# Supporting Information

# for

# The role of L-Cysteine and introduced surface defects in reactive oxygen species generation by ZnO nanoparticles

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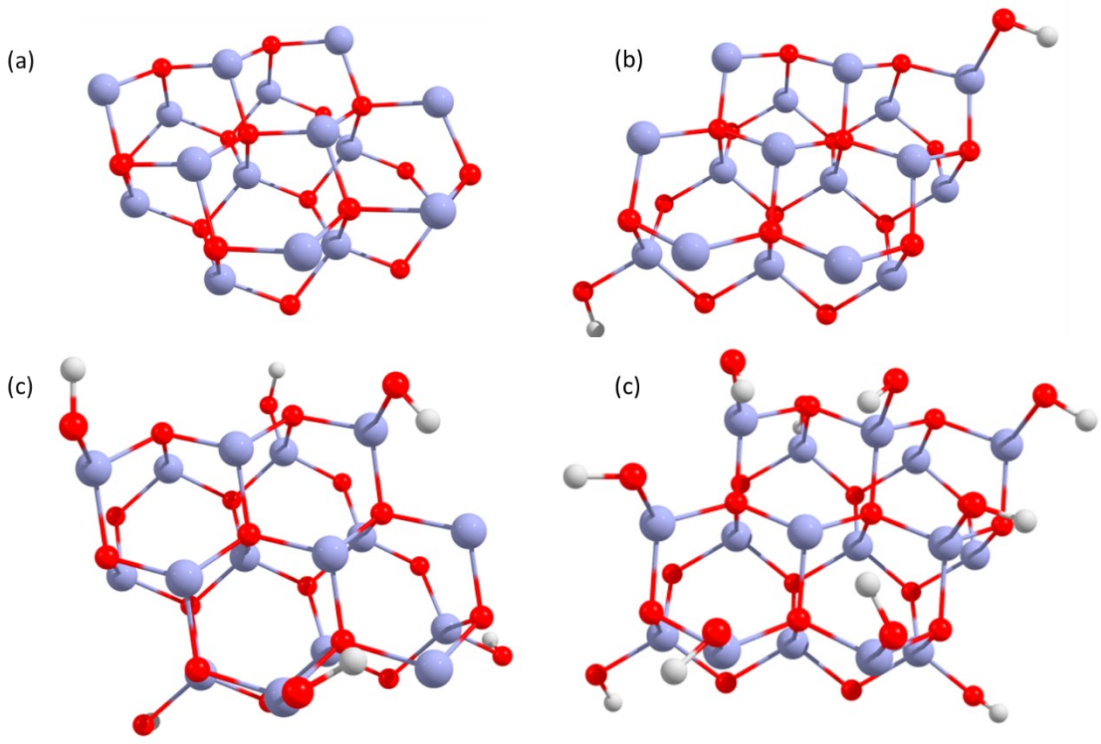


**Figure S1** Unoptimized geometries of the $Zn_{16}O_{16}$ clusters with the (a) 0, (b) 2, (c) 6 and (d) 10 OH groups adhered to the cluster's surface.

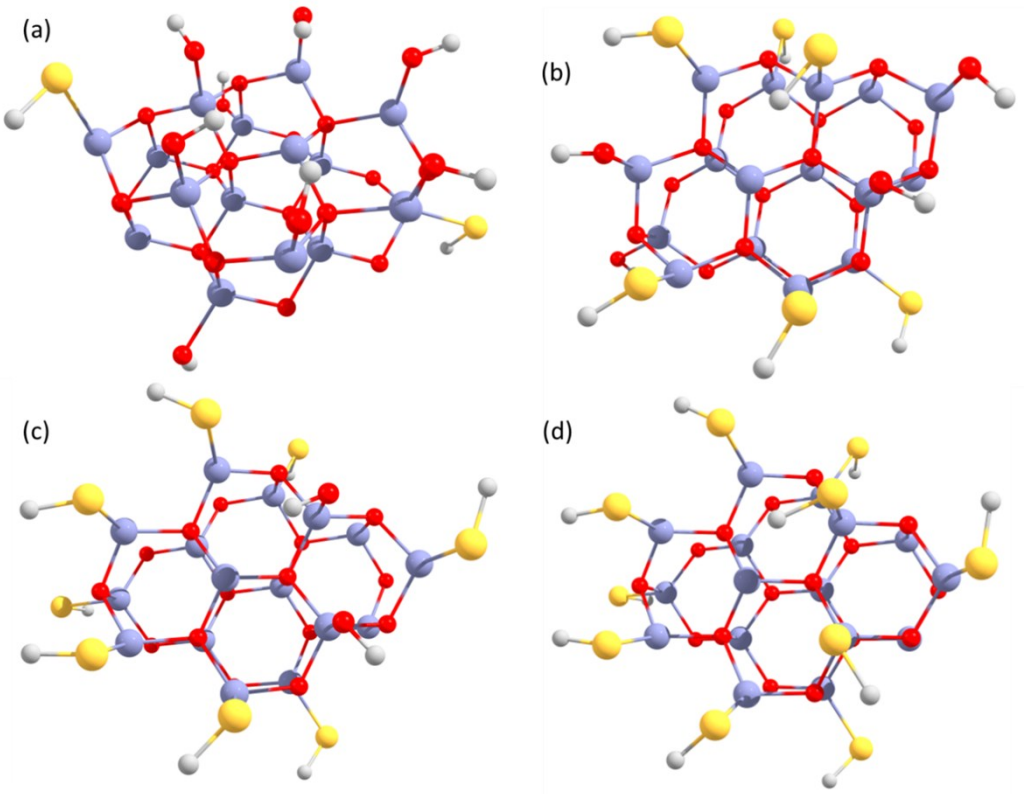


**Figure S2** The unoptimized geometries of the $Zn_{16}O_{16}$ clusters with the (a) 2xSH, 8xOH (b) 6xSH, 4xOH (c) 8xSH, 2xOH and (d) 10 SH groups adhered to the cluster's surface.

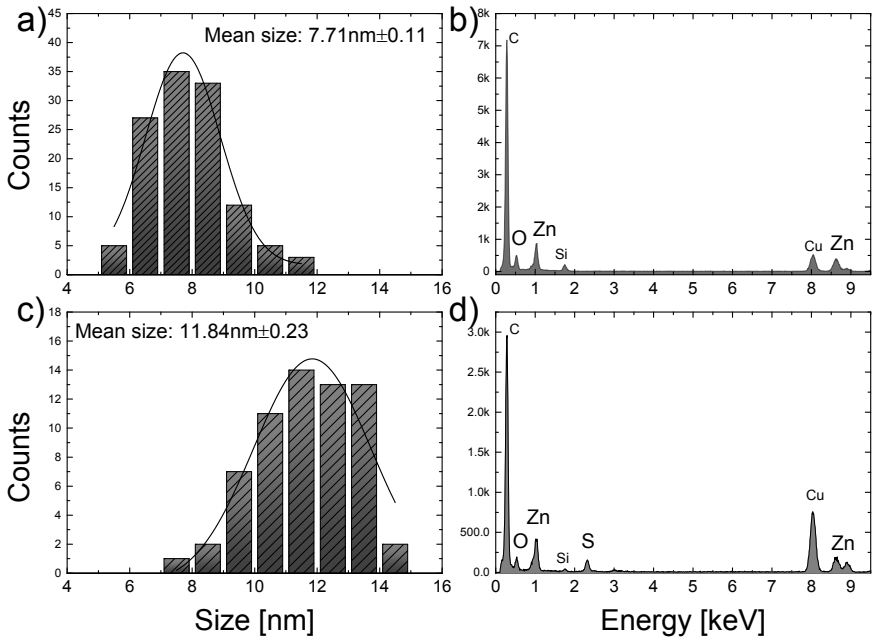


**Figure S3** Size distribution histograms of as-synthesized raw-ZnO NPs (a) and after surface functionalization with L-Cysteine molecules (2 mmol) (c) calculated based on TEM images, together with EDS spectrum before (b) and after (d) surface functionalization.

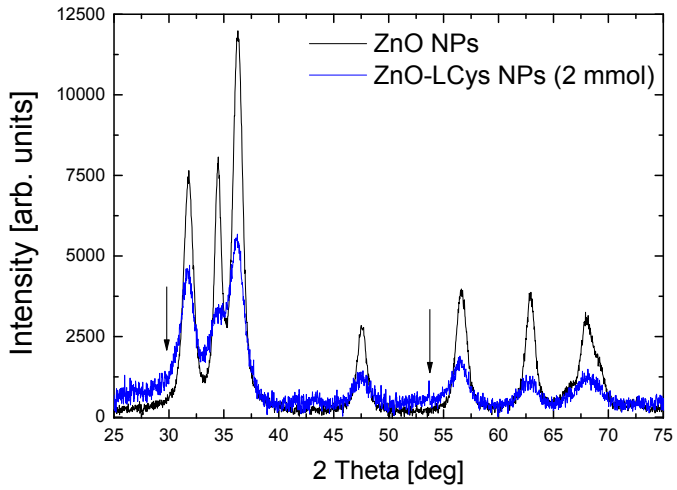


**Figure S4** XRD patterns of as synthesized ZnO NPs powder (black) and the powder obtained after drying a dispersion of ZnO-LCys NPs (blue).

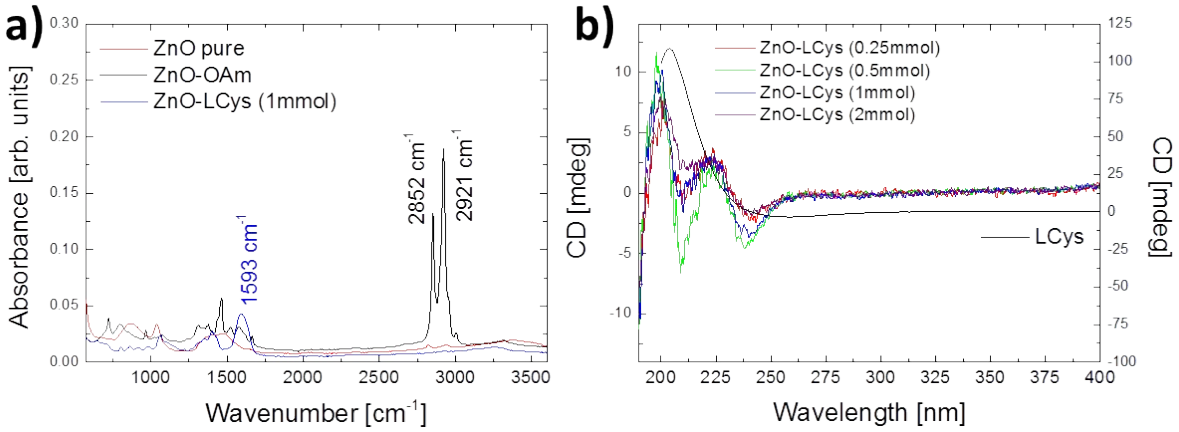


**Figure S5** Representative FTIR spectra of ZnO NPs before and after surface functionalization with L-Cysteine and Oleylamine molecules (a), and CD spectra of L-Cysteine functionalized ZnO NPs compared to the spectra of pure L-Cysteine molecules in water.

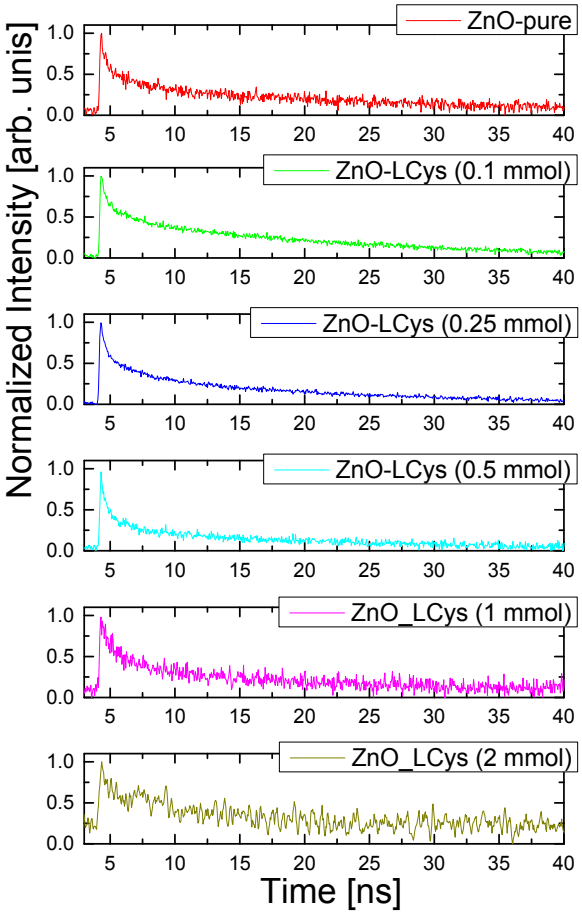


**Figure S6** Luminescence decays curves for visible ($\lambda_{EM.}$=540 nm) emission in ZnO NPs functionalized with different amounts of L-Cys molecules.

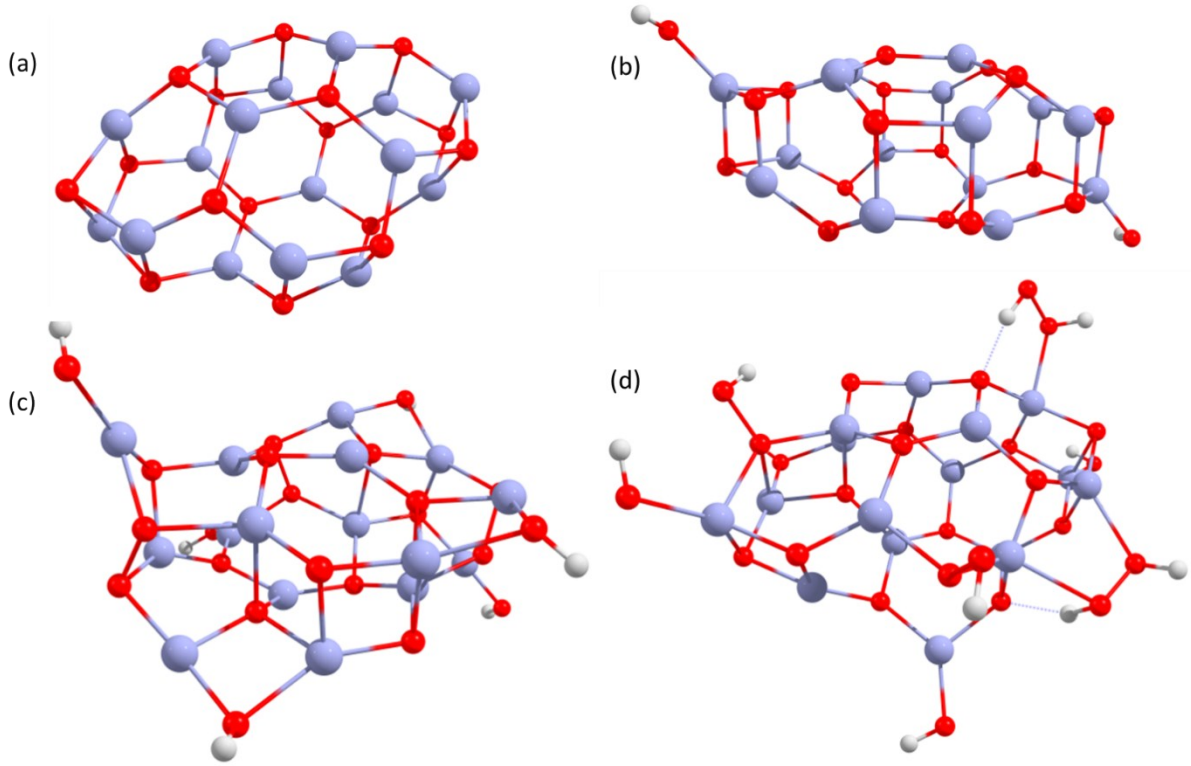


**Figure S7** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with the (a) 0, (b) 2, (c) 6 and (d) 10 OH groups adhered to the cluster's surface.

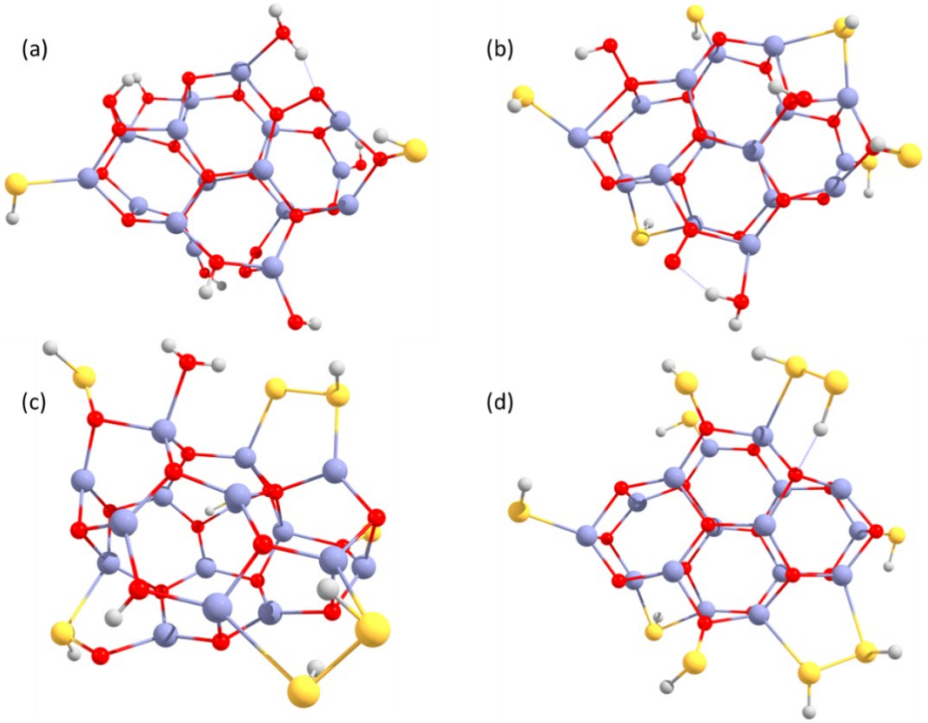


**Figure S8** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with the (a) 2xSH, 8xOH (b) 6xSH, 4xOH (c) 8xSH, 2xOH and (d) 10 SH groups adhered to the cluster's surface.

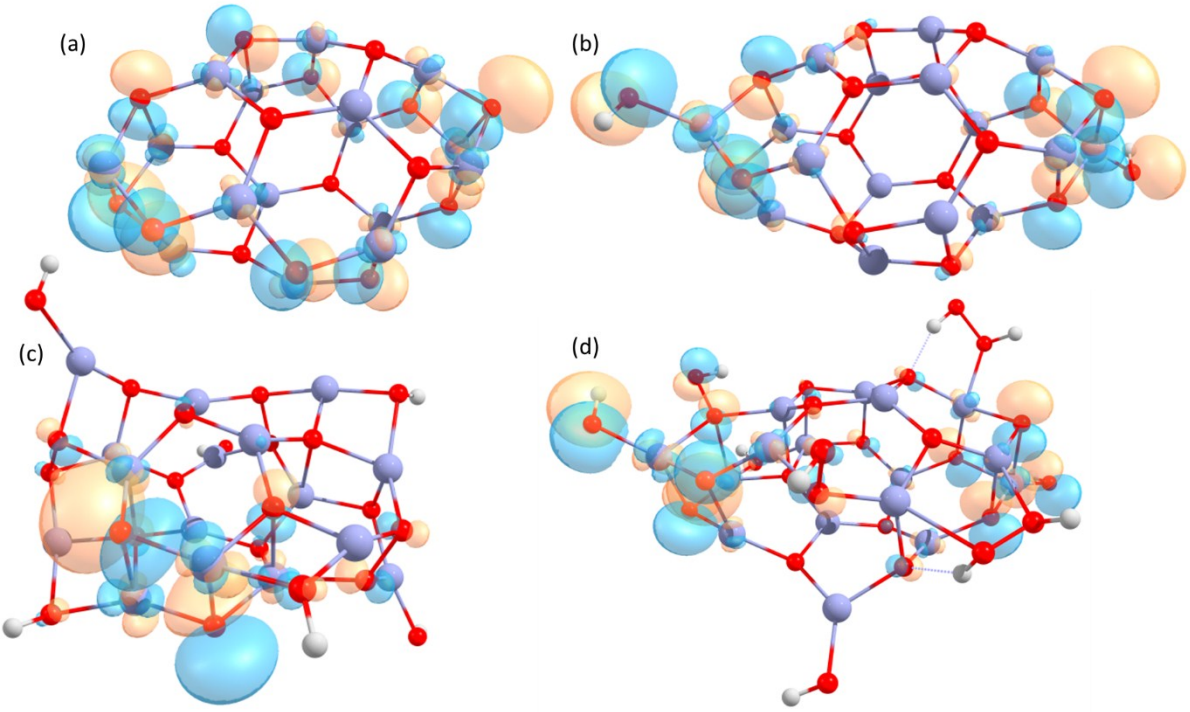


**Figure S9** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with various number of the OH groups attached to the surface i.e. (a) 0×OH, (b) 2×OH, (c) 8×OH and (d) 10×OH. The HOMO orbitals are shown for each optimized structure.

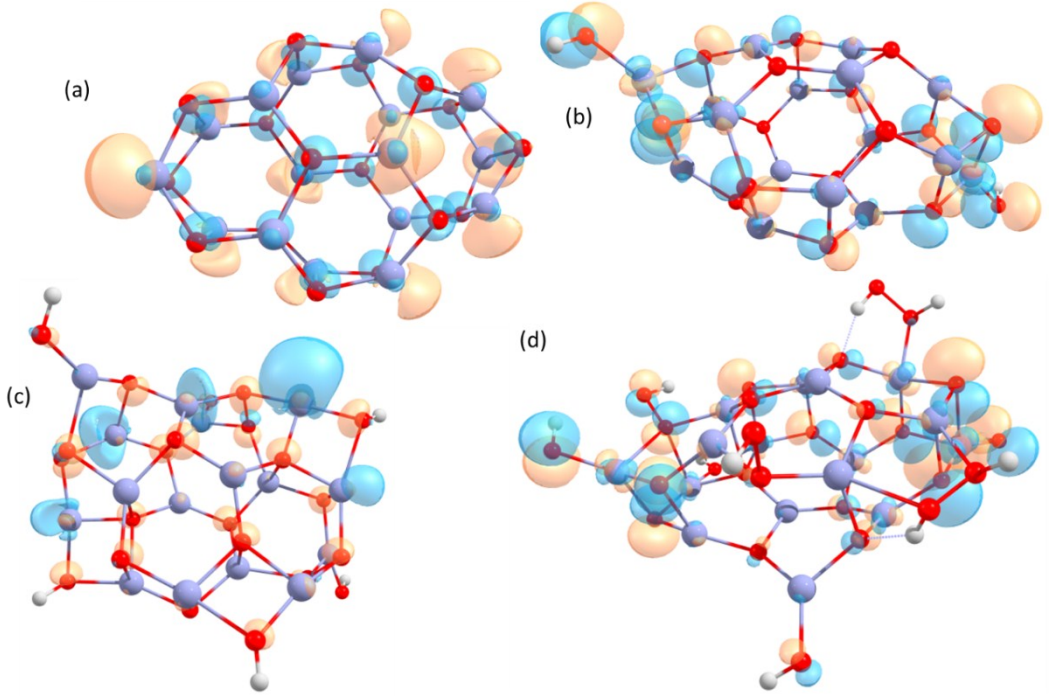


**Figure S10** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with various number of the OH groups attached to the surface i.e. (a) 0×OH, (b) 2×OH, (c) 8×OH and (d) 10×OH. The LUMO orbitals are shown for each optimized structure.

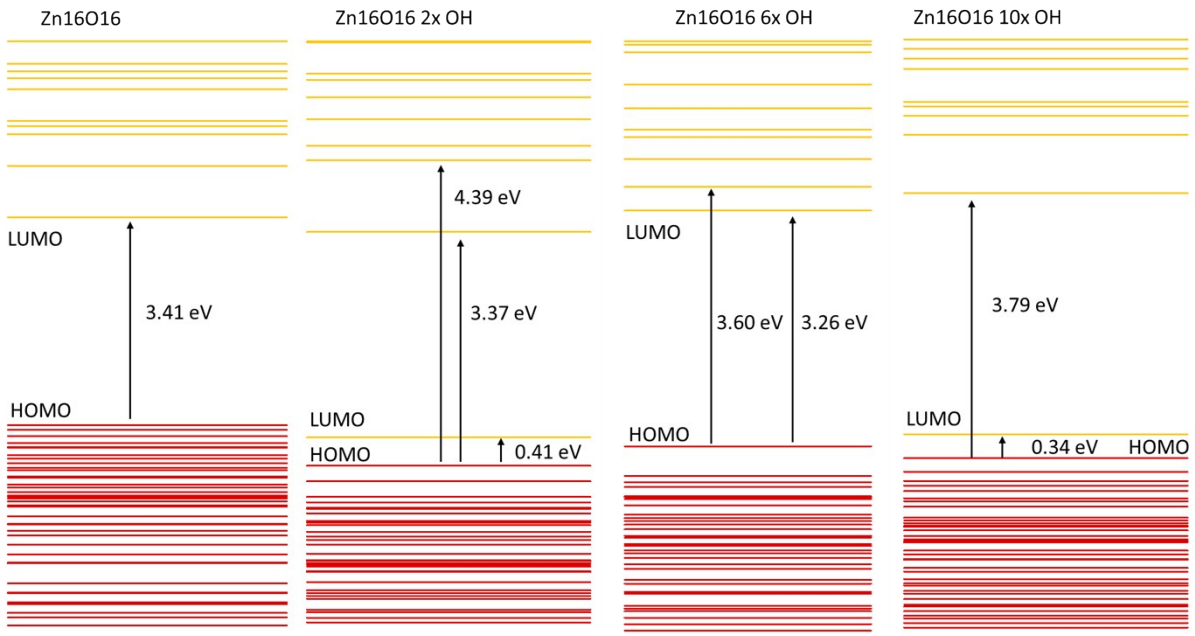


**Figure S11** The energy diagrams for the $Zn_{16}O_{16}$ clusters with various number of the OH groups attached to the surface i.e. (a) 0×OH, (b) 2×OH, (c) 8×OH and (d) 10×OH.

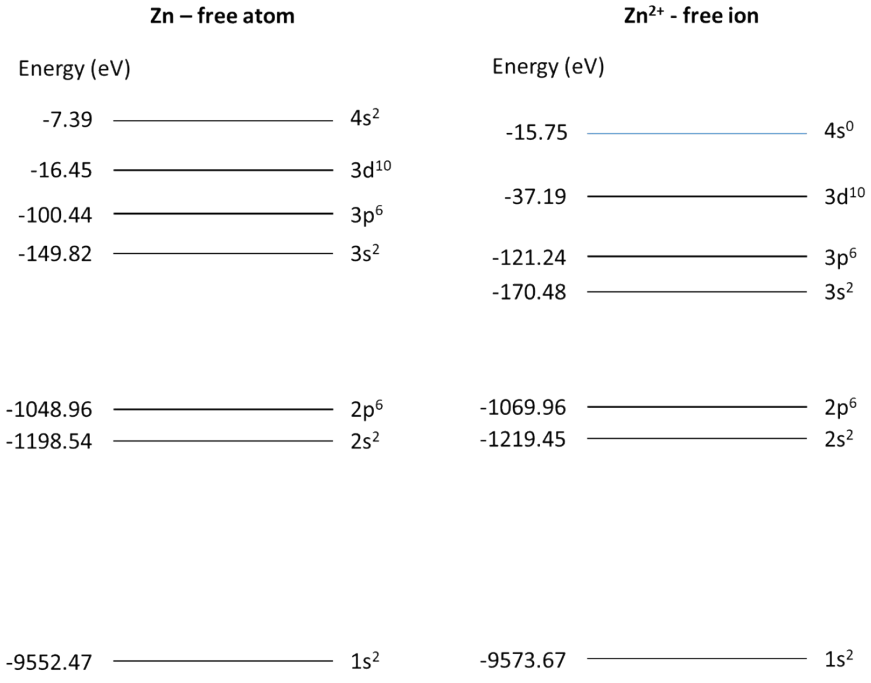


**Figure S12** The energies of the atomic orbitals calculated for the (a) neutral Zn atom and the (b) free $Zn^{2+}$ ion. The first virtual orbital was related to the 4s state has been colored in blue.

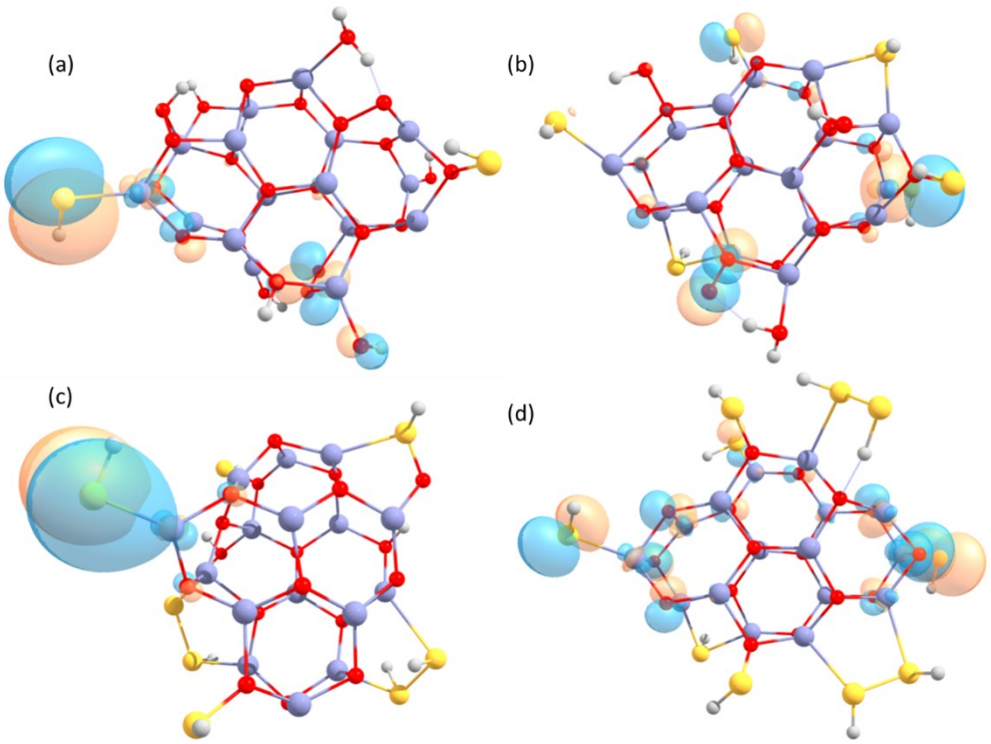


**Figure S13** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with the (a) 2xSH, 8xOH (b) 6xSH, 4xOH (c) 8xSH, 2xOH and (d) 10 SH groups adhered to the cluster's surface. HOMO orbitals has been depicted.

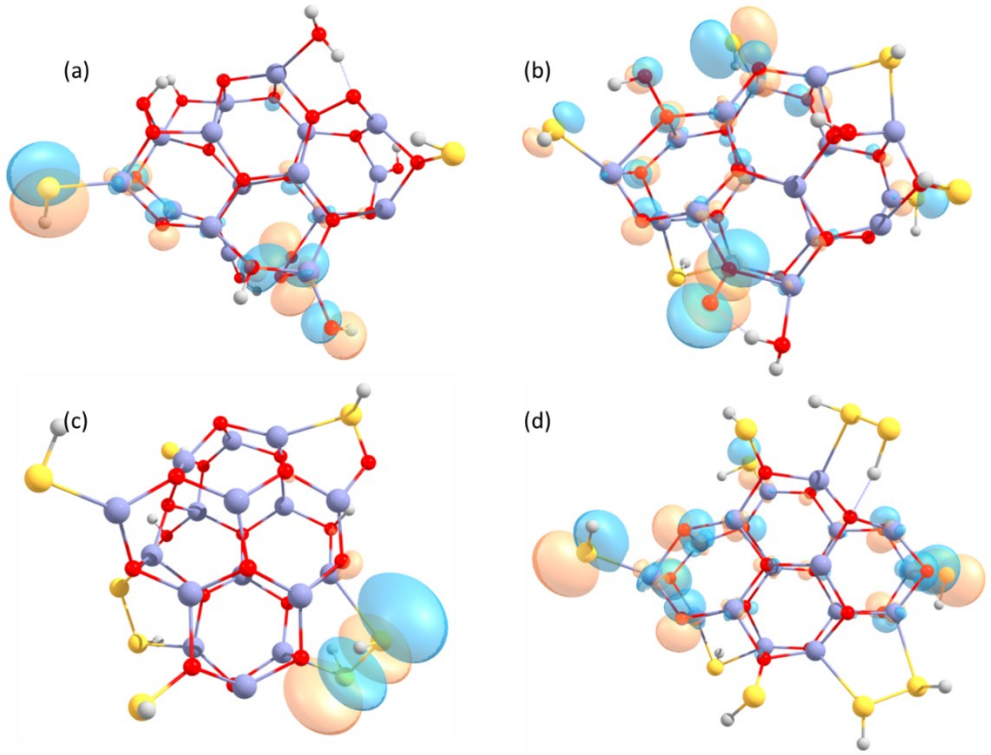


**Figure S14** The stationary point geometries of the $Zn_{16}O_{16}$ clusters with the (a) 2xSH, 8xOH (b) 6xSH, 4xOH (c) 8xSH, 2xOH and (d) 10 SH groups adhered to the cluster's surface. HOMO orbitals has been depicted.

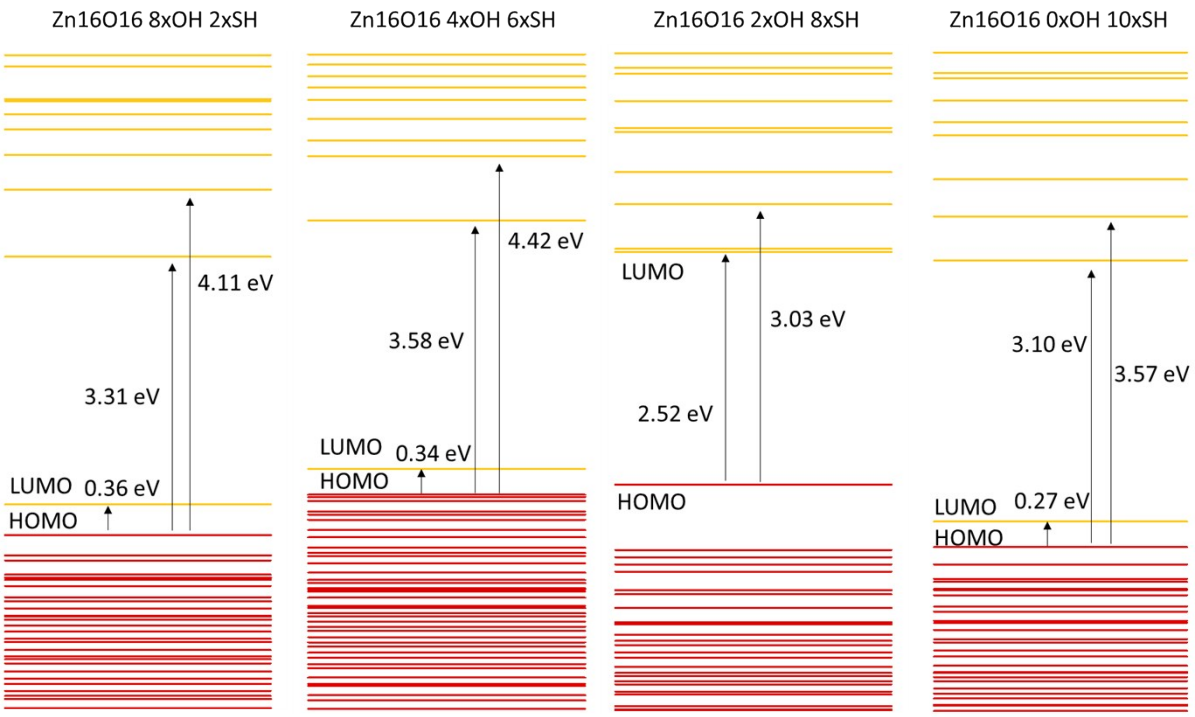


**Figure S15** The energy diagrams for the $Zn_{16}O_{16}$ clusters modified by the (a) 2xSH, 8xOH (b) 6xSH, 4xOH (c) 8xSH, 2xOH and (d) 10 SH groups adhered to the cluster's surface.