In-Depth Study of ZnS Nanoparticle Surface Properties with a Combined Experimental and Theoretical Approach – SUPPORTING INFORMATION

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Motivations and considerations justifying the slab model

In this study, the ZnS surface was modelled employing slab models with periodic boundaries conditions, thus neglecting the finite size of the particles. This approach is justified because the computational cost of explicitly treating a nanoparticle in the nanometer range grows rapidly, and in our case would be too computationally demanding. For instance, Khalkhali *et al.*^{1,2} performed a molecular dynamics investigation based on the empirical potential developed by Hamad *el al.*,³ which allowed to simulate full sized particles up to 5 nm (approx. 3500 atoms). The particles studied in the present investigation have an average diameter of 21 nm (approx. 125000 atoms), which is prohibitively high. On the other hand, we need accurate predictions of vibrational frequencies of adsorbed species, which are given by an ab initio calculations. For these reasons, we relied on an approach based on the density functional theory and slab models and DFT. The same strategy was employed by Balantseva *et al.*⁴ for the simulation of the vibrational frequencies for CO interacting with the ZnS nanoparticle surface. Because of this choice, we assumed that the influence of the particle size is negligible in our samples.

The quality of the size-independency assumption was assessed both by theoretical considerations and experimental evidences. Khalkhali *et al.*^{1,2} predicted that important deviation from the regular sphalerite structure may occur for particles smaller than 2 mn. In ultra-small particles it is possible to hypothesize that peculiar structures and properties may appear, that, in turn, severely effects the properties of the surface. On the other hand, particles larger than 2 nm are instead expected to display the common cubic ZnS features, thus prevalently exposing the (110) surface. Moreover, with reference to the work of Balantseva *et al.*⁴, the CO stretching frequency was almost entirely unchanged in the case of a 35 nm nanoparticles in comparison with the bulk sample. Much larger CO stretching frequency shifts were instead observed while changing the dosage of the gaseous CO, likely due to different coverage of the surface. Thus, the lateral interaction between adsorbates influenced the observed frequency shift more than the NPs size. In our study, 21 nm NPs were employed, which are expected to show surface properties much closer to 35 nm NPs rather than to 5 nm NPs. This can be determined qualitatively by assuming that the variation in surface properties is directly related to the relative amount of exposed surface atoms. Indeed, as the NPs size is reduced the ratio of atoms being exposed to the surface increases, together with the number of dandling bonds. The ratio of atoms exposed on the topmost layer of the NPs over the total number of atoms in a particle can be roughly estimated by assuming:

- Spherical shape of the NPs
- Unstrained ZnS cubic structure
- Only (110) surface exposed

Under these approximations, it is possible to write the following equations.

$$N^{\circ}_{TOT} \approx 4 \frac{V_{NP}}{V_{cell}} \approx \frac{2}{3} \pi \left(\frac{d}{a}\right)^3$$

 N°_{TOT} is total number of atoms in a NP having a diameter *d* and a ZnS sphalerite structure with a cubic unit cell of lateral size *a*. V_{NP} is the volume of the NP, while V_{cell} is the volume of the crystallographic unit cell.

$$N^{\circ}_{TM(110)} \approx \frac{A_{NP}}{A_{cell(110)}} \approx \sqrt{2}\pi \left(\frac{d}{a}\right)^2$$

 $N^{\circ}_{TM(110)}$ is the number of atoms on the topmost layer. A_{NP} is the surface area of the NP, while $A_{cell(110)}$ is the surface area of the (110) surface unit cell.

Consequently, $R_{s/b}$, being ratio of atoms exposed on the topmost layer of the ZnS NPs over the total number of atoms, can be approximated as follows.



Figure S1. Ratio of atoms exposed on the topmost layer of the ZnS NPs over the total number of atoms plotted as a function of the NP size.

From the plot in Figure S1 is possible to see that the estimated $R_{s/b}$ value for the 21 nm NPs we employed is much closer to the one of 35 nm NPs (form 5% to 3%) than to the one of 5 nm NPs (from 5% to approx. 20%). Consequently, since Balantseva *et al.*⁴ reported a bulk-like behavior in her adsorption experiments for 35 nm NPs, only minor and likely negligible variations are

expected for 21 nm NPs. Thus, we believe that neglecting the contribution induced by NPs size and using a slab-based approach represented a viable option to obtain accurate results.

Calculated ZnS bulk parameters

Table S1. Predicted values for bulk sphalerite ZnS: cell parameter a_0 , compressibility modulus k_0 , and first derivative of the compressibility modulus respect pressure dk_0 .

	<i>a</i> ₀ (Å)	ko (GPa)	dk_0
PBE	5.450	72.4	1.37
PBE D2	5.371	68.9	1.42
Expt. ⁵	5.4102	78.0	4.91
	5.395	74.8	4
	5.41	79.5	

DRIFT spectra of ZnS heated at 400°C



Figure S2. (a) DRIFT spectra of ZnS NPs heated *in-situ* at 400°C. (b) Detail of the adsorbed H_2O stretching region for ZnS NPs recorded at RT (red curve) and at 400°C (blue curve), showing the signal attributed to –OH stretching at 3691 cm⁻¹ disappearing in the heated sample.



Figure S3. Survey XPS spectra of ZnS NPs.

Table S2. Observed peaks and calculated Auger Parameter (AP) in the XPS spectra of ZnS NPs.

XPS peak	Experimental (eV)	Reference (eV)
Zn2s	1196.2	1196.06
Zn2p _{3/2}	1021.8	1021.7 ⁷ , 1022.0 ⁷
Zn3s	139.8	139.9 ⁷ , 140.3 ⁶ , 141.5 ⁸
Zn3p	89	88.47
Zn3d	9.8	9.8 ⁷ , 10.1 ⁹ , 10.7 ⁶
S2s	225.8	225.6 ⁸ , 226.0 ⁷ , 226.3 ⁶
S2p	161.8	162.2 ¹⁰ , 161.9 ¹⁰
ZnAP-2p _{3/2} ,L ₃ M ₄₅ M ₄₅ (1G)	2011.5	2011.3 ⁷ , 2011.9 ⁶ , 2011.7 ⁷

TGA-DSC of ZnS NPs



Figure S4. TGA-DSC profiles of the ZnS samples. TGA: red line; DSC: blue line (exothermic down). Dashed lines separate the profile in five segments (labeled I - V), where different phenomena occur (see main text).

Calculated structural and vibrational properties of free and interacting methanol



Figure S5. Reference structure for methanol.

Table S3. Calculated structural parameters for methanol as free molecule and when interacting with the ZnS(110) surface.

	Free $\theta = 1 \text{ ML}$			$\theta = 0.5 \text{ N}$	ſĹ	
	PBE	PBE-D2	PBE	PBE-D2	PBE	PBE-D2
dО-Н (Å)	0.974	0.974	0.994	0.997	0.992	1.007
dC-O (Å)	1.429	1.430	1.437	1.438	1.442	1.462
dC-H (Å)	1.103	1.104	1.100	1.100	1.099	1.116
	1.103	1.104	1.097	1.097	1.099	1.113
	1.096	1.097	1.096	1.097	1.095	1.116
θ C-O-H (deg)	108.570	108.293	110.599	108.494	110.555	111.054
θ H-C-H (deg)	108.376	108.491	109.854	110.066	109.338	110.417
	108.376	108.491	109.215	109.486	109.669	109.666
	108.939	108.984	109.326	109.639	110.272	109.716

		$\theta = 1 \text{ ML}$		$\theta = 0.5 \text{ ML}$			
	Free	Interacting	Δv	Interacting	Δv		
	(cm ⁻¹)	(cm^{-1})	(cm ⁻¹)	(cm^{-1})	(cm ⁻¹)		
A' modes							
v_1	3795	3381	-414	3426	-369		
v_2	3048	3100	52	3071	23		
<i>V</i> 3	2919	2950	30	2956	37		
<i>V</i> 4	1440	1449	9	1441	1		
<i>V</i> 5	1454	1472	19	1467	13		
<i>V</i> 6	1318	1354	37	1357	39		
\mathcal{V}_7	1048	1085	37	1095	47		
V8	1003	982	-21	1006	3		
A" modes							
V9	2971	3017	46	3028	57		
<i>V</i> 10	1420	1425	6	1423	3		
<i>v</i> ₁₁	1129	1151	22	1141	13		
<i>v</i> ₁₂	290	700	410	581	291		

Table S4. Calculated vibrational frequencies for methanol as free molecule and when interacting with the ZnS(110) surface.

Calculated structural and vibrational properties of free and interacting pyridine



Figure S5. Reference structure for pyridine.

Table S5. (Part 1 of 2) Calculated structural parameters for pyridine as free molecule and when interacting with the ZnS(110) surface.

		$\theta = 0.5 \text{ ML}$		
	Free	PBE	PBE-D2	
dC(1)-N (Å)	1.339	1.343	1.342	
<i>d</i> C(1)-C(2) (Å)	1.395	1.389	1.389	
<i>d</i> C(2)-C(3) (Å)	1.392	1.392	1.393	
<i>d</i> C(1)-H(1) (Å)	1.093	1.089	1.090	
<i>d</i> C(2)-H(2) (Å)	1.090	1.089	1.088	
<i>d</i> C(3)-H(3) (Å)	1.090	1.090	1.090	

		$\theta = 0.5 \text{ ML}$		
	Free	PBE	PBE-D2	
θ H(1)-C(1)-N (deg)	116.109	115.985	115.765	l
θ H(1)-C(1)-C(2) (deg)	120.355	121.647	122.003	
θ H(2)-C(2)-C(1) (deg)	120.247	119.696	119.686	
θ H(2)-C(2)-C(3) (deg)	121.236	121.431	121.520	
θ H(3)-C(3)-C(2) (deg)	120.707	120.614	120.537	
$\theta C(1)$ -N-C(1) (deg)	117.308	118.751	119.232	
$\theta C(2)$ -C(1)-N (deg)	123.537	122.366	122.232	
$\theta C(1)-C(2)-C(3)$ (deg)	118.585	118.869	118.779	
$\theta C(2)$ -C(3)-C(2) (deg)	118.517	118.770	118.922	

Table S5. (Part 2 of 2) Calculated structural parameters for pyridine as free molecule and when interacting with the ZnS(110) surface.

	Free	$\theta = 0.5$ ML	Δv		Free	$\theta = 0.5 \text{ ML}$	Δv
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)		(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
Al mode	5			B2 mode.	5		
v_1	590	630	39	v_{14}	648	648	-1
<i>V</i> 2	975	1010	35	V 15	1042	1064	22
<i>V</i> 3	1017	1026	9	V16	1135	1145	10
\mathcal{V}_4	1079	1067	-12	v_{17}	1294	1305	10
<i>V</i> 5	1215	1207	-8	<i>V</i> 18	1342	1339	-3
<i>V</i> 6	1450	1469	18	V 19	1427	1437	11
\mathcal{V}_7	1573	1596	23	V20	1577	1572	-5
v_8	3078	3100	22	<i>v</i> ₂₁	3073	3107	34
V9	3099	3115	15	V22	3112	3127	14
v_{10}	3122	3135	13				
A2 mode	S			B1 mode.	S		
<i>v</i> ₁₁	359	369	9	V23	401	417	16
<i>V</i> 12	870	850	-20	V24	696	680	-16
<i>V</i> 13	970	963	-8	V25	744	744	0
				V26	927	924	-3
				V 27	988	988	-1

Table S6. Calculated vibrational frequencies for pyridine as free molecule and when interacting with the ZnS(110) surface.

DFT starting configurations for adsorption simulations



Figure S7. Starting configurations employed for the simulation of the adsorption of small molecules on the ZnS(110) surface: (a) pyridine, (b) CO₂ as Lewis base, (c) CO₂ as Lewis acid, (d) CO, (e) H₂O, (f) methanol.

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