Accepted Manuscript

Title: Nature of surface oxygen intermediates on TiO_2 during photocatalytic splitting of water

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PII: S1001-8417(17)30371-6
DOI: http://dx.doi.org/10.1016/j.cclet.2017.09.029
Reference: CCLET 4235

To appear in: *Chinese Chemical Letters*

Received date: 28-6-2017
Revised date: 3-8-2017
Accepted date: 8-9-2017

Please cite this article as: Charles A.Roberts, Somphonh P.Phivilay, Israel E.Wachs, Nature of surface oxygen intermediates on TiO2 during photocatalytic splitting of water, Chinese Chemical Lettershttp://dx.doi.org/10.1016/j.cclet.2017.09.029

Communication

Nature of surface oxygen intermediates on TiO_2 during photocatalytic splitting of water

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Graphical Abstract

Nature of surface oxygen intermediates on TiO_2 during photocatalytic splitting of water

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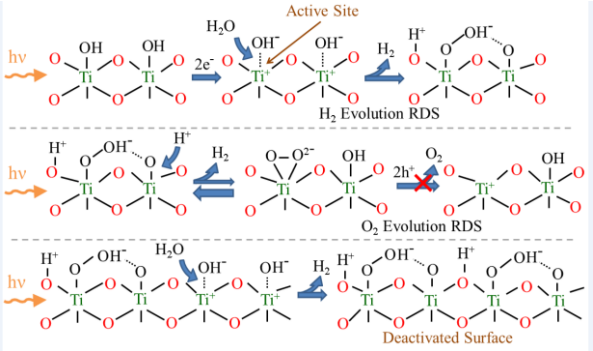

The surface oxygenated intermediates present on TiO_2 during photocatalytic water splitting have been identified and their accumulation on the titania surface is responsible for the deactivation of H_2 evolution rate during photocatalysis.

*ARTICLE INFO:Article history:*Received 28 June 2017 Received in revised form 3 August 2017 Accepted 22 August 2017 Available online

ABSTRACT
Titanium dioxide (TiO_2) is the most widely studied solid photocatalyst, but when applied to photocatalytic splitting of water to H_2 and O_2, the evolution rate of H_2 is low and decreases with reaction time. The origin of the decreasing evolution rate for the photocatalytic splitting of water was investigated for the first time by directly monitoring the surface species on TiO_2 during water photocatalysis with *in situ* attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) spectroscopy. The *in situ* ATR-FTIR spectroscopic analysis during UV illumination of TiO_2 immersed in water reveals that surface dioxygen and hydroxyl species are formed on TiO_2: charged Ti-OOH^-, peroxo Ti$(O_2)^{2-}$, and bridging Ti-(OH^+)-Ti groups. The accumulation of these surface oxygenated species on the TiO_2 photocatalyst blocks the activation of H_2O on the surface titania sites and is responsible for the decreasing H_2 evolution rate and absence of O_2 evolution.

Keywords:Photocatalysis ATR FTIR Spectroscopy TiO_2 Water Splitting In Situ

Photocatalytic splitting of H_2O to H_2 and O_2 has been identified as a possible green route to produce alternative, sustainable non-carbon fuel, and potential improvements to the efficiency of this process have motivated the study of this photocatalytic reaction. Titania-based photocatalysts are the most studied heterogeneous photocatalysts, being intensively investigated for water splitting and oxidation of pollutants in water and building surfaces [1-9]. Titania-based materials, however, are semiconductors with wide bandgap energies (3.0 eV for rutile and 3.2 eV for anatase) and are inefficient photocatalysts for H_2 production compared to other water splitting photocatalysts [2,3,5,7,10]. Furthermore, TiO_2 does not efficiently utilize the solar spectrum as activation requires excitation in the limited UV region (< 400 nm). Modification of TiO_2 photocatalysts improves efficiency by broadening light absorption into the visible range (> 400 nm) or preventing recombination of photoexcited electron (e^-) and hole (h^+) pairs [11-16]. These improvements focus