Letter to the Editor

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Dual surface doping of Co+N in the anatase TiO2(100) for water splitting process

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ABSTRACT

TiO_2 photocatalyst by generating electron-hole pairs dissociates the adsorbed water to the reactive oxygen species (ROS) by which environmental pollutants are degraded. There are many experimental and theoretical studies on the band gap reduction of rutile/anatase by single and dual doping of metals and non-metals. In all these works, the dopants are considered to be doped in bulk, and by band gap reduction, the more photocatalytic activity is explained. In this letter, by periodic DFT method, the role of dopants that adsorbed on the surface is studied. To do this, the synergistic effects of Co and N surface doping on the dissociation of water to H+OH radicals are studied.

To the Editor

Nowadays, DFT methods are widely used for the prediction of the structural and the electronic properties of novel materials [1, 2]. TiO_2 photocatalyst by generating electron-hole pairs dissociates the adsorbed water to the reactive oxygen species (ROS) by which environmental pollutants are degraded. There are many experimental and theoretical studies on the band gap reduction of rutile/anatase by single and dual doping of metals and non-metals. In all these works, the dopants are considered to be doped in the bulk, and by band gap reduction, the more photocatalytic activity is explained [3]. However, the minor portion of the dopants may present in the surface, but this part is not considered in the modeling. In this letter, by periodic DFT method the role of dopants which adsorbed on the surface is studied. To do this, synergistic effects of Co and N surface doping on the dissociation of water to H+OH radicals is studied.

All calculations were done by a (2×1) supercell model of TiO_2(100) with 5 TiO_2 layers (20 Ti and 40 O atoms) and 15□ vacuum. A K-grid of 4×3×1 according to the Monkhorst-Pack algorithm [4] and spin-collinear version of self-consistence field method were used for all cases. PBE functional [5] and dispersion potential of the Grimm type were chosen for optimizations and post processing calculations [6]. The charge SCF and force convergence criteria were set to be less than 2×10^{-5} and 0.05 eV/□. Three bottom layers were fixed to simulate the bulk phase. Transition state findings were done by ASE-NEB [7] and SIESTA [8] as calculator.

Fig. 1 shows the optimized TiO_2(100) supercell with lattice parameters of a=7.66 □, b=9.8 □, and c=22.66, α=90, β=90, and γ=90. Fig. 2 shows the structures of transition states of dissociation of water to H+OH radicals. Pure anatase TiO_2(100) has the barrier energy of 0.60 eV for water dissociation, while the barrier energy of the water molecule on the Co single doped and (N, Co) dual-doped TiO_2 are 0.52 and 0.33 eV, respectively. In other words, the energy required for water splitting is reduced by half. Presence of nitrogen atom is necessary for this reduction. Table 1 compares important bond lengths and angles between the transition state structures of Co single and (N, Co) dual doped anatase TiO_2(100). Table 1 shows that the presence of Co and its better interaction with OH stabilizes transition structure of Co-doped TiO_2(100) by only 0.08 eV. On the other hand, relaxation of the

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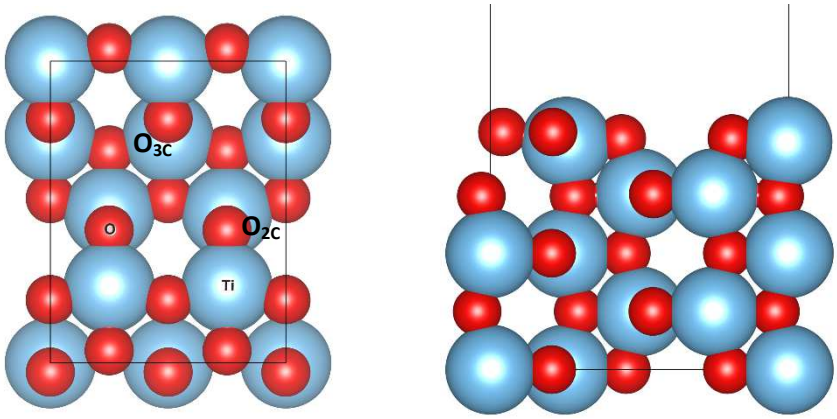

Fig. 1. Optimized structure of TiO_2(100) supercell from top (left) and side (right) views.

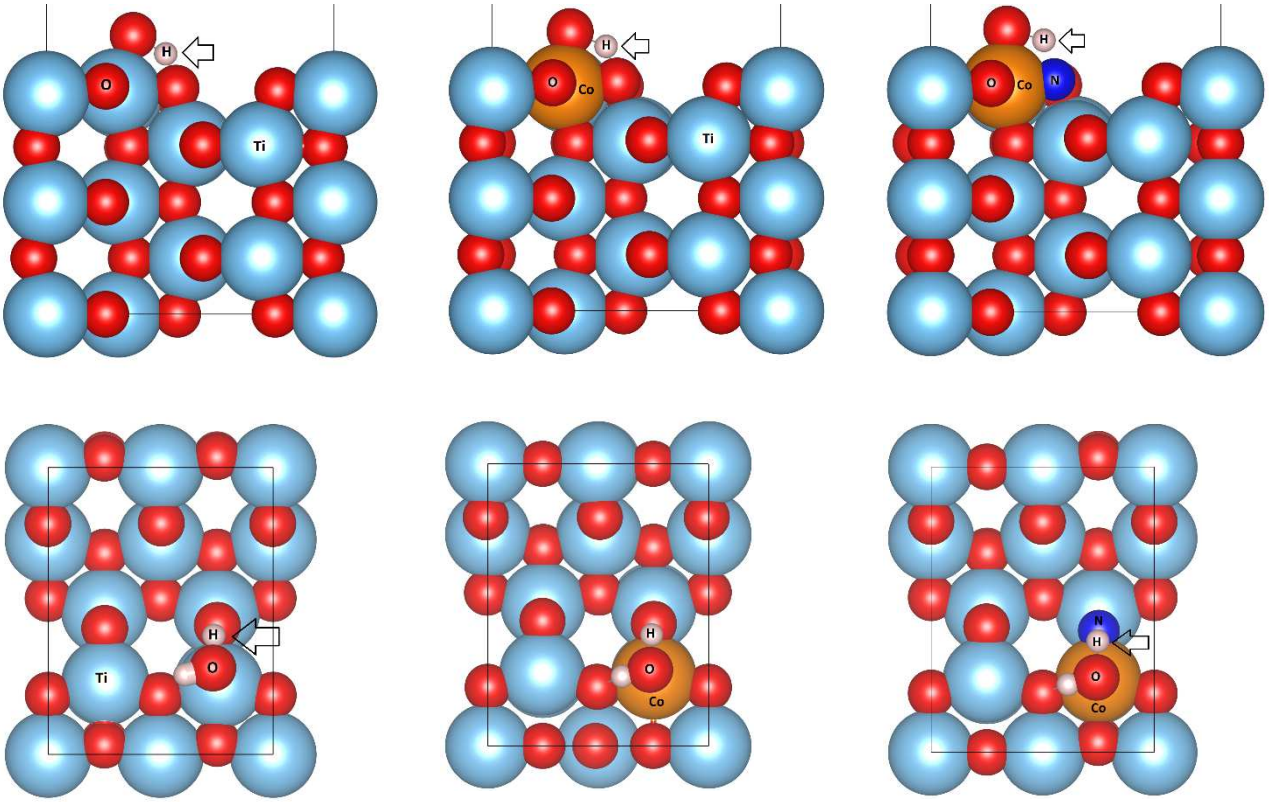

Fig. 2. TS structures of H_2O dissociation on pristine (left), Co-doped (middle), (Co,N)-doped (right) TiO_2(100). The side and top views are shown in up and down figures, respectively.

Table 1. Important bond lengths and angle in the transition structures of single and dual doped TiO_2(100). The unit for bond lengths are picometer, and for bond angle is degree.

	H–N(O)[a]	O–Co(Ti)[b]	H–O–Co(Ti)[c]	O–H[d]
Pristine	122.9	202.0	100	97.7
Co-doped	124.4	188.5	92.1	99.0
(N, Co) doped	137.0	190	93.4	99.3

a: distance of dissociating water's hydrogen from N (in dual doped) or O (in single doped or pristine TiO_2)
b: the bond length between O of adsorbed OH radical and Co (or Ti in the pristine TiO_2).
c: the bond angle between the adsorbed OH radical and Co (or Ti in the pristine TiO_2).
d: the bond length of O and H in the adsorbed OH radical.

H–O–Co angle by simultaneously nitrogen doping decreases the energy of TS by ~0.2 eV.

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Conflict of interests
The authors declare that they have no conflicts of interest.

References

[1] S. Kamalinahad, H.R. Saud, H. Bashir, T.A. Qassem, H. Tariq, Theoretical Study on the Enhancement of Nonlinear Optical and Electronic Responses of Sumanene through Interaction with Alkali Metals (Li, Na, and K), Chemical Review and Letters (2024). https://doi.org/10.22034/crl.2024.392027.1219.
[2] M.R. Jalali Sarvestani, Z. Doroudi, Fullerene (C20) as a potential sensor for thermal and electrochemical detection of amitriptyline: A DFT study, Journal of Chemistry Letters, 1 (2020), 63-68. https://doi.org/10.22034/jchemlett.2020.119493.
[3] U.M. Khan Shahed, M. Al-Shahry, B. Ingler William, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO2, Science, 297 (2002), 2243-2245. https://doi.org/10.1126/science.1075035.
[4] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B, 13 (1976), 5188-5192. https://doi.org/10.1103/PhysRevB.13.5188
[5] B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, Phys. Rev. B, 59 (1999), 7413-7421. https://doi.org/10.1103/PhysRevB.59.7413.
[6] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, J. Comput. Chem., 27 (2006), 1787-1799. https://doi.org/10.1002/jcc.20495.
[7] A. Hjorth Larsen, J. Jørgen Mortensen, J. Blomqvist, I.E. Castelli, R. Christensen, M. Dułak, J. Friis, M.N. Groves, B. Hammer, C. Hargus, E.D. Hermes, P.C. Jennings, P. Bjerre Jensen, J. Kermode, J.R. Kitchin, E. Leonhard Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. Bergmann Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiøtz, O. Schütt, M. Strange, K.S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, K.W. Jacobsen, The atomic simulation environment—a Python library for working with atoms, J. Phys.: Condens. Matter, 29 (2017), 273002. https://doi.org/10.1088/1361-648x/aa680e.
[8] A. García, N. Papior, A. Akhtar, E. Artacho, V. Blum, E. Bosoni, P. Brandimarte, M. Brandbyge, J.I. Cerdá, F. Corsetti, R. Cuadrado, V. Dikan, J. Ferrer, J. Gale, P. García-Fernández, V.M. García-Suárez, S. García, G. Huhs, S. Illera, R. Korytár, P. Koval, I. Lebedeva, L. Lin, P. López-Tarifa, S.G. Mayo, S. Mohr, P. Ordejón, A. Postnikov, Y. Pouillon, M. Pruneda, R. Robles, D. Sánchez-Portal, J.M. Soler, R. Ullah, V.W.-z. Yu, J. Junquera, Siesta: Recent developments and applications, J. Chem. Phys., 152 (2020). https://doi.org/204108, 10.1063/5.0005077.