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

Supporting information for:

The Effect of Particle Size and Composition on the Optical and Electronic Properties of CdO and CdS Rocksalt Nanoparticles

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Table S1 -IP, -EA, fundamental gap (Δ_F), optical gap (Δo) and exciton binding energy (EBE) predicted for the CdS nanoparticles using ev*GW*-BSE starting from B3LYP orbitals and the different basis-sets and method combinations. In the case of the optical gap both the optical gap based on the lowest excited and the lowest bright excited state (in bold) are given. Similarly, exciton binding energies calculated for the lowest and the lowest bright excited state are presented.

Particle	Basis-set		-IP	-EA	Δ_F	Δo	EBE
$(CdS)_4$	def2-SVP	AC	-7.941	-1.588	6.35	2.42/**2.46**	3.94/3.89
$(CdS)_4$	def2-SVP	AC/2c	-7.978	-1.694	6.28		
$(CdS)_4$	def2-SVP	SR	-8.352	-1.845	6.51	2.56/2.63	3.95/3.88
$(CdS)_4$	def2-TZVPP	AC	-8.366	-1.876	6.49	2.55/**2.61**	3.94/3.88
$(CdS)_4$	def2-TZVPP	SR	-8.352	-1.845	6.51	2.56/**2.63**	3.95/3.88
$(CdS)_{32}$	def2-SV(P)	AC	-6.751	-2.295	4.46	2.10/**2.29**	2.36/2.16
$(CdS)_{32}$	def2-SVP	AC	-6.751	-2.468	4.28	1.93/**2.13**	2.35/2.15
$(CdS)_{32}$	def2-TZVPP	AC	-7.170	-2.837	4.33	2.00/**2.18**	2.33/2.16
$(CdS)_{32}$	Def2-TZVPP	CD	-7.170	-2.836	4.33	2.02/**2.19**	2.31/2.14
$(CdS)_{108}$	def2-SV(P)	AC	-6.331	-2.572	3.76	1.97	1.79

Table S2 -IP, -EA, fundamental gap (Δ_F), optical gap (Δo) and exciton binding energy (EBE) predicted for the CdO nanoparticles using using ev*GW*-BSE starting from B3LYP orbitals and the different basis-sets and method combinations. In the case of the optical gap both the optical gap based on the lowest excited and the lowest bright excited state (in bold) are given. Similarly, exciton binding energies calculated for the lowest and the lowest bright excited state are presented.

Particle	Basis-set		-IP	-EA	Δ_F	Δo	EBE
$(CdO)_4$	def2-SVP	AC	-7.430	-1.586	5.84	**1.46**	4.38
$(CdO)_4$	def2-SVP	AC/2c	-7.547	-1.677	5.87		
$(CdO)_4$	def2-SVP	SR	-8.049	-1.871	6.18	**1.80**	4.38
$(CdO)_4$	def2-TZVPP	AC	-8.054	-1.900	6.15	**1.77**	4.38
$(CdO)_4$	def2-TZVPP	SR	-8.049	-1.871	6.18	**1.80**	4.38
$(CdO)_{32}$	def2-SV(P)	AC	-6.548	-1.833	4.72	2.08/**2.17**	2.64/2.55
$(CdO)_{32}$	def2-SVP	AC	-6.560	-2.013	4.55	1.92/**2.01**	2.62/2.54
$(CdO)_{32}$	def2-TZVPP	AC	-7.079	-2.497	4.60	2.01/**2.07**	2.59/2.53
$(CdO)_{32}$	def2-TZVPP	CD	-7.108	-2.482	4.63	2.08/**2.11**	2.55/2.52
$(CdO)_{108}$	def2-SV(P)	AC	-6.178	-2.110	4.07	1.96	2.10

Table S3 optical gap (Δo) predicted for the CdO and CdS nanoparticles using LR-CCSD/def2-TZVPP for geometries optimised using B3LYP/def2-TZVPP.

Particle	Δo
$(CdO)_4$	2.02
$(CdS)_4$	2.85

Table S4 -IP, -EA, fundamental gap (Δ_F), optical gap (Δo) and exciton binding energy (EBE) predicted for the CdO and CdS nanoparticles using G_0W_0-BSE/def2-SVP starting from B3LYP orbitals. In the case of the optical gap both the optical gap based on the lowest excited and the lowest bright excited state (in bold) are given. Similarly, exciton binding energies calculated for the lowest state are presented.

Particle	Basis-set		-IP	-EA	Δ_F	Δo	EBE
$(CdO)_{32}$	def2-TZVPP	AC	-6.637	-2.118	3.95		
$(CdO)_{32}$	def2-SVP	AC	-6.184	-6.184	3.92	1.33	2.59
$(CdO)_{32}$	def2-SV(P)	AC	-6.148	-2.118	4.03	1.42	2.52
$(CdO)_{108}$	def2-SV(P)	AC	-5.877	-2.370	3.51	1.44	2.01
$(CdS)_{32}$	def2-TZVPP	AC	-6.908	-3.035	3.87		
$(CdS)_{32}$	def2-SVP	AC	-6.542	-2.724	3.82	1.49	2.33
$(CdS)_{32}$	def2-SV(P)	AC	-6.532	-2.587	3.95	1.60	2.34
$(CdS)_{108}$	def2-SV(P)	AC	-6.172	-2.855	3.32	1.55	1.77

Table S5 -IP, -EA, fundamental gap (Δ_F), optical gap (Δo) and exciton binding energy (EBE) predicted for the CdO and CdS nanoparticles with methylamine capping agents using ev*GW*-BSE/def2-SVP starting from B3LYP orbitals.

Particle	$NH_2(CH_3)$		-IP	-EA	Δ_F	Δo	EBE
$(CdO)_{32}$	4	AC	-5.757	-0.905	4.85	2.292	2.56
$(CdO)_{32}$	16	AC	-5.140	0.116	5.26	2.834	2.42
$(CdO)_{32}$	28	AC	-4.764	0.594	5.36	2.989	2.37
$(CdS)_{32}$	4	AC	-6.410	-1.377	5.03	2.770	2.26
$(CdS)_{32}$	16	AC	-5.154	0.039	5.19	3.192	2.00
$(CdS)_{32}$	28	AC	-4.523	0.780	5.30	3.247	2.06

Table S6 -IP, -EA, fundamental gap (Δ_F), optical gap (Δo) and exciton binding energy (EBE) predicted for a CdO nanoparticle using G_0W_0-BSE starting from HSE03 orbitals for a geometry optimised with B3LYP/def2-TZVPP.

Particle	Basis-set		-IP	-EA	Δ_F	Δo	EBE
$(CdO)_{32}$	def2-TZVPP	AC	-6.571	-2.611	3.96	1.436	2.52

Table S7 NBO charges for atoms in the centre and on the corner of $(MgO)_{32}$, $(CdO)_{32}$ and $(CdS)_{32}$ as calculated with B3LYP/def2-TZVPP.

Particle	Centre		Corner	
	Charge Mg/Cd	Charge O/S	Charge Mg/Cd	Charge O/S
$(MgO)_{32}$	1.78	-1.82	1.80	-1.77
$(CdO)_{32}$	1.65	-1.77	1.61	-1.48
$(CdS)_{32}$	1.46	-1.62	1.43	-1.22

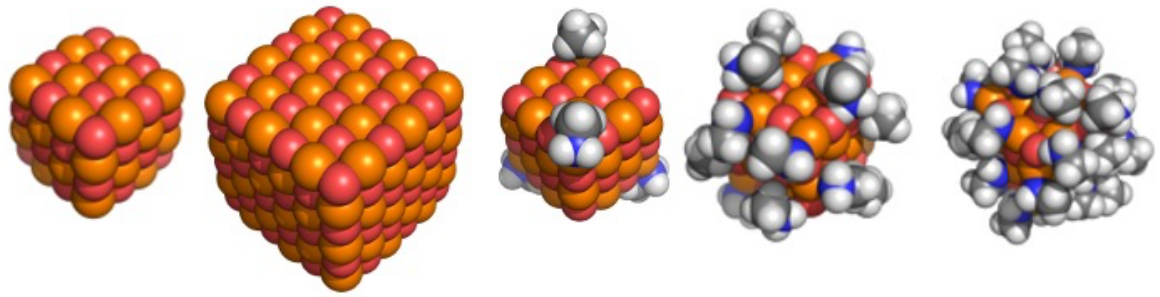

Fig. S1 *DFT optimised structures of the* $(CdO)_{32}$, $(CdO)_{108}$ *and the* $(CdO)_{32}(NH_2(CH_3))_4$, $(CdO)_{32}(NH_2(CH_3))_{16}$ and $(CdO)_{32}(NH_2(CH_3))_{28}$ particles.

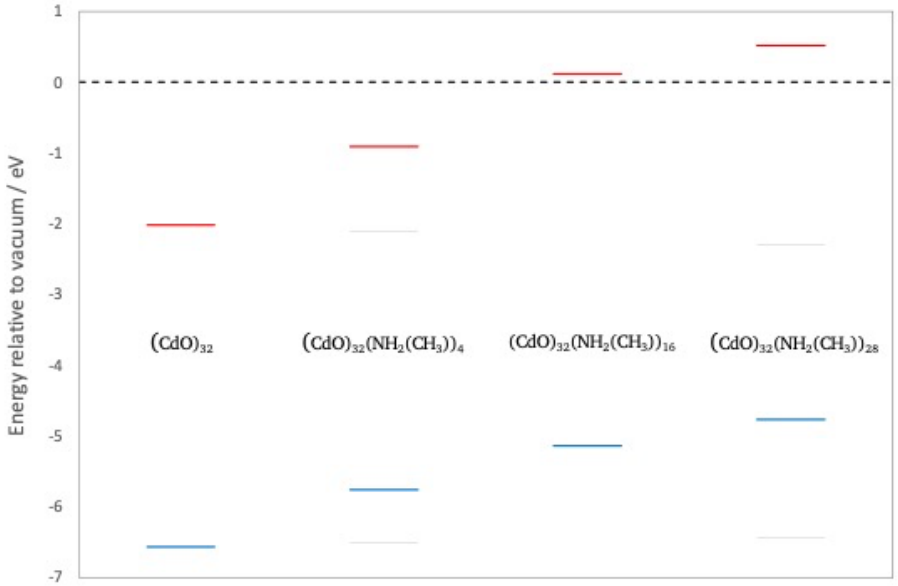

Fig. S2 *Change in the predicted optical spectra of* $(CdS)_{32}$ *with number of capping agents on the surface as calculated with evGW(AC)-*BSE*/def2-SV(P). Red lines -EA, blue lines -IP, grey lines -IP and -EA of particles.*

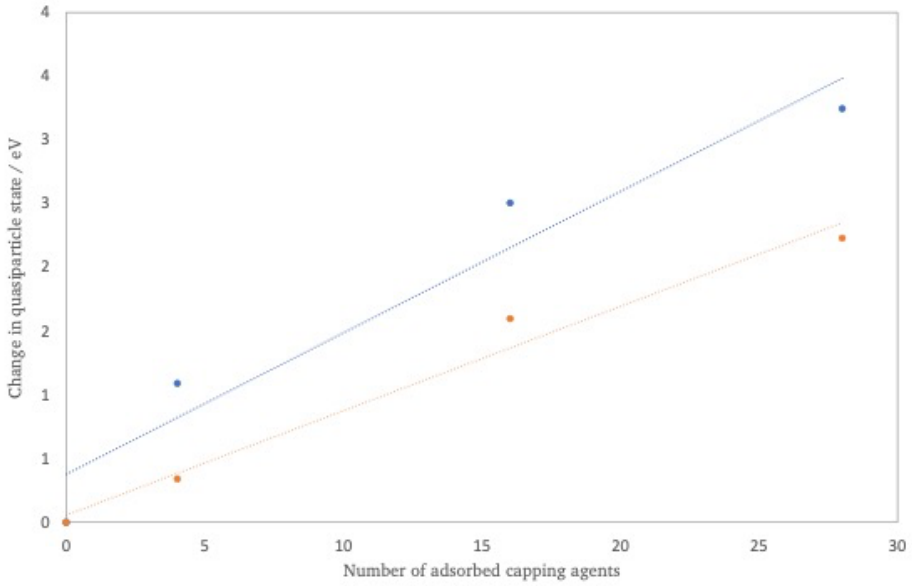

Fig. S3 *Change in the occupied (red points) and unoccupied (blue points) quasiparticle states of* $(CdS)_{32}$ *as function of the number of adsorbed capping agents. Red and blue dashed lines are lines of best fit.*

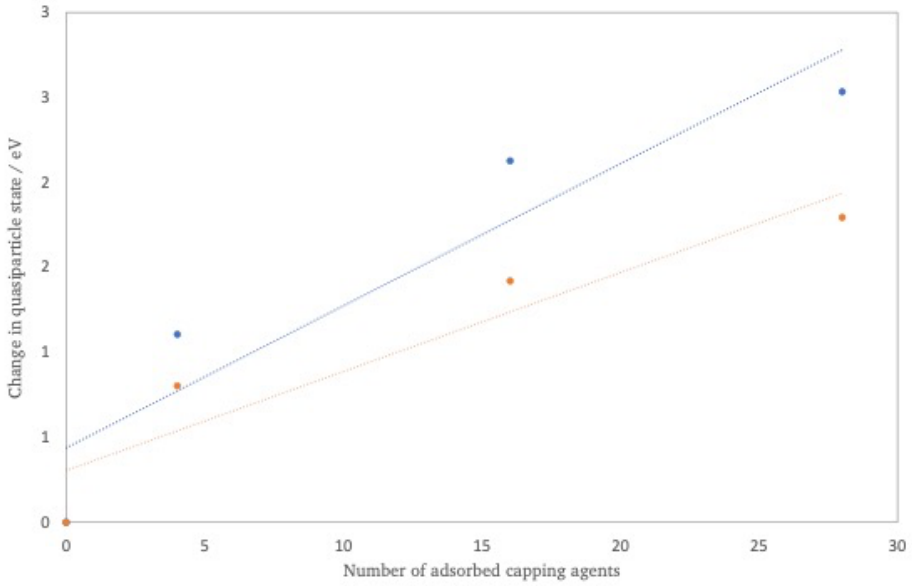

Fig. S4 *Change in the occupied (red points) and unoccupied (blue points) quasiparticle states of* $(CdO)_{32}$ *as function of the number of adsorbed capping agents. Red and blue dashed lines are lines of best fit.*