Supporting Information

Superparamagnetic Fe$_3$O$_4$ Nanoparticles-Carbon Nitride Nanotube Hybrids for Highly Efficient Peroxidase Mimetic Catalysts

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Experimental

CNNTs synthesis: In this paper, the carbon nitride nanotubes (CNNTs) were synthesized with microwave plasma enhanced chemical deposition (MPECVD). For catalyst preparation, the iron film of 7 nm was deposited on the Si-substrate which has 5000 Å oxide layer by RF magnetron sputtering at power of 100 and the pressure was maintained to 15 mTorr by feeding Ar gas. The substrate was then moved to the MPECVD chamber and the chamber was evacuated to about 0.1 Torr. The substrate was heated to 550 ˚C in a vacuum. 85 sccm of N$_2$ gas was subsequently flowed into the chamber, and the substrate was treated with N$_2$ plasma with a microwave power of 700 W for 1 minute. 15 sccm of CH$_4$ gas was then introduced at 700 °C with N$_2$ gas simultaneously under a microwave power of 700 W. The growth time was 20 minutes. The outer diameter of the as-produced CNNTs ranged from 5 to 25 nm.

NP and CNNT hybrid materials synthesis: Fe$_3$O$_4$NP-CNNT hybrid materials were synthesized by microwave heating method with iron oxide precursor dissolved in triethylenglycol (TEG, Aldrich). As a typical procedure, 5 mg of CNNTs was dispersed in a vial with 50 ml of TEG by sonication. And then, 20-800 mg of iron(III) acetylacetonate (Fe(acac)$_3$, Aldrich) were mixed with the solution. The vial was placed in the center of a household microwave oven and heated for 60-150 seconds. The black products were separated by centrifugation at 6000 rpm for 50 min, washed with acetone and dried at 60 °C for 8 hr under vacuum.

Peroxidase mimetic activity of Fe$_3$O$_4$NP-CNNT was characterized via the catalytic oxidation analysis of 3,3,5,5,-tetramethylbenzidine (TMB) substrate in the presence of H$_2$O$_2$ measuring color change with absorbance 652 nm at 298K as described in the reference.(1) 9-72 µg of Fe$_3$O$_4$NP-CNNT in 1.8 ml of 0.2 M sodium acetate buffer (NaAc, pH 3.5) were used as catalyst with 600 µl of 2.65 M H$_2$O$_2$ solution using 600 µl of 4.08 mM TMB as a substrate at 298 K upto 600 seconds. Also, the 72 µg of commercial Fe$_3$O$_4$NP was used for reference.
The morphology and structure of as grown samples were analyzed by field emission SEM (FESEM, FEI Sirion) and high resolution TEM (HRTEM, FEI Tecnai F20, FEI Tecnai F30, JEM 2100F). The magnetic properties of NPs on MWCNNT were measured using the vibrating sample magnetometer (VSM, Lake Shore 7300) with magnetic field up to 17k Oe. Also, the field-cooled and the zero field-cooled magnetic properties were characterized with a superconducting quantum interference device magnetometer. The X-ray diffractometer (XRD, Rigaku D/Max-RC, Cu Kα radiation) was used to analyze crystal structure of NPs-CNNTs with the range of 2θ =10 ~ 70 °. The Fourier transform infrared spectroscopy (FT-IR, Bruker Optiks IFS66V/S & HYPERION 3000) was used for the surface analysis of Fe3O4NP-CNNT for hydroxyl group with ATR mode. The peroxidase mimetic reactions were analysed by UV-Vis-NIR (UV-Vis-NIR, Shimadzu UV-3101PC) spectrometer with 652 nm wavelength absorption.

The XPS measurements were performed at the U7 beam line of the Pohang Light Source (PLS). The photoelectrons were collected using photon energy is 700 and 820 eV for CNNT and Fe3O4NP-CNNT measurement, respectively. The binding energies were corrected for specimen charging by referencing the Pt 4f7/2 peak to 70.9 eV. The experiment was performed in an ultrahigh vacuum (UHV) chamber with a base pressure ≤ 5×10−10 Torr. The energy of the photoelectrons emitted from the surface of the NPs-CNNTs nanotubes was analyzed with an electron energy analyzer (Physical Electronics: model PHI 3057 with a 16-channel detector). The analyzer was located at an angle of 55° from the surface normal. The N K-edges XANES measurement was also performed at the same beam line. The spectral resolving power (E/ΔE) of the incident photons is about 5000 at 400 eV. All of the spectra were taken in total electron yield mode in which the sample current was recorded at room temperature.

![Fig. S1. a) HAADF image and EDS line scan profile for H-1 whose structure was synthesized under the Fe(acac)3 concentration of 200 mg and the reaction time of 90 s, b) quantitative percentages for each element existing on the surface layer of H-1, and c) 4.0 nm size of NPs on CNNTs under the Fe(acac)3 concentration of 400 mg.](image-url)
Fig. S2. TEM images of NPs-CNNTs synthesized in 200 mg-90 s (a), 200 mg-120 s (b), 200 mg-135 s (c), 200 mg-150 s (d), and 400 mg-120 s (e), respectively.

Fig. S3. FT-IR spectrum of Fe$_3$O$_4$ NP-CNNT hybrids. A broad band appeared in the region of 2700-3600 cm$^{-1}$ corresponds to the O-H stretching vibration.

Fig. S4. TEM images of reference pure Fe$_3$O$_4$ NPs sizes of a) 5 nm and b) 30 nm. The NPs are agglomerated each other even though there is the dispersion observed with the severe sonication.
Fig. S5. TEM image of NP-CNNT hybrids after a leaching test.

Fig. S6. SQUID analyses at 50 Oe of NPs-CNNT hybrids.

The blocking temperatures of the NPs-CNNT hybrids are 30 K to 120 K, where it shows the smaller size of NPs showed the lower blocking temperature value. Meanwhile, we find that the NPs-CNNT hybrids exhibit the superparamagnetism up to room temperature where it has no coercive field.

References