Theoretical and experimental investigation of N-doped WO_3 for photocatalytic solar energy conversion

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Introduction

Further to our recent work upon the effects of cation substitution in bismuth tungsten mixed oxides [1], we report here upon anion doping in a tungsten oxide photocatalyst. Anion doping of TiO_2 has been shown to be effective in increasing photocatalytic activity through mixing of N2p states with the O2p valance band [2]. Although less widely investigated, pure WO_3 exhibits impressive chemical stability has a band gap significantly lower than either pure rutile or anatase. Early indications are that anion doping also leads to band gap narrowing in the WO_3 materials system [3].

TiO_2-WO_3 photocatalytic systems have shown a number of interesting properties including energy storing which allows photocatalytic reactions to continue for some time after illumination has ceased. If the benefits of anion doping are to be exploited in such systems then it is important that it is equally well understood in the tungsten component of the system.

The semiconducting band gap is one of the key materials properties which must be optimised for high efficiency solar energy conversion through photocatalysis. The thermodynamic arguments developed by Shockley and Queisser for maximum useful photon energy absorption in single junction solar cells are combined with the electrochemical requirement that both the oxygen and hydrogen formation reaction potentials are bridged by the conduction and valance bands for a photocatalytic reaction to proceed. Together these indicate an optimum semiconductor band gap of 1.7 eV. Much current research within the field of photocatalysis is focussed upon the need to decrease effective semiconducting band gaps to converge upon this value without sacrificing chemical stability.

Theoretical

Monoclinic $P21$-c nitrogen doped WO_3 crystals have been modelled using Density Functional Theory as implemented in the CASTEP software package [4] and the CA-PZ Local Density Approximation. The unit cell of undoped WO_3 is presented in figure 1. Geometrically optimised cells have been used to calculate the density of states for each structure, allowing the determination of the semiconductor band gap and cell parameters (undoped, E_g = 1.26 eV, V_{WO3} = 60.50 $Å^3$). The results of these calculations compare well to recent work upon pure WO_3 that used customised pseudopotentials to determine a band gap of 1.71 eV and unit volume of 56.90 $Å^3$ [5].
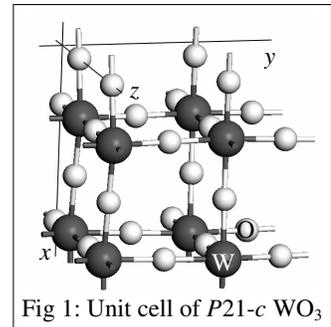

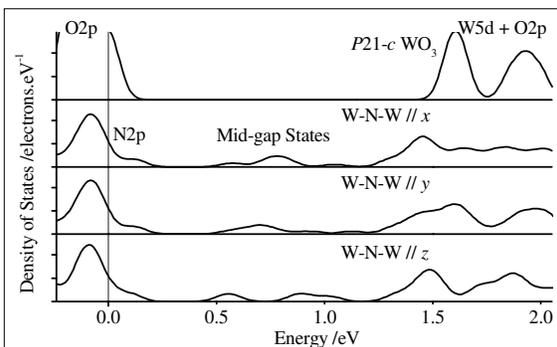Fig 1: Unit cell of $P21$-c WO_3

Fig 2: Calculated density of states for N-doped WO_3

Nitrogen doped unit cells have been analysed at concentrations of 1:31 (N:O). The densities of states for WO_3 with the W-N-W bonds aligned to the x, y and z axes are shown in figure 2 compared to pure $P21$-c WO_3. In all three cases the presence of substitutional nitrogen results in both the introduction of mid-gap states and a narrowing of the band gap via broadening of the conduction and valence bands.

Experimental

WO$_3$ nano-particulate films have been synthesised using a modified Augustynski method [6]. Concentrated tungstic acid produced via ion exchange was collected in ethanol mixed with an organic amine to form a nitrogen doped WO$_3$ precursor sol. This was then spread onto glass slides, gelled, and heated to 490 °C for one hour under flowing nitrogen to remove the solvents, react and crystallize.

Fig 3: UV-vis spectra of pure and N-doped WO$_3$ samples.
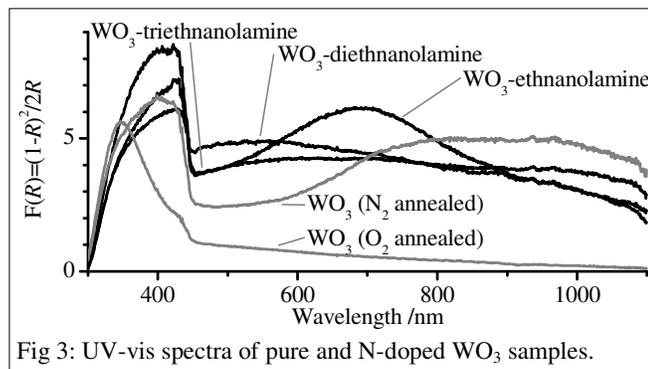
UV-vis spectra for these samples calculated from their diffuse reflectance using the Kubelka-Munk approximation are illustrated in figure 3. All samples exhibit a direct semiconductor band gap of 2.5 eV ± 0.2 eV in common with pure WO$_3$. However, the undoped sample annealed under N$_2$ shows an additional feature at 900 nm characteristic of oxygen deficient WO$_{3-x}$. The three samples nitrogen doped with organic amines exhibit strong absorption between 500 nm to 1000 nm, analysis of which suggests the presence of a second indirect electronic transition, 1.0 eV to 1.3 eV in energy.

Discussion and Conclusions

Both theoretical and experimental work suggest that nitrogen doping into the *P*21-*c* WO$_3$ lattice alters the electronic structure in such a way to as to increase light absorption for wavelengths above 450 nm. Theoretically, this occurs through both the introduction of mid-gap states and narrowing the semiconductor band gap although the experimental data collected indicates only the presence of additional sub-band gap transitions. The mid-gap states were found to be comprised of W5d and O2p orbitals similar to those which form the base of the conduction band in pure WO$_3$. Thus, the doping is not expected to compromise the excellent stability of this material with respect to photo-oxidation in water.

In conclusion, although many questions remain outstanding, nitrogen doping has the potential to increase the theoretical maximum solar energy conversion efficiency of WO$_3$ nano-crystalline films and TiO$_2$-WO$_3$ photocatalytic systems.

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