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Supporting information

Dendritic Fibrous Nano-Silica Supported Gold Nanoparticles as an Artificial Enzyme

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Synthesis of DFNS/APTS

DFNS (4 mg) was dispersed in 250 ml of toluene by sonicating it for 30 min. 4 mL of 3-aminopropyltriethoxysilane (APTS) was added and the reaction mixture was heated at 80 °C for 24 hours under stirring. Solid product was isolated by centrifugation and washed with toluene (three times) and ethanol (three times) and dried in oven at 80 °C for overnight.

Synthesis of DFNS/Au

500 mg of DFNS/APTES was added to 50 ml of deionized water and sonicated for 15 minutes and then stirred at room temperature. 0.32 mL (for 1wt% Au loading) or 1.43 mL (for 5wt% Au loading) of aq. $HAuCl_4$ (100 mg/mL) was added to the DFNS/APTES solution and stirred it for 15 min and then stirred for 24 hours. 5 mL of freshly prepared aq. $NaBH_4$ solution (1M) was then added and reaction mixture was further stirred for 2 hours. Product was isolated by centrifugation and washed with water and ethanol. DFNS/Au was dried under vacuum and stored under inert atmosphere.

Peroxidase-like activity and kinetic study of DFNS/Au

To study the peroxidase like study of DFNS/Au for TMB oxidation, we used a total of 2 mL solution and all the absorption measurements were carried out using JASCO V770 UV-Vis spectrophotometer. In a 3 ml cuvette, we added 1 ml, X (X= 200, 500, 800, 1000) µg/mL aqueous solution of DFNS/Au-x (x=1, 5), 200 µL of phosphate buffer solution (25 mM, pH=3), Y (Y=1 to 120) µL of TMB (25 mM in ethanol) and 45 µL of 30 % H_2O_2 and the remaining volume was made up by adding deionized water.

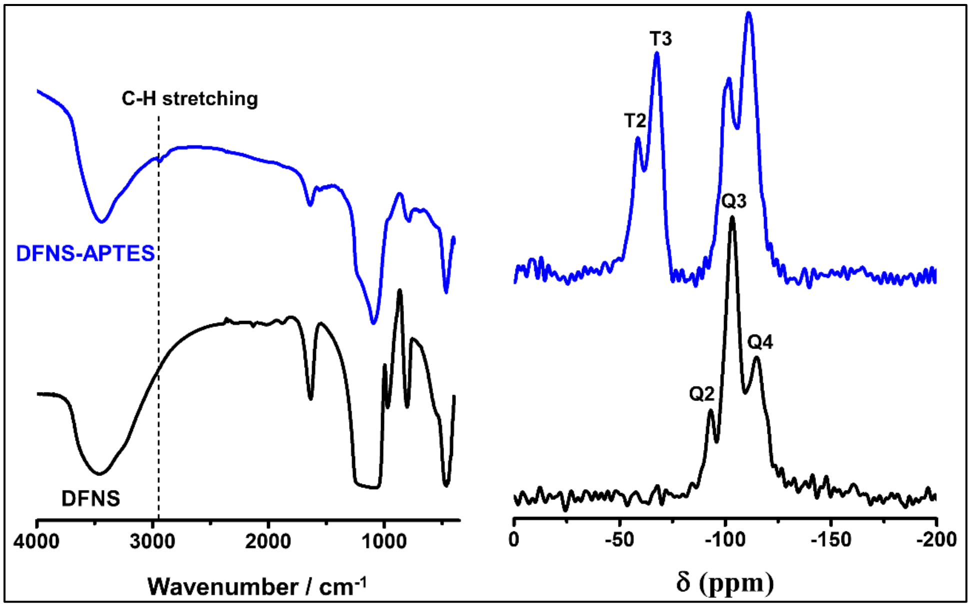


Fig. S1 FT-IR (left) and ^{29}Si-CPMAS solid state NMR (right, adapted from our own ref. Polshettiwar et al. *J. Mat. Chem. A.* **2017**, 5, 1935-1940) of DFNS and DFNS/APTS.

In FT-IR spectra, the peak at wavenumber 2850-3000 cm^{-1} belongs to the C-H stretching frequency from the APTS molecules attached to DFNS surface. However, to find out whether it is physisorbed or chemically attached to the silica surface, ^{29}Si-CPMAS was performed which confirms the covalent attachment. The appearance of the T^2 and T^3 peaks that belongs to the CSi(OSi)$_2$OH and CSi(OSi)$_3$, respectively in DFNS/APTS sample confirms the covalent attachment. Also, the decrease in the Q^2 (Si(OSi)$_2$(OH)$_2$) and Q^3 (Si(OSi)$_3$(OH)) peaks intensity with respect to the that of Q^4 (Si(OSi)$_4$) suggest that the surface silanols groups were the attachment sites for the APTS.

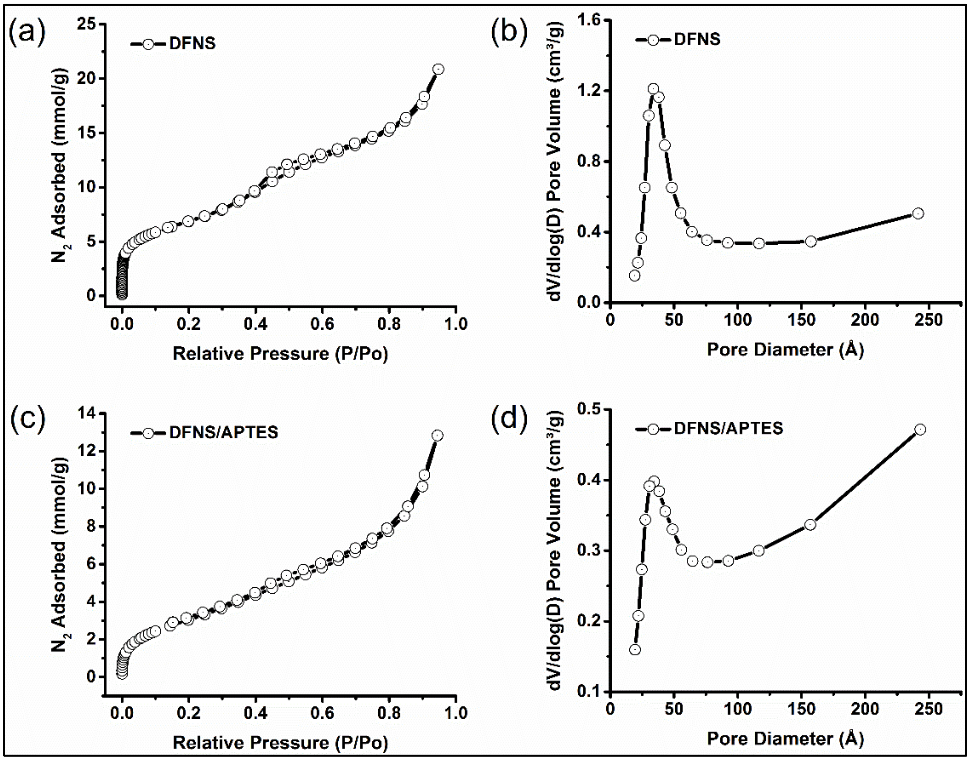


Fig. S2 Nitrogen (N_2) gas sorption isotherm (a, c) and pore size distribution (b, d) of DFNS and DFNS/APTS.

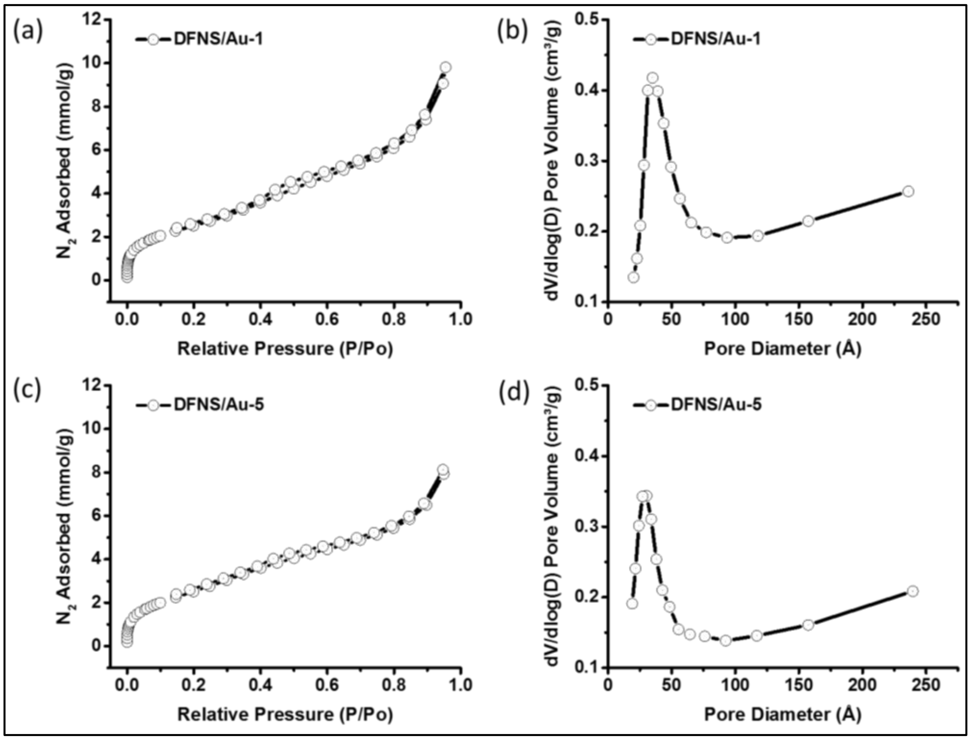


Fig. S3 Nitrogen (N_2) gas sorption isotherm (a, c) and pore size distribution (b, d) of DFNS/Au-1 and DFNS/Au-5.

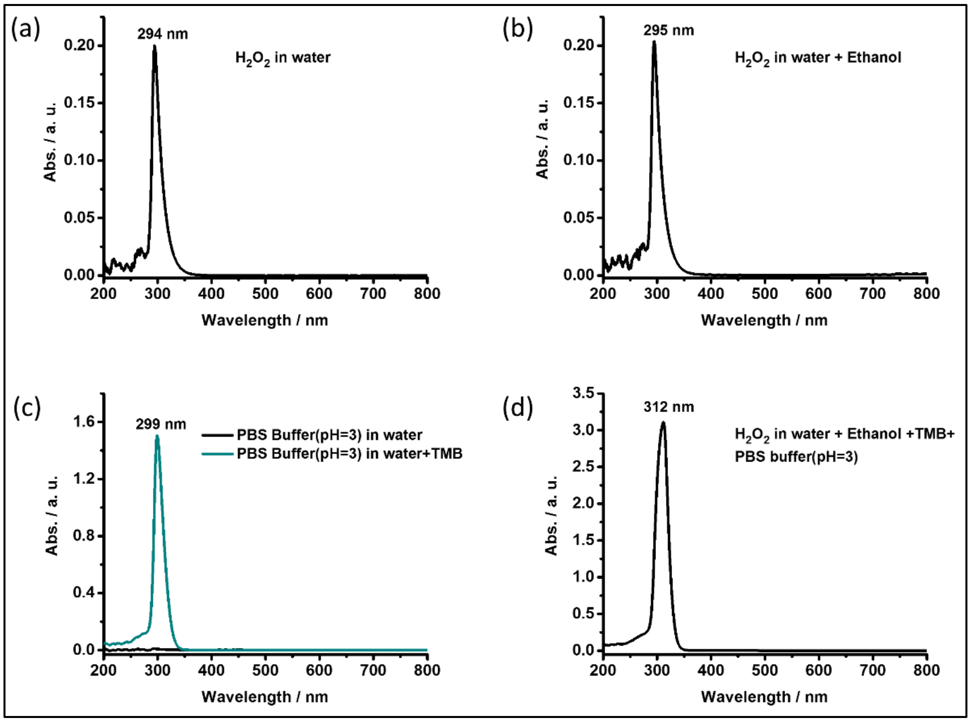


Fig. S4 The absorption spectra of (a) H_2O_2 in water (b) H_2O_2 in water + Ethanol (c) PBS buffer with pH =3 in water and TMB (d) H_2O_2 in water + Ethanol + PBS buffer (with pH =3) + TMB.

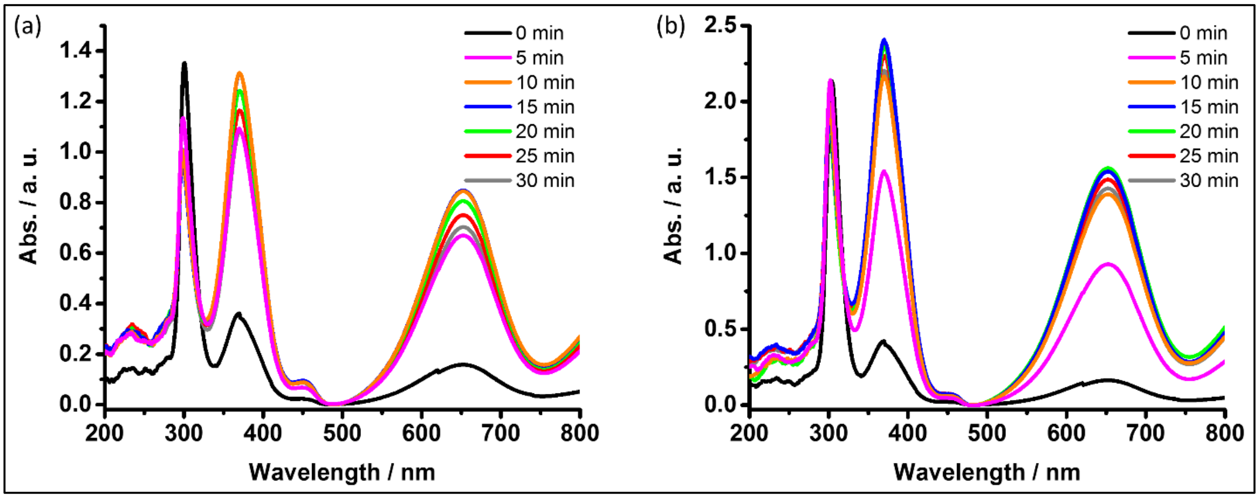


Fig. S5 The absorption spectra of (a) DFNS/Au-5(250 µg/ml) +TMB (100 µM) +H_2O_2(50 mM), PBS buffer (200 µL, pH=3), Total volume = 2mL (b) DFNS/Au-5(250 µg/ml) +TMB (200 µM) +H_2O_2(50 mM), PBS buffer (200 µL, pH=3), Total volume = 2mL.

Calculation for Michaelis–Menten kinetics:

For a typical TMB oxidation reaction, we have monitored the change in the absorption profile of TMB oxidation with the reaction time. The absorbance to concentration conversion of TMB^+ at $\lambda_{max.}$= 652 nm was done by using an extinction coefficient value of 39000 $M^{-1}cm^{-1}$ in the lambert beers law equation, $A_{652} = \epsilon cl$, where path length l=1 cm. Thereafter, the TMB^+ concentration vs time graph was plotted and the initial rate of the reaction was calculated by finding a slope to the initial time measurements. This initial rate of the reaction was designated as V *(or* V_o*)* for a fixed concentration of the TMB substrate. The concentration of the TMB substrate was varied and the initial rate for all these reactions were calculated using the same procedure as mentioned above. The initial rate vs substrate concentration graph was plotted and fitted to Michaelis–Menten kinetic model.

$$E + S \xleftrightarrow{k_1,k_{-1}} ES \xleftrightarrow{k_2,k_{-2}} E + P$$

$$V = \frac{V_{max}\,[S]}{K_m + [S]}$$

Where S and P are TMB and TMB^+. The Lineweaver–Burk plot was used to find the V_{max} and K_m values, where $\frac{1}{V}$ vs $\frac{1}{[S]}$ was plotted using the following equation.

$$\frac{1}{V} = \frac{1}{V_{max}} + \frac{K_m}{V_{max}}\frac{1}{[S]}$$

Table S1. The reaction conditions for various reaction is summarized below (T= 30℃):

Catalysts	**Catalysts Amount**	**TMB Amount**	**H_2O_2 Amount**	**PBS (pH=3) Vol.**	**Total Vol.***	**K_m [mM]**	**V_{max} X 10^{-8} [$M.s^{-1}$]**
DFNS/Au-1 (Fig. S5-a1, a2)	1mL of 200 µg/mL [100 µg/mL]	1 to 120 µL [10 to 1200 µM]	11 µL [50 mM]	200 µL	2 ml	0.059	0.3
DFNS/Au-1 (Fig. S5-b1, b2)	1mL of 200 µg/mL [100 µg/mL]	80 µL [800 µM]	1 to 66 µL [10 to 300 mM]	200 µL	2 ml	389	2.9
DFNS/Au-1 (Fig. S5-c1, c2)	1mL of 200 µg/mL [100 µg/mL]	1 to 120 µL [10 to 1200 µM]	45 µL [200 mM]	200 µL	2 ml	0.076	1.4
DFNS/Au-1 (Fig. S5-d1, d2)	1mL of 500 µg/mL [250 µg/mL]	1 to 120 µL [10 to 1200 µM]	45 µL [200 mM]	200 µL	2 ml	0.103	3.2
DFNS/Au-5 (Fig. S5-e1, e2)	1mL of 200 µg/mL [100 µg/mL]	1 to 120 µL [10 to 1200 µM]	45 µL [200 mM]	200 µL	2 ml	0.124	5.8
DFNS/Au-5 (Fig. 3-a, b)	1mL of 500 µg/mL [250 µg/mL]	1 to 120 µL [10 to 1200 µM]	45 µL [200 mM]	200 µL	2 ml	0.220	17.1
DFNS/Au-5 (Fig. 3-c, d)	1mL of 500 µg/mL [250 µg/mL]	80 µL [800 µM]	1 to 44 µL [10 to 200 mM]	200 µL	2 ml	245	29.5

values written inside square brackets represents final concentrations in 2mL solution of the reaction mixture.

§ TMB stock solution was 25 mM in ethanol, PBS stock solution was 25 mM in water.

* The known amount of deionized water was added to the reaction system such that the total volume of reaction mixture becomes 2 ml.

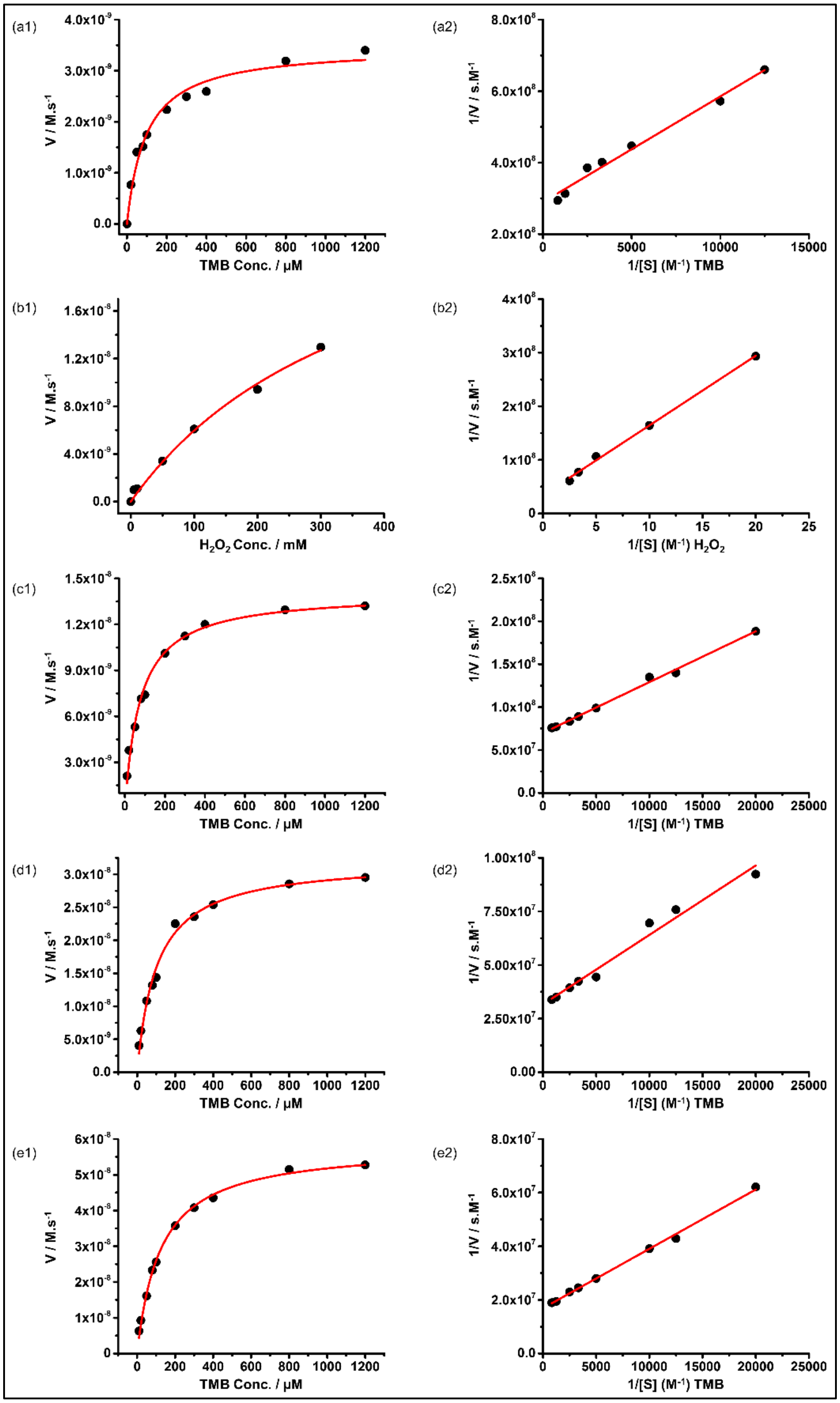


Fig. S6 (a1-e1) Michaelis–Menten Steady-state kinetic assay of DFNS-AuNPs. (a2-e2) Lineweaver–Burk plot of the reciprocals of initial rate vs. substrate concentration for the determination of kinetic parameters K_m and V_{max} of DFNS/AuNPs with TMB or H2O2 as the substrate.

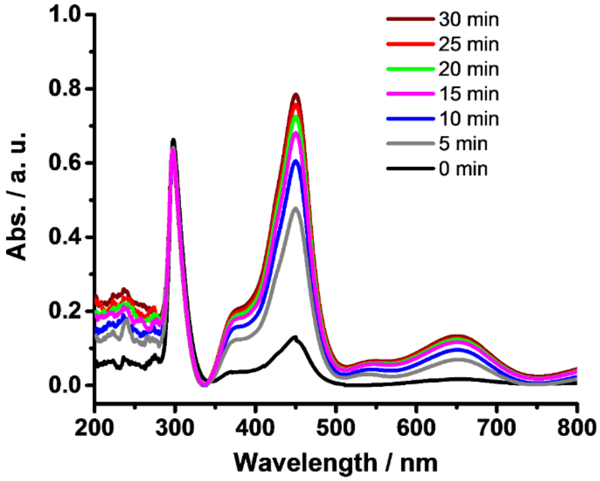


Fig. S7. The absorption profile of TMB oxidation at pH =1.

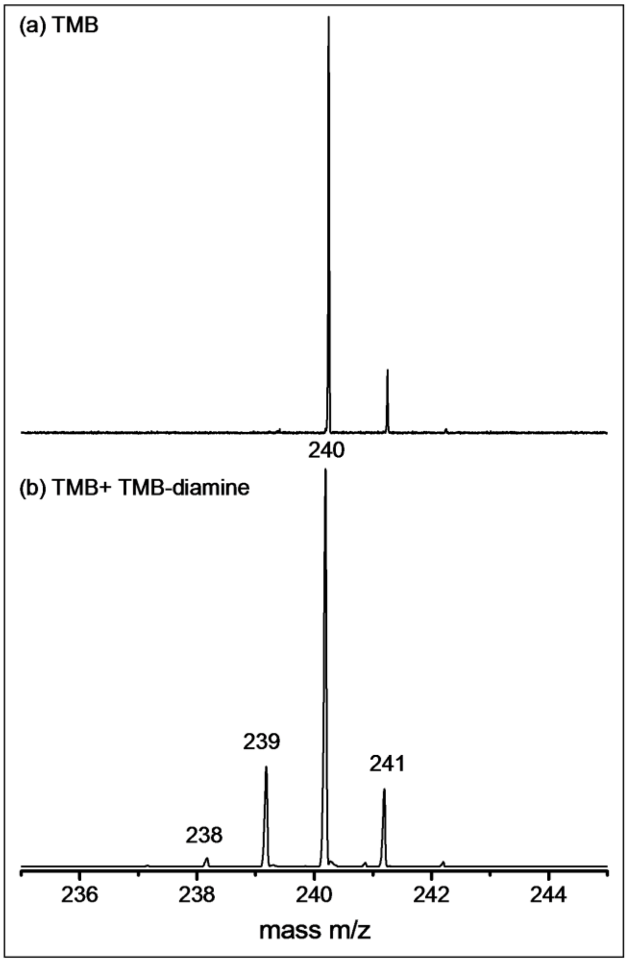


Fig. S8. Matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry data of TMB and TMB-diamine.

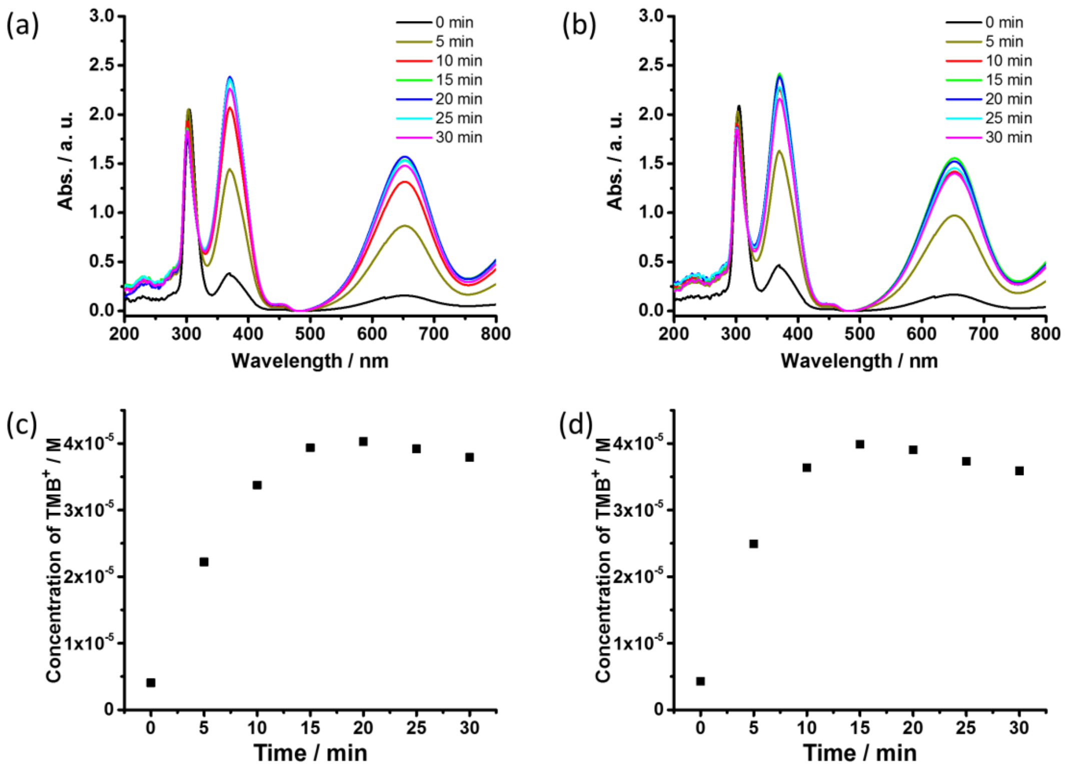
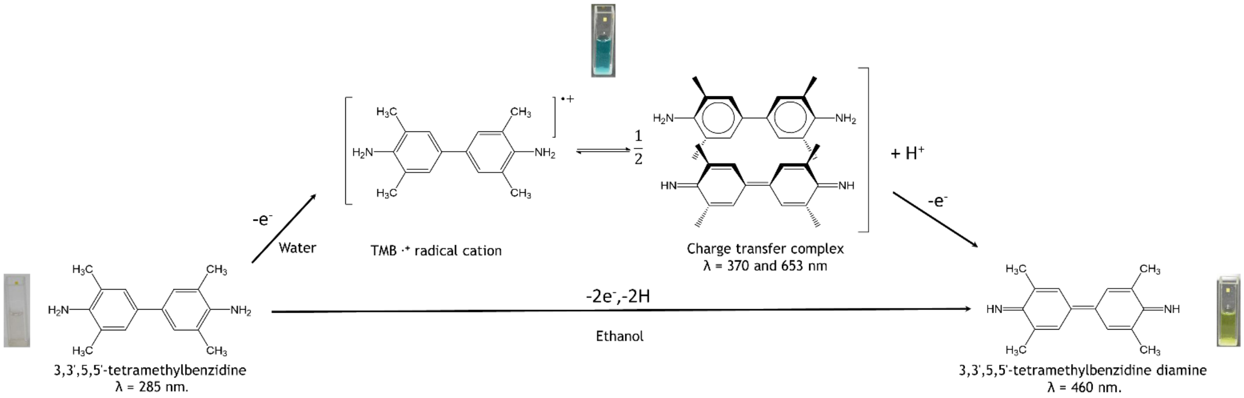


Fig. S9. Catalytic activity of DFNS/Au-5 at after heating the catalysts at 200 ^{0}C for 2h in air (a,c) and in nitrogen (b,d). Conditions: DFNS/Au-5 (250 µg/ml) +TMB (200 µM) +H_2O_2 (200 mM), PBS buffer (200 µL, pH=3), Total volume = 2mL, Temperature – 30 ^{0}C



Scheme 1. One electron and two electrons oxidation pathways of TMB