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**Abstract**

→ Oriented (0001) CdX (X = S, Se) crystals selectively adsorb  $\text{MoS}_4^{2-}$  onto the <sup>Cadmium</sup> Cd-rich faces. Binding of  $\text{MoS}_4^{2-}$  is effected by dipping the CdX crystals into  $\text{CH}_3\text{CN}$  containing 20 mM  $[\text{Et}_4\text{N}]_2\text{MoS}_4$ . Removal of the crystal from the solution followed by rinsing with  $\text{CH}_3\text{CN}$  leaves  $\text{MoS}_4^{2-}$  on the Cd- but not X-rich face of the crystal as detected by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The specificity for Cd-face vs. X-face binding is typically 5:1 as determined by XPS and AES data for both faces of the same crystal. S element maps for the  $\text{MoS}_4^{2-}$ -modified, Cd-face of CdSe crystals reveal non-uniform binding of  $\text{MoS}_4^{2-}$ . There is a correlation of the regions of  $\text{MoS}_4^{2-}$  binding with the crystal planes revealed in the pretreatment/etch procedure.



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Face-Specific Interaction of  $\text{MoS}_4^{2-}$  with  
Oriented Crystals of (0001)  $\text{CdX}$  ( $X = \text{Se}, \text{S}$ )

by

James J. Hickman and Mark S. Wrighton

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[Prepared for publication as a Communication to the Editor  
of the Journal of the American Chemical Society]

**Face-Specific Interaction of  $\text{MoS}_4^{2-}$  with Oriented Crystals  
of (0001) CdX (X = Se, S)**

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**Abstract**

Oriented (0001) CdX (X = S, Se) crystals selectively adsorb  $\text{MoS}_4^{2-}$  onto the Cd-rich faces. Binding of  $\text{MoS}_4^{2-}$  is effected by dipping the CdX crystals into  $\text{CH}_3\text{CN}$  containing 20 mM  $[\text{Et}_4\text{N}]_2\text{MoS}_4$ . Removal of the crystal from the solution followed by rinsing with  $\text{CH}_3\text{CN}$  leaves  $\text{MoS}_4^{2-}$  on the Cd- but not X-rich face of the crystal as detected by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The specificity for Cd-face vs. X-face binding is typically >5:1 as determined by XPS and AES data for both faces of the same crystal. S element maps for the  $\text{MoS}_4^{2-}$ -modified, Cd-face of CdSe crystals reveal non-uniform binding of  $\text{MoS}_4^{2-}$ . There is a correlation of the regions of  $\text{MoS}_4^{2-}$  binding with the crystal planes revealed in the pretreatment/etch procedure.

We wish to communicate that  $\text{MoS}_4^{2-}$  adsorbs selectively on the Cd-rich face of oriented crystals of (0001) CdX (X = S, Se) and that the binding to the Cd-rich face is non-uniform. We have used X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to demonstrate the selectivity of the  $\text{MoS}_4^{2-}$  adsorption on CdX. In this work we have extended previous studies on the interaction of anionic S-donor species such as dithiocarbamates,<sup>1</sup> thiolates,<sup>2-4</sup> and polysulfides<sup>5-7</sup> on CdX crystals. Such studies reveal that anionic S-donors can strongly and favorably influence the CdX/electrolyte interface energetics to give highly efficient photoelectrochemical devices.<sup>1-3,5-7</sup> Differential capacitance measurements have shown that the Cd-, but not S-, face of (0001) CdS interacts strongly with  $\text{S}^{2-}$ .<sup>8</sup> More recently it has been shown that  $\text{Fe}(\text{CN})_6^{3-/4-}$  interacts favorably only with the Cd-rich face of CdX.<sup>9</sup> This study was undertaken to better understand the role of crystal orientation in determining the degree of interaction of CdX with anionic S-donor compounds. We chose to investigate  $\text{MoS}_4^{2-}$  as an adsorbate, because of its high charge to size ratio.

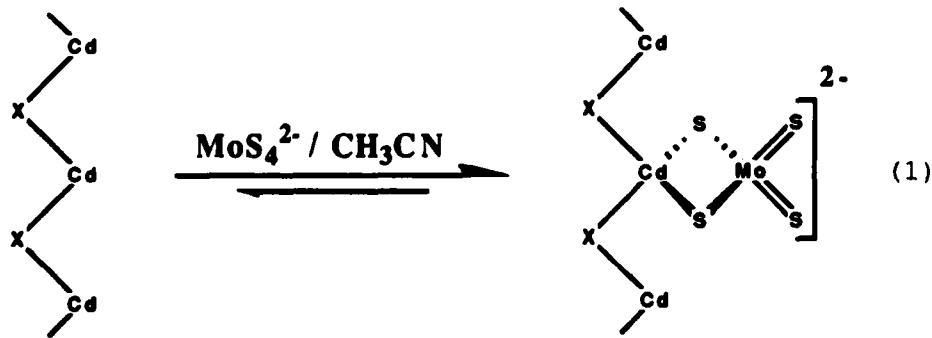
Experiments were carried out using n-type CdX single crystals (1-2 mm thick and 0.2-0.4 cm<sup>2</sup> in area from Cleveland Crystals, Cleveland, Ohio) cut perpendicular to the c-axis to expose the (0001) face. The CdX crystals were first cleaned in concentrated  $\text{H}_2\text{SO}_4$  to remove C-containing

deposits. The CdS crystals were then etched in 12 M HCl<sup>10</sup> for 30 s and rinsed with copious amounts of H<sub>2</sub>O and then with CH<sub>3</sub>CN. The CdSe crystals were etched in a 3:1 mixture of HCl:HNO<sub>3</sub> for 15 s, rinsed with H<sub>2</sub>O, and then exposed to a 1 M KCN solution for 5-10 min.<sup>10</sup> The crystals were finally rinsed with H<sub>2</sub>O and then with CH<sub>3</sub>CN. AES analysis of the etched CdX crystals indicates the presence of some adventitious C and O, but no other contaminating elements were detected.

The CdX crystals were modified with MoS<sub>4</sub><sup>2-</sup> by immersing them for 5 min in a 20 mM solution of [Et<sub>4</sub>N]<sub>2</sub>MoS<sub>4</sub><sup>11</sup> dissolved in distilled and deoxygenated CH<sub>3</sub>CN. The crystals were then rinsed with CH<sub>3</sub>CN for 1-2 min and stored under vacuum prior to introduction into the spectrometer. The crystals were examined by XPS and/or AES.<sup>12</sup>

CdS crystals modified with MoS<sub>4</sub><sup>2-</sup> were examined principally by XPS because the element Mo is much more easily detected by XPS than AES. CdSe crystals were examined by AES (for S) and XPS (for Mo and S). Both AES and XPS show selective binding of MoS<sub>4</sub><sup>2-</sup> to the Cd-rich face of CdX. Representative XPS data are shown in Figure 1 for CdS. Spectra were taken on both sides of the same crystal to eliminate artifacts arising from differences between crystals, and essentially the same result was found for each of >10 independently prepared samples. The Mo signal on the Cd-rich face is at least five times that on the X-rich face. The peak energy of the Mo 3d<sub>5/2</sub> signal is 232.6 eV (using

$\text{Cd}^{2+} 4d_{5/2}$  at 405.1 eV as a reference) which is consistent with  $\text{Mo(VI)}^{13}$  and suggests that the  $\text{MoS}_4^{2-}$  remains intact after adsorption onto the surface of the crystal. The Mo/S ratio and peak positions in the XPS of  $\text{MoS}_4^{2-}$ -treated CdSe are the same as for pure  $[\text{Et}_4\text{N}]_2\text{MoS}_4$ . The S 2s peak (on CdS) and Se 3s peak (on CdSe) in XPS measurements were used to calibrate the absolute magnitude of the Mo 3d peaks, and we conclude that there is roughly one monolayer of  $\text{MoS}_4^{2-}$  on the Cd-rich face of CdX. Prolonged washing of the  $\text{MoS}_4^{2-}$ -treated CdX with  $\text{CH}_3\text{CN}$  does lead to removal of the Mo signal. The results are consistent with reversible binding of intact  $\text{MoS}_4^{2-}$  to the Cd-rich face of (0001) CdX represented in equation (1).



The SEM of the Cd-rich face of CdSe, Figure 2, shows a surface with many sharp ridges, irregularities, and etch pits. The etch pits consist of planes of differing crystallographic orientation. Comparison of the S map from AES to the SEM indicates that the  $\text{MoS}_4^{2-}$  interacts only with certain features on the Cd-rich face of CdSe. This pattern of S AES signals does not arise from differential charging,



because the Cd map from AES is uniform over the region where there is significant variation of the S. The results for (0001) CdSe show that  $\text{MoS}_4^{2-}$  adsorbs selectively on the Cd-rich face, but the binding on the Cd-face is non-uniform.

Studies are in progress to pursue the relation between the extent of surface non-uniformity (and crystal orientation) and the magnitude of the flat-band potential shift of CdX in solvent/electrolyte media as a function of adsorbate ( $\text{MoS}_4^{2-}$ ) concentration. Frequency dependent interfacial capacitance measurements<sup>14</sup> have been interpreted to mean that the Cd face of (0001) CdS is composed of regions with different flat-band potentials. Differences in surface morphology of the Cd-rich face and the S-rich face are revealed by SEM and may be a factor in the face selective binding of  $\text{MoS}_4^{2-}$ . For now, however, it is tempting to conclude that selective binding of  $\text{MoS}_4^{2-}$  occurs at sites that can best accommodate the structure represented in equation (1).

Aside from CdX/adsorbate interactions, several III-V semiconductor/adsorbate systems are of interest. These include GaAs functionalized with Ru,<sup>15</sup> Co,<sup>16</sup> and Os<sup>17</sup> and the selective modification of (111) InP on the P-rich face.<sup>18</sup> These systems are to be investigated by scanning AES to establish whether modification is uniform.

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eV. AES and XPS reference data for Cd, S, Se, and Mo can be found in: Handbook of Auger Electron Spectroscopy, 1978 (AES) and Handbook of X-ray Photoelectron Spectroscopy, 1979 (XPS) published by Perkin-Elmer Corp., Eden Prairie, MN.

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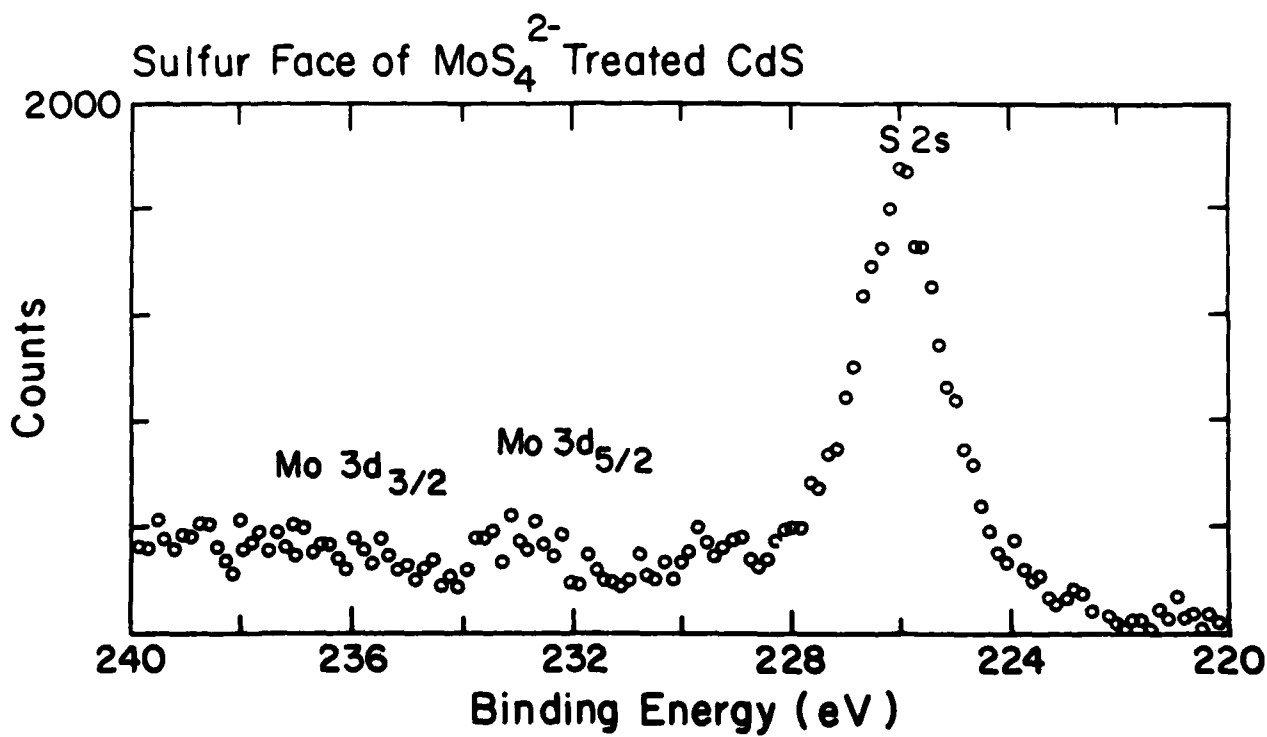
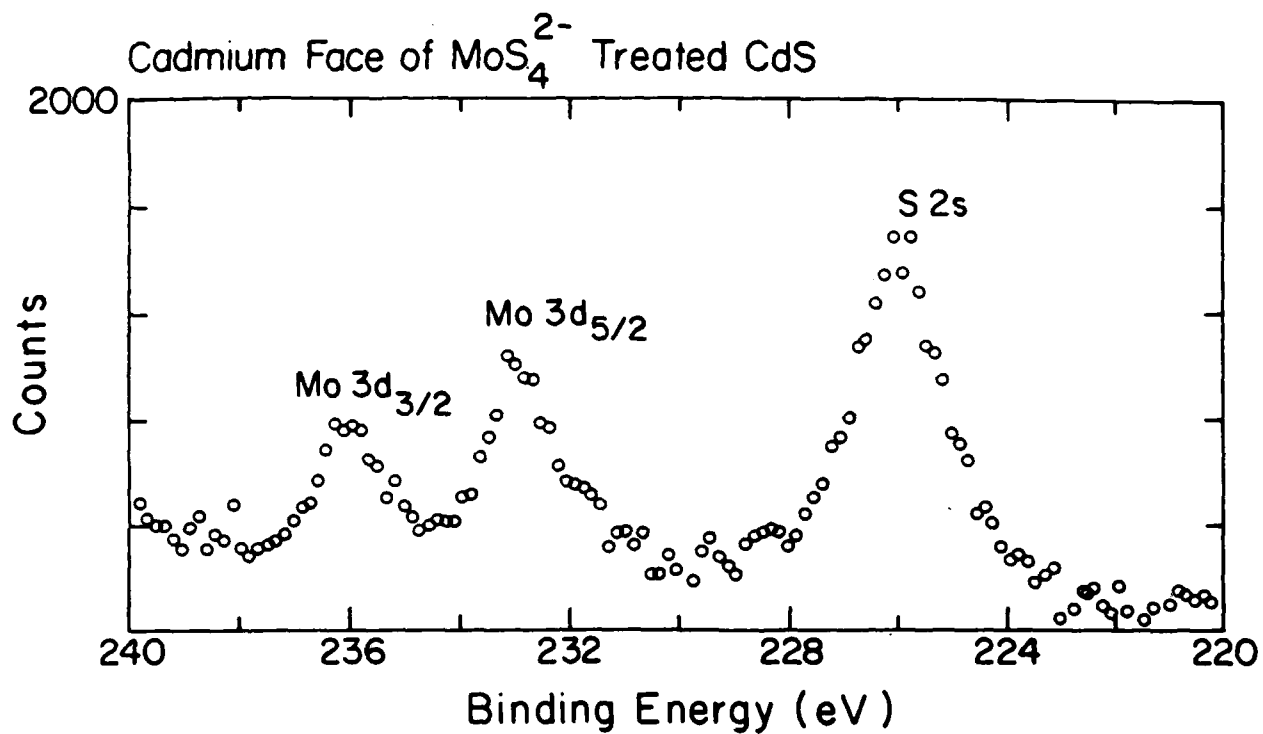
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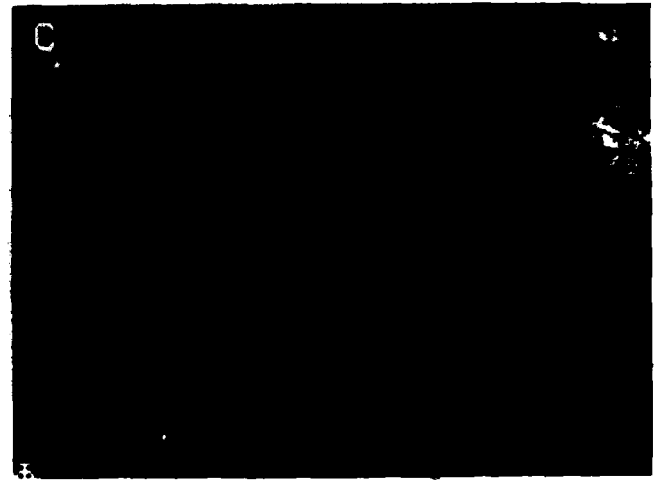
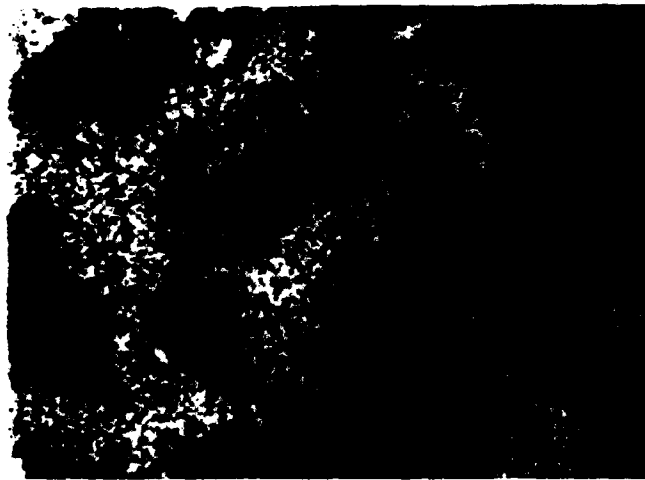
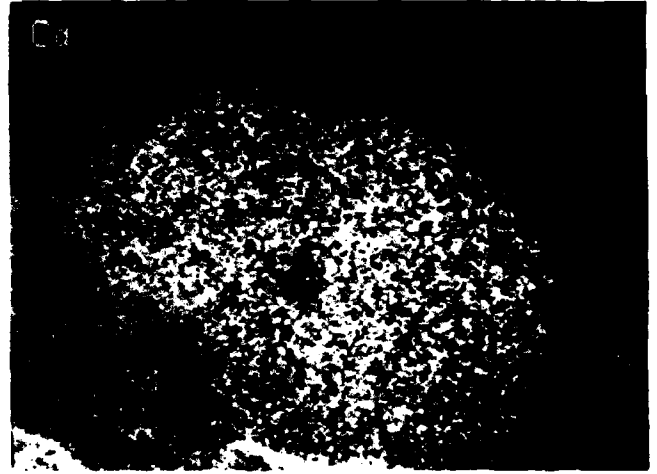
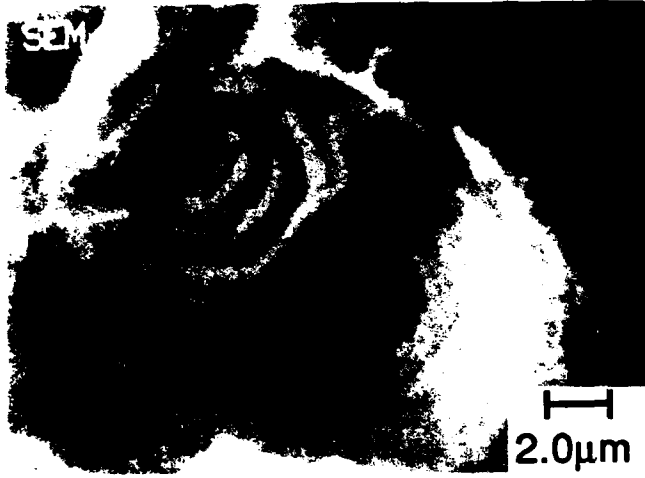
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**Figure Captions**

**Figure 1.** XPS data showing  $\text{MoS}_4^{2-}$  adsorption on only the Cd-rich face of oriented (0001) CdS.

**Figure 2.** Three element maps (S, C, and Cd) of an etch-pit on the Cd-rich face of (0001) CdSe depicted in the SEM in upper left corner. The surface concentration of the elements is proportional to the brightness in each photograph. Carbon is adventitious from exposure to atmosphere after  $\text{MoS}_4^{2-}$  interaction. Note the Cd signal is obscured where the C coverage appears large.







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