

Supporting Information:

**Ultrathin-nanosheets-assembled Bi_2MoO_6 mesoporous framework
for realizing optimized sunlight-driven photocatalytic water
oxidation**

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Experimental section:

Preparation of ultrathin-layers-assembled Bi_2MoO_6 mesoporous hollow sphere (UA- Bi_2MoO_6).

First, 150 mg sodium oleate was dissolved in 10 ml boiling ethylene glycol with strong stirring for 10 min. Then 210 mg bismuth nitrate and 50 mg sodium molybdate were added into above solution, respectively. After stirring for about 35 min, 30 ml absolute ethyl alcohol was slowly injected into above mixed solution and still stirring for 30 min. Finally, the mixture was transferred into a 50 ml Teflon-lined autoclave, sealed and heated at 160 °C for 30 h. The product was allowed to cool down to room temperature naturally, and the resultant sample was obtained by centrifugally separated, washed with cyclohexane and absolute ethanol several times, and dried under vacuum condition. In addition, the control samples were also prepared in the same way as UA- Bi_2MoO_6 but under different crystallization time (24 h and 36 h).

Preparation of ultrathin Bi_2MoO_6 nanosheet (U- Bi_2MoO_6). Similar with above synthesis process, 150 mg sodium oleate was dissolved in only 40 ml deionized-water with strong stirring for 10 min. Then 210 mg bismuth nitrate and 50 mg sodium molybdate were added into above solution, respectively. After stirring for about 40 min, the mixture was transferred into a 50 ml Teflon-lined autoclave, sealed and heated at 140 °C for 24 h. The product was allowed to cool down to room temperature naturally, and the resultant sample was obtained by centrifugally separated, washed with cyclohexane and absolute ethanol several times, and dried under vacuum condition.

Preparation of conventional Bi_2MoO_6 hollow. 242 mg bismuth nitrate and 60 mg sodium molybdate were added into 10 ml ethylene glycol with strong stirring, respectively. After stirring for about 35 min, 30 ml absolute ethyl alcohol was slowly injected into above mixed solution and still stirring for 30 min. Then, the mixture was transferred into a 50 ml Teflon-lined autoclave, sealed and heated at 160 °C for 24 h. The product was allowed to cool down to room temperature naturally, and the resultant sample was obtained by centrifugally separated, washed with water and absolute ethanol several times, and dried under vacuum condition.

Preparation of conventional bulk Bi_2MoO_6 . Specifically, 4.2 mmol bismuth nitrate and 2 mmol sodium molybdate were mixed together, then 40 ml of de-ionized water was added into above mixture solution. After stirring for 30 min, the suspension was transferred into a 50 ml Teflon-lined autoclave. The product was allowed to cool down to room temperature naturally, and the resultant sample was

obtained by centrifugally separated, washed with de-ionized water several times, and dried under room temperature. .

Characterization: The TEM analyses were performed by a JEOL JEM-2100F transmission electron microscope. SEM images were taken using a field-emission scanning electron microscope (JSM-7800F, JEOL). The crystallinity and the purity of the as-prepared samples were characterized by powder X-ray diffraction (XRD) analysis on a Shimadzu XRD-6100 diffractometer at 40 kV and 40 mA with Cu K α radiation. Data were recorded at a scan rate of 0.07°/s in the 2Theta range 10°-70°. X-ray photoelectron spectroscopy (XPS) measurement by a Thermo VG ESCALAB-250 system with Al-K α and Mg-K α source operated at 15 kV. Light absorption property was evaluated by UV-vis diffuse reflectance spectra (UV-vis DRS, CARY 100&300, VARIAN), BaSO₄ was used as a reflectance standard. The PL spectra of the photocatalysts were analysis using Hitachi F-7000 fluorescence spectrophotometer. The N₂-sorption measurement was performed by using Micromeritics Tristar 3000 at 77 K, the poresizedistribution were estimated using the Barrett-Joyner-Halenda (BJH) methods. In addition, the elemental analysis was carried out using ICP-OES (Perkin Elmer,Optima 8000).

Measurement ofphotocatalytic water oxidation performance. All the photocatalytic water oxidation experiments were conducted at room temperature; and, under simulated sunlight irradiation of a 300 W Xe lamp. For water oxidation, 100 mg as-prepared catalysts was added into 100 ml aqueous solution containing 0.1 M NaOH and 0.02 M Na₂S₂O₈ in a reactor, which was equipped with water circulation (20°C). Before light irradiation, the suspension was purged with nitrogen for about 90 min to drive off the inside air. In addition, Co₃O₄(5%) was loaded on the surface of the as-prepared photocatalysts as co-catalyst, and the analysis of the O₂ generation was performed using an online gas chromatograph (TECHCOMP GC-7900, TCD).

Photoelectrochemical measurements.Electrochemical and photoelectrochemical measurements were carried out in a standard three-electrode electrochemical cell using an electrochemical workstation (CHI 660E). The platinum sheet, saturated calomel electrode and modified glassy carbon were used as counter, reference, and working electrodes, respectively. For working electrode modification, 4 mg catalysts and 30 μ l of Nafion solution (5 wt%) were dispersed in 1 ml of water-ethanol solution with a volume ratio of 1:3, after ultrasonication for 20 min, an aliquot of 5 μ l mixture solution was pipetted onto the glassy carbon electrode to achieve the catalyst loading, and finally dried under room temperature. For photocatalytic water oxidation experiments, Linear sweep voltammogram (LSVs)

with a scan rate of 20 mV s^{-1} was conducted in $0.1 \text{ M Na}_2\text{SO}_4$ or Na_2SO_3 solution under simulated sunlight irradiation (300 W Xe lamp; PLS-SXE 300, Beijing Perfect Light Co., Ltd.).

The ECSA ($\text{ECSA} = R_f S$) of electrode was determined by the real surface area of smooth metal electrode (S) and the roughness factor of electrode (R_f). In this experiment, the S could be considered as the geometric area of glassy carbon electrode (0.07 cm^2), the R_f could be estimated from the ratio of double-layer capacitance C_{dl} for the working electrode and the corresponding smooth metal electrode¹⁻³. Referencing the previous researches, the average double-layer capacitance of a smooth metal surface is about $20 \mu\text{F cm}^{-2}$, that means the roughness factor R_f could be calculated by: $R_f = C_{dl}/20 \mu\text{F cm}^{-2}$. Additionally, the double-layer capacitance C_{dl} was estimated by investigating the cyclic voltammetric plots (-0.4 V to -0.2 V) which were measured in $0.1 \text{ M Na}_2\text{SO}_4$ solution under different scan rate (20 mV s^{-1} , 30 mV s^{-1} , 50 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} and 120 mV s^{-1}), the slope of charging current density differences ($\Delta j = (j_a - j_c)$ at -0.3 V) plotted against scan rates fitted to a linear regression could be considered as the twice of C_{dl} ⁴. Moreover, the ECSA-corrected Tafel slopes were estimated from the corresponding ECSA-corrected current densities, which were obtained by normalizing the kinetic current to the ECSA ($j_k = j / \text{ECSA}$).

Electrochemical impedance spectroscopy (EIS) was conducted with an alternating current signal (10 mV) in the frequency range of $0.1\text{-}10^5 \text{ Hz}$ at open circuit potential (OCP). In addition, the incident photon-to-current efficiency (IPCE) at each wavelength was measured using illumination from a 300 W Xe lamp passed through band pass filters to produce monochromatic light with different wavelength, the light output was measured with a light intensity meter. IPCE were measured at 0.8 V vs. SCE and calculated by the following formula:

$$\text{IPCE}(\lambda) = \frac{1240 j(\lambda)}{\lambda E(\lambda)} \times 100$$

The carrier separation efficiency ($P_{\text{Charge separation}}$) can be calculated by a comparison study between the photocurrent density measuring from oxidizing Na_2SO_3 as well as the theoretical maximum photocurrent density using Eq. 1, where $J_{\text{Na}_2\text{SO}_3}$ is the photocurrent density measured in Na_2SO_3 electrolyte, and J_{abs} is the photon absorption rate, which is calculated assuming 100% APCE¹. J_{abs} of the UA- Bi_2MoO_6 , U- Bi_2MoO_6 and C- Bi_2MoO_6 photoelectrode were calculated to be 4.834 mA/cm^2 , 4.379 mA/cm^2 and 3.745 mA/cm^2 , respectively. ϕ_{sep} is the yield of the photo-generated holes arrived on the surface, and ϕ_{ox} is the yield of the holes diffusion from the surface to the solution. In the

process of calculation, we can think $\phi_{ox}=1$, because in the sodium sulfite (Na_2SO_3) solution, surface recombination can be ignored. Accordingly, the carrier separation efficiency can be calculated by *Eq. 2*

$$J_{\text{Na}_2\text{SO}_3} = J_{\text{abs}} \times \phi_{\text{sep}} \times \phi_{\text{ox}} \quad (1)$$

$$P_{\text{Charge separation}} = J_{\text{Na}_2\text{SO}_3} / J_{\text{abs}} \quad (2)$$

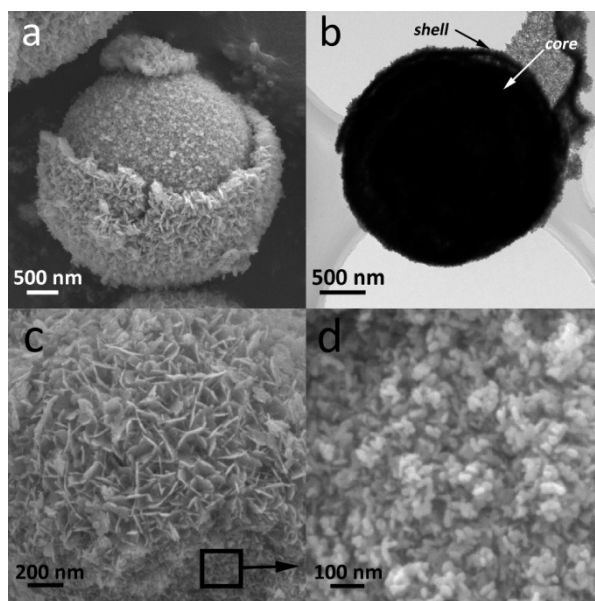
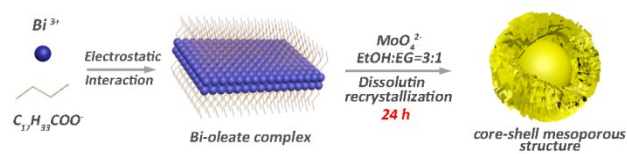


Fig. S1 SEM and TEM images of the resultant sample synthesized after 24 h crystallization process.

Obviously, the shorter crystallization time could affect the crystallization process, in which the dissolution-recrystallization process could not perform completely, thus, a core-shell structure was constructed. However, the “core” which consisted of nanoparticles possesses poor crystallinity; and, the ultrathin nanosheet could not completely form, which are very unfavorable for the enhancement of catalytic activity.

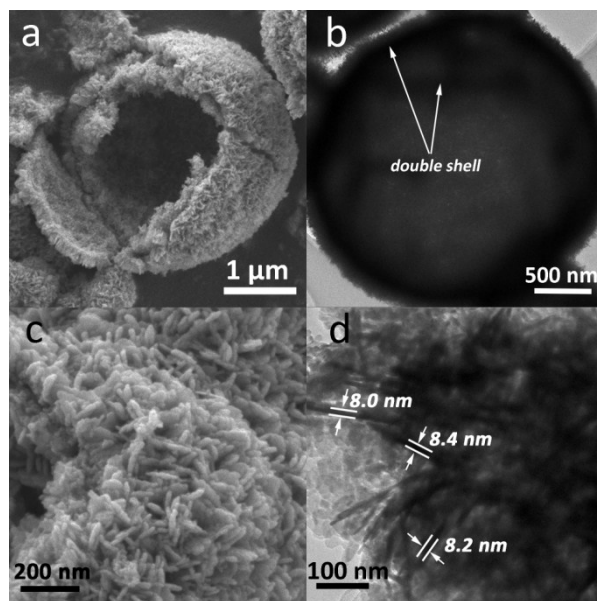
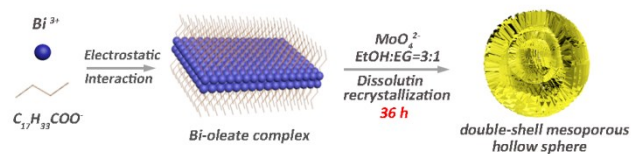


Fig. S2 SEM and TEM images of the resultant sample synthesized after 36 h crystallization process.

After extending the reaction time to 36 h, the secondary ripening process was occurred, leading to the formation of double-shell structure. But, unfortunately, owing to the too long crystallizing time, the thickness of every layer will thicken, which is unbeneficial for the exposure of active sites and the enhancement of intrinsic activation ability.

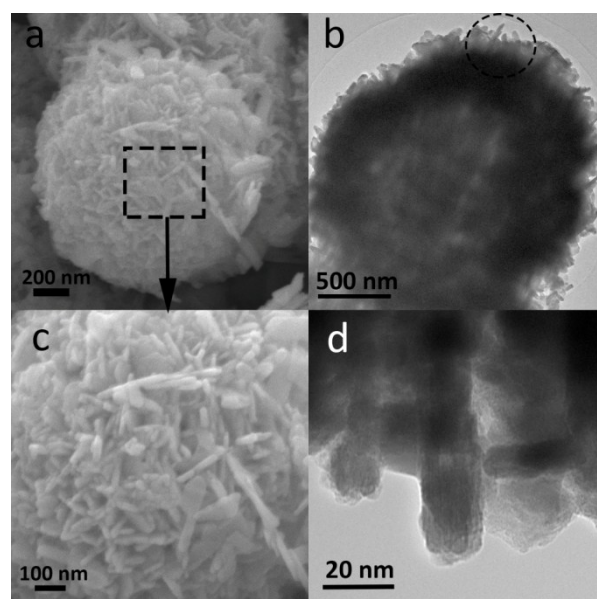


Fig. S3 SEM and TEM images of the resultant sample without adding sodium oleate.

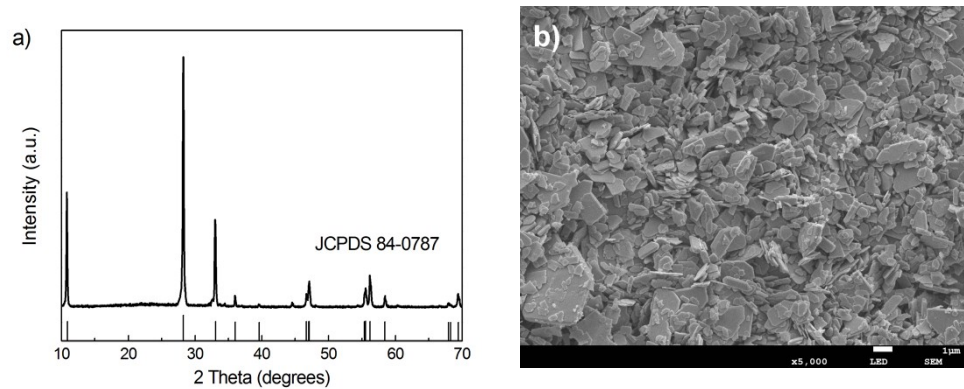


Fig. S4 a)XRD pattern and b) SEM image for bulk Bi_2MoO_6 (C- Bi_2MoO_6).

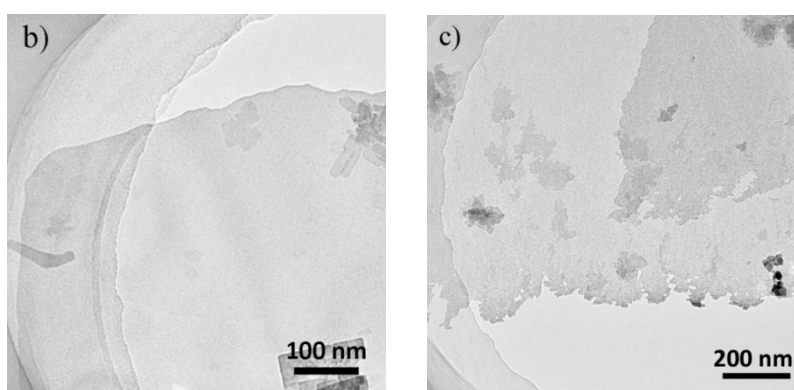
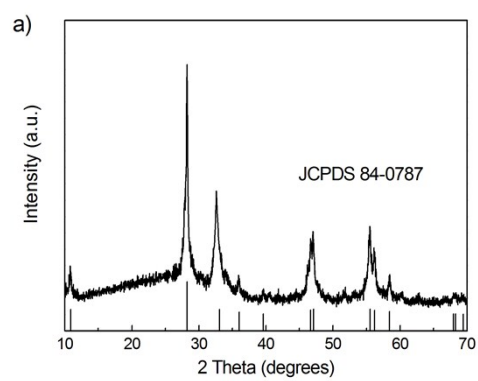


Fig. S5 XRD pattern and TEM images for ultrathin Bi_2MoO_6 layers (only using water as solvent).

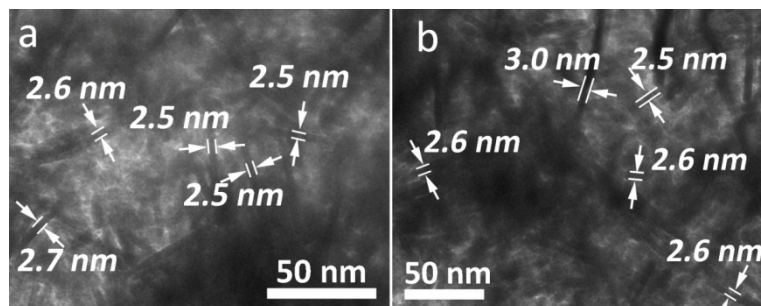


Fig. S6 TEM images for the surface of as-prepared UA-Bi₂MoO₆.

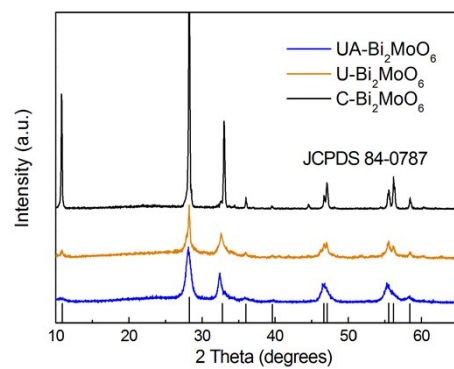


Fig. S7 XRD pattern for the as-prepared UA-Bi₂MoO₆, U-Bi₂MoO₆ and C-Bi₂MoO₆.

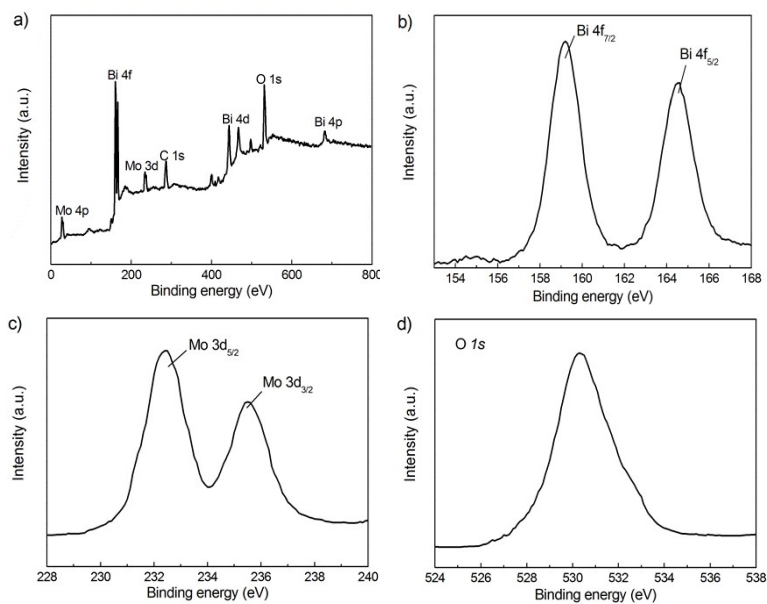


Fig. S8 XPS spectrum for the as-prepared UA-Bi₂MoO₆

As shown in Fig. S8, the high-resolution Bi 4f spectrum shows obvious peaks at 164.3 eV (Bi 4f_{7/2}) and 159.2 eV (Bi 4f_{5/2}), which can be ascribed to Bi³⁺. The Mo 3d peaks centered at about 232 eV (Mo 3d_{5/2}) and 235.5 eV (Mo 3d_{3/2}), respectively. The high-resolution O 1s spectrum with the observed peak at 530 eV can be attributed to the lattice oxygen in crystalline Bi₂MoO₆.

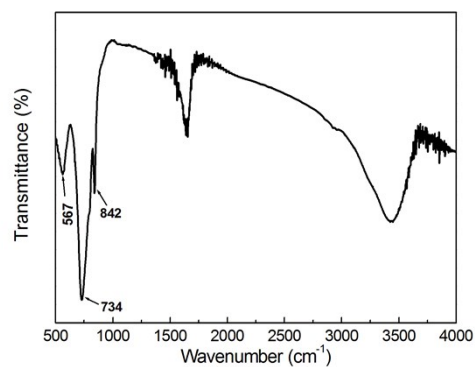


Fig. S9 FT-IR spectrum for the as-prepared UA-Bi₂MoO₆.

Obviously, the band at 567 cm⁻¹ and 734 cm⁻¹ could be considered as the asymmetric stretching mode and the bending vibration of the MoO₆. The band center at 842 cm⁻¹ could be identified based on asymmetric and symmetric vibration modes (Mo-O stretching) of the corner sharing (MoO₆)⁶⁻ octahedron. All these results confirm the as-prepared sample possesses pure phase and without any oleate ions on the surface.

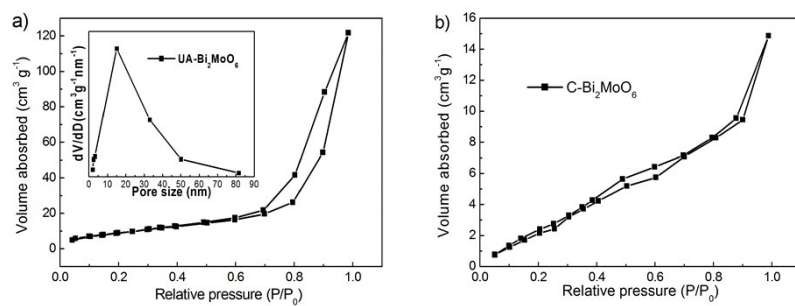


Fig. S10 N_2 -sorption isotherms of as-prepared a) UA-Bi₂MoO₆ and b) C-Bi₂MoO₆.

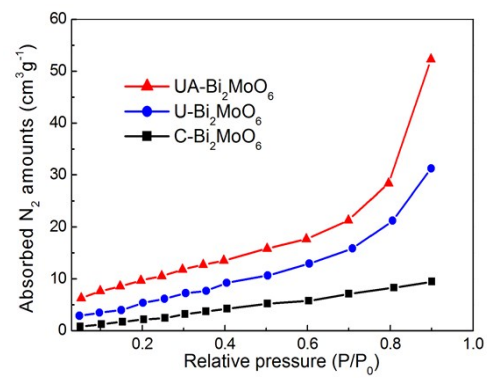


Fig. S11 N₂ absorption isotherms of different sample.

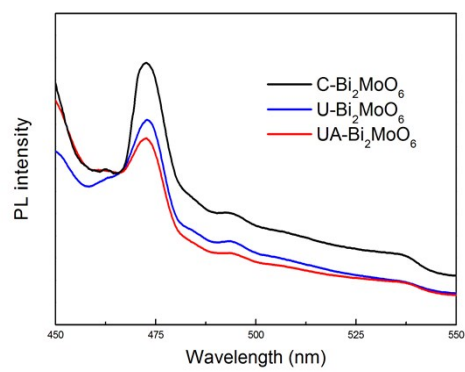


Fig. S12 PL spectrum for different samples.

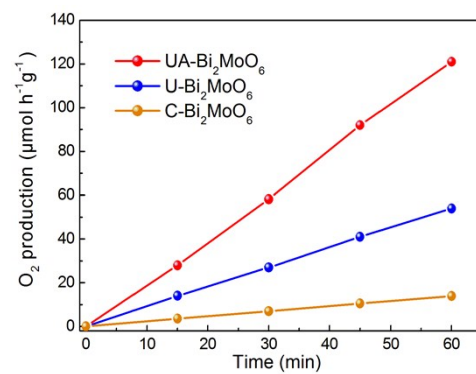


Fig. S13 Oxygen evolution rates of different samples under simulated sunlight irradiation without using any other co-catalysts.

Reference

- [1] A. Murphy, P. Barnes, L. Randeniya, I. Plumb, I. Grey, M. Horne and J. Glasscock, *Int. J. Hydrogen Energy*, 2006, 31, 1999.