Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Two-Step Synthesis of Agglomeration-free Peroxidase-like Co_3O_4 Nanoparticles-Carbon Nitride Nanotube Hybrids Enabling a High Redox Activity

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The growth and characterization of CNNTs. CNNTs were grown by a plasma-enhanced chemical vapor deposition (PECVD) method using Fe catalysts prepared through Radio Frequency (RF) magnetron sputtering on a SiO_2/Si substrate. Fig. S1 (a) shows that the CNNTs are vertically aligned at the length of 17.1 μm on the substrate and that the inner structure of the CNNTs resembles bamboo. In addition, the CNNTs show the peak matching with the (002) planes of graphite (JCPDS, 41-1487) at $2\Theta = 25.96\ ^{o}$ in the X-ray diffraction (XRD) patterns (Fig. S1 (b)). This peak is ascribed to the ~ 3.4 Å graphene interlayer distance between the nanotube layers. In an X-ray photo-electron spectroscopy (XPS) analysis (Fig. S1 (c)), the nitrogen content of the nanotubes is 3.21 at% and the nitrogen doping configuration of the CNNTs intricate that there are three Gaussian peaks with binding energies of 399.0 eV (N1), 401.5 eV (N2) and 404.9 eV (N3) in the range of the N1s peak. N1, N2 and N3 indicate pyridine-like nitrogen (Pry-N), graphite-like nitrogen (Gra-N), and gaseous nitrogen molecules encapsulated in the core tube, respectively.[1] These nitrogen configurations act as defect sites and can bind more strongly Co_3O_4 particles on the CNNTs.

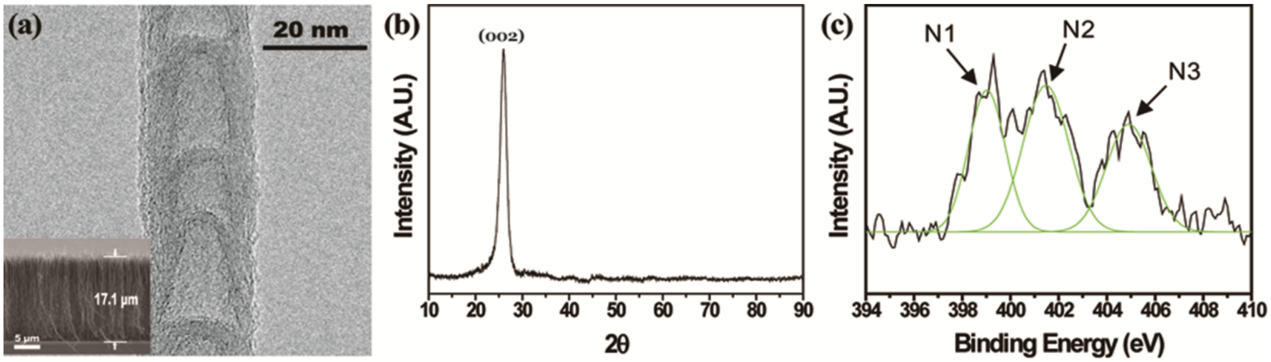

Fig. S1. (a) TEM images of CNNTs (SEM image inclusion), (b) XRD pattern and (c) XPS spectra of CNNTs.

The peroxidase-like redox activities of the Co_3O_4 NPs-CNNT hybrid according to the pH, the H_2O_2 concentration, the temperature and the Co_3O_4 NPs-CNNT hybrid concentration.

The catalytic activity of the Co_3O_4 NPs-CNNT hybrid is dependent on the pH, the Co_3O_4 NPs-CNNT hybrid concentration, the temperature, and the H_2O_2 concentration. The peroxidase-like redox activity of the Co_3O_4 NPs-CNNT hybrid was measured by varying 1) the pH from 3 to 7, 2) the Co_3O_4 NP-CNNT hybrid concentration from 1 - 5 µg / mL, 3) the temperature from 25 °C to 50 °C, and 4) the H_2O_2 concentration from 5 mM to 1.0 M. The catalytic activity of the Co_3O_4 NPs-CNNT hybrid is higher under the acidic solutions (pH 3 - 5) than that in the neutral solutions. We find that the optimal pH is 4.5 (Fig. S2 (a)). The Co_3O_4 NPs-CNNT hybrid shows no inhabitation of its catalytic activity in a H_2O_2 concentration range of 5 mM to 1.0 M (Fig. S2 (b)). This finding is similar to that of prisitine Co_3O_4 NPs.[3] The optimal temperature of the Co_3O_4 NPs-CNNT hybrid is 40 °C, as seen in Fig. S2 (c). We also find that the optimal temperature is similar to that observed with Co_3O_4 NPs.[2] In addition, Fig. S2 (d) shows that the TMB oxidation rate is dependent on the concentration of the Co_3O_4 NPs-CNNT hybrid. Fig. S3 shows the comparison of the peroxidase-like redox activity of the Co_3O_4 NPs-CNNT hybrid and HRP[2] according to the pH, the H_2O_2 concentration, the temperature. The results of Fig. S3 indicate that the catalytic activity of the Co_3O_4 NPs-CNNT hybrid is more stable than HRP at a high H_2O_2 concentration and temperature. In addition, the pH distribution of the Co_3O_4 NPs-CNNT hybrid is similar to HRP, but a maximum velocity of the Co_3O_4 NPs-CNNT hybrid (2.55×10^{-7} M S^{-1}) is much higher than the 8.71×10^{-8} M S^{-1} of HRP. Consequently, these results show that the Co_3O_4 NPs-CNNT hybrid can be applied to the conditions where the pH, the temparature and the salt concentration vary widely. From the analyses of the pH, the temperature, and the Co_3O_4 NPs-CNNT hybrid concentration of Figure S2, we adopted the pH at 4.5, the room temperature (~ 25 °C), and the 2 μg/mL of the Co_3O_4 NPs-CNNT hybrid as the standard conditions to determine the peroxidase-like ability. We investigated the ability of Co_3O_4 NPs (sigma Aldrich), Fe_3O_4 NPs (alfa aesar) and the Co_3O_4 NP-CNNT hybrid as catalysts for the peroxidase-like activity of the substrates (TMB, H_2O_2) under the standard condition. (Fig. S4).

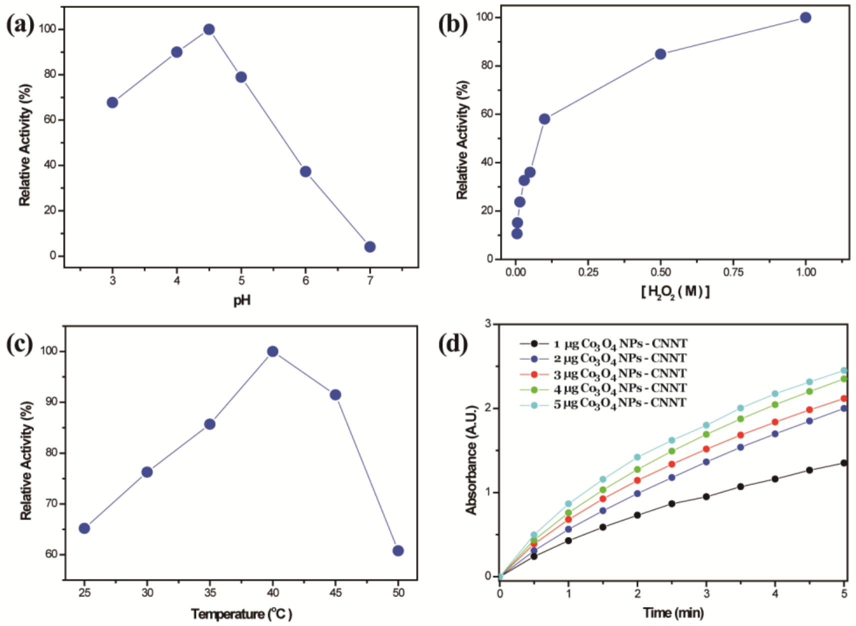

Fig. S2. Dependency of the peroxidase-like redox activity according to (a) the pH, (b) the H_2O_2 concentration, (c) the temperature and (d) the Co_3O_4 NPs-CNNT hybrid concentration. Experiments were conducted by changing the pH ((a), pH 3 - 7) of the acetate buffer solution, the H_2O_2 concentration ((b), 5 mM - 1 M), the Temperature ((c), 25 - 50 °C), and the Co_3O_4 NPs-CNNT hybrid concentration ((d), 1 - 5 μg / mL), respectively. Other conditions were set in 3 ml acetate buffer solution (0.1 M, pH 4.5) with 0.1 M H_2O_2, 0.3 mM TMB, 2 μg/mL of the Co_3O_4 NPs-CNNT hybrid at room temperature.

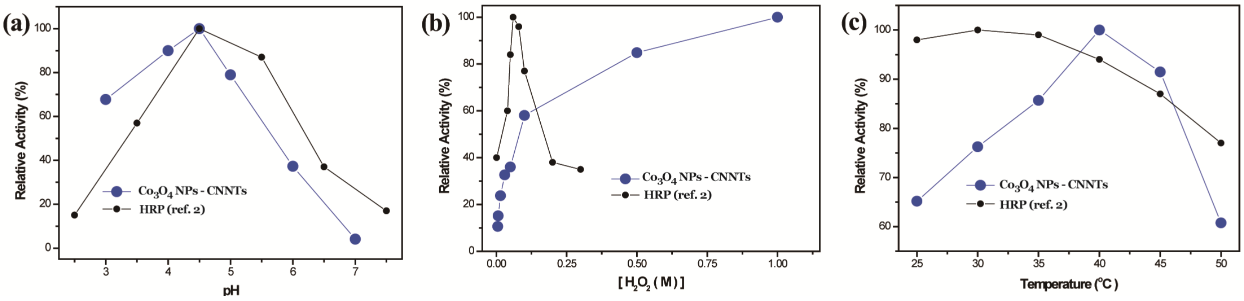

Fig. S3. Comparison of the peroxidase-like redox activity of the Co_3O_4 NPs-CNNT hybrid and HRP[2] according to the pH, the H_2O_2 concentration, the temperature.

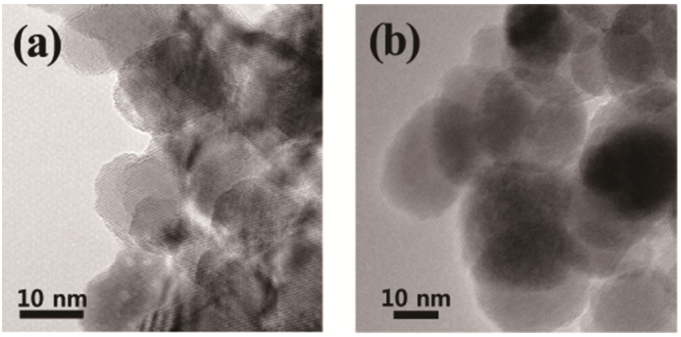

Fig. S4. TEM images of pristine (a) Co_3O_4 NPs and (b) Fe_3O_4 NPs grown on conventional methods

The steady-state kinetic assay of the Co_3O_4 NPs-CNNT hybrid. To analyze the kinetics of the peroxidase activity of the Co_3O_4 NPs-CNNT hybrid, we also determined the steady-state kinetic parameters of the reaction. The kinetic parameters were acquired by changing one substrate concentration while holding the other substrate concentration constants steady. The initial reaction rates were calculated through the absorbance of a TMB oxidation reaction catalyzed by Co_3O_4 NPs-CNNT hybrid, where the absorbance rate follows the typical Michaelis-Menten behavior in the presence of TMB and H_2O_2 concentrations. Typical Michaelis-Menten curves were observed for the Co_3O_4 NPs-CNNT hybrid (Fig. S5 (a), (b)). The data were fitted to the Michaelis–Menten equation ($1 / \nu = (K_m / V_{max}) \cdot (1 / [S]) + 1 / V_{max}$), and the Michaelis constant (K_m) and the maximal velocity (V_{max}) were obtained using Lineweaver-Burk plots (Fig. S4 (c), (d)).

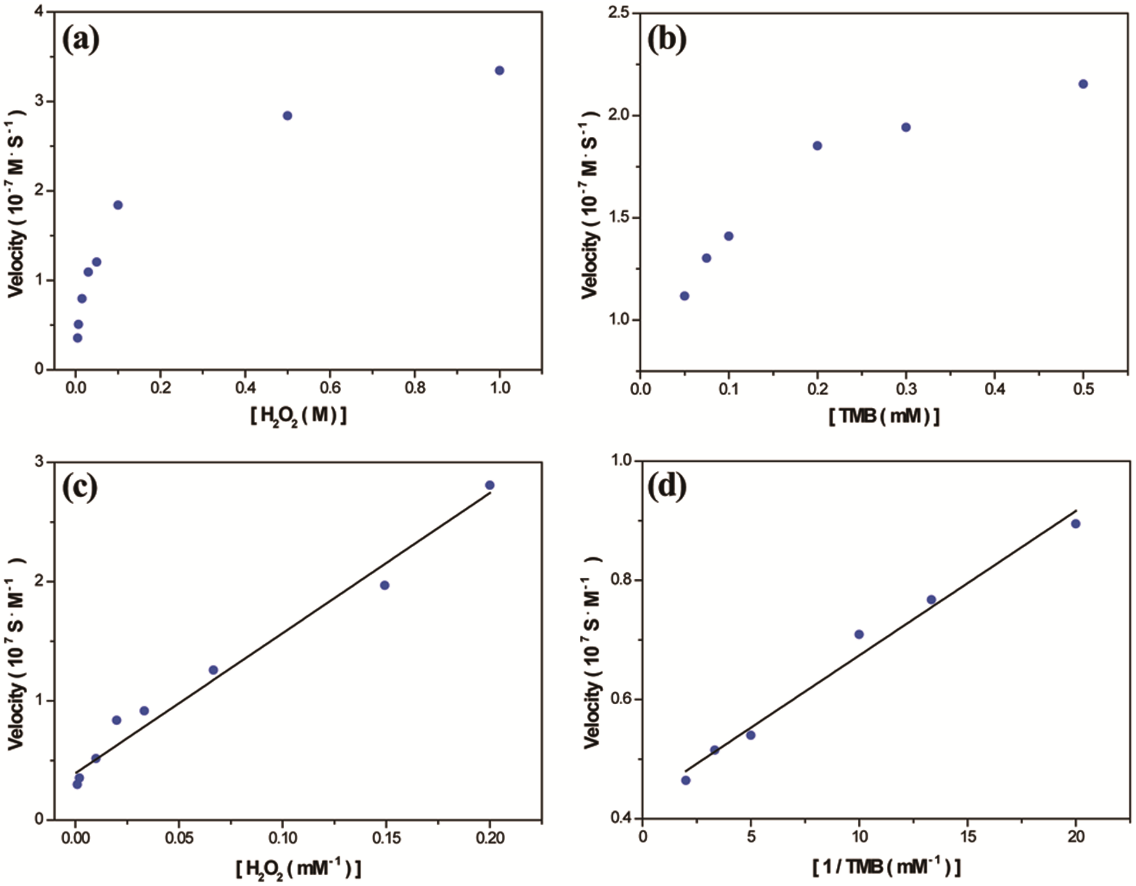

Fig. S5. Kinetic assay for the Co_3O_4 NPs-CNNT hybrid. The velocity of the reaction by the Co_3O_4 NPs-CNNT hybrid with different concentrations of (a) H_2O_2 and (b) TMB. (c) and (d) are Lineweaver-Burk plots of (a) and (b), respectively. The reaction condition is in the 3 ml acetate buffer solution (0.1 M, pH 4.5) and the 2 μg /mL Co_3O_4 NPs-CNNT hybrids at room temperature. (a, c) The concentration of TMB was 0.3 mM and the H_2O_2 concentration was changed (5mM - 1M). (b, d) The concentration of H_2O_2 was 0.1 M and the TMB concentration was alternated (0.05 - 0.5 mM).

The structure of the Co_3O_4 NPs-CNNT hybrid before and after the catalytic reaction. The Co_3O_4 NP-CNNT hybrid was dispersed in an acetate buffer aqueous solution (0.1M, pH 4.5), and it was used to catalyze the oxidation of TMB (0.3 mM) by H_2O_2 (0.1M) at 652 nm on a UV-Vis spectrometer and at room temperature. We confirmed that the structure of the Co_3O_4 NP-CNNT hybrid before and after the catalytic reaction was maintained without any changes through XRD analysis (Fig. S6). The x-ray diffraction pattern depends on the electron density of the sample. The maintenance of Co_3O_4 NPs-CNNT structure through XRD measurements means that the electron density of the Co_3O_4 NPs-CNNT hybrid after reaction does not change and the Co_3O_4 NPs-CNNT performs the role of catalyst in the peroxidase-like redox reaction.

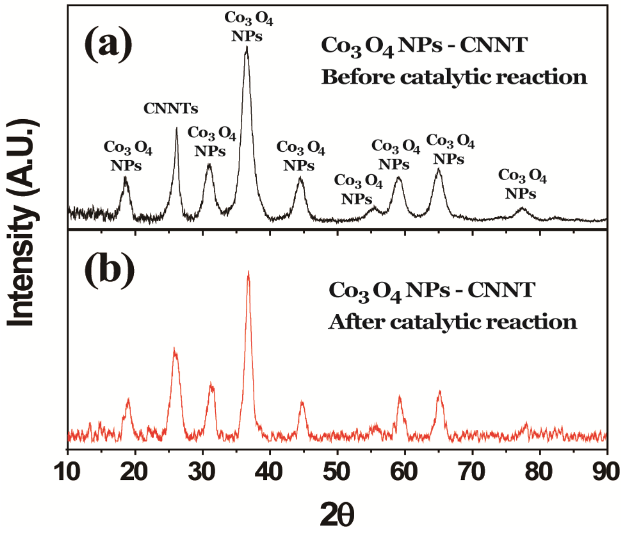

Figure S6. X-Ray Diffraction patterns of Co_3O_4 NPs-CNNT (a) before and (b) after the catalytic reaction.

References

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