ARTICLE OPEN $Co_6Se_8(PEt_3)_6$ superatoms as tunable chemical dopants for two-dimensional semiconductors

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Electronic, optoelectronic, and other functionalities of semiconductors are controlled by the nature and density of carriers, and the location of the Fermi energy. Developing strategies to tune these parameters holds the key to precise control over semiconductors properties. We propose that ligand exchange on superatoms can offer a systematic strategy to vary these properties. We demonstrate this by considering a WSe₂ surface doped with ligated metal chalcogenide $Co_6Se_8(PEt_3)_6$ clusters. These supperatoms are characterized by valence quantum states that can readily donate multiple electrons. We find that the WSe₂ support binds more strongly to the Co_6Se_8 cluster than the PEt₃ ligand, so ligand exchange between the phosphine ligand and the WSe₂ support is energetically favorable. The metal chalcogenide superatoms serves as a donor that may transform the WSe₂ p-type film into an n-type semiconductor. The theoretical findings complement recent experiments where WSe₂ films with supported $Co_6Se_8(PEt_3)_6$ are indeed found to undergo a change in behavior from p- to n-type. We further show that by replacing the PEt₃ ligands by CO ligands, one can control the electronic character of the surface and deposited species.

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INTRODUCTION

Semiconductors used in most technological applications are doped with impurities whose kind, concentration, and location of impurity level determine the electronic, optical, and transport characteristics of the semiconductor.¹⁻³ For bulk materials, the doping is generally carried out by implanting the impurities in an intrinsic material where the dopants can occupy interstitial sites or substitute for host atoms.^{4,5} This has limitations, as not all semiconductors allow an unlimited pathway to incorporation of any impurity in any amount.⁶ For two-dimensional or thin film semiconductors, an alternative approach to overcome this limitation is to deposit dopants on surface that can chemically bind to surface sites and change the carrier density either through fields and/or donation of carriers through charge transfer.^{7–10} For example, alkali atoms have been used as donors of electrons as they have low ionization potentials.¹¹ However, atoms can generally donate only one electron with low ionization energy as the ionization energy increases substantially beyond the removal of first electron. It would be ideal if donors could donate multiple electrons with low ionization energies, and it would also be ideal if the impurity level of the donors could be manipulated. The aim of the present theoretical studies is to propose a first step towards such an objective by using superatoms as tunable multiple electron donors.¹²⁻¹⁵

The purpose of this paper is to carry out theoretical studies to understand how the donor and acceptor behaviors of selected superatomic clusters bound to a semiconductor surface can be affected through ligand exchange, ligand removal, and through the doping of the semiconductor. This paper is motivated in part by the study of Yu et al.³ who found that by depositing $Co_6Se_8(PEt_3)_6$ superatoms on a p-type WSe₂ support, the WSe₂ was transformed from a p-type to an n-type semiconductor. These materials could be made air stable and offer a simple strategy for

doping of two-dimensional semiconductors. We will examine not only how a superatom can be used as a super donor to transform the nature of carriers but how they can be used to modulate the location of the impurity level and even induce magnetic carriers. It was some time ago that one of the present authors proposed that the quantum confinement in small compact metal clusters, that leads to bunching of quantum states into groups, could also lead to stable motifs with well-defined valence enabling their description as superatoms.¹² These superatoms exhibit electronic characteristics similar to atoms and over the past years, superatoms mimicking a large variety of elements have been identified.¹⁶⁻²¹ In particular, superatoms with closed electronic shells are found to be more stable but have higher ionization energies. Our first objective is to demonstrate how such units could be transformed into effective multiple electron donors. While the larger size of superatoms reduces the rate of increase of energy as multiple electrons are withdrawn, compared to single atoms, the increase in energy is still large. We have just identified a novel approach by which one can not only reduce the first ionization energy of the superatoms but also reduce the energy to withdraw multiple electrons. We have found that this can be accomplished by attaching ligands that form charge transfer complexes.^{22,23} In such ligated species, every time an electron is withdrawn, the crystal field generated by the ligands pushes up the electron manifold and in particular the highest occupied molecular orbital (HOMO), thus reducing the cost for withdrawing the subsequent electron. The effect, which is especially prominent in charge donating ligands such as phosphines is so powerful that the energy reduction can be several electron volts. For example, consider the ligated chalcogenide cluster Co₆Se₈(PEt₃)₆. The successive energies required to remove the first four electrons in a Co₆Se₈(PEt₃)₆ superatom are 4.76, 7.48, 10.38, and 12.88 eV, respectively, due to the stabilization by the ligands.²⁴ For

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Fig. 1 Structure of WSe_2, Co_6Se_8(PEt_3)_6, Co_6Se_8(PEt_3)_5 on WSe_2, and Co_6Se_8(PEt_3)_6 on WSe_2

comparison, the ionization potential of the bare clusters are 7.42, 10.83, 14.83, and 18.85 eV. These ionization potentials are significantly lower than those of atoms, and we note that the energy required to remove even the 4th electron is less than the first ionization energy of a Hydrogen atom. The comparison of ionization potentials and work functions can be tricky due to the size difference, and the work function of a surface is usually roughly half the ionization potential of the atom. Since we are focusing on the use of clusters as charge transfer dopants, we compare the I.Ps with atoms and clusters which would be alternative charge transfer dopants. Furthermore, several materials have been identified in which the Co₆Se₈(PEt₃)₆ cluster is found to be in the +2 oxidation state.^{14,15,25,26} The location of the Fermi energy in such systems can be controlled by changing the ligands providing the ability to control the band gap energy using the same metallic core.^{22,23} We also show that superatoms acquire a spin magnetic moment for partial coverage with ligands offering potential for creating magnetic semiconductors unless the metal core can relax through a Jahn–Teller distortion.^{27,28} The properties of these semiconductors with supported superatomic clusters can be understood by considering the surface as a ligand that stabilizes a superatomic cluster. The binding of the superatom cluster to the support and the ligands may be understood by examining the balance of donor and acceptor properties of the surface, ligand, and superatomic cluster allowing both the tuning of electronic properties and the use of the cluster as a probe of the character of the carriers in the semiconductor surface.

RESULTS

While bulk WSe₂ is an indirect band gap semiconductor, previous studies have shown that monolaver transition metal chalcogenides are direct band gap semiconductors.²⁹⁻³² We start with the band structure of a single layer of WSe2, which has a direct band gap. The semiconductor layer was modeled by a supercell with edges of size 22.975 Å and containing 147 atoms (Fig. 1a). The electronic structure was investigated within generalized gradient approximation (GGA) using the gradient corrected functional proposed by Perdew et al.³³ Since GGA functionals usually underestimate the band gaps, supplementary calculations of the band gaps were performed using the HSE06 hybrid functional.³⁴ The calculated band gap using PBE was 1.98 eV. The corresponding gap using HSE06 functional was 2.54 eV compared to the measured band gap of 2.02 eV. Because the gap was closer to measured value using the PBE functional, all results in the main text will use the PBE functional, while HSE06 results are shown in the supplemental information.

As mentioned in the introduction, doping of thin film semiconductors such as metal chalcogenides and graphene may be achieved by using charge transfer dopants that bind to the surface and act as either a charge donor or acceptor. Studies by Javey and co-wrokers found that NO₂ could act as a p-type dopant when bound to WSe_{27}^{35} and further studies found O_2 also acted as a ptype dopant.³⁶ For n-type doping, amines bound to MoS₂ were successful,³⁷ and K may also act as an n-type donor when deposited on WSe₂.¹¹ The judicious choice of redox-active molecules has been demonstrated for tuning the work function in WSe₂.³⁸ Also, platinum and palladium nanoparticles have been used to tune the electrical properties of WSe₂.³⁹ Interestingly, not every molecule studied has effectively changed the electronic properties of the semiconductor. For example, C₆₀, an excellent electron acceptor was studied on MoS₂, and no doping effect was observed.⁴⁰ These studies show that when a molecule is bound to a thin layer semiconductor, the characteristics of the semiconductor may be changed, although in these studies the dopants appear to be single electron donors or acceptors. Here, we wanted to examine if superatomic clusters like Co₆Se₈(PEt₃)₆ that have multiply degenerate HOMO and low ionization energy could be used as donors.

The electronic structure of the superatomic cluster Co₆Se₈(-PEt₃)₆ was first calculated using a cubic supercell with 25 Å lattice vectors. The large supercell avoids any interaction between the periodic images. The ground state structure of the cluster is shown in Fig. 1b. The cluster has an ionization energy of 4.76 eV, which is less than that of a Sodium atom. The successive ionization energies of the cluster were 7.48 eV, 10.38 eV, and 12.88 eV for the removal of second, third, and fourth electron. All these are an indication that the cluster has the ability to donate multiple electrons without a significant increase in ionization energy making it an excellent donor. We also calculated that the energy required to remove a PEt₃ ligand is 2.45 eV. We then examined if the cluster could be used to change the transport characteristics of a WSe₂ semiconductor. The fully ligated cluster was placed on the surface of the WSe₂ and the structure was optimized, as shown in Fig. 1c. The cluster was bound to the surface by 1.37 eV and the band gap energy was 0.24 eV. Since the PEt₃ ligands are bound to the metallic core by only 2.45 eV, we examined the possibility that the cluster binds by removing the ligand attached to the Co site and the Co site binds directly to the Se atom on the surface, as shown in Fig. 1d. The binding energy of Co₆Se₈(PEt₃)₅ to the WSe₂ surface was 3.19 eV, around 1.81 eV higher than that of $Co_6Se_8(PEt_3)_6$. Since it takes 2.45 eV to remove a PEt_3 ligand from the Co₆Se₈(PEt₃)₆ cluster, it is energetically more favorable for the $Co_6Se_8(PEt_3)_5$ cluster to bind to the surface than to the ligand, with the WSe₂ surface acting as a sixth ligand. The lone pair on the Se atom in WSe₂ may act as a charge transfer complex in an analogous way as the lone pair of phosphine ligands,



Fig. 2 Structure of Co₆Se₈(PEt₃)_{5-n}(CO)_n clusters on WSe₂



Fig. 3 a) Energies of the valence band, HOMO, LUMO of the Cluster, and the Conduction band, and b) Work function of Co₆Se₈(PEt₃)_n(CO)_{5-n} on WSe₂

explaining the large binding energy. Note that the addition of the $Co_6Se_8(PEt_3)_5$ has decreased the band gap energy of the WSe_2 from 2.02 eV to a HOMO-LUMO gap of 0.52 eV due to filled donor states that are mostly localized on the ligated cluster and the acceptor states below the conduction band of the WSe_2 that are also derived from the superatom. The density of states (DOS) of $Co_6Se_8(PEt_3)_5$ on WSe_2 can be seen in Figure S1, and the

corresponding HSE06 based DOS are shown in Figure S2. One can therefore conduct by exciting electrons from the filled cluster donor to available superatomic states or the conduction band making it an n-type semiconductor. We note that the metal chalcogenide cluster has transferred 0.05 e⁻ to the WSe₂ surface according to a Bader analysis, despite the fact that the interaction is a charge transfer complex that usually assigns the electron to

the species with the lone pair, in this case the WSe₂ surface. While the donor band using the HSE06 is lower in energy than when using the PBE functional both are clearly donors. It is important to highlight that unlike bulk semiconductors, the transition to n-type does not entail breaking of bonds in the pure semiconductor but a chemical linking of the dopant to the surface. In conventional doping, the impurity states have a large radius due to the dielectric function of the host. Here, the nature of the doped semiconductor is very different as the impurity states are largely localized on the ligated cluster but chemically bonded to the host states.

Next we consider the possibility that by substituting the ligands, the electronic structure of the WSe₂ may be controlled. In a recent paper, Champsaur et al. demonstrated that ligand exchange may lead to the synthesis of $Co_6Se_8(PEt_3)_n(CO)_{6-n}$ clusters containing a combination of CO and phosphine based ligands.⁴¹ They further showed that the CO ligands are fairly mobile and can be substituted by diisocyanide ligands allowing the formation of diand tri- superatomic molecules. Here, we are primarily interested in how the donor characteristics could be tuned by replacing PEt₃ ligands by CO ligands. Figure 2 shows the ground state geometry of $Co_6Se_8(PEt_3)_n(CO)_{5-n}$ clusters for n = 0-5. In each case, we examined the geometries corresponding to different locations of CO molecules to determine the most stable configuration. Figure 3a shows the location of the valence and conduction bands of WSe₂ the changes in the Fermi energy of the system, and the LUMO of the cluster orbitals. The formation of donor levels with such a large variation of energies is unprecedented and shows the advantage of using ligated superatoms as donors. A more detailed analysis shows that this effect is directly related to the crystal field created by the ligands that shifts the electronic spectrum of the metallic core. This quantum aspect is best seen in Figure S1 where we show the DOS of the cluster-surface complex as a function of



Fig. 4 The binding energy of $Co_6Se_8(PEt_3)_n(CO)_{n-5}$ to WSe_2 as compared to the binding energy of PEt_3 and CO to $Co_6Se_8(PEt_3)_n_{+1}(CO)_{5\text{-}n}$

the number of CO molecules using the PBE functional whereas Figure S2 shows the corresponding results using the HSE06 functional.

Phosphine ligands tend to act as charge donors, while CO molecules tend to act as charge acceptors.²² The deepening of the electronic spectrum, or downward shift in the energy of the cluster states, as phosphine ligands are replaced with CO is directly related to the crystal field created by the ligands. The charge donating phosphine ligand push the superatomic electronic states up in energy, while CO pulls them slightly down in energy. As a direct consequence of this, the downward shift of the spectrum increases the work function as the number of CO ligands is increased, while the phosphine ligands push up the Fermi energy resulting in a smaller work function. Figure 3b shows the variation of the work function and the band gap that results from this shift, with the results for the HSE06 functional shown in Figure S3.

We next examine the effect of ligand exchange on the binding energy of the $Co_6Se_8(PEt_3)_{5-n}(CO)_n$ cluster to the WSe₂ surface. The binding energy is of special interest because if the surface is acting as an acceptor, and the cluster is acting as a donor, then the binding energy will be enhanced.^{42–44} The change in the binding energy of the cluster to the surface and the binding energy of PEt₃ and CO ligands as a function of the composition of the cluster are shown in Fig. 4. The binding energy is a maximum for $Co_6Se_8(PEt_3)_5$, and the binding energy decreases as the PEt₃ is exchanged for CO. As the PEt₃ acts is a powerful donor, this shows that the WSe₂ surface is acting as an acceptor. The substitution of PEt₃ by CO leads to a change in the polarity of the supported cluster as the cluster is transformed from a donor to an acceptor. This aspect of the system is also demonstrated by the electric dipole moment of the surface, as shown in Figure S4. As the number of CO molecules increases, the dipole becomes more positive, while the dipole becomes more negative with the addition of PEt₃ ligands, consistent with the change in the donor/ acceptor characteristics of the deposited species. For comparison, we show the binding energy of the WSe₂ versus the binding energy of the PEt₃ and CO ligands. This shows that for $Co_6Se_8(PEt_3)_n(CO)_{5-n}$ n = 2-5, the WSe₂ binds the cluster more strongly than the cluster binds the ligand, although for the cluster where n = 0 or 1, the CO and PEt₃ binds more strongly than the WSe₂ surface.

The use of superatoms also offers the possibility of magnetic carriers. The bare Co_6Se_8 cluster has a spin magnetic moment of 10 μ_b and it is reasonable to ask if one could create magnetic species by changing the number of ligands. The structure of the $Co_6Se_8(PEt_3)_n$, n = 4-0 are shown in Figure S5. We examined the ground state of the system as the PEt₃ ligands were successively removed from the superatom. The ground state of $Co_6Se_8(PEt_3)_h$ had a spin magnetic moment of 2 μ_B . The spin magnetic moment increased to 4 μ_B and 6 μ_B for $Co_6Se_8(PEt_3)_n$ n = 3, and 2, and 0,



Fig. 5 The binding energy of $Co_6Se_8(PEt_3)_5$ and $Co_6Se_8(CO)_5$ to WSe_2 with 1–4 Re n-type dopant atoms, and 1–4 Nb p-type dopant atoms, and the binding enhancement energy of $Co_6Se_8(PEt_3)_{5-n}(CO)_n$ to the 4-doped Nb and Re WSe_2 surfaces as compared to the undoped WSe_2

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and 4 μ_B are found for Co₆Se₈(PEt₃) and the bare Co₆Se₈ cluster on WSe₂, respectively. Figure S6 shows the variation of the work function, the PEt₃ binding energy and Figure S7 shows the location of the impurity states as a function of the number of PEt₃ molecules. This shows that one can potentially induce magnetic carriers into the semiconductor by controlling the number of ligands surrounding the superatomic core.

One of the most significant aspects of any semiconductor is the determination of whether it is a p-type or n-type. These determinations are usually carried out by transport measurements. Are there alternate approaches to ascertain the n- and pcharacteristics of the semiconductor? We now show that the superatomic clusters can provide a chemical probe to identify the n- or p- nature of the underlying semiconductor. To demonstrate this fascinating aspect, we first created a p-type semiconductor by replacing one to four W sites by Nb atoms. We similarly created an n-type semiconductor by replacing 1-4W sites with Re atoms. $Co_6Se_8(PEt_3)_5$ is a donor superatom while $Co_6Se_8(CO)_5$ is an acceptor superatom. A donor superatom is expected to bind strongly to a p-type semiconductor while an acceptor superatom is expected to bind to a n-type semiconductor as it can supply electrons more easily than a p-type materials. We therefore monitored the progression of the binding energy of $Co_6Se_8(PEt_3)_5$ and Co₆Se₈(CO)₅ to the semiconductor doped with different number of Re and Nb atoms. Figure 5 shows the variation of the binding energy for both the species, and the structures are shown in Figure S8 and S9. It is remarkable that the binding energy shows a jump across the undoped species. Whereas Co₆Se₈(CO)₅, an acceptor superatom clusters binds more strongly to Re-doped species that are n-type, the Co₆Se₈(PEt₃)₅, a donor superatom, binds more strongly to Nb doped species that are p-type.

To test whether the cluster is donating multiple charges to the support, we next examine the charge transfer from the Co₆Se₈(PET₃)₅ cluster to the doped WSe₂ support. Adding a single p-type dopant, Nb, results in the charge transfer from the cluster to the support increasing from 0.06 e⁻ to 0.56 e⁻. A full electron is not transferred in part because the Se lone pair that binds to the Co is partially assigned to the Co atom, and in part because charge transfer between only one donor and one acceptor is rarely an integer. After a second, third and fourth acceptor are added, the charge transfer increases to +0.72,+0.77, and +0.81 e⁻, respectively. This significant increase following the addition of the second dopant is consistent with the Co₆Se₈ cluster serving as a two electron donor. It appears that the cluster transfers two electrons per cluster when two acceptors are available, consistent with what is observed in superatom-fullerene assemblies.¹⁵ We next examine ligand displacement on heavily n-type doped and ptype doped WSe₂. Figure 5 shows that in the p-type Nb doped system, the Co₆Se₈(PEt₃)₅ has the largest binding enhancement, and as the phosphine ligand is replaced with CO, the binding energy monotonically decreases. The addition of phosphine is enhancing the binding energy. Combined with the fact that multiple doping increases the binding energy of cluster, it shows that adding phosphine leads to the cluster donating multiple electrons to the p-type support. For the n-type WSe₂ support, the addition of CO enhances the binding energy, showing that the addition of the CO make the cluster a better acceptor. These results offer a demonstration that clusters may be used as probes to tune and determine the nature of n- and p- type semiconductors, and that superatom clusters may act as multiple electron donors.

DISCUSSION

To conclude, present studies show that ligated chalcogenide superatomic clusters ($Co_6Se_8(PEt_3)_6$) can be employed to be efficient donors or acceptors by changing the ligands from PEt₃ to CO. We find that it is energetically favorable for the WSe₂ surface

to act as ligand that exchanges with the PEt₃ ligand, resulting in a direct bond between the surface and cluster. When supported on the surface of a layered WSe₂, the efficient donation can transform the surface from a p-type to n-type semiconductor. The Co₆Se₈(PEt₃)₆ cluster may act as a multiple electron donor, due to its very low multiple ionization potential and high degeneracy of HOMO. In particular, for $Co_6Se_8(PEt_3)_{67}$, the energy require to withdraw even the fourth electron is less than the ionization energy of a H atom. The distinguishing feature of the new dopants is that the Fermi energy of the doped system can be varied over a wide range by selectively replacing the PEt₃ ligands by CO ligands. Such a control is important for optoelectronic properties and even for creating semiconductors where the dopants carry magnetic moments. We also show that the variation in the binding energy of Co₆Se₈(PEt₃)₅ and Co₆Se₈(CO)₅ units can be used to characterize the change from p- to n-type in the semiconductor surface, as shown by the intriguing study by Yu et al.³ We hope that the present investigations will stimulate further experimental effort to create semiconductors with tunable chemical potential and nature of carriers.

METHODS

Theoretical studies are based on the dispersion corrected density functional theory (DFT) within the GGA proposed by Perdew, Burke and Ernzerhof (PBE) for the exchange and correlation functional,³³ while using DFT-D2 to include the Van der Waals corrections.⁴⁵ The computations are performed using the VASP code using a plane wave basis set with a cutoff set to 400 eV.^{46,47} The WSe₂ support was modeled by taking a periodic cell with edges of size 22.975 Å and containing 147 atoms, and the layers were separated by 34 Å. Due to the large size of the surface supercell only the Γ point was used for Brillouin zone integration. The structures were not considered optimized until the forces on the atoms were minimized to 0.01 eV/Å or less. Bader charges were used to determine the charge of the individual atoms. Supplementary calculations were performed using the HSE06 hybrid functional.³⁴ The projector-augmented wave method was used to treat electron-ion interactions.⁴⁷ A dipole correction was incorporated along the z-axis of the slab. The dipole correction improves the convergence and allowed for the calculation of the electrostatic potential in the vacuum that was used to calculate the work function of the system.^{48,49} The calculations of the ionization potentials of the free clusters were performed using the ADF code. The structures from the periodic calculation were then optimized with ADF.⁵⁰ The ADF calculations also used the PBE functional along with a TZ2P basis set, and the calculated ionization potentials are adiabatic.³³

Data availability

Supporting information includes the structures, density of states, comparison using a hybrid functional, and other supporting figures.

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ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the *npj Computational Materials* website (https://doi.org/10.1038/s41524-018-0092-9).

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