Electronic Structure of High Pressure Phases TiO_2: A Hybrid Functional and GW Method's Study

B. Wang,[1] X. Jiang,[1] C. Århammar,[2] and R. Ahuja[1,3]

[1] *Department of Material Science and Engineering, Royal Institute of Technology, Stockholm, S-10044, Sweden.*
[2] *Sandvik Machining Solutions R&D S-126 80 Stockholm, Sweden.*
[3] *Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, S-751 21 Uppsala, Sweden.*

Semiconductors with proper band gap can be used as the photoelectrodes for photochemical energy conversion processes. Titanium dioxide has good corrosion resistance in aqueous solutions and is a good candidate for photoelectrodes. The limitation of the anatase phase of TiO_2 is its large band gap,which make it unable to absorb sunlight in the visible range. High pressure phases of TiO_2 like fluorite and pyrite have optimal band gap given by DFT [1]. In this paper, the electronic properties of high pressure phases of TiO_2, flourite, pyrite and cotunnite, have been investigated by hybrid funtional and GW methods. Our calculations suggest that the band gap of fluorite and pyrite are 1.72 eV and 2.34 eV using the hybrid functional HSE06, respectively. The calculated band gap by GW methods is larger than hybrid functional methods, which gives 2.15 eV and 2.45 eV for the fluorite and pyrite phases. For the comparison of the calculated results of anatase phase, we claim that the calculated band gap of fluorite and pyrite phases have the optimal band gap to absorb visible light for photocatalysis to decompose water. The imaginary part of the dielectric function has also been calculated for fluorite, pyrite, and anatase phases using the Bethe-Salpether (BSE) method. The dielectric function calculated by BSE for the anatase phase agrees well with experiment and with previous studies, using the same level of theory. Therefore we expect that we are also able to predict the optical properties of the high pressure phases of TiO_2 by the BSE method.

[1] M. Mattesini, J. S. de Almeida, L. Dubrovinsky, N. Dubrovinskaia, B. Johansson, and R. Ahuja, Phys. Rev. B **70**, 115101 (2012).

Contact: baochang@kth.se