Multifunctional photo/thermal catalysts for the reduction of carbon dioxide

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ABSTRACT

The photochemical fixation of CO_2 to energy rich products for solar energy storage or feedstock chemicals is an attractive, albeit daunting, challenge. The overall feasibility of CO_2 conversion is limited by the availability of efficient photo-active materials that meet the energetic requirements for CO_2 reduction and are optically matched to the solar spectrum. Surface modification of TiO_2 with earth abundant metal oxides presents one approach to develop visible active photocatalysts through band gap narrowing, while providing catalytic sites to lower the activation energy for CO_2 reduction. In this work density functional theory was used to model the effect of surface modification of rutile and anatase using MnO_x nanoclusters. The results indicate the formation of inter-band gap states following surface modification with MnO_x, but surface water can change this. Oxygen vacancies are predicted to form in supported MnO_x and the interaction with CO_2 was investigated. MnO_x-TiO_2 was synthesized and characterised using surface analytical methods and photoelectrochemistry. The interaction of CO_2 with the materials under irradiation was probed using in-situ FTIR to interrogate the role of oxygen vacancies in CO_2 binding and reaction. These results provide insights into the requirements of a multifunctional catalyst for CO_2 conversion.

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1. Introduction

The photochemical fixation of CO_2 to energy rich products is an attractive, albeit daunting, challenge that attracts a great deal of recent interest [1–8]. The reduction of CO_2 has a steep uphill thermodynamic barrier and the overall feasibility of CO_2 conversion is limited by the availability of efficient photo-active materials that can meet the energetic requirements, while also being optically matched to the solar spectrum [9].

There are many reports of the heterogeneous photocatalytic reduction of CO_2 on oxide semiconductors, particularly TiO_2. CO_2 reduction is observed, but reaction efficiencies are very low. The conversion of CO_2 by photoactive oxides to energy-rich products is a complex system of reactions requiring novel, multifunctional nanoarchitectures that can harvest visible light, stabilize charge separation, activate CO_2, and control the reaction pathway.

Fig. 1 provides a sketch of a potential catalytic cycle for the reduction of CO_2. Small domains of reducible oxides (for MnO_x, but this is extendable to other earth-abundant oxides) are synthesized on supports of appropriate or modified band gap materials for light harvesting (shown here as TiO_2). MnO_x clusters are examined because they may create band gap states that red-shift TiO_2 for visible light activation – previous work has shown that Mn doping can create in-gap states [10] – and broaden the valence band to favor charge injection in the regeneration cycle (Rx. 4). Reduced metal centers and oxygen deficiencies are created thermally on MnO_x clusters and are sites of CO_2 adsorption and activation (Rx. 1, *thermal catalysis*). A photochemically generated electron (Rx. 2) is transferred to MnO_x and donated to the carboxylate (a specific form of adsorbed CO_2) to achieve a 2-eletron reduction of CO_2, cleaving the C-O bond to produce CO and heal the oxygen vacancy. Water oxidation at the oxidized MnOx (Rx. 3), possibly photo- and thermo-driven, regenerates the active O-vacancy sites by the reverse of the classic Mars-van Krevelen mechanism and injects electrons into the TiO_2 hole (Rx. 4). Crucially, reoxidation of surface vacancies with O_2, which would short-cut the catalytic cycle, is avoided by maintaining very low pO_2. Overall, then, the
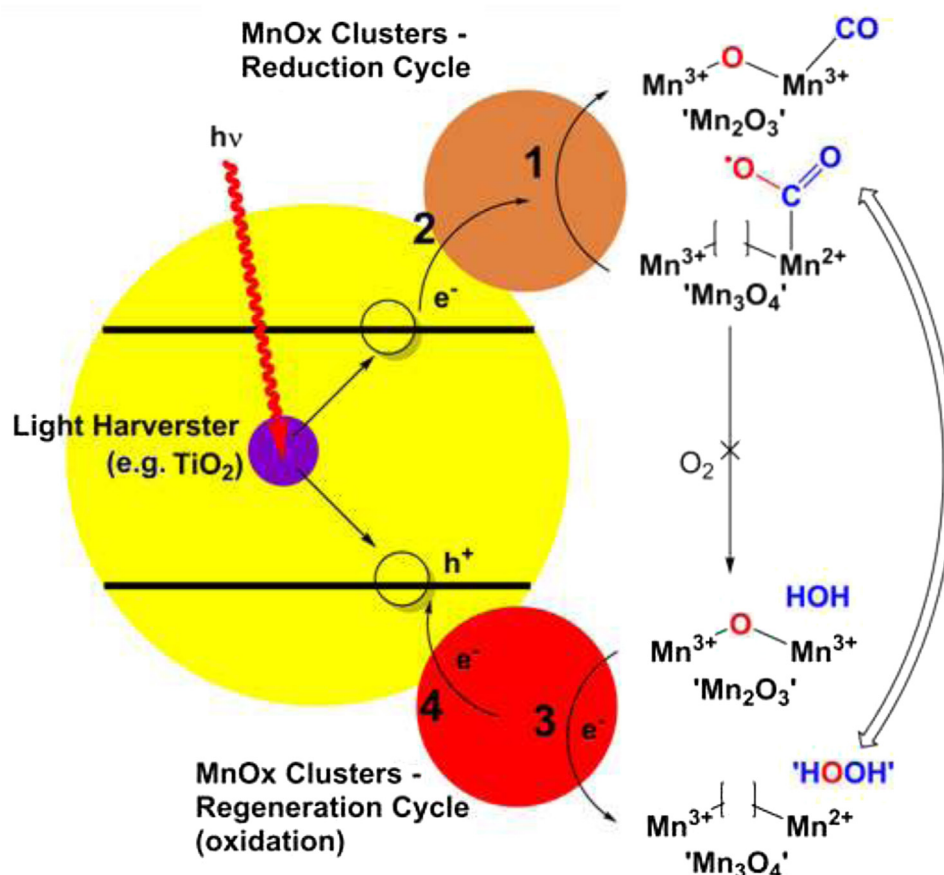
Fig. 1. Potential photo-thermal catalytic cycle for the reduction of CO_2 on a proposed nanostructured material using MnO_x-TiO_2 as the example.

proposed multi-functional system combines both thermochemical and photochemical cycles for CO_2 reduction and water oxidation.

The purpose of this paper is to probe the efficacy of this model theoretically and experimentally. Using first principles simulations, the effects of supporting MnO_x clusters on various crystal facets of either anatase or rutile TiO_2 [11–13] are explored to determine the extent of band-gap narrowing, the ease of forming oxygen vacancies and the mode of CO_2 surface binding. To validate the theoretical findings experimentally, we compare the influence of synthesis conditions (precursor, support, loading) on light absorption, catalyst reduction and CO_2 activation. The integration of theoretical and experimental findings yields deep insight into the structure and function of this TiO_2-based nanocomposite and indicates the critical features of a multifunctional photo/thermal catalyst tailored for CO_2 reduction.

2. Methodology

2.1. Computational modelling

To model the MnO_x-modified TiO_2 rutile (110) and anatase (101) surfaces, we use a three dimensional periodic slab model within the VASP code [14]; full details of the methodology are given in the supporting information. The cut-off for the kinetic energy is 396 eV and the core-valence interaction is described by PAW potentials [15]. The Perdew-Wang 91 exchange-correlation functional [16] and a Monkhorst-Pack $(2 \times 1 \times 1)$ k-point sampling grid and smearing width of 0.1 eV are used. To describe the Ti 3d and Mn 3d states DFT + U [17–19] is used where U = 4.5 eV for both cations. This value of U is sufficiently large to described localised Ti^{3+} [20–22] and

Mn oxidation states and this set-up has been shown to be reliable [12,20].

The rutile (110) and anatase (101) surfaces have two-fold coordinated bridging O atoms terminating the surface layer and 5-fold/6-fold coordinated surface Ti atoms. For both surfaces (2×4) surface supercell expansions, 6 O-Ti-O trilayers thick are employed with a 12 Å vacuum gap. We employ stoichiometric surfaces (no defects and no adsorbed hydroxyls) and surfaces with different water coverages [13] (adsorption energies are computed similarly to Eq. (1)) to examine the effect of a wet substrate on nanocluster absorption and the energy gap change.

The convergence criteria for the electronic and ionic relaxations are 0.0001 eV and forces smaller than 0.02 eV/ Å. The Mn_2O_3 nanoclusters are less than 1 nm diameter and based on our previous work [12,21–24] can shift the absorption edge of TiO_2 into the visible. The adsorption energy of the nanoclusters is computed from:

$$E^{ads} = E((Mn_2O_3)\text{-}TiO_2) - \{E(Mn_2O_3) + E(TiO_2)\} \qquad (1)$$

where $E((Mn_2O_3)\text{-}TiO_2)$ is the energy of an Mn_2O_3 stoichiometry nanocluster supported on a TiO_2 surface and $E(Mn_2O_3)$ and $E(TiO_2)$ are the total energies of the free Mn_2O_3 stoichiometry nanocluster and unmodified TiO_2. A negative adsorption energy indicates that cluster adsorption is stable.

The formation of oxygen vacancies is examined, using the formation energy to assess vacancy stability. After removing different oxygen atoms the vacancy formation energy is calculated from:

$$E^{vac} = \{E(Mn_2O_{3-x}\text{-}TiO_2) + 1/2E(O_2)\} - E(Mn_2O_3\text{-}TiO_2) \qquad (2)$$

where $E(Mn_2O_{3-x}\text{-}TiO_2)$ is the energy of modified TiO_2 with an oxygen vacancy in the Mn_2O_3 nanocluster, $1/2\ E(O_2)$ is the energy of oxygen and $E(Mn_2O_3\text{-}TiO_2)$ is the energy of the stoichiometric com-