter electrode, a polymer membrane separator (Celgard 2400), and an electrolyte of 1 M $LiPF_6$ in 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate (Techno Semichem). Electrochemical test was performed using battery cycler (Maccor, Series 4000) with current rates from 20 to 1000 mA g^{-1} at voltage range of 2.0-4.5 V.

Confirmation of amorphous $FePO_4$ formation onto CNT surface

Fourier Transform Infrared (FT-IR) spectra of the acid-treated CNTs before and after the mineralization are shown in Figure S1. Precedent to the mineralization, two peaks near 1570 and 1730 cm^{-1} were detected, which are attributed to vibrations of aromatic C=C and carboxyl C=O bonds respectively.[S1] This implies that the surface of CNTs was functionalized with carboxyl group by acid treatment. Due to the polar carboxyl groups displayed on their surface, CNTs could be used as a template for the synthesis of inorganic materials through mineralization process. After the mineralization of $FePO_4$, a new peak near 1063 cm^{-1} appeared. This phenomenon indicates that Fe-O-P bond exists in the outer shell.[S2,S3] The decrease of the former two peaks related to the C=C and C=O bonds implies that the amount of coated $FePO_4$ is much greater than that of CNTs. Raman spectra also confirm the formation of PO_4^{3-} bond after the mineralization (Figure S2). D and G bands observed near 1350 and 1580 cm^{-1} are related to bonding nature of carbon in CNT core.[S4] Additional peaks near 455, 620, 1000, and 1065 cm^{-1} that appeared after the mineralization are well matched with the vibration spectra of PO_4^{3-} polyanion.[S2]

$FePO_4$ possesses various kinds of polymorphs depending on its synthetic conditions. As trigonal and hexagonal $FePO_4$ phases are electrochemically inactive,[S5,S6] it is essential to maintain outer $FePO_4$ shell in an electrochemically-active, amorphous phase. In addition, the amorphous phase is free from the internal stress induced by the lattice mismatch that is usually observed in two-phase reaction compounds. Thus, the amorphous phase can ensure more reliable long-term operation. Crystallinities of pristine CNTs and CNT-amorphous $FePO_4$ core-shell nanowires are compared by the X-ray diffraction (XRD) in Figure S3. Diffraction peaks of CNTs precedent to the mineralization are indexed based on those from the graphite's (JCPDS no. 41-1487). Note that a strong (002) plane peak is related with the perpendicular direction of multi-wall CNT. After the mineralization, there is no appearance of any additional peaks, this indicates that the outer $FePO_4$ shell is in a completely amorphous phase. Furthermore, all the diffraction peaks of

CNT are decreased and broadened due to the small fraction of CNTs in the CNT-amorphous $FePO_4$ nanowires.

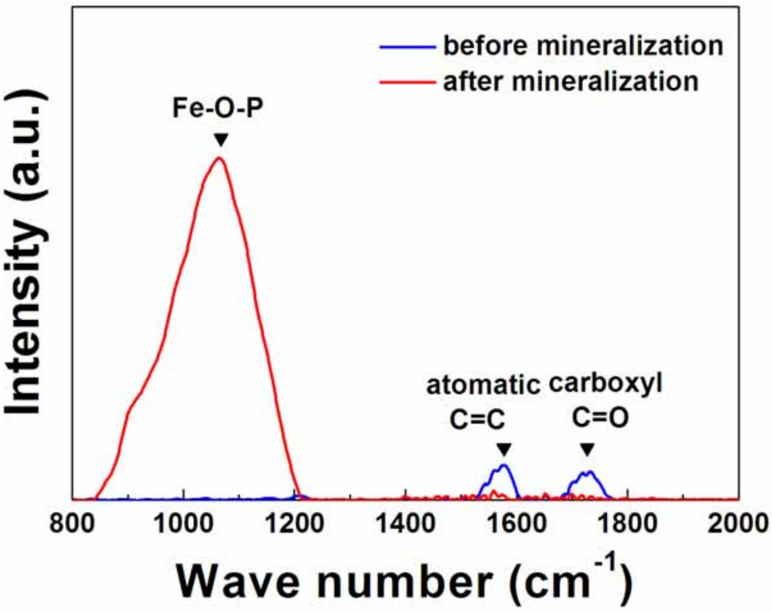

Figure S1. FT-IR spectra of CNT before (blue) and after the mineralization (red).

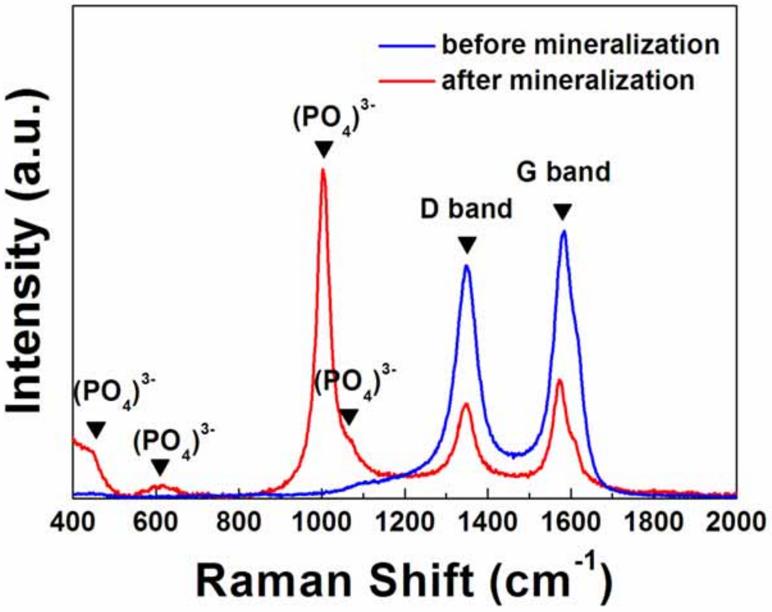

Figure S2. Raman spectra of CNT before (blue) and after the mineralization (red).

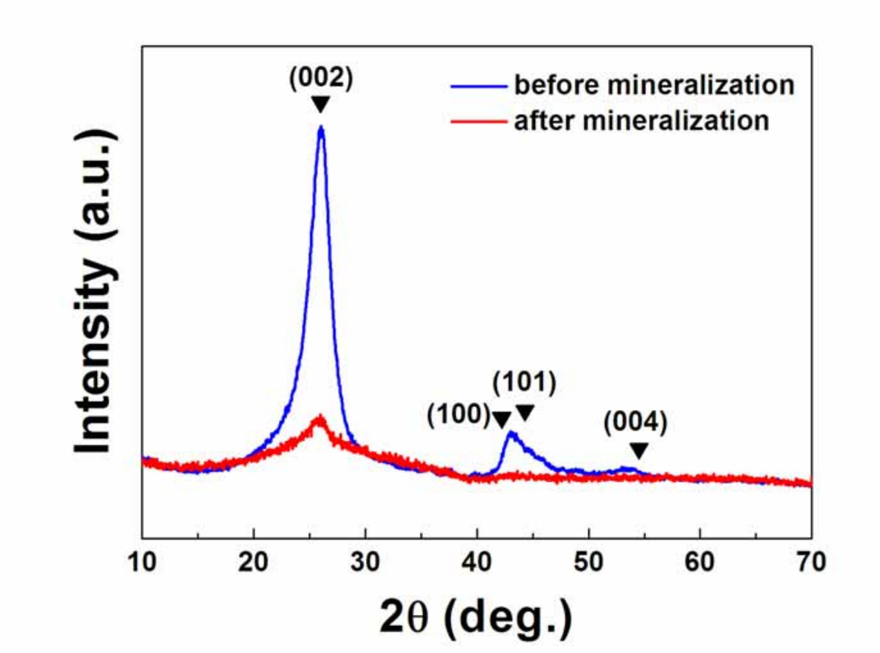

Figure S3. XRD patterns of CNT before (blue) and after the mineralization (red).

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