

Superatom Molecular Orbital as an Interfacial Charge Separation State

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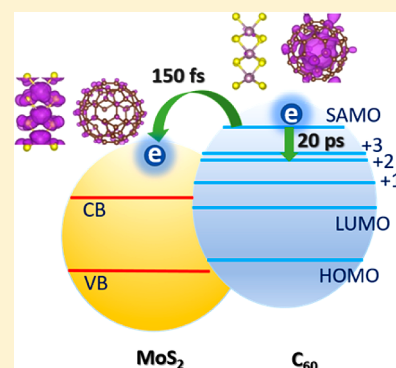
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Supporting Information

ABSTRACT: Hot electron cooling by energy loss to heat through electron–phonon (e–ph) interaction is an important mechanism that can limit the efficiency of solar energy conversion. To avoid such energy loss, sufficient charge separation needs to be realized by extracting hot carriers from the photoconverter before they cool, which requires fast interfacial charge transfer and slow internal hot carrier relaxation. Using ab initio time-dependent nonadiabatic molecular dynamics and taking C_{60}/MoS_2 as a prototype system, we show that the superatom molecular orbitals (SAMOs) of fullerenes, which are bound by the central potential of the whole molecule induced by the charge screening, are ideal media for charge separation. The diffuse character of SAMOs results in extremely weak e–ph interaction and therefore acts as a “phonon bottleneck” for hot electron cooling. Furthermore, it also leads to significant hybridization with other atoms at the interface that induces fast charge transfer. The interfacial charge-transfer rate at the C_{60}/MoS_2 interface is found to be 2 orders of magnitude faster than the hot electron cooling from s-SAMO in C_{60} . This conclusion is generally applicable for different carbon nanostructures that have SAMOs. The proposed SAMO-induced charge separation provides unique and essential insights into the material design and function for solar energy conversion.



Due to the abundance of sunlight, solar power is an important source of clean renewable energy, which can be utilized for the production of alternative fuels with enormous potential for society.¹ A remaining fundamental challenge is the development of efficient methods of harvesting solar energy that are accessible and cost-effective. This challenge has motivated a large number of experimental and theoretical studies aiming at finding materials feasible for either transforming solar energy into electricity (photovoltaics)^{2–7} or inducing chemical reactions (photocatalysis).^{8–11}

In typical solar energy conversion systems, many hot charge carriers (excited electrons and holes) generated by photons with energies above the semiconductor bandgap quickly cool before all of their energies can be captured, which is a typical

process that limits device efficiency.¹ The excess energy of hot carriers will be lost as heat through electron–phonon (e–ph) scattering in a nonradiative process and subsequent phonon emission, as the carriers relax to their respective band edges [conduction band minimum (CBM) for electrons and valence band maximum (VBM) for holes] and recombine. One way to utilize the hot carriers for enhancing the efficiency of photo energy conversion is to realize a charge separation at the interfaces by extracting the hot carriers from the photo-

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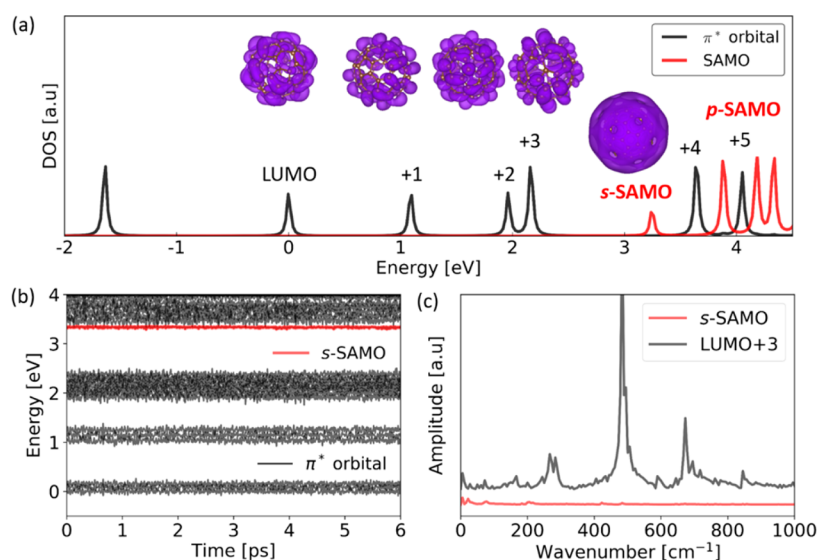


Figure 1. (a) DOS and orbital distribution of an isolated C_{60} . (b) Time evolutions of the energy states of an isolated C_{60} in NAMD simulations. (c) FT spectra of the time evolution of one LUMO+3 state and s -SAMO in an isolated C_{60} .

converter before they cool, which can also produce an enhanced photovoltage and suppress the electron–hole recombination.^{12,13} In order to realize this, the interfacial charge transfer across the contacts must be faster than the rate of carrier cooling.¹⁴ Although numerous experimental and theoretical studies have been carried out to investigate the charge separation mechanism at the interface of hybrid solar cells in order to develop high-efficiency photovoltaic or photocatalysis materials,^{15–26} it is still one of the most important and challenging problems in this field.

Here, using an *ab initio* time-dependent nonadiabatic molecular dynamics (NAMD) approach, we propose that the superatom molecular orbitals (SAMOs) of fullerenes, which were discovered by Feng et al. in 2008,²⁷ and other nanomaterials are ideal medias for interfacial charge separation. Instead of being bound to individual carbon atoms, SAMOs are bound to the central potential of the whole fullerene induced by charge screening through the short-range exchange and correlation and long-range Coulomb interactions. SAMOs are fundamentally different from the well-known π^* antibonding molecular orbitals of the carbon framework. Thus, SAMOs exhibit very diffuse and nearly free electron (NFE) character.^{28,29} This diffuse character, on one hand, leads to an extremely weak e–ph interaction and thus the cooling of the hot electrons on SAMO is suppressed significantly because of the “phonon bottleneck”.³⁰ Based on our NAMD simulations, for an isolated C_{60} the lifetime of electron excited into s -like SAMO can be estimated to be around 20 ps. On the other hand, the diffuse character induces significant orbital hybridization at the interface of fullerene with other materials and then the ultrafast interfacial charge transfer. Taking C_{60}/MoS_2 as an example, our results show that the interfacial charge transfer from s -like SAMO of C_{60} to MoS_2 takes place within 200 fs, which is 2 orders of magnitude faster than the SAMO electron cooling in an isolated C_{60} . This demonstrates that the SAMO of fullerene is a promising charge separation state for solar energy conversion, and we propose that this conclusion is widely applicable for different carbon nanostructures that stabilize SAMOs. Our results provide unique and essential

insights into the design and function of novel devices for optoelectronic and photovoltaic applications.

The NAMD simulations are carried out using Hefei-NAMD code,³¹ which augments the Vienna *ab initio* simulation package (VASP)^{32,33} with the NAMD capabilities implementing the decoherence-induced surface hopping (DISH) technique^{34–37} within time-dependent density functional theory (TDDFT)^{38,39} in the Kohn–Sham representation.^{40–42}

The generalized gradient approximation functional of Perdew–Burke–Ernzerhof (PBE)⁴³ in conjunction with D2 van der Waals corrections was used.⁴⁴ We used the projector augmented wave (PAW)⁴⁵ approximation for the core electrons. For the simulation involving a single C_{60} molecule, we used a $20 \text{ \AA} \times 20 \text{ \AA} \times 20 \text{ \AA}$ supercell with more than $10 \text{ \AA}$ of vacuum in each direction. To model the C_{60}/MoS_2 interface, one C_{60} molecule was adsorbed on a $3 \times 3 \text{ MoS}_2$, forming a close-packed two-dimensional (2D) C_{60} film. After geometry optimization, we used velocity rescaling to bring the temperature of the system to 300 K. A 6 ps microcanonical *ab initio* molecular dynamics trajectory was then generated using a 1 fs time step. The NAMD results are based on averaging over 100 different initial configurations obtained from the MD trajectory. For each chosen structure, we sampled 1×10^3 trajectories for the last 4 ps. More calculation details can be found in the Supporting Information.

Before describing the NAMD results, it is instructive to revisit the SAMO properties of C_{60} . The density of states (DOS) of isolated molecule and the orbital distribution of lowest unoccupied molecular orbital (LUMO) (3-fold), LUMO +1 (3-fold), LUMO+2 (3-fold), LUMO+3 (5-fold), and lowest SAMO, which is analogous to the s atomic orbital (s -SAMO), are shown in Figure 1a. In agreement with previous investigations, s -SAMO is located $\sim 1 \text{ eV}$ above LUMO +3.^{27–29} Compared with other π^* orbitals (LUMO–LUMO +3), SAMO is delocalized all over the whole C_{60} , showing a NFE character. Note that, there are also SAMOs showing p and d characters at higher energies. However, because of the close proximity in energy of these states to the nearby π^* orbitals, it is difficult to distinguish them in the NAMD simulations.^{27–29} Therefore, we focus our investigations on s -SAMO only.

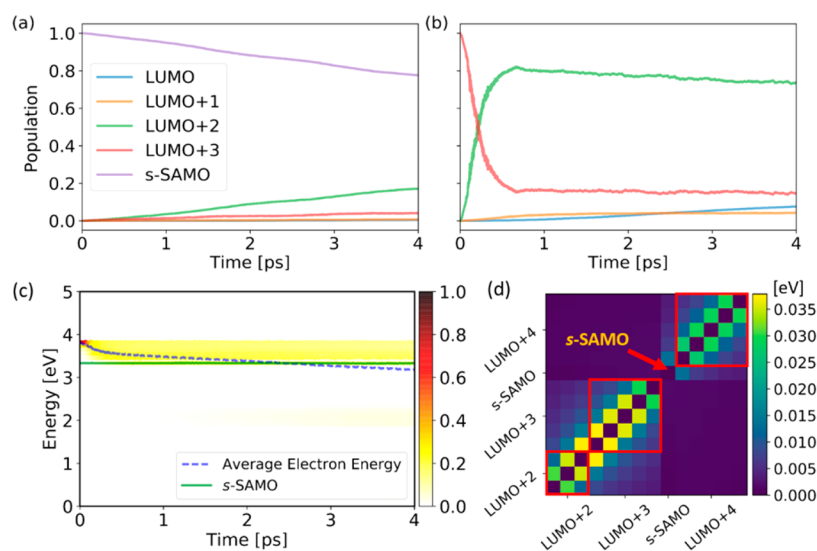


Figure 2. Time-dependent state population evolutions for LUMO to *s*-SAMO when the hot electron is excited initially at (a) *s*-SAMO or (b) LUMO+3. (c) The time-dependent averaged energy evolution for hot electron initiated from a state 0.5 eV above the SAMO. The color strip indicates the hot electron distribution on different energy states, and the dashed line represents the averaged hot electron energy. (d) The NACs among different states from LUMO+2 to LUMO+4. (Because of the degeneracy, LUMO+2, +3, and +4 are framed by red boxes).

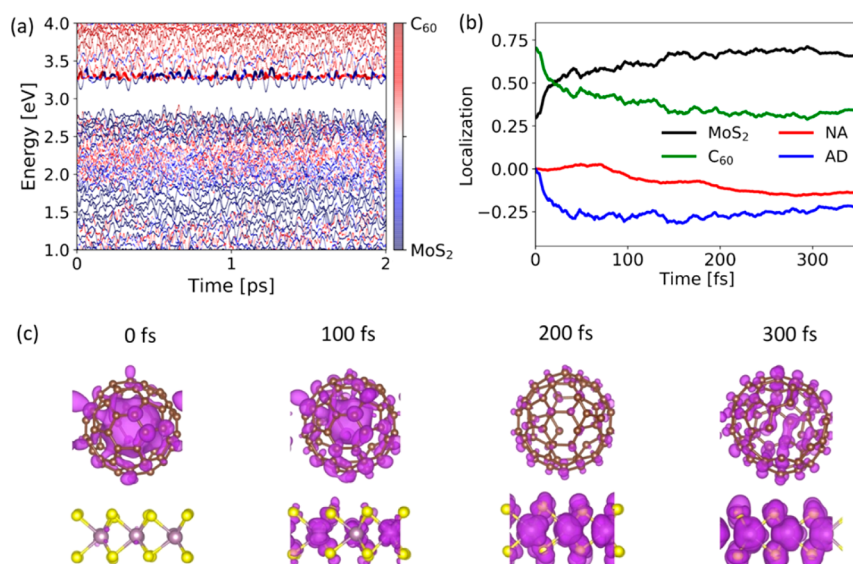


Figure 3. (a) Time evolutions of the energy states of C₆₀/MoS₂ in NAMD simulations. The color strip indicates the state distribution on C₆₀ and MoS₂. The *s*-SAMO state is marked using a thicker line. (b) Time-dependent electron transfer from *s*-SAMO of C₆₀ to MoS₂ and the NA/AD contribution. (c) Snapshots of the orbital distribution in the NAMD simulation at 0, 100, 200, and 300 fs.

Instead of individual C atoms, SAMOs are bound to the central screening potential of C₆₀. Therefore, previous investigations have proposed that the delocalized NFE character of SAMOs will induce a weak e–ph interaction.^{28,46} This is supported by our NAMD simulations. The e–ph coupling of different electronic states can be understood from the time-dependent energy evolution of the electronic states and their Fourier transform (FT) spectra (Figure 1b,c). The amplitude of electronic state energy fluctuation is correlated with the strength of e–ph coupling, and the FT spectra reveal the responsible dominant phonon modes. It can be seen that, for all π^* states, the degeneracy due to the symmetry of C₆₀ breaks in the MD and their energies oscillate because of the e–ph interaction. By taking one of the 5-fold LUMO+3 states as a representative of π^* orbital, the FT spectra show that the

phonon modes at 300, 500, and 700 cm^{−1} have strong coupling with it. In contrast, the energy of *s*-SAMO is almost kept as a constant during the 6 ps MD simulation. As a result, there are no strong phonon peaks for SAMO in the FT spectra shown in Figure 1c.

Nonradiative hot electron cooling is mostly mediated by e–ph interaction. Our NAMD investigations demonstrate that because of the weak e–ph interaction, the lifetime of a hot electron on *s*-SAMO is significantly longer compared to the π^* states. As shown in Figure 2a,b, when *s*-SAMO and one of LUMO+3 states are compared, the hot electron on LUMO+3 decays by more than 80% within 0.5 ps, while a *s*-SAMO hot electron decays by 20% within 4 ps. Thus, the lifetime of *s*-SAMO can be estimated to be around 20 ps using an exponential fitting, which is 40 times longer than that of the

LUMO+3. Such a slow decay rate is in agreement with the Ehrenfest simulation in Usenko et al.'s work.⁴⁷ Therefore, the *s*-SAMO will slow the internal hot electron cooling in C₆₀. As shown in Figure 2c, our results show that when a hot electron is generated at 0.5 eV above *s*-SAMO, it will decay to *s*-SAMO within 1 ps. After that, the relaxation to lower energy states becomes much slower; that is, *s*-SAMO behaves exactly like a "bottleneck" for hot electron cooling.

The slowdown of hot electron cooling can be understood by the phonon bottleneck concept, which has been widely discussed in regard to the hot carrier relaxation process in quantum dots and halide perovskite solar cells.^{30,48–51} Previous theoretical investigations proposed that the e–ph and the energy level spacing are important factors for the phonon bottleneck.^{30,52–55} According to NAMD simulation, the phonon bottleneck induced by *s*-SAMO can be understood quantitatively by looking into the nonadiabatic coupling (NAC) between different states, which determines the hopping probability of hot electrons from one state to another. The NAC between two electronic states *j* and *k* can be expressed as

$$d_{jk} = \left\langle \varphi_j \left| \frac{\partial}{\partial t} \right| \varphi_k \right\rangle = \frac{\langle \varphi_j | \nabla_R H | \varphi_k \rangle}{\epsilon_k - \epsilon_j} \dot{R} \quad (1)$$

where *H* is the Kohn–Sham Hamiltonian; φ_j , φ_k , ϵ_k , and ϵ_j are the wave functions and eigenvalues for electronic states *k* and *j*; $\dot{R}$ is velocity of the nuclei.⁵⁶ Thus, the NACs mainly depend on the energy difference term $\epsilon_k - \epsilon_j$, the e–ph coupling term $\langle \varphi_j | \nabla_R H | \varphi_k \rangle$, and the nuclear velocity term $\dot{R}$. For *s*-SAMO, as we already discussed, the e–ph coupling is very weak. In addition, the energy difference between *s*-SAMO with lower LUMO+3 is as large as 1 eV. These two factors induce a small NAC between *s*-SAMO and lower energy levels, as can be seen from Figure 2d.

We have demonstrated that *s*-SAMO in C₆₀ can slow the hot electron cooling process. Now, it is important to understand the interfacial charge-transfer rate. We chose MoS₂ as a substrate coupled with C₆₀ because it is one of the most important newly developed 2D semiconductors, which has been proposed to have important applications in photonics and photovoltaics.^{57–61} Figure 3a shows the energy evolution of electronic states of C₆₀/MoS₂. One can see that MoS₂ contributes high DOS above *s*-SAMO, and during the molecular dynamics (MD) simulation, the MoS₂ levels cross the *s*-SAMO many times. Because of the diffuse character of *s*-SAMO, there is significant hybridization between *s*-SAMO and MoS₂ when their energies are close to each other. Below *s*-SAMO there is a small band gap of 0.3 eV. The states of MoS₂ below this band gap behave as electron acceptors during the hot electron dynamics.

The time-dependent electron localization at C₆₀/MoS₂ shown in Figure 3b suggests the hot electron transfer from *s*-SAMO of C₆₀ to MoS₂ happens within 200 fs. The electron localization on MoS₂ increases rapidly from 30% to 60% within the first 50 fs. After that, it slowly converges to 70% within 200 fs. To understand this ultrafast charge-transfer process at the interface, we divide the charge-transfer population into two parts: (i) the nonadiabatic (NA) process which corresponds to the direct tunneling or hopping between the states and (ii) adiabatic (AD) charge transfer that is provoked by nuclear motion, where NAC distinctly increases as the nuclear motion causes energy states to cross. These two mechanisms can be distinguished as described in the Supporting Information. As

shown in Figure 3b, the ultrafast charge transfer in the first 50 fs is dominated by an AD process. This can be explained because the donor (*s*-SAMO) and acceptor (MoS₂) states are sufficiently close in energy and have many crossings between them during an MD path. After that, the NA process contributes to the relatively slow convergence of charge transfer, which corresponds to the electron hopping from *s*-SAMO to MoS₂ states at lower energy across the 0.3 eV band gap. This charge-transfer dynamics at C₆₀/MoS₂ interface is illustrated by the snapshots of time-dependent orbital distribution in Figure 3c.

The *s*-SAMO in C₆₀ is shown to be an ideal charge separate state because of the slow internal hot electron cooling and the fast interface charge transfer. Both of these factors are due to the NFE character of SAMO. First, because SAMO is not bound to the individual carbon atoms, the e–ph interaction is very weak. Thus, the phonon bottleneck for the hot electron cooling is generated. Second, SAMO has very diffuse orbital wave function, making it easy to be hybridized with other orbitals at the interfaces. In this study we chose MoS₂ as a substrate, which is a "van der Waals" layered semiconductor. The lone-pair electrons of the chalcogen atoms terminate the surfaces of the layers, and the absence of dangling bonds indicates a weak interaction between C₆₀ and MoS₂. We propose that charge transfer will be even faster if another substrate with stronger interaction with C₆₀ is selected. In fact, in the two-photon photoemission measurements by X. Y. Zhu, they obtain a time scale of 4–20 fs of the charge transfer from *s*-SAMO of C₆₀ layer to Au(111), which is in good agreement with our results.^{29,62}

SAMOs in C₆₀ are bound by the central potential which can be traced to the screening of an electron charge through the short-range exchange and correlation and long-range Coulomb interactions, which are analogous to the image potential states for 2D graphene.^{29,63} Therefore, such SAMOs were proved to generally exist in all hollow nanostructures such as different fullerenes and carbon nanotubes (in nanotubes one-dimensional NFE states are formed⁶⁴). The high energies of SAMOs in C₆₀ may limit their applications in solar energy conversion. However, in other nano materials, the SAMOs or NFE states can have lower energy. For example, the C₆F₆ molecules can form a 2D SAMO band whose energy locates at the conduction band minimum (CBM).⁶⁵ By chemical doping, the energies of SAMOs of C₆₀ can be lowered effectively.^{27,28} By hydrogen modification, graphene can be changed into graphane, where the NFE states can be stabilized to CBM by both the image potential and the dangling hydrogen.⁶⁶ Recently, Khazaei et al. proposed that the NFE states in OH-terminated MXenes can be stabilized.⁶⁷ The SAMOs and NFE states have the same character, namely NFE-like diffuse orbital wave function. Therefore, we propose the slow hot electron relaxation induced by the phonon bottleneck and the fast interface charge transfer generally exists in all the interfaces formed by hollow carbon nanostructure with other materials, where the SAMOs and NFE states are important charge separation states for solar energy conversion.

To summarize, by performing time-dependent ab initio NAMD simulations, we demonstrate that *s*-SAMO is an important charge separation state at the C₆₀/MoS₂ interface. Because of its diffuse NFE character, *s*-SAMO generates a phonon bottleneck inducing slow internal hot electron cooling. Simultaneously, fast interface charge transfer is achieved at C₆₀/MoS₂ interface due to the strong orbital hybridization. We

propose that the conclusion based on C_{60}/MoS_2 is widely applicable for different carbon nanostructure interfaces with other materials, providing unique and essential insights into material design and function for solar energy conversion.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b01302.

Nonadiabatic molecular dynamics with time-domain density functional theory (PDF)

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Notes

The authors declare no competing financial interest.

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