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2016 2017

Molecular spin-switch for effective electron-hole separation at hybrid interfaces for application in photocatalysis

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KTiO3,

(Cr-TPP)

KTiO3   Cr-TPP   Cr-TPP

KTiO3

I used the DFT approach to calculate the work functions of KTaO3, Cr-TPP-Cl (Cr is 3+ charge), Cr-TPP (Cr is 2+ charge) and Pt. Then I assumed a system as follow KtaO3, Cr-TPP-Cl (Cr is 3+ charge), Cr-TPP (Cr is 2+ charge) and Pt. In this system the work functions follow the following dependence: 2.3 eV; 4.6 eV; 3.8 eV; 5.6 eV. Such work functions will lead to electron transfer from KTaO3 to Cr-TPP-Cl (Cr is 3+ charge). As a result, Cr 3+ will become C3 2+ and the Cl will migrate to the second Cr-TPP molecule which will simultaneously donate electron to Pt. As a result, the work functions will be reordered for the new system of KtaO3, Cr-TPP (Cr is 2+ charge), Cr-TPP-Cl (Cr is 3+ charge), and Pt as follows: 2.3 eV; 3.8 eV; 4.6 eV; 5.6 eV.

chemistry

DFT

１．研究開始当初の背景

In this work we investigated the irreversible electron transfer between potassium tantalite KTaO3, Cr-tetra phenyl porphyrin (several layers) Cr-TPP, and platinum nanoparticle. Upon photo excitation an electron hole separation occurs in the KTaO3 and the electron is transferred to the Cr-TPP system. Further, the electron is transferred from the Cr-TPP system to the Pt nanoparticle. The interesting point about this system is that electron-hole recombination does not occur and all transferred electrons from the KTaO3 are transported to the Pt nanoparticle. This phenomenon has not been clarified until now. Several important problems exist in the proposed research. The first is the correct surface termination of KTaO3. KTaO3 is a polar perovskite with Tasker type 3 surface. This means that the surface will undergo severe surface reconstruction in order to eliminate the strong dipole momentum. Estimating the correct surface termination is crucial to determine the correct workfunction of KTaO3 and also to understand its interaction with the Cr-TPP molecule.

２．研究の目的

In my original proposal I suggested that the reason for electron transfer in direction oxide -> porphyrin -> metal is spin switching within the Cr-TPP molecule which would block the backdonation of electrons. While such process is observed for the Cr-TPP in homogeneous solution its effect is minimal on the oxide surface. That is why in addition to the spin-switching mechanism, additional approach of work function evaluation was used.

３．研究の方法

Periodic, plane wave DFT calculations and first principle molecular dynamics were performed with the Vienna Ab initio Software Package. The Perdew-Burke-Ernzerhof exchange-correlation functional was applied using projector augmented wave pseudopotentials. Electron energies were converged to 10^{-5} eV using the tetrahedron smearing method with Bloch correction for bulk systems and Gaussian smearing for surfaces. The calculations were performed with 400 eV cut-off energy and Monkhorst-Pack k-points mesh of $6 \times 6 \times 6$ for the bulk systems and $2 \times 2 \times 1$ for the slab systems. Geometry optimization was performed using the conjugated gradient algorithm. For bulk systems relaxation was performed of the cell volume, cell shape, and atomic positions. For slab models, relaxation was performed for the atomic positions only. The relaxation was performed until the forces converged to values bellow 0.03 $eV/Å^2$. Throughout this study, we have used the graphical visualization package VESTA.

４．研究成果

To solve the problem, I used the DFT approach to calculate the work functions of KTaO3, Cr-TPP-Cl (Cr is 3+ charge), Cr-TPP (Cr is 2+ charge) and Pt. Work function is estimated in plane wave DFT approach as the difference between the vacuum level energy and the Fermi level energy of the material. The workfunction difference between two materials can evaluate the probability of an electron to be transferred between them. The electrons are transferred from materials with small workfunction to materials with big workfunction. I assumed a system as follow: KtaO3, Cr-TPP-Cl (Cr is 3+ charge), Cr-TPP (Cr is 2+ charge) and Pt. The system is schematically presented in Figure 1. In this system the computed with DFT workfunctions follow the following dependence: 2.3 eV; 4.6 eV; 3.8 eV; 5.6 eV. Such work functions will lead to electron transfer from KTaO3 to Cr-TPP-Cl (Cr is 3+ charge). As a result, Cr 3+ will become Cr 2+ and the Cl will migrate to the second Cr-TPP molecule which will simultaneously donate electron to Pt. As a result, the workfunctions will be reordered for the new system of KtaO3, Cr-TPP (Cr is 2+ charge), Cr-TPP-Cl (Cr is 3+ charge), and Pt as follows: 2.3 eV; 3.8 eV; 4.6 eV; 5.6 eV.

Now, the electron on Cr-TPP (Cr is 2+ charge) will have the opportunity to transfer to KTaO3 (electron hole recombination) but such transfer is unlikely due to the difference in work functions. It is more likely to occur a transfer between Cr-TPP (Cr is 2+ charge) and Cr-TPP-Cl (Cr is 3+ charge) which is an electron transfer in the direction of Pt. Thus, the original system will be restored. The electron transfer between

KTaO3 and Pt is achieved by the Cr 3+ / Cr 2+ redox pair in two Cr-TPP molecules with a Cl anion migrating between them.
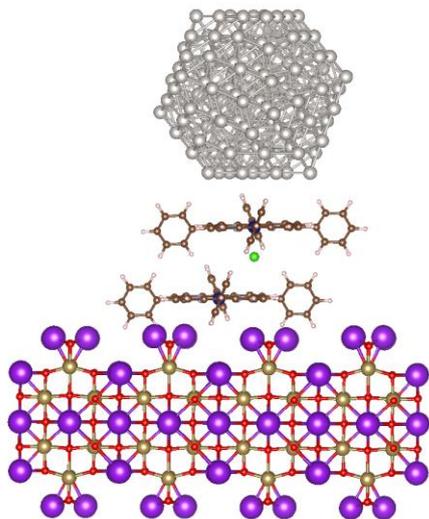
Figure 1: Investigated model consists of three layers of KTaO3 with surface reconstruction; two layers of Cr-TPP with one Cl- ion, and Pt nanoparticle surface.

This reordering of the workfunctions would correspond to the formation of Cr 3+/ Cr 2+ redox pair which will switch every time an excited electron from the KTaO3 is transferred to the Cr-TPP molecules. Such a redox pair switching will ensure the proper flow of electrons from the KTaO3 to Pt without electron hole recombination on the interface.
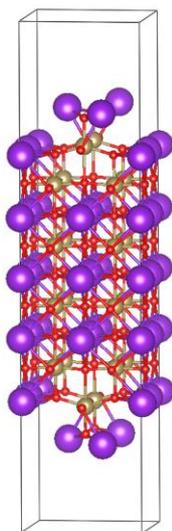
Figure 2: Model for which the workfunction of KTaO3 was determined.

In Figure 2 is shown the slab model for which the workfunction of KTaO3 was determined the model consists of 4 layers and reconstructed surface. KTaO3 is a polar perovskite characterized with strong dipole momentum which should lead to severe surface reorganization. Perovskites are characterized with AO-surface termination which in case of KTaO3 will be KO-termination. Further reconstruction, however, will be necessary to compensate the dipole momentum. The reconstruction is a result of small radius high charge Ta 5+ cations. Due to the high charge those cations are very unstable without an anionic coordination sphere. Owing to their small size they would easily migrate in the subsurface layers and form coordination sphere. Thus, the outermost layers will be depleted from Ta and will be compose by K and O only. We have found the same value of the workfunction for model with three layers. Due to very large computational model we will use n our calculations three-layer model of KTaO3.
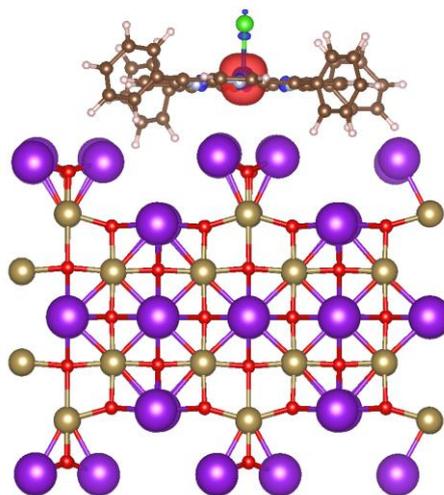
Figure 3: Model for which the charge transfer between KTaO3 and Cr-TPP was determined.

In Figure 3 is shown the computed model of KTaO3 surface with Cr-TPP for electron transfer at the heterointerface. The phenyl rings of the Cr-TPP molecule occupy the pore regions on the surface between the KO-chains. Thus, the Cr-TPP molecule is

situated close to the surface. The Cr atom is 3.8 Ang. away from a surface oxygen atom. An electron exchange Cr-O bridge is formed which allow for electrons to be transferred between the surface and the molecule. The results show that one electron was transferred from the oxide to the Cr-TPP molecule.
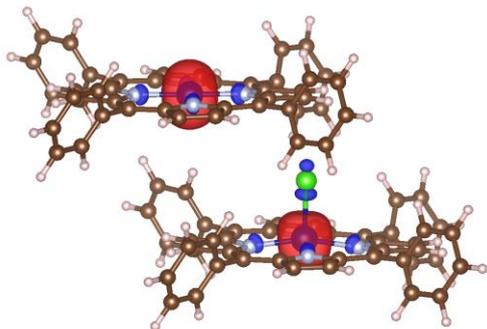
Figure 4: Model two Cr-TPP molecules with Cr 3+ and Cr 2+ respectively. The electron transfer was in direction from Cr 2+ molecule to Cr 3+ molecule.

In Figure 4 is shown a model of two Cr-TPP molecules. One of the molecules has Cr 3+ at the metal site while the second molecule has Cr 2+ at the metal site. Thus, the both Cr-TPP molecules would form a Cr 3+ / Cr 2+ redox pair. The both molecules are linked by a Cl- anion which can be situated in the middle in case of intermediate valence state for the both Cr 2+ ions. However, it can be situated next to each of the Cr 2+ molecules. The molecule to which Cl- is situated is characterized with 3+ charge while the other is characterized with Cr 2+ charge. The migration of Cl- between the both molecules would transfer one electron between them and in this wat the Cr 3+ / Cr 2+ positions will be switched. We could estimate that charge transfer can occur between the molecules in the direction of Cr-TPP with Cr 2+ to Cr-TPP with Cr 3+. In an additional electron is added to the system, i.e., negative charge, then the system is characterized with two Cr 2+ molecules and Cl-.

The Cr 3+ / Cr 2+ electron pair is crucial for the operation of the device. Owing to the difference in wave functions between the both molecules a blocking electron gradient is created on the KTaO3 / Cr-TPP interface. The molecules at the interface are always Cr 3+ Cr-TPP. Thus, they maintain the large workfunction difference with the KTaO3. The workfunction of KTaO3 is 2.3 eV while the workfucntion of Cr-TPP (Cr 3+) if 4.6 eV. This workfunction gradient would always lead to electron transfer from the oxide to the molecule. However, it would be impossible to overcome the gradient and achieve transfer in the opposite direction. Thus, electrons and holes will remain separated efficiently.

To operate properly the device would need at least two layers of Cr-TPP which is the minimum required to form a Cr 3+ / Cr 2+ redox pair. Any higher number of layers would certainly work; however, it will slow down the electron transfer and give rise to significant resistance. A single layer would also actively participate in the electron transfer, however, the work function difference at the KTaO3 / Cr-TPP (Cr 2+) would be smaller: KTaO3 is 2.3 eV and Cr-TPP (Cr 2+) is 3.8 eV and this will reduce the effective separation of electrons and holes.

In conclusion we have estimated the operation of the KTaO3 / Cr-TPP / Pt system. The system is a complex cascade of workfunctions and the electron transfer is driven by a Cr 2+ / Cr 3+ redox pair. In order to optimize the system, one should further reduce the work function of the oxide by choosing a more suitable material. Optimizing the molecule is possible by designing a redox pair with greater difference between the work functions of reduced and oxidized forms. However, a limit exists and those are the boundary conditions set by the workfunction of the oxide as a source electrode than the workfunction of the Pt on the drain electrode.

Optimizing the devise thickness is impossible due to greater resistance in larger devices and no operating redox pair in thinner devices.

５．主な発表論文等

Publication is in preparation

（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　　件）

〔学会発表〕（計　　件）

〔図書〕（計　　件）

〔産業財産権〕

○出願状況（計　　件）

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況（計　　件）

名称：
発明者：
権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕
ホームページ等

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