Supporting information

Insight mechanism revealing the peroxidase mimetic catalytic activity of quaternary CuZnFeS nanocrystals: colorimetric biosensing of hydrogen peroxide and glucose

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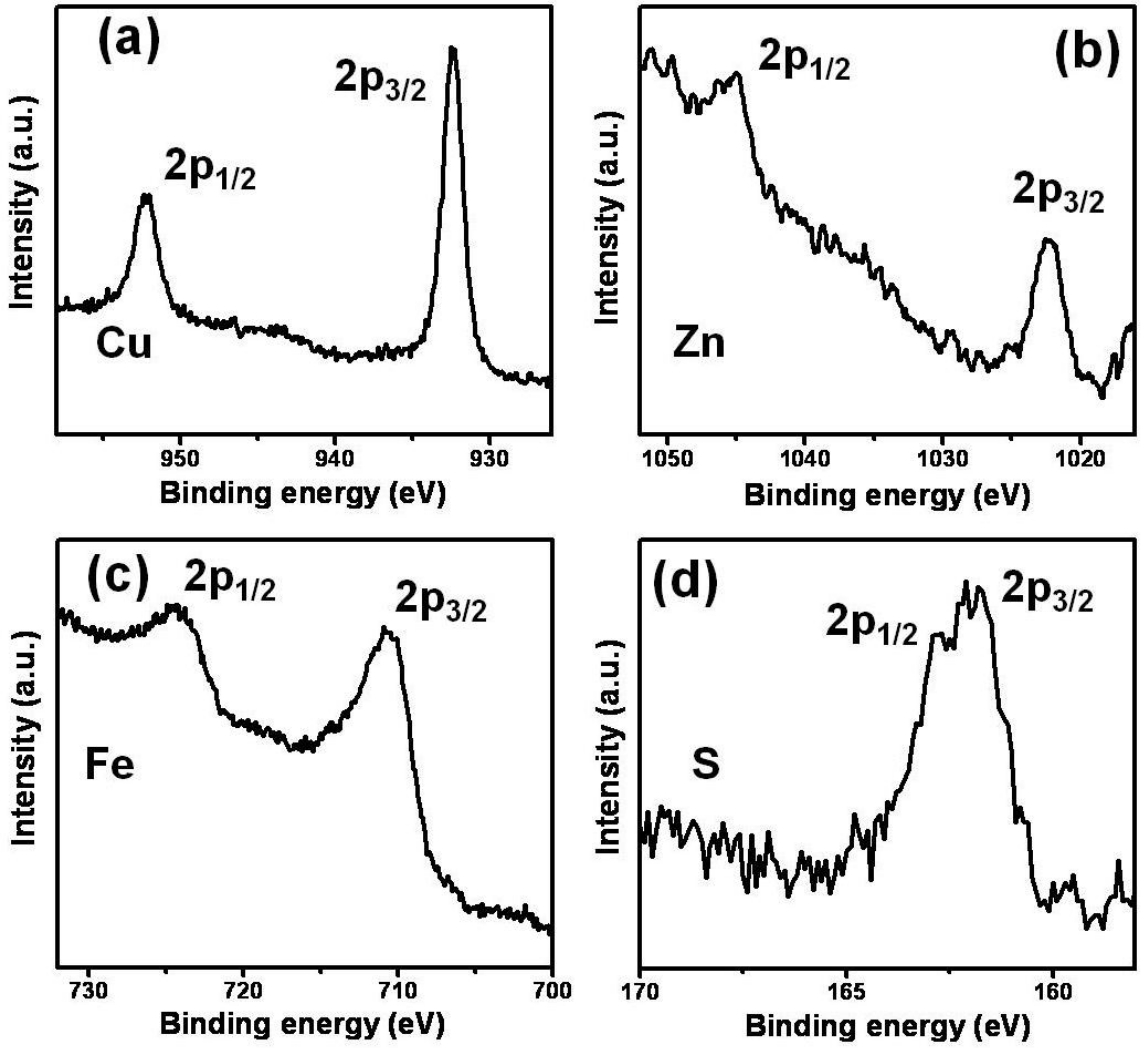

Figure S1. High resolution XPS spectrums of the as synthesized CZIS NCs revealing the peaks corresponding to the constituent elements, like (a) Cu, (b) Zn, (c) Fe and (d) S respectively. The 'Cu-2p' doublet peaks ($2p_{1/2}$ and $2p_{3/2}$) appear at binding energies of ~952.1 eV and ~932.4 eV respectively with a splitting energy of ~19.7 eV indicates the presence of monovalent Cu. The 'Zn-2p' doublet peaks ($2p_{1/2}$ and $2p_{3/2}$) appears at binding energy of ~1044.9 eV and ~1022.3 eV with a separation energy gap of ~22.6 eV are indicative of presence of divalent 'Zn'. The 'Fe-2p' doublet peaks ($2p_{1/2}$ and $2p_{3/2}$) arise at binding energies of ~724.4 eV and ~710.7 eV with a separation of ~13.7 eV is attributed to trivalent 'Fe'. The 'S-

2p' doublet peaks at binding energies of ~161.9 eV and ~162.9 eV are consistent with the 'S' in alloyed metal sulfides nanocrystals.

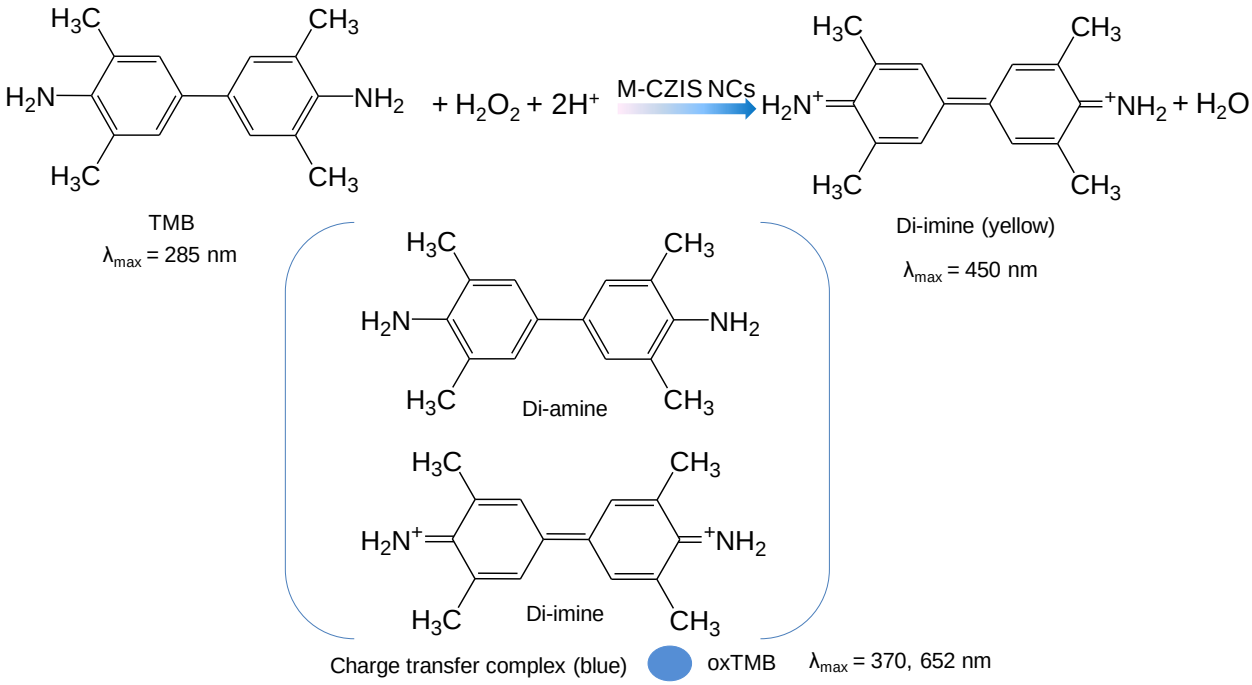

Figure S2. Schematic presentation of reaction pathways occurred during the conversion of TMB to oxidized TMB (oxTMB) in presence of M-CZIS NCs and H_2O_2 in acetate buffer (pH= 4.2).The color of oxidized TMB (blue color) and the wavelength of maximum absorption peaks are leveled in the bottom of the each structures.

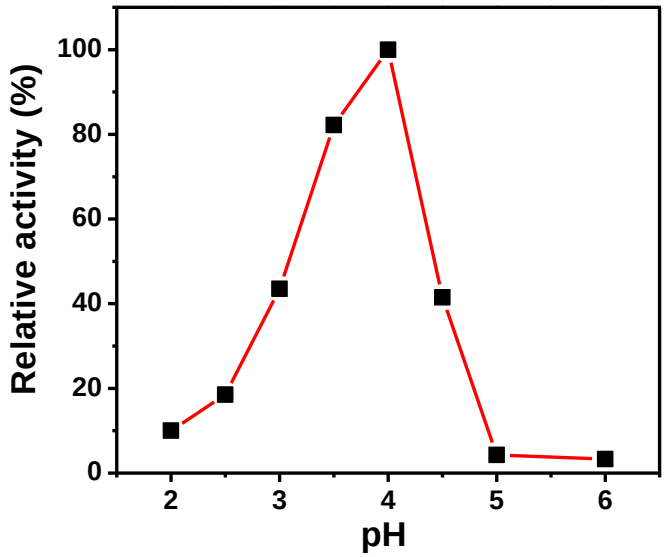

Figure S3. pH dependent peroxidase like activity of M-CZIS NCs of the reaction medium. The relative activity of 100% is set where the absorbance at 652 nm is highest and relative activity for other are calculated accordingly.

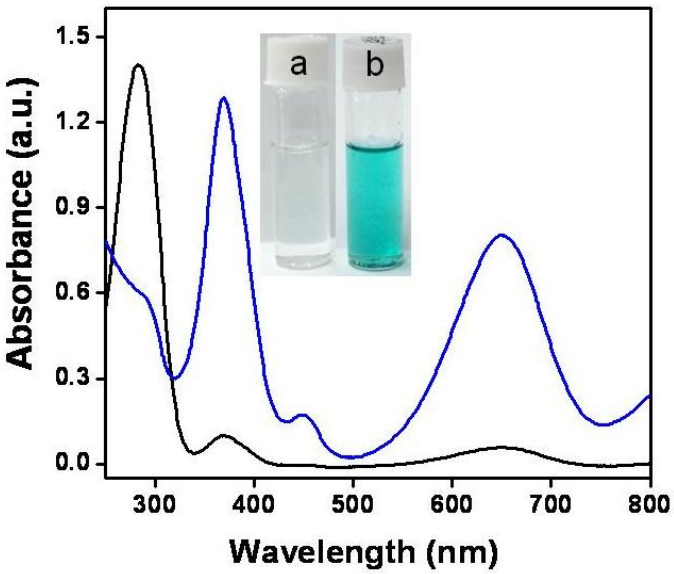

Figure S4. Comparison of absorption spectra of oxTMB produced by the ion leached solution (black curve) and M-CZIS NCs (blue curve). Inset showing the photograph of reaction color solution produced by the leached ion solution (a) and M-CZIS NCs (b) respectively.

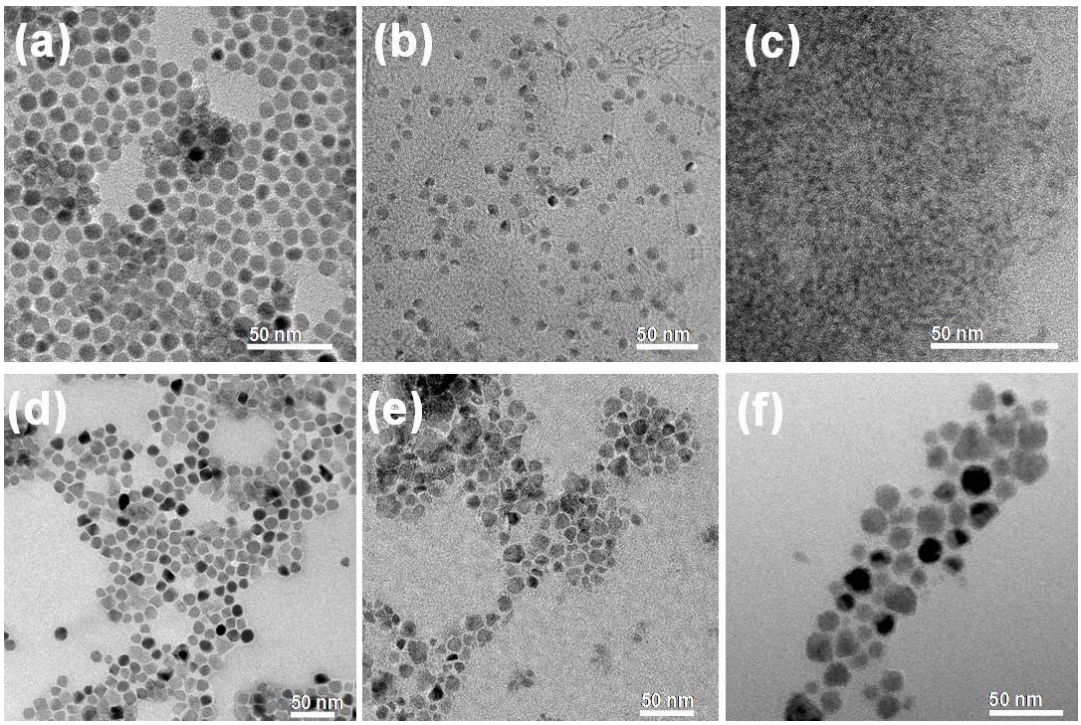

Figure S5. Transmission electron microscope images of the nanocrystals used in the peroxidase-like catalytic activities. (a) copper sulfide (~9 ± 1 nm), (b) zinc sulfide (~10 ± 2 nm), (c) iron sulfide (~3 ± 2 nm), (d) copper-zinc-sulfide (~14 ± 2 nm), (e) copper-iron-sulfide (~10 ± 2 nm) and (f) copper-zinc-iron-sulfide (~12 ± 3 nm).

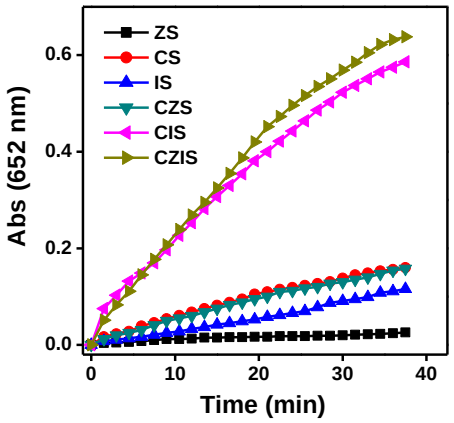

Figure S6. Effect the elemental composition of the NCs capped with MPA on the peroxidase-like catalytic activity by monitoring the absorbance change at 652 nm exhibited by different NCs; ZS (zinc sulfide), CS (copper sulfide), IS (iron sulfide), CIS (copper-iron-sulfide) and CZIS (copper-zinc-iron-sulfide).

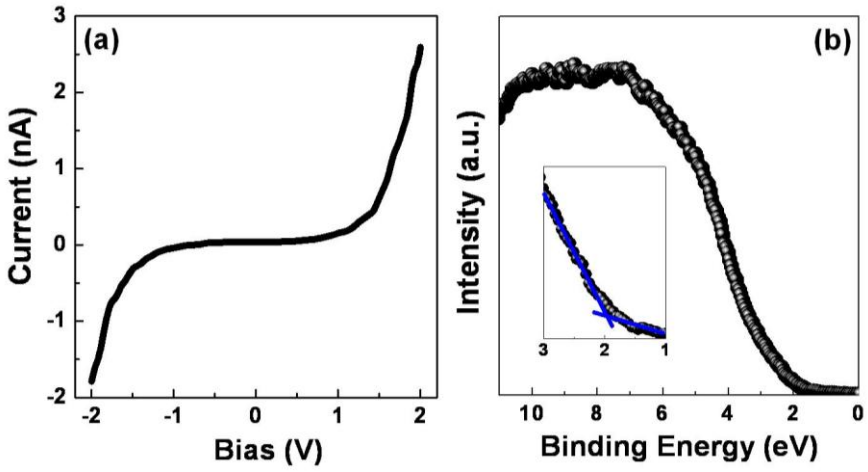

Figure S7. (a) I-V curve measured on isolated M-CIZS NCs. Typically ~50 I-V curves are averaged to improve the signal to noise ratio. The I-V measurements were performed at set-voltage of 1 V and set-current of 0.1 nA. (b) UPS spectrum of M-CIZS NCs measured in UHV conditions. Inset: enlarged threshold position showing the onset binding energy of ~1.95 eV.

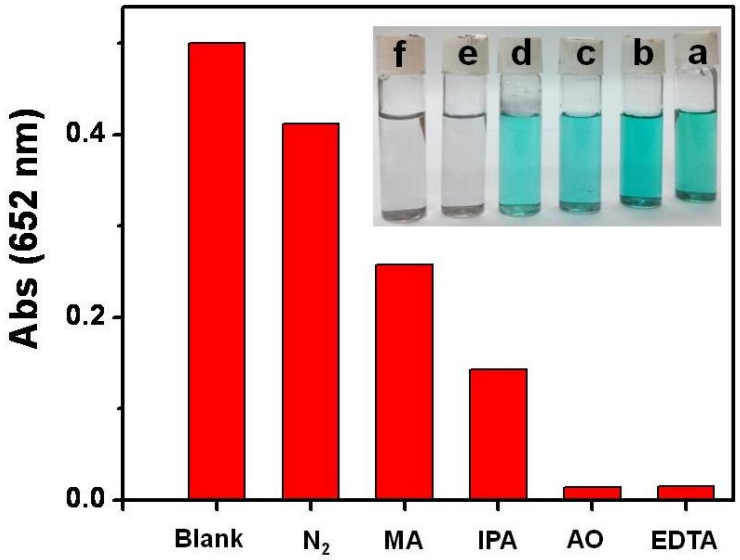

Figure S8. Change in absorption of oxTMB in presence of scavenger during the catalytic TMB oxidation. Absorbance of oxTMB at 652 nm have been monitored in presence of different radical scavenger: blank (without any scavenger), N_2 (at inert atmosphere), MA (methyl alcohol), IPA (iso-propylalcohol), AO (ammonium oxalate), EDTA (ethylenediaminetetraacetic acid).

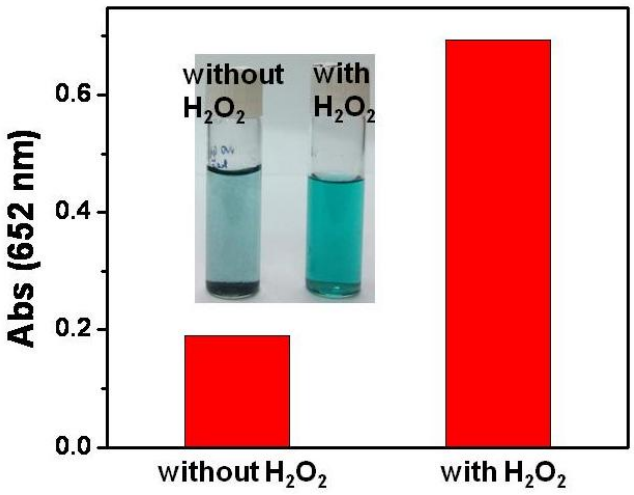

Figure S9. Peroxidase-like activity of M-CZIS NCs performed in presence of H_2O_2 and absence of H_2O_2. For without H_2O_2 experiment, 0.9 mM TMB, 200 µg of M-CZIS NCs are used and solution is illuminated with UV light of 365 nm wavelength for 20 minutes. While for with H_2O_2 experiment, 0.1mM TMB, 50 µg of M-CZIS NCs, 5 mM H_2O_2 are used and reaction performed at normal day light. Absorption spectrum and photograph (inset of the figure) are taken after 20 minutes of the reaction.

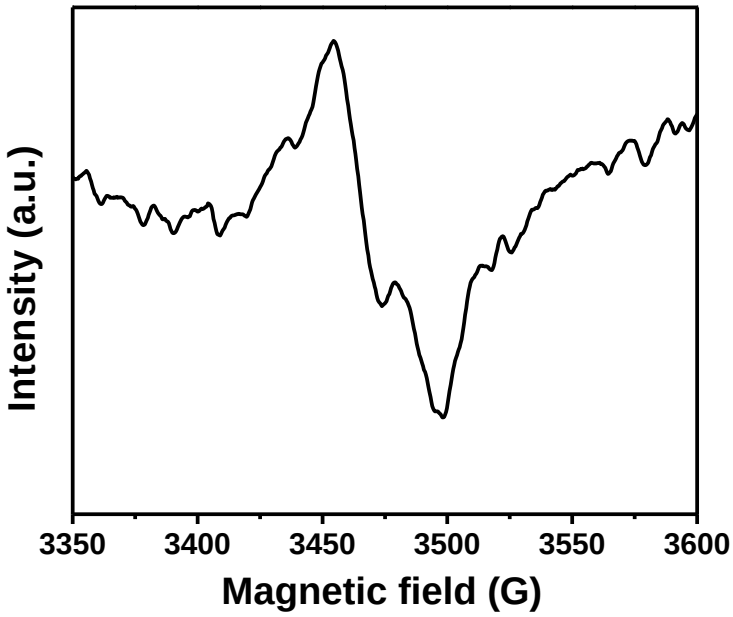

Figure S10. EPR spectrum of the DMPO-$^{\bullet}$OH radical adduct.

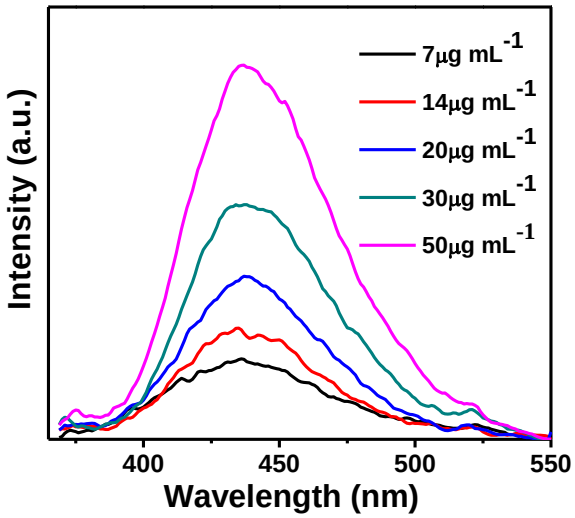

Figure S11. Evolution of PL spectra of the 2-hydroxy terephthalic acid measured in presence of different M-CZIS NCs concentration in acetate buffer medium. The excitation wavelength was 315 nm.

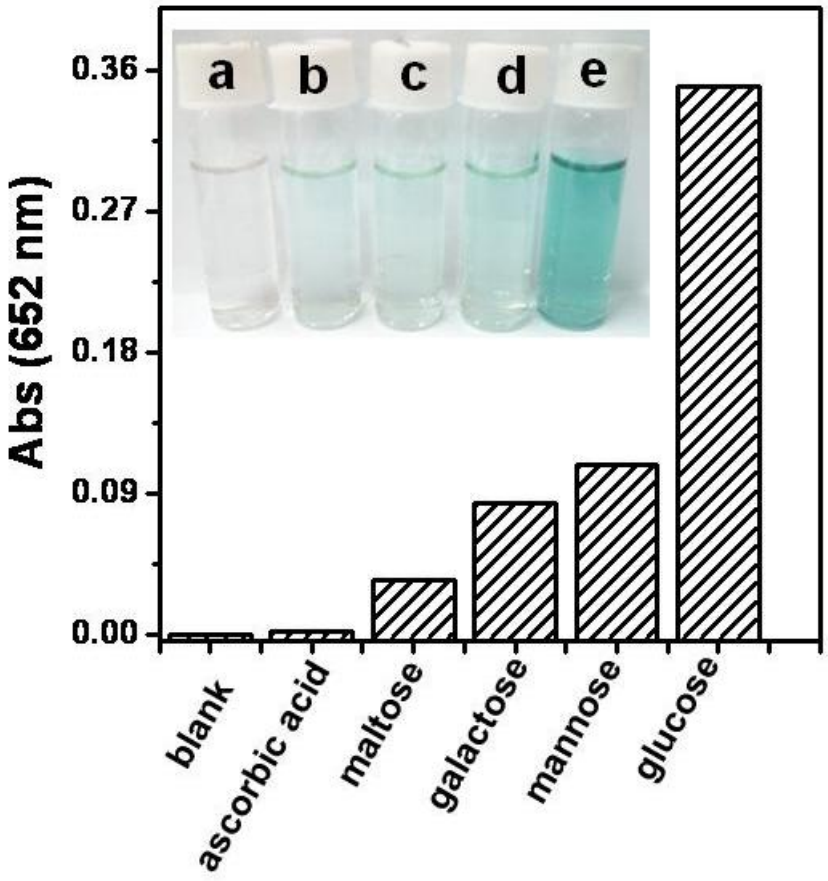

Figure S12. Absorbance changes at 652 nm of TMB oxidation by hydrogen peroxide produced by glucose and other saccharides or interferents. Glucose was used 1mM while the other materials were used five times higher concentration than glucose. Inset showing the color of the reaction solution produced by the different materials. Although the glucose concentration was five times lower the greater absorbance for glucose indicates greater selectivity towards glucose. Inset photograph showing the color reaction produced by the different materials started from (a) ascorbic acid (b) maltose (c) galactose (d) mannose and (e) glucose respectively.

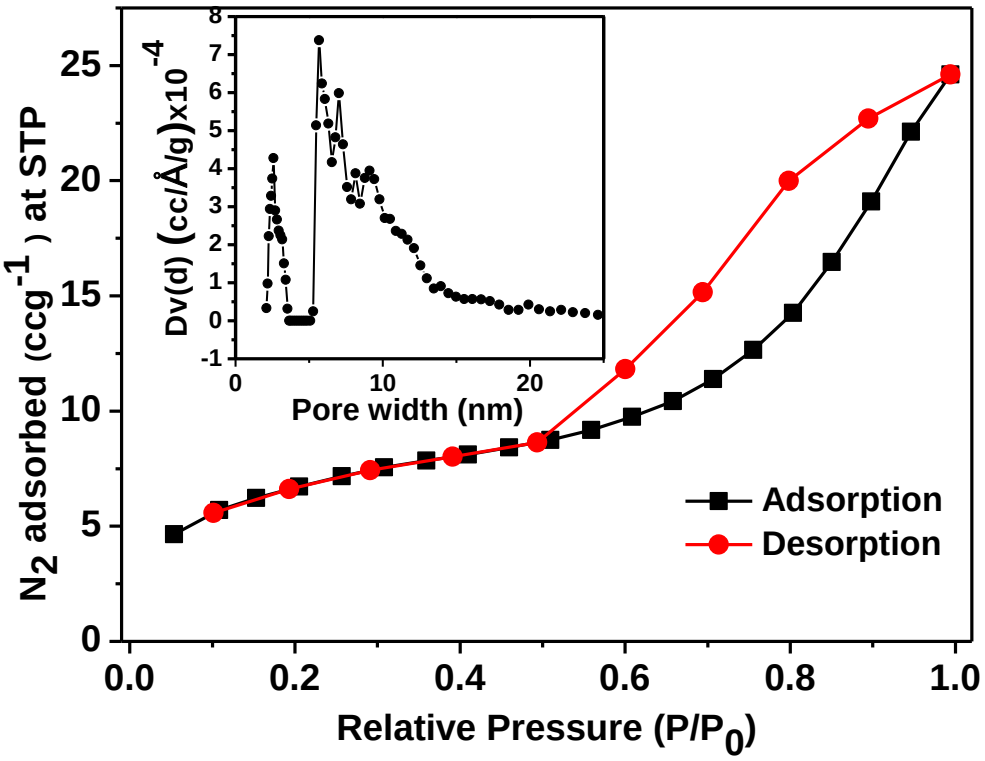

Figure S13. N_2 adsorption isotherm of M-CZIS NCs measured using Brunauer-Emmett-Teller (BET) method to obtain surface area. Inset graph is showing the pore width distribution of M-CZIS NCs calculated using non-local density functional theory (NLDFT) method.