

The Role of the Nanoscale in Surface Reactions: CO₂ on CdSe

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Cd-rich CdSe nanocrystals below a critical size, under illumination, catalyze CO₂ fixation, but bulk CdSe surfaces do not. We report first-principles calculations in which we determine the roles of faceting, deviations from stoichiometry, photoexcitation, and electron confinement, and the specific physics of the nanoscale. We further establish that catalysis does *not* occur at the nanocrystal surface; instead, neutral molecules adsorb, desorb negatively charged, and react elsewhere. Finally, we predict that *n*-type doped CdSe nanocrystals would be effective catalysts without photoexcitation.

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It is well known that nanoscale systems show new physical properties, for example, the opening of the semiconductor band gap due to electron confinement [1–6]. Semiconductor nanocrystals have been shown to be effective photocatalysts for the artificial fixation of CO₂, i.e., its incorporation in organic molecules such as formic acid, which is a major environmental issue [7–10]. It has been assumed that catalysis occurs on the semiconductor surface: Adsorbed CO₂ molecules become negatively charged and thus more reactive. Although bulk CdS [11,12] and ZnS [11,13] surfaces catalyze CO₂ fixation in the presence of light, CdSe surfaces do not [3]. However, Cd-rich CdSe *nanocrystals* below a certain critical size *are* efficient photocatalysts [3]. Several possible mechanisms have been invoked to account for the significance of the nanoscale, with model calculations that provided supporting evidence for some of these effects [3–6,14–18], but a comprehensive atomic-scale description of the entire process, documenting the precise role of the nanoscale, is not available.

In this Letter, we report a set of parameter-free first-principles calculations that were designed to probe precisely the distinct role of the nanoscale and identify the origin of the contrasting behavior between bulk surfaces and nanocrystals below a critical size. Here is a summary of the sequence of calculations and results. First, we examined whether a CO₂ molecule chemisorbs on flat stoichiometric CdSe surfaces. We found only very weak physisorption, when the molecule is no more reactive than in the free state. Then we examined possible chemisorption at Cd or Se surface vacancies. We found that CO₂ bonds metastably only at Se vacancies with a specific backbond arrangement [Figs. 1(a)–1(c)]. In the bonded state, the molecule draws extra electron density from the back bonds [Figs. 1(d) and 1(e)], becoming negatively charged, thus becoming reactive with organic molecules in the catalytic system. Such a process confirms the observed need for a Cd-rich (Se deficient) surface, *but would not depend on whether one uses a flat or a nanocrystal surface as long as*

both are Se deficient. We noted that the barrier for desorption is small, ~ 0.5 eV (Fig. 2), suggesting that, even at room temperature, CO₂ molecules would be constantly chemisorbing and desorbing. We inquired, therefore, whether a chemisorbed molecule can desorb and carry an extra electron with it. It does *not* on its own, because of a high energy cost (1.3 eV). The reason for the high energy cost is that the electron must come from states near the semiconductor's valence band edge, whereas the CO₂ lowest unoccupied molecular orbital (LUMO) state is quite high (Fig. 3). That is the reason why photoexcitation is essential for the catalytic process to occur. One must first excite electrons to the conduction bands. In order to mimic the effect, we replaced a Cd atom below the surface with an In atom, doping the crystal *n*-type. The energy cost for a bonded CO₂ molecule to desorb negatively charged dropped to only 0.4 eV and the barrier for desorption became smaller (~ 0.3 eV) (Fig. 2). *It is at this last step that a nanocrystal enters the scene as an absolute necessity*. As is well known, the energy gap of a nanocrystal increases with decreasing size. Using existing calculations [2] for the dependence of the CdSe nanocrystal energy gap on diameter (Fig. 4), we estimate that the critical diameter to enable the free flow of crystal electrons to desorbing CO₂ molecules is about 3.5 nm, which compares well with the experimental value of 5 nm [3].

The net result is that, fundamentally, the most important role of the nanoscale is the opening of the band gap. Other nanocrystal factors are secondary. For example, one can form the right kinds of vacancies on typical CdSe surfaces, but, of course, nanocrystals provide a natural way to expose more surface area. Similarly, one can have Cd-rich free surfaces, though the nanocrystal faceting may play a role in enhancing the right kind of nonstoichiometry. Though there is experimental evidence that CdSe nanocrystals are intrinsically Cd rich [19], there is no indication that the density of Se vacancies is a function of nanocrystal size. We note, however, that Inoue *et al.* [20] attributed the observed enhancement of photocatalysis by smaller ZnS

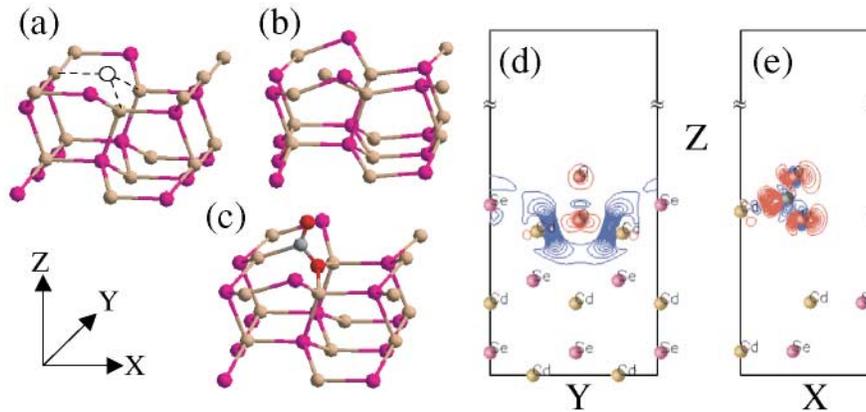


FIG. 1 (color). Surface atomic configurations and charge densities. (a) Schematic showing the atomic arrangements on a CdSe(10 $\bar{1}$ 0) surface containing a Se vacancy with all the atoms frozen at their original positions. (b) The optimized atomic geometry of the Se vacancy. (c) The optimized atomic geometry for a CO₂ molecule adsorbed in the Se vacancy. (d) and (e) Plots of charge density difference $\Delta\rho = \rho(\text{surf} + \text{vac} + \text{CO}_2) - \rho(\text{surf} + \text{vac}) - \rho(\text{CO}_2)$; (d) the XZ plane with $Y = 0.5$ and (e) the YZ plane with $X = 0.5$; red lines represent a gain of charge and blue lines a loss of charge.

nanocrystals to a possible increase of nonstoichiometry with decreasing size. Such issues are beyond the reach of first-principles calculations.

It is intriguing to contrast the above results for CdSe with experimental results for CdS and ZnS. In the latter cases, nanocrystals are not essential, but cation enrichment and photoexcitation are. The reason is that bulk CdS and ZnS already have a large enough band gap.

We now give technical information about the calculations and analyze the results in more detail. The calculations were performed using density functional theory [21,22], the generalized-gradient approximation for the exchange-correlation potential [23], Vanderbilt ultrasoft pseudopotentials [24], and a plane-wave basis set [25,26]. The energy cutoff for the basis was set at 350 eV, as determined by convergence studies. We considered

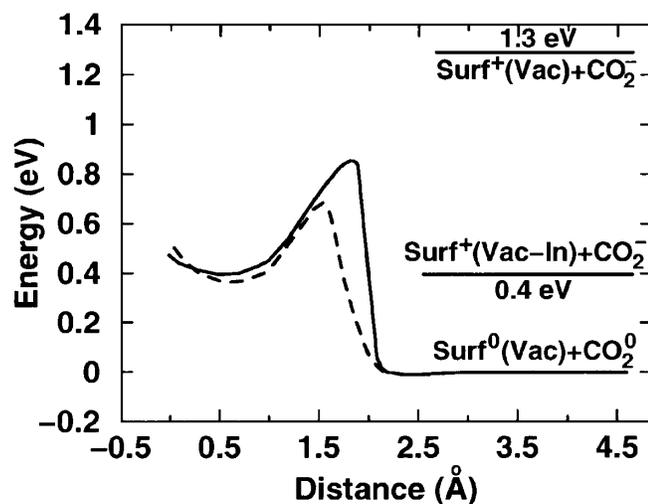


FIG. 2. The total energy of a CO₂ molecule chemisorbed in a Se vacancy on the CdSe(10 $\bar{1}$ 0) surface as a function of the vertical distance between the C atom and the ideal truncated surface.

several different surfaces, i.e., (10 $\bar{1}$ 0), (0001), (000 $\bar{1}$), and (10 $\bar{1}$ 2), which may appear in a CdSe nanocrystal [27]. A 2×2 supercell with six atomic layers separated by a vacuum layer of 14 Å was used. Two special k points were used in the irreducible wedge of the Brillouin zone in conjunction with the Monkhorst-Pack scheme. The surface atomic arrangements and the configuration of the adsorbed CO₂ molecule were optimized until the forces on atoms were smaller than 0.05 eV/Å. The convergence of the results was checked with respect to supercell size, the slab and vacuum thickness, and k points.

The more detailed results are as follows. First of all, CO₂ molecules do not chemisorb on flat stoichiometric CdSe surfaces. They only physisorb with a binding energy that is much less than 0.1 eV, the limit of computational accuracy.

In Fig. 1 we show the atomic bonding at a typical Se vacancy before and after bonding of a CO₂ molecule. Only Se vacancies on the (10 $\bar{1}$ 0) surface or on the (10 $\bar{1}$ 0) terraces of the (10 $\bar{1}$ 2) surface bind the molecule in this fashion because such a vacancy provides a suitable geometry for bidentate binding to three Cd atoms. The CO₂ molecule is

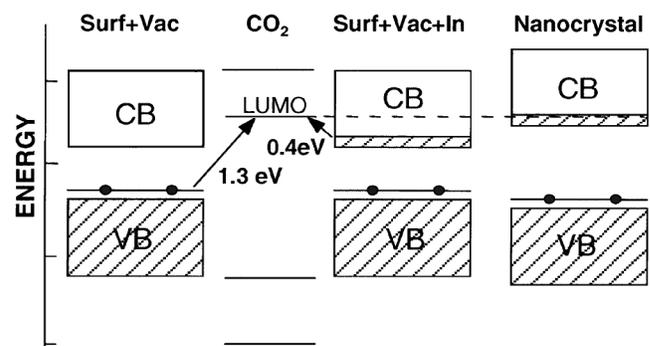


FIG. 3. Illustration of electron transfer from surfaces or nanocrystals to the CO₂ molecule. The localized energy level near the valence band edge is caused by a Se vacancy.

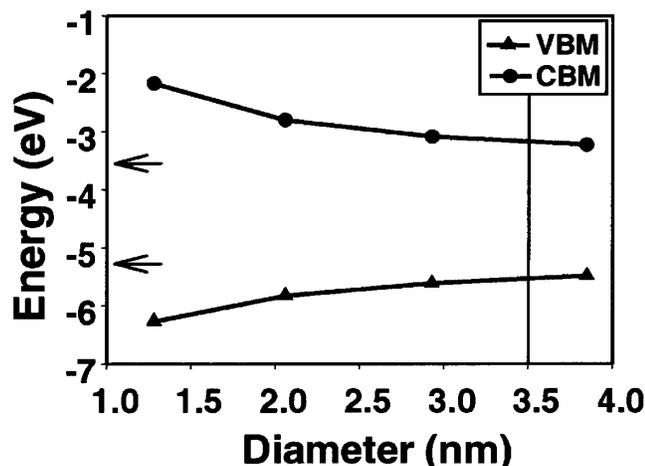


FIG. 4. Dependence of the valence band maximum (VBM) and the conduction band minimum (CBM) on the nanocrystal size. The arrows indicate the VBM and CBM of bulk CdSe. The vertical line shows the nanocrystal size predicted in the present work. The theoretical values are from Wang and Zunger [2].

asymmetric with one C—O bond 1.21 Å (the upper bond in the figure) and another one 1.34 Å (the lower one). The bond angle between two C—O bonds is 127°. Other Se vacancies such as those on the (000 $\bar{1}$) surface do not chemisorb a CO₂ molecule. We also note that the Se vacancy on the (10 $\bar{1}$ 0) surface exhibits a nonsymmetric rebonded atomic configuration which is similar to the P vacancy on the InP(110) surface [28].

In the bonded state, CO₂ attracts electrons from the backbonds as shown in Figs. 1(d) and 1(e). We integrated the electron density within atomic spheres surrounding each atom of the CO₂ molecule and the sum of electrons is roughly 17.6 (i.e., a gain of 1.6 electrons). Though the number obviously depends on the size of the spheres, the resulting large number indicates a definite excess electron density. The result is consistent with the fact that the free negatively charged CO₂ molecule is bent, very much like the molecule bonded at a vacancy as shown in Fig. 1(c). Previous studies also found that CO₂ gains electrons when it adsorbs on semiconductor or metal surfaces, assuming the bent geometry of CO₂⁻ [4,29].

In Fig. 2, we show the total energy of a CO₂ molecule plus a CdSe surface containing a Se vacancy as a function of the vertical distance between the C atom and the ideal truncated surface (solid curve). It is clear that binding is metastable; i.e., the bound state has a higher energy than the free state (earlier calculations of the binding of CO₂ in S vacancies on CdS nanocrystal surfaces resulted in much larger values and a stable bonding state because the surface was simulated by only the nearest neighbors as a very small molecule [4]). The present calculations show that CO₂ chemisorbed in a S vacancy on the CdS(10 $\bar{1}$ 0) surface is metastable. The barrier for adsorption is 0.9 eV, whereas the barrier for reemission is 0.5 eV.

Reemission of a neutral molecule is described by the same solid curve describing adsorption, as shown in Fig. 2. If an electron is carried by the molecule, leaving a positively charged surface, the final state would have a total energy that is 1.3 eV higher, as shown in the figure. Thus, reemission of a negatively charged CO₂ molecule is not favored energetically. The relevant energy levels of the crystal and the molecule are shown in Fig. 3.

The dashed curve in Fig. 2 corresponds to a CO₂ molecule approaching a CdSe surface with a Se vacancy when one of the Cd atoms far from the vacancy is replaced by an In atom. The effect of the substitution is to place an electron in the conduction bands of CdSe, which is then available to be carried away by the molecule. We see that the barrier is lowered by 0.2 eV. This result indicates that it is easier for negatively charged CO₂ molecules to desorb from nanocrystal surfaces in the presence of light, but it still costs 0.4 eV. The relevant energy levels are again seen in Fig. 3.

In Fig. 4 we show the variation of the band gap of CdSe as a function of nanocrystal size, as calculated by Wang and Zunger [2]. As shown in the figure, nanocrystals of diameter 3.5 nm or smaller cause the conduction band minimum to move up by 0.4 eV, *allowing the free transfer of conduction electrons from the nanocrystal to the departing CO₂ molecule*. This prediction is comparable with the experimentally determined nanocrystal size of 5 nm [3]. It should be noted that, whereas the nanocrystal calculations of Ref. [2] have the correct experimental band gap by the use of empirical potentials, the present calculations have no empirical adjustments. The LDA value of the energy gap is, as usual, smaller than the experimental value. The value of 3.5 nm for the critical nanocrystal size is obtained by using the same scaling of the gap with size as in Ref. [2].

The above results illustrate a unique case where the precise role of the nanoscale has been elucidated and the atomic-scale mechanisms have been unraveled. Note that there was no need to perform any chemisorption calculations on a real nanocrystal to deduce the information. All calculations were performed on structures that were selected to provide answers to specific questions, testing a particular scenario for the complete process. Fixation occurs *remote* from the nanocatalyst; the role of the nanocrystal is to convert neutral CO₂ to negatively charged CO₂ which is highly reactive. The use of a dopant atom to simulate photoexcitation (the latter is difficult to implement directly in a calculation) led to an extra bonus prediction that In-doped nanocrystals would not require light to achieve fixation of CO₂.

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