Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information for

Optical excitation of MgO nanoparticles; A computational perspective

Milena C. C. Wobbe[1], Andrew Kerridge[1,2], and Martijn A. Zwijnenburg[1,*]

[1] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K. Email: m.zwijnenburg@ucl.ac.uk
[2] Department of Chemistry, Lancaster University, Lancaster LA1 4YB, U.K.

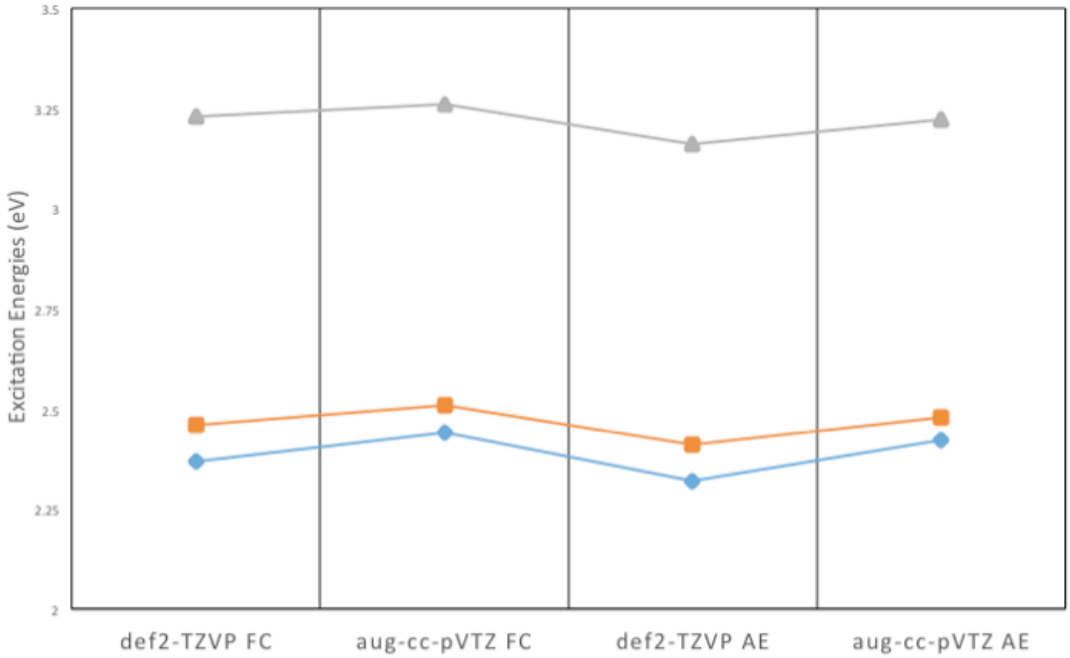

Fig. S1 Effect of the frozen core approximation on the lowest EOM-CCSD excitation energies of $(MgO)_2$. Blue diamonds 1-$^1b_{1g}$ state, orange squares 1-$^1b_{3u}$ state, and grey triangles 1-$^1b_{1g}$ state.

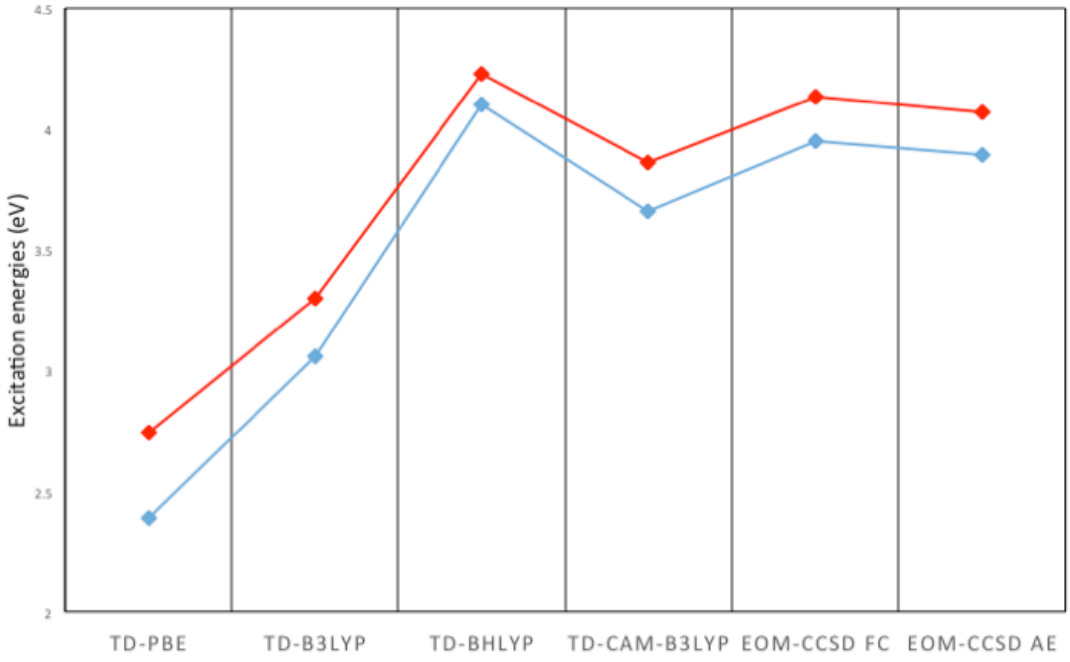

Fig. S2 Excitation energies of the two lowest excitations of the $(MgO)_4$ cluster as calculated using TD-DFT and EOM-CC. Blue diamonds 1-^{1}t state, red diamonds 2-^{1}t state. Calculations were performed in the D_2 sub of the full T_d point group because the EOM-CCSD implementation cannot handle non-Abelian point groups, and hence we cannot distinguish t_1 from t_2 states.

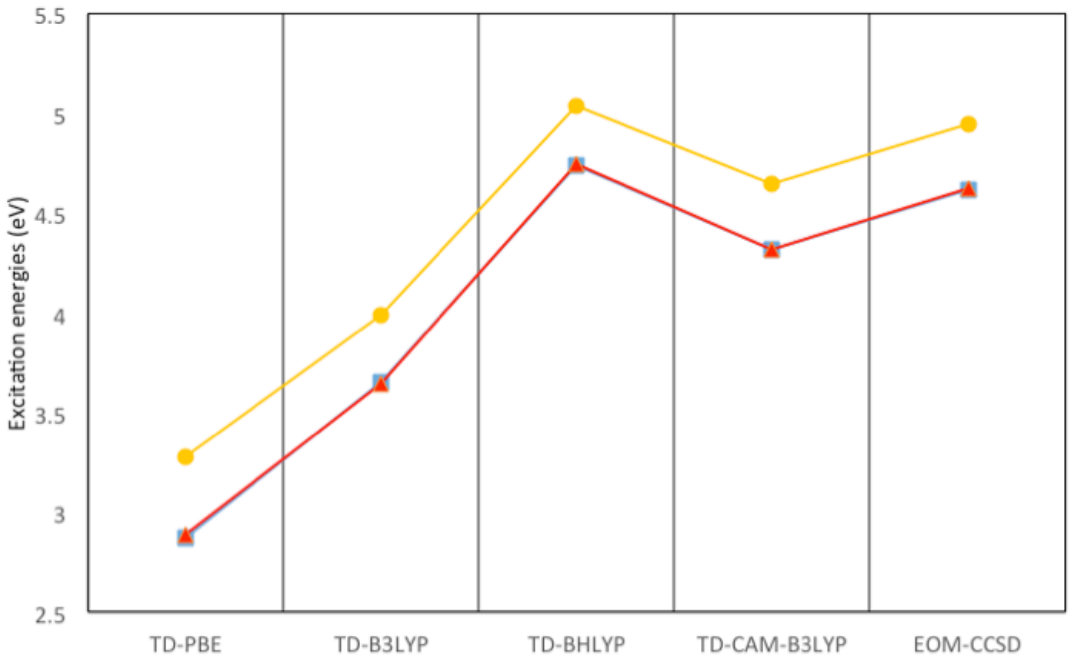

Fig. S3 Excitation energies of the three lowest excitations of the hexagonal $(MgO)_6$ cluster as calculated using TD-DFT and EOM-CC. Blue squares 1-^{1}a state, red diamonds 1-^{1}e state, and yellow circles 2-^{1}e state. Calculations were performed in the C_s sub of the full D_{3d} point group because the EOM-CCSD implementation cannot handle non-Abelian point groups, and hence we cannot distinguish e_g from e_u states, nor a from b states.

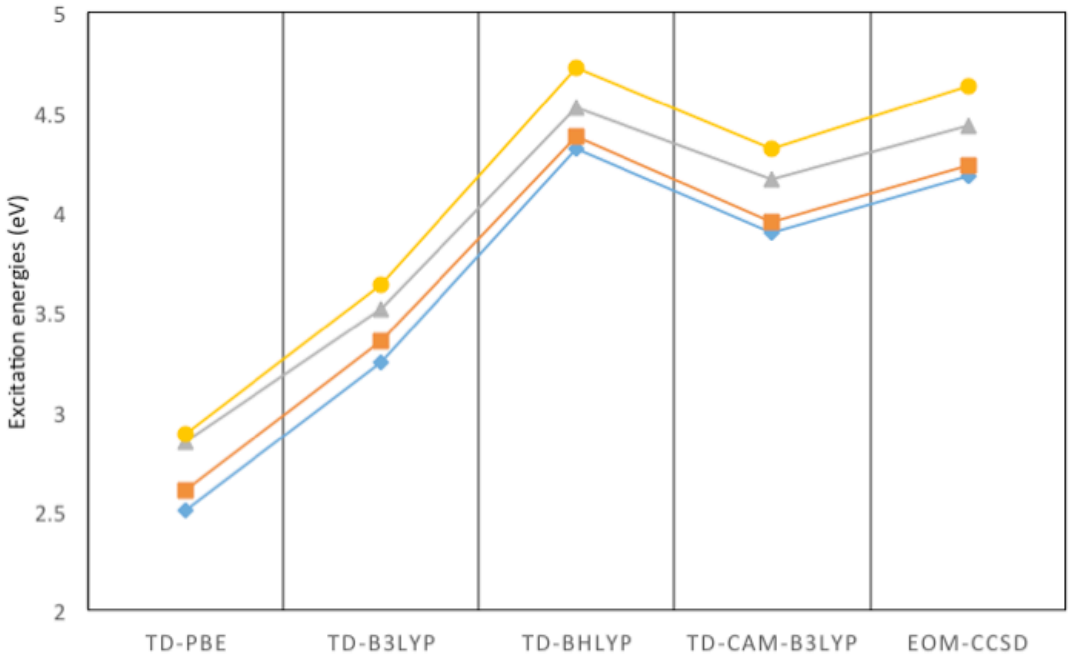

Fig. S4 Excitation energies of the four lowest excitations of the cubic $(MgO)_6$ cluster as calculated using TD-DFT and EOM-CC. Blue diamonds 1-^1b_2u state, red squares 1-^1b_3g state, grey triangles 1-^1b_1g state, and yellow circles 1-^1a_g state.

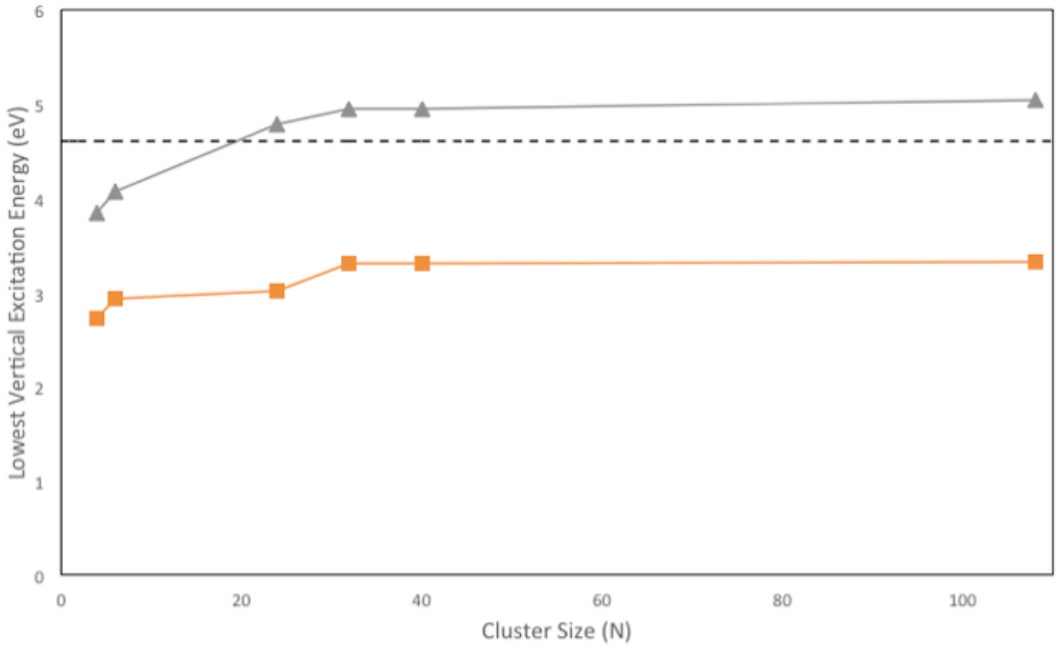

Fig. S5 Lowest vertical excitation energy (LVEE) of $(MgO)_4$ to $(MgO)_{108}$ nanocubes calculated using TD-B3LYP and TD-BHLYP and the DZ(D)P basis-set. Orange squares represent TD-B3LYP results, grey triangles TD-BHLYP results and the dashes lines the experimental absorption on-set of 3 nm particles.

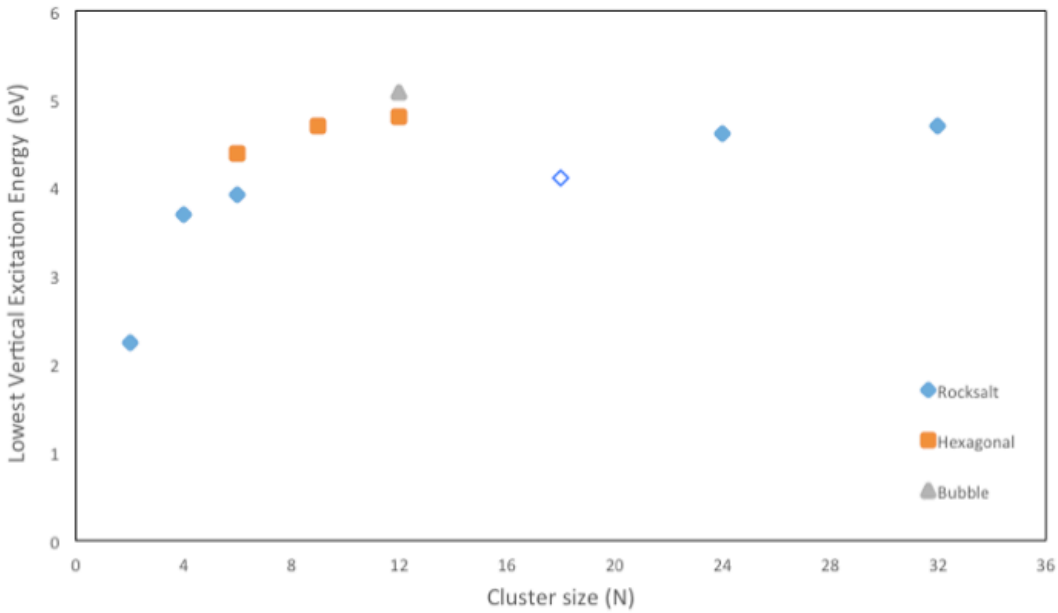

Fig. S6 Lowest vertical excitation energy (LVEE) of $(MgO)_1$ to $(MgO)_{32}$ calculated using TD-CAM-B3LYP. Open symbols correspond to particles with faces containing odd number of atoms.

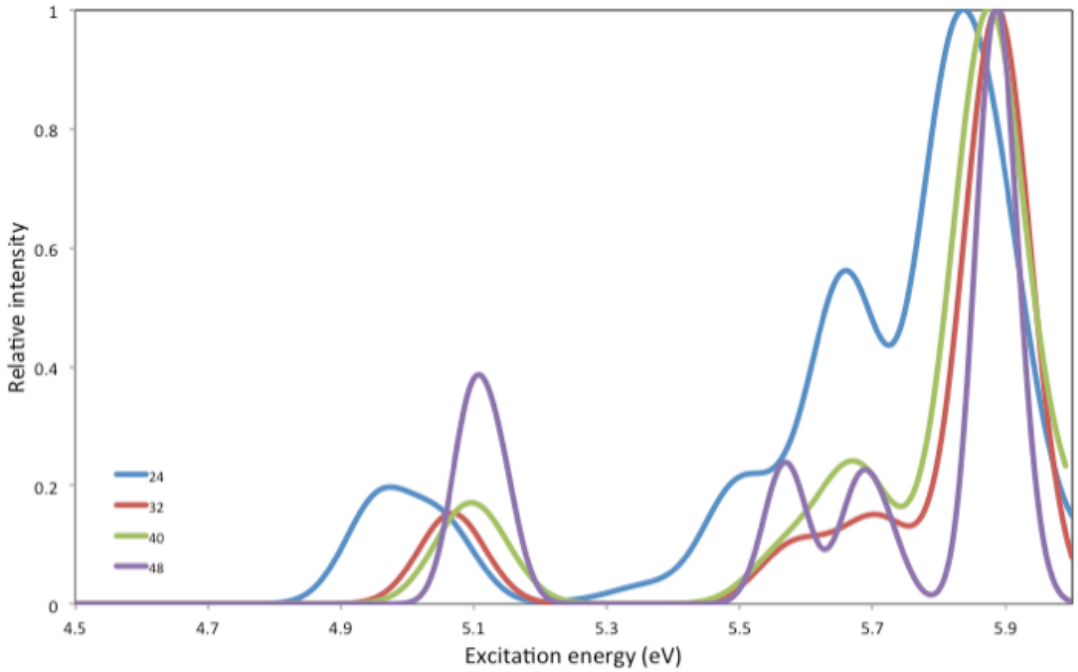

Fig. S7 unshifted TD-BHLYP calculated absorption spectra (without the 0.5 eV rigid blue-shift discussed in the text) of $(MgO)_{24}$, $(MgO)_{32}$, $(MgO)_{40}$ and $(MgO)_{48}$.

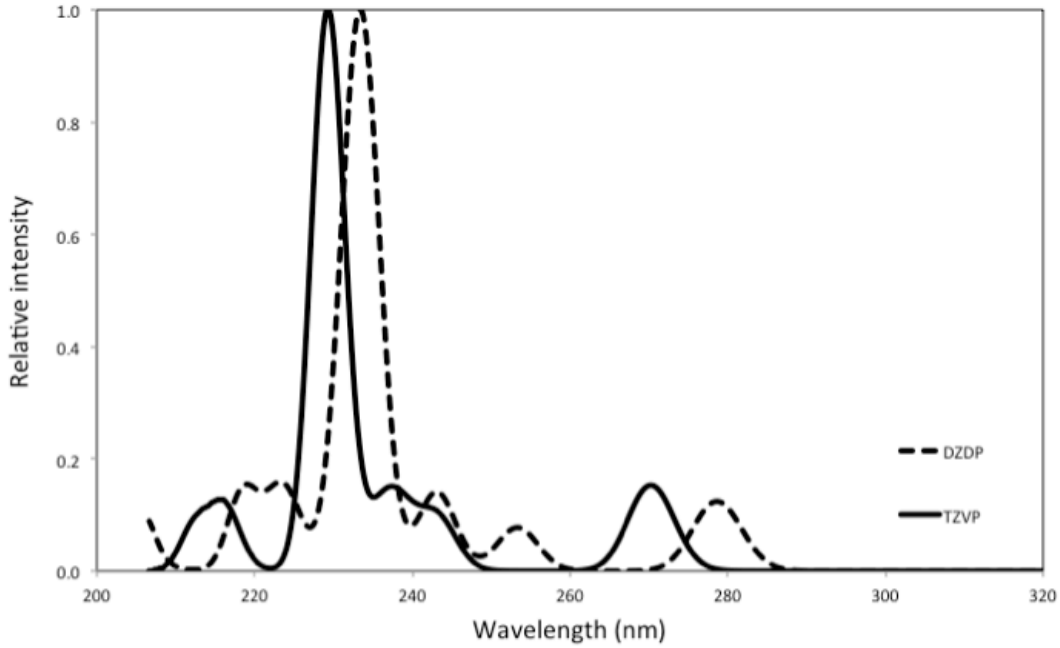

Fig. S8 Comparison of the absorption spectra of the def2-TZVP and DZ(D)P TD-BHLYP spectra of $(MgO)_{32}$ (including the 0.5 eV rigid red-shift discussed in the text).

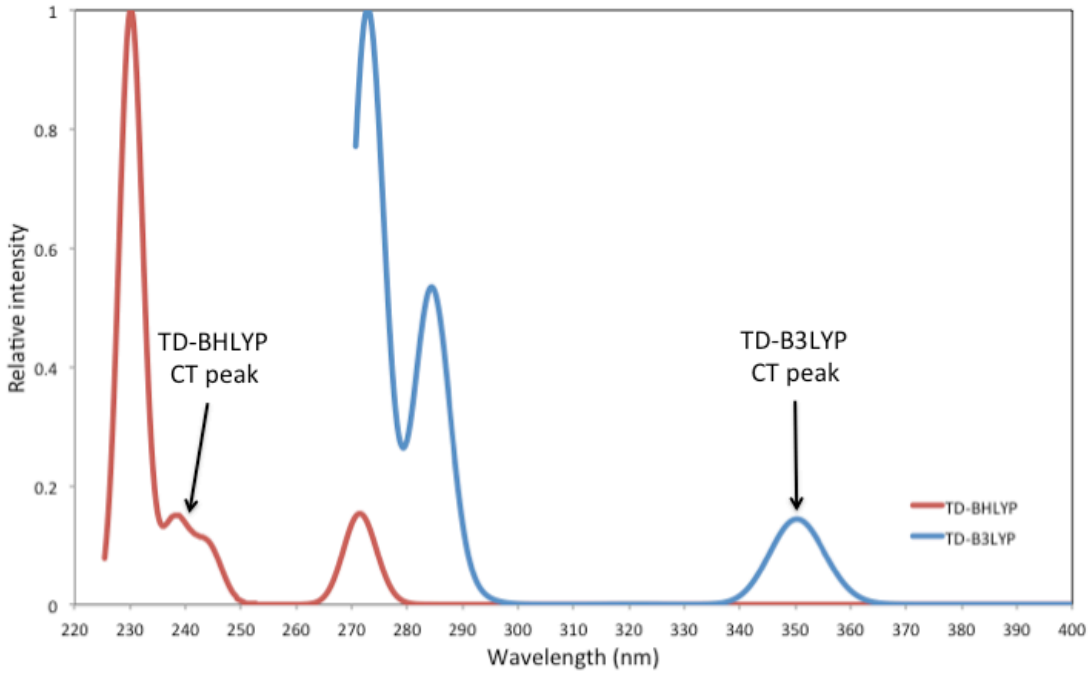

Fig. S9 Comparison of the absorption spectrum of $(MgO)_{32}$ as calculated with TD-B3LYP and TD-BHLYP.

Table S1 Length of the edges and body diagonal of the DFT optimised cuboid MgO nanoparticles.

Particle	Edges (nm)	Body diagonal (nm)
$(MgO)_{24}$	0.59 (2x) / 0.4	0.94
$(MgO)_{32}$	0.59 (3x)	1.02
$(MgO)_{40}$	0.79 / 0.59 (2x)	1.16
$(MgO)_{48}$	1.01 / 0.59 (2x)	1.32
$(MgO)_{108}$	0.99 (3x)	1.72