Supplementary materials

Non-covalent surface modification of boron nitride nanotubes for enhanced catalysis

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Materials

Amorphous B powder (95%-97%) was purchased from Fluka, MP-11 (microperoxidase-11), TMB (3, 3', 5, 5'-Tetramethylbenzidine) and H_2O_2 were purchased from Sigma-Aldrich (Sydney, Australia).

Experimental section

1. Synthesis of BNNTs

Boron nitride nanotubes (BNNTs, Figure S1) were synthesized by a boron (B) ink method.[1, 2] Amorphous B powder (95% - 97%, Fluka) was first ball milled in dehydrated ammonia (NH_3) gas at a static pressure of 300 kPa for 150 h, to produce highly reactive B particles of nanosizes. The milled B particles were then dispersed into ferric nitrate (Fe $(NO_3)_3$) ethanol solution in an ultrasonic bath for 0.5 h to form an ink-like solution (B ink). The B ink was heated in nitrogen with 15% hydrogen (N_2 + 15% H_2) reaction gas at 1100 ºC for 3 h to form BNNTs.

2. Self-assembly of BNNTs with MP-11

Hybride BNNTs (Figure S2) was prepared by self-assembly of BNNTs with MP-11. In a typical experiment, 1.0 ml of 20 mM MP-11 solution in 1.5 ml eppendorf tube was mixed with 200 μg BNNTs suspension in the presence of 20 mM phosphate buffer solution (pH 7.0, which can be varied in control groups). After been shaken gently for 30 ~ 90 seconds, the tube was left to stand still overnight at room temperature to be ready for investigation.

During the next day, the new nanohybrids MP-11/BNNTs were characterised by Cary 300 Bio ultraviolet-visible (UV–Vis) spectrophotometer (Figure S3), Jasco J-815 circular dichroism spectrometer (Figure S4) and transmission electron microscopy (Figure 1) compared with pure MP-11. By keeping the nanohybrids at 4℃,the stability and peroxidase activity can be maintained for at least three weeks, and the stability in the diverse pH conditions has also been investigated (Figure S6 and S7). It would be further studied and investigated in future work, especially on the thermal stability of BNNT/MP-11 hybrids and stability in the presence of denaturing agents. UV-Vis spectroscopy was employed to reveal the optical properties of the BNNT/MP-11 nanohybrids. The peak shifts suggest electron transfers, which originated from the strong π-π stacking interactions, existed between the FMNs and BNNTs.[3] CD spectra of BNNTs functionalized with a special peptide have also revealed the tryptophan residues cooperatively interacted with the hydrophobic BNNT surface via π-π interactions.[4] Thus, spectroscopic changes of functionalized BNNTs are mainly due to π-π interactions and this is further proved by the TEM results, kinetic studies and computational calculations.

3. Kinetics study of the new hybride BNNTs

In a typical experiment of kinetics study, 50 μM MP-11/BNNTs were used to catalyze oxidation reaction of 1.0 mM TMB in the presence of 10 mM H_2O_2 at room temperature. TMB (3, 3', 5, 5'-Tetramethylbenzidine) is a kind of chromogenic substrates, which can be oxidized by H_2O_2 to give a clearly visible colour change from colourless to blue (Figure S5).

After monitored the reactions by kinetics mode at 652 nm using Cary 300 Bio UV-Vis spectrometer (Figure S6, S7, S8), Lineweaver-Burk Plot, which provides a useful graphical method for analysis of the Michaelis–Menten equation[5]

$$v = \frac{v_m \cdot [S]}{K_m + [S]},$$

$$\frac{1}{v} = \frac{K_m}{v_m} \cdot \frac{1}{[S]} + \frac{1}{v_m}$$

was used to calculate the Michaelis constant. In the above equation, K_m is the Michaelis constant; v_m is the maximal reaction velocity, [S] is the concentration of substrate.

At the same time, pure MP-11 and pure BNNT were also introduced in the kinetics study as control experiments. To investigate the mechanism, assays were carried out under standard reaction conditions as described above by varying concentrations of TMB at a fixed concentration of H_2O_2 or vice versa (Figure S8). With the detection of TMB color change, the alternation of the new products' catalytic efficiency can be investigated.[6-8]

Computational Details

Our first-principles calculations are based on density-functional theory (DFT) with the Perdew–Burke–Ernzerhof gradient corrected functional,[9] as implemented in the PWSCF package.[10] Ultrasoft pseudopotential is used and spin-polarization is included through all the calculations. A (5 × 5) boron-nitride nanotube containing 220 atoms plus a MP-11 fragment (83 atoms) are set in a supercell (27.17 Å × 27.17 Å × 27.17 Å). Only gamma point is used due to the large size of supercell. The cut-off energy for plane waves is chosen to be 400 eV, and the vacuum space is at least 15 Å, which is large enough to avoid interaction between periodical images. Geometry optimization procedures have been performed until the residual forces were smaller than 0.01 eV/ Å.

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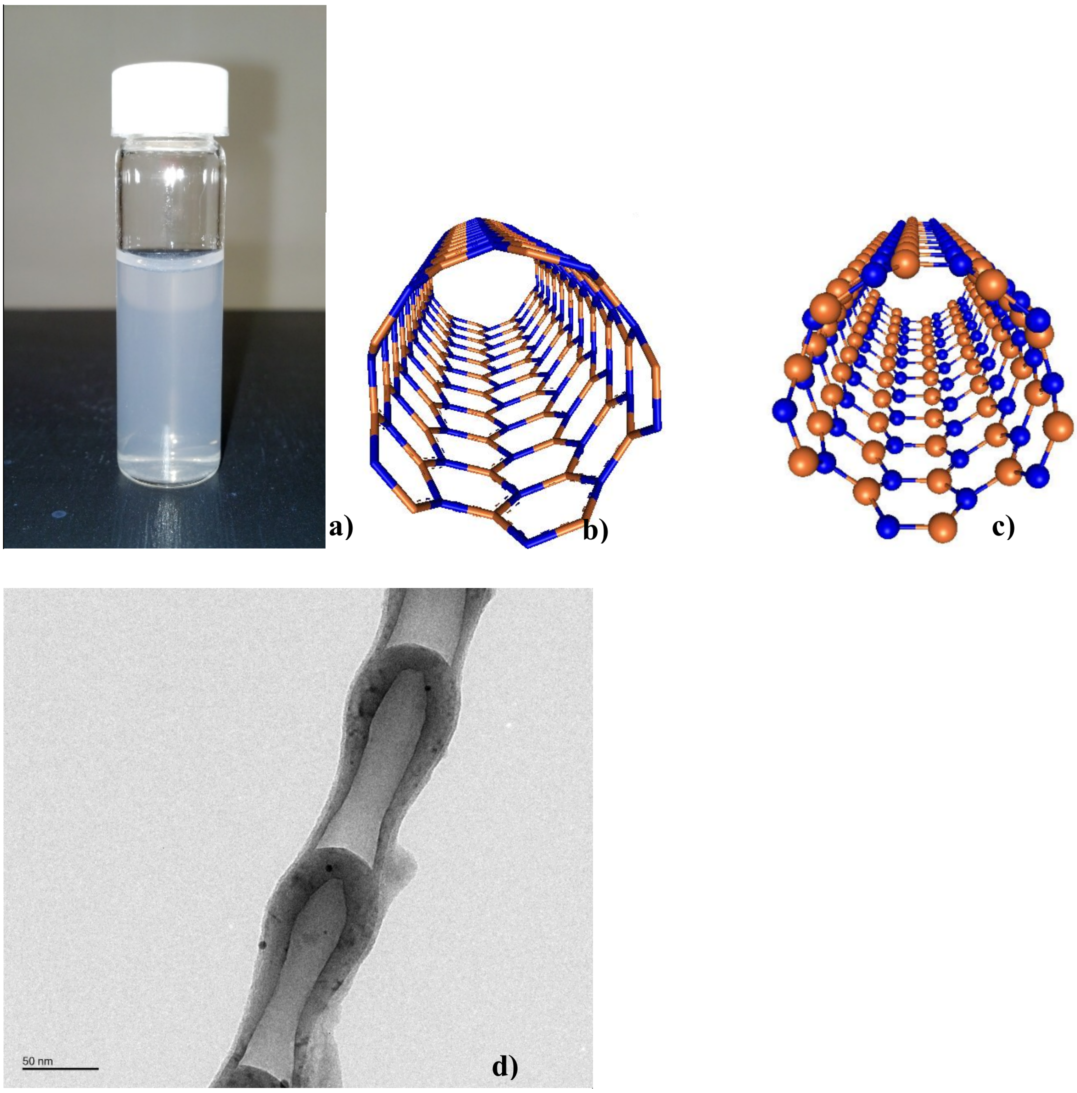

Fig. S1 a) The photo image of BNNT suspension in water; b, c) optimized geometries for BNNT, blue and yellow atoms represent N and B atoms, as a structural analogue to carbon nanotubes (CNTs), BNNTs have boron and nitrogen atoms distributed equally in hexagonal rings; d) TEM image of BNNTs, their resolutions were 50 nm and 20 nm respectively.

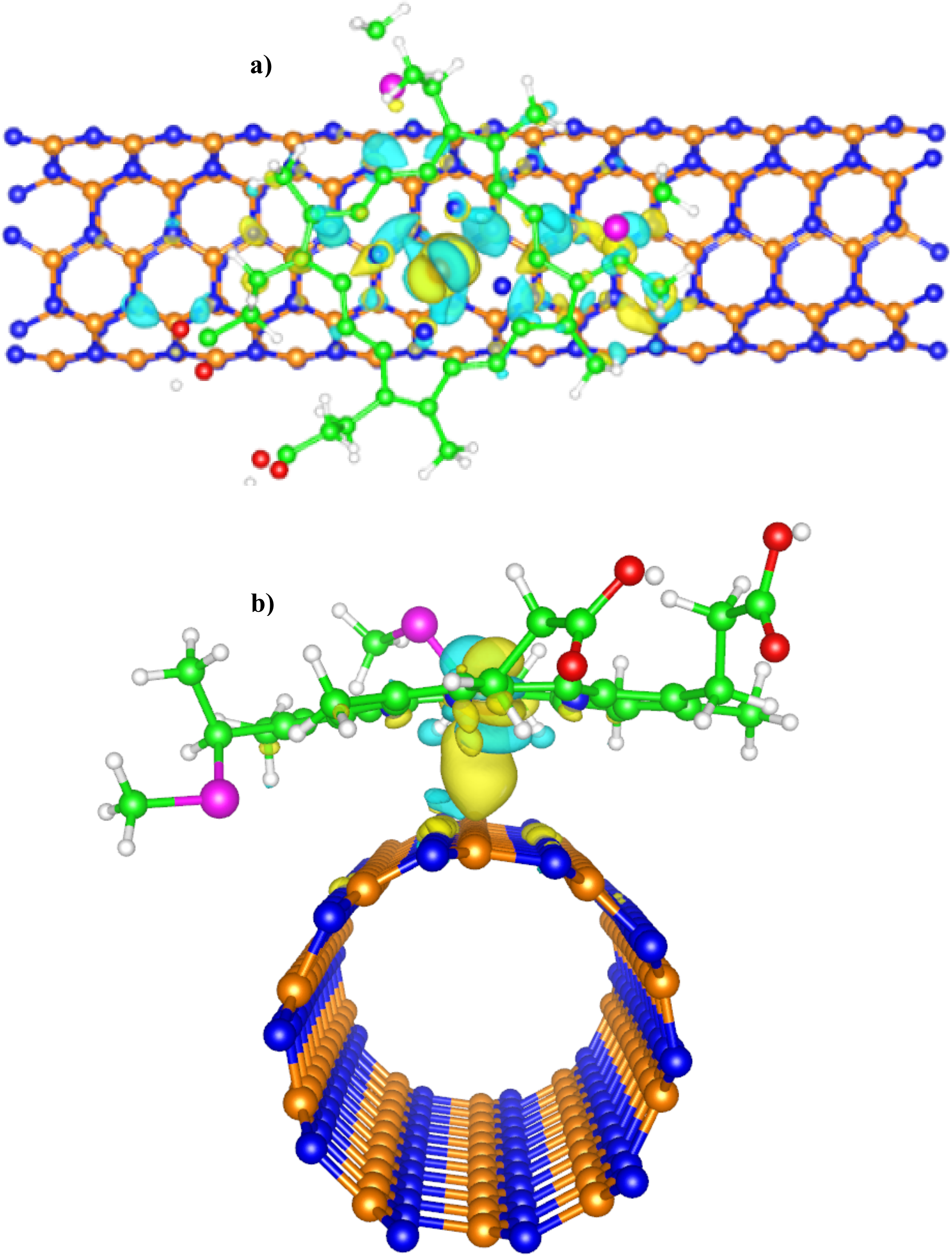

Fig. S2 Three dimensional charge density difference plot for the hybrid Porphyrin and BNNt complex with respect to BNNT and porphyrin fragment. Blue, yellow, green, magenta, red, white and grey atoms represent N, B, C, S, O, H and Fe atoms, respectively. Yellow and light blue isosurface represent respectively charge accumulation and depletion. There is a strong electron coupling between d-orbital of Fe and π orbital of BNNT, which will affect the catalytic performance of porphyrin.

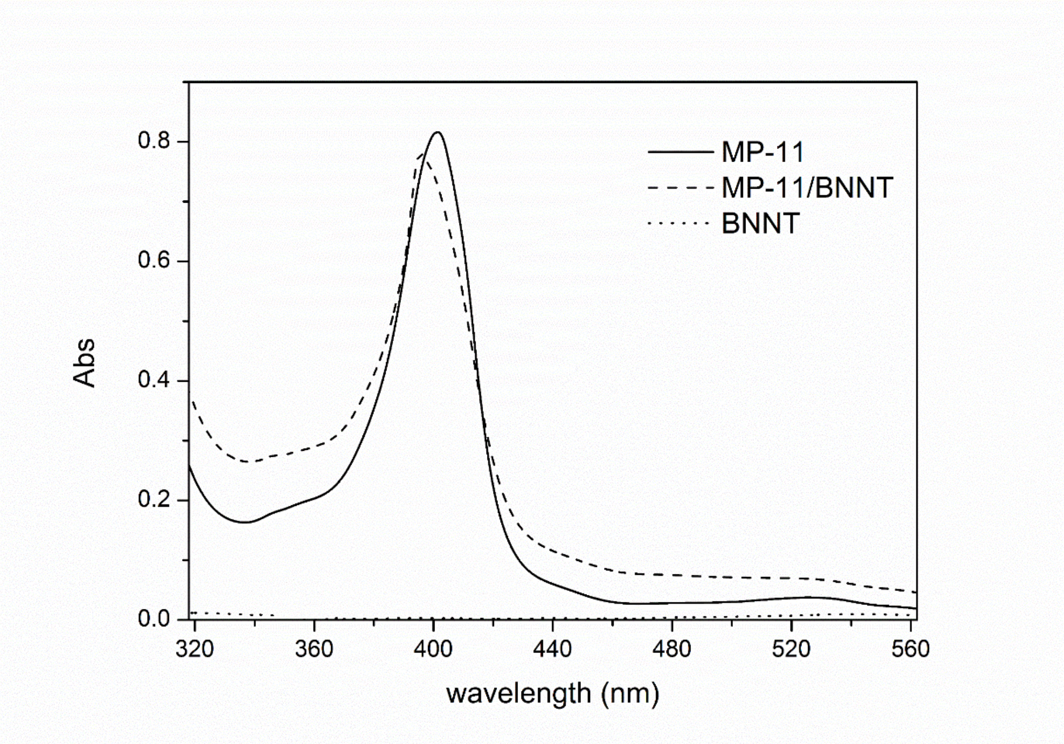

Fig. S3 UV-visible spectrum of MP-11 coated BNNT. The solid, dotted and dashed lines represented the absorbance of pure MP-11 BNNT, and MP-11/BNNT respectively. After coating with MP-11, the soret band at 405 nm shift to 396 nm, indicating π-π stacking interactions between MP-11 and BNNTs.

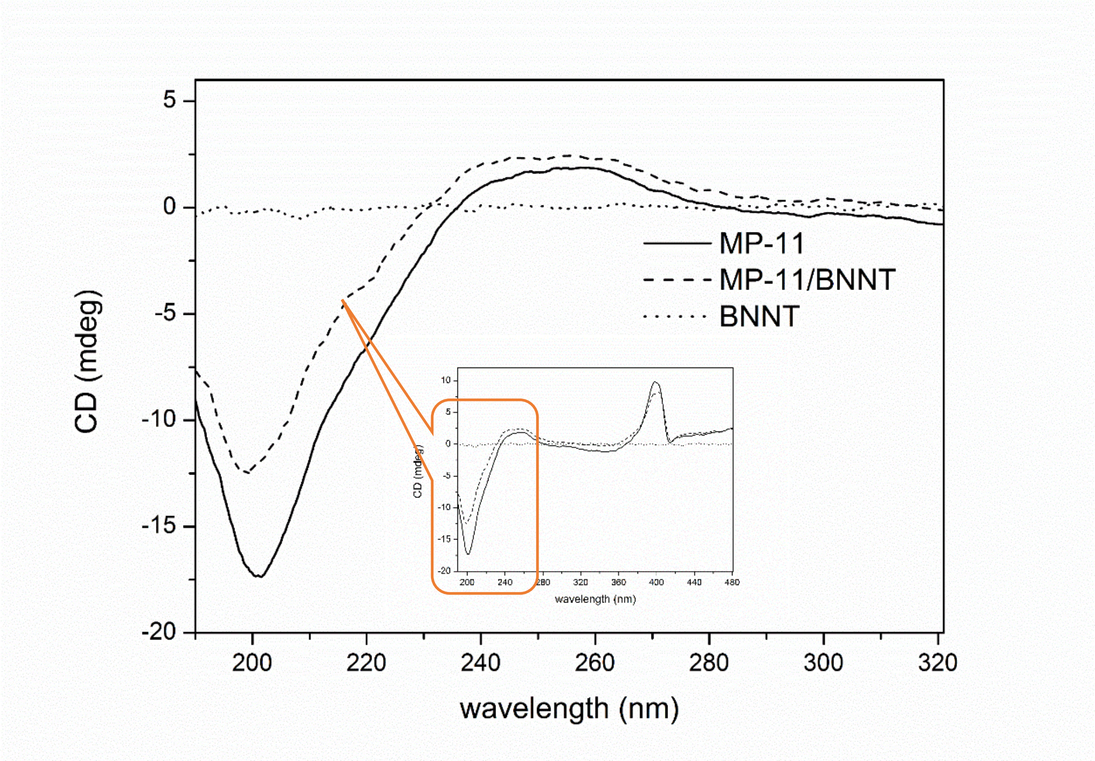

Fig. S4 The CD spectrum of MP-11, BNNT and MP-11/BNNT. The negative band at 203 nm was shifted to 197 nm, indicating the secondary structure of MP-11 molecules was changed after coating with BNNTs.

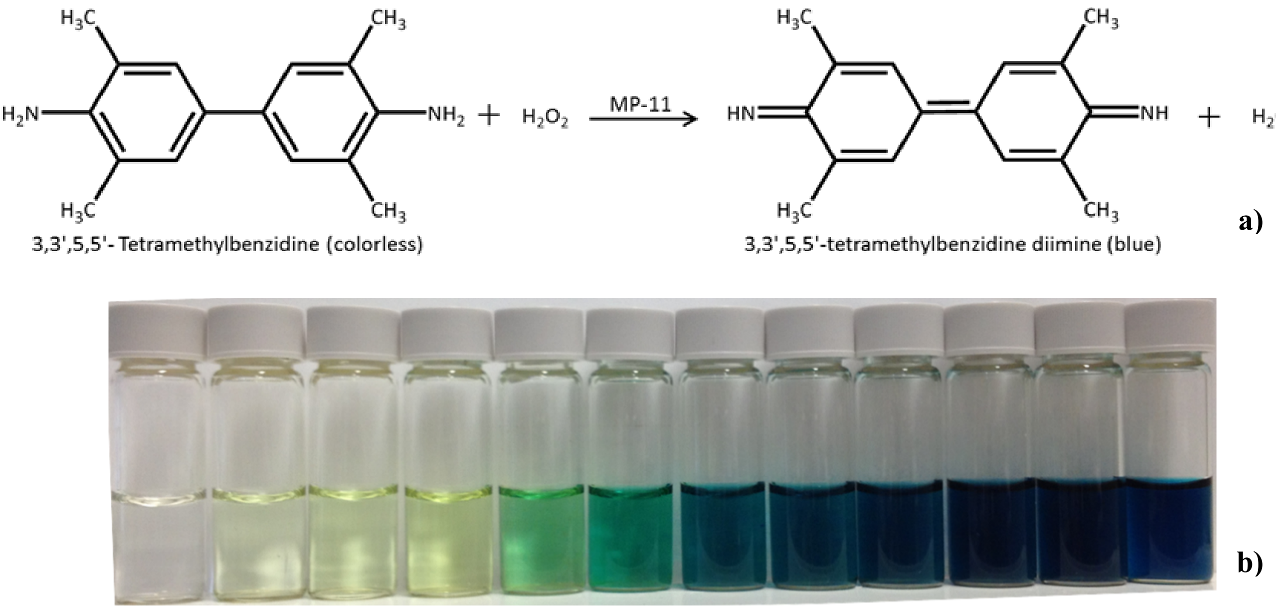

Fig. S5 a) The Chemical Equation of TMB photochromic reaction; b) A group of functionalized BNNT samples with TMB and H_2O_2, the concentrations of TMB increased from left to right: 0, 22.4 μM, 44.8 μM, 67.2 μM, 89.6 μM, 112.0 μM, 179.2 μM, 224.0 μM, 268.8 μM, 336.0 μM, 403.2 μM, 448.0 μM; the concentrations of H_2O_2 were 7mM in all the twelve samples. With the increase of TMB concentration, their colours varied from colourless to dark blue obviously, these alternation of colours would be used in the drawing of TMB standard curve for Lineweaver-Burk plot.

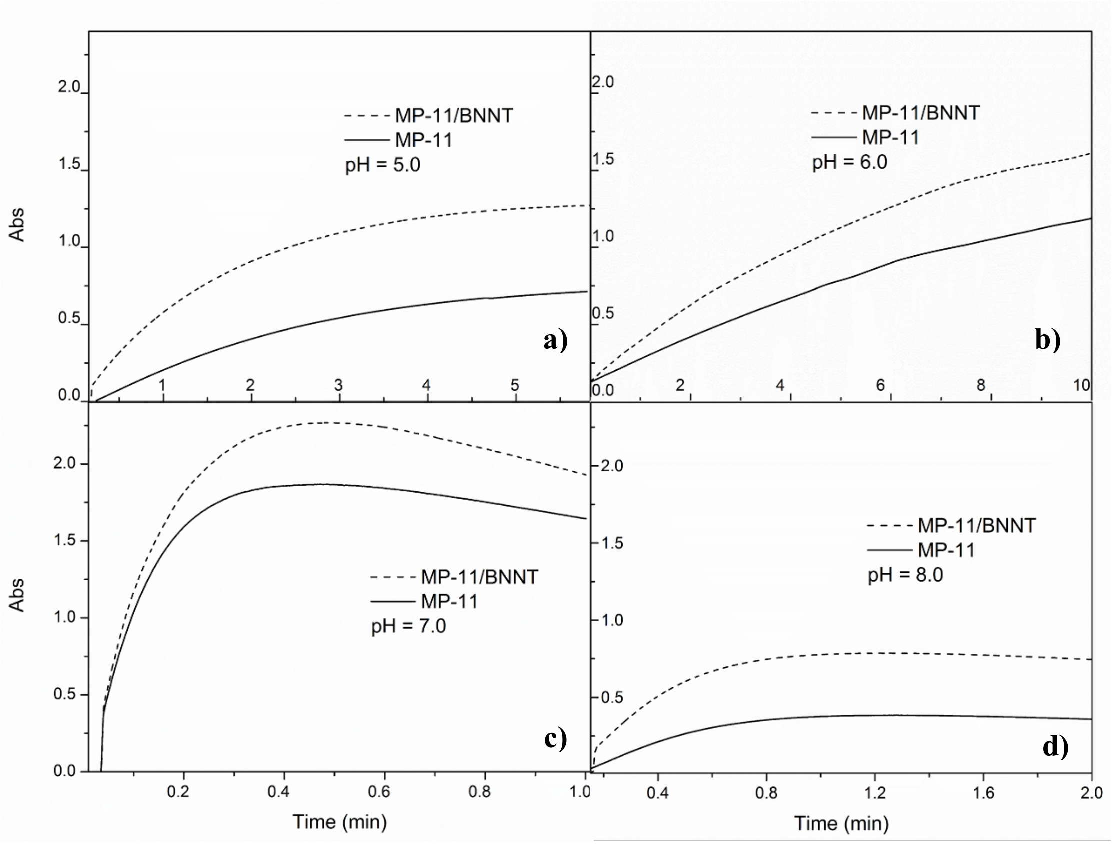

Fig. S6 The plots of absorbance against time at different pH conditions, used to monitor the reactions by kinetics mode at 652 nm using UV-vis spectrometer; the stability of the catalysts in the diverse pH conditions have been investigated; a), b), c) and d) stand for pH 5.0, 6.0, 7.0 and 8.0, respectively; highest value of absorbance was found in pH 7.0, indicating reaction would be the most efficient when catalyzed by MP-11 /BNNTs nanohybrids at this pH condition.

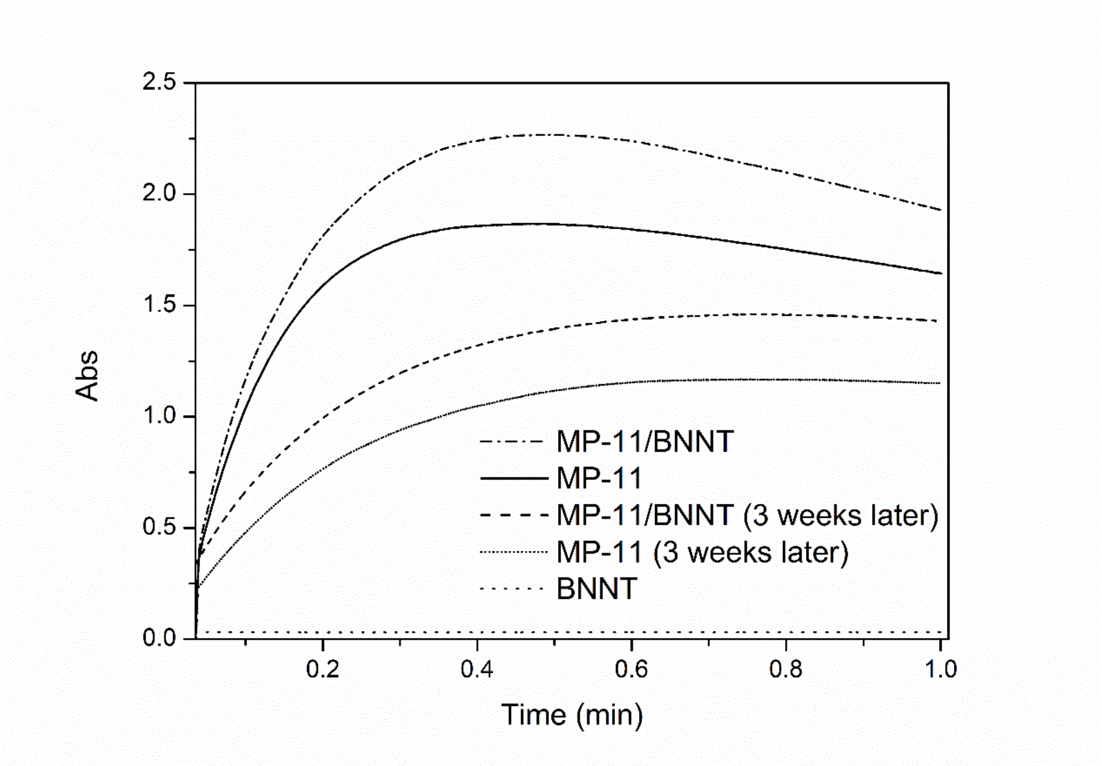

Fig. S7 Monitored the reactions by kinetics mode at 652 nm using UV-vis spectrometer; the stability of the catalysts with various time have been preliminarily examined: The top two lines represent the samples left overnight at room temperature just after self-assembly of MP-11 on BNNTs, the next group have been stored at 4℃ to maintain the stability for three weeks for investigation.

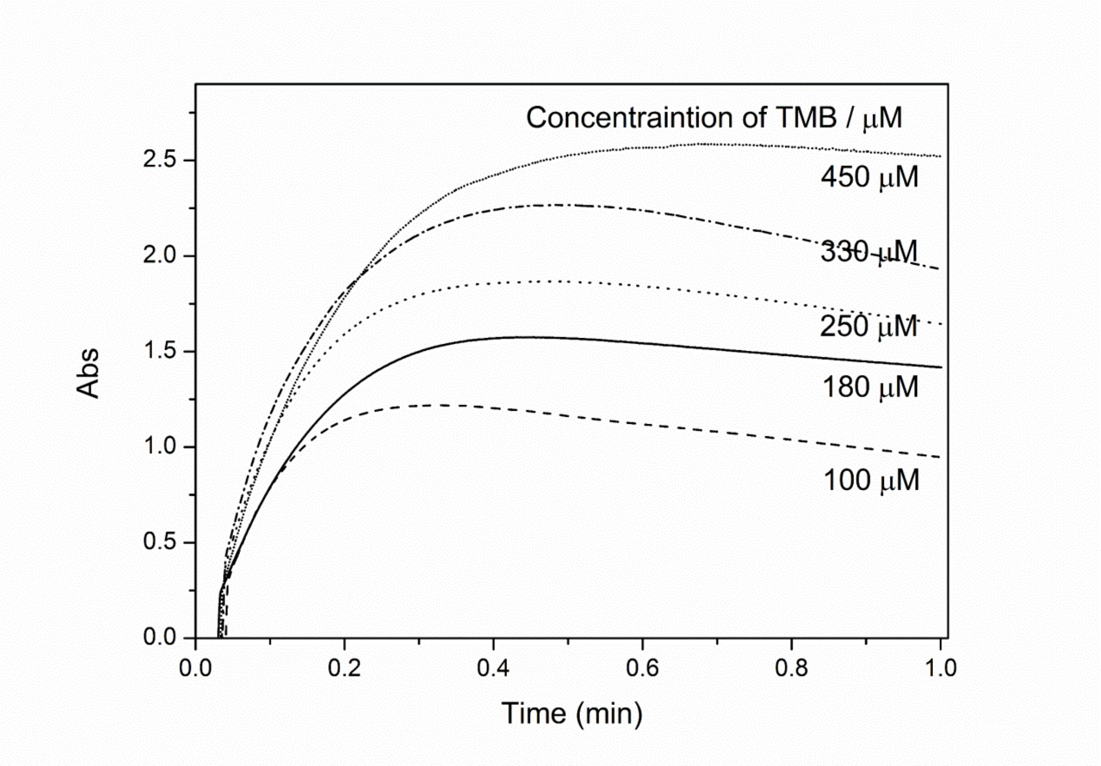

Fig. S8 TMB oxidation profile catalyzed by MP-11/BNNTs (10 μM MP-11 equivalent). The concentrations of TMB range from 100 μM, 180 μM, 250 μM, 330 μM to 450 μM, which can be used for double reciprocal plots of peroxidase activity of MP-11/BNNTs.