Photocatalysis in Metal Oxide Nanotubes

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1. Introduction

As an important wide-band gap versatile semiconductor, TiO_2 has been widely applied in a lot of research fields [1-2]. Stimulated by the discovery of carbon nanotubes, a series of low dimensional TiO_2 nanoarchitectures have been prepared with the development of synthesis technology on nanomaterials. Among them, TiO_2 nanotubes have attracted more attention during the past decade due to the combination of semiconducting, photoelectrochemical properties of bulk TiO_2 and the structural characteristics of nanotubes.

We systematically investigated the formation, properties of a series of metal oxide nanotubes (for example TiO_2[3-5], ZnO[6], V_2O_5[7]). The photocatalysis in these metal oxide nanotubes is different from that on the surface due to the enhancement of molecule adsoption, diffusion and dissociation by the confinement effect.

2. Computational Method

The computations have been carried out using the plane-wave approach, together with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional, and ultrasoft pseudopotentials with PWSCF code implemented in Quantum-Espresso.
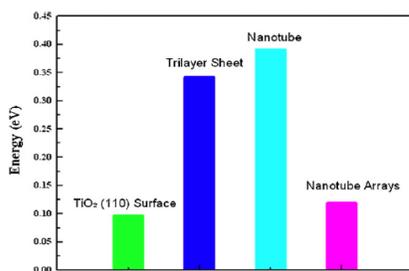
3. Results and discussion

Fig.1 The formation energies of rutile TiO_2(110) surface, tri-layer sheet, TiO_2 nanotube and nanotube arrays

The formation energies of TiO_2 nanotube arrays and other TiO_2 structures are shown in Fig.1. It can be seen that the formation energy of TiO_2 nanotube arrays is 0.12 eV, which is very close to the most stable rutile TiO_2 (1 1 0) surface and much more stable than the tri-layer sheet and single-walled nanotubes.
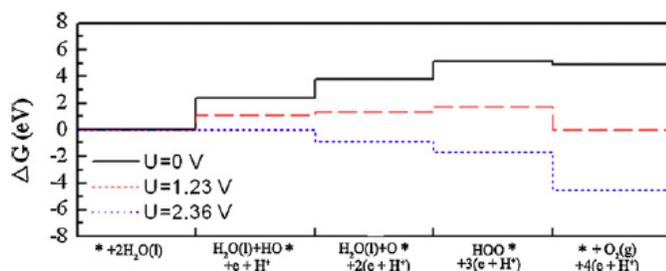

Fig.2 Calculated free energies of intermediates following the oxygen evolution from H_2O splitting inside TiO_2 nanotube of an array at three potentials (relative to the standard hydrogen electrode); zero potential (U= 0 V), the equilibrium potential (U= 1.23 V) and the lowest potential at which all steps are downhill in free energy(U= 2.36 V).

The thermodynamic properties of H_2O splitting on the TiO_2 nanotube and nanotube array have been discussed based on the Gibbs free energy diagrams (Fig. 2). The overpotential of H_2O splitting is 0.51 eV and 1.0 eV on the outside and inside of nanotube respectively, and 1.13 eV on the inside of nanotube arrays. Based on the thermodynamic point of view from the Gibbs free analysis, the rate-limiting step is to obtain the OH from the dissociation of the first H_2O on both TiO_2 nanotube and nanotube arrays.

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