v# Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Remarkable oxygen barrier films based on layered double hydroxide/chitosan hierarchical structure

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1. Experimental section

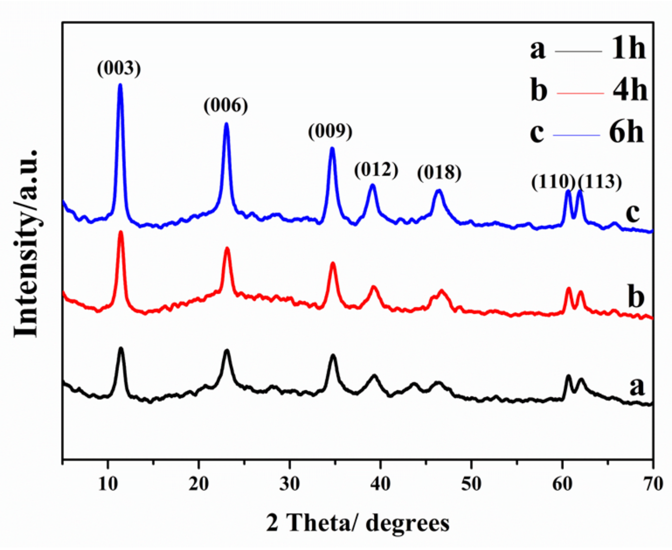

Fig. S1 XRD patterns of reconstructed H-LDH powders with different rehydration time: (a) 1 h; (b) 4 h and (c) 6 h.

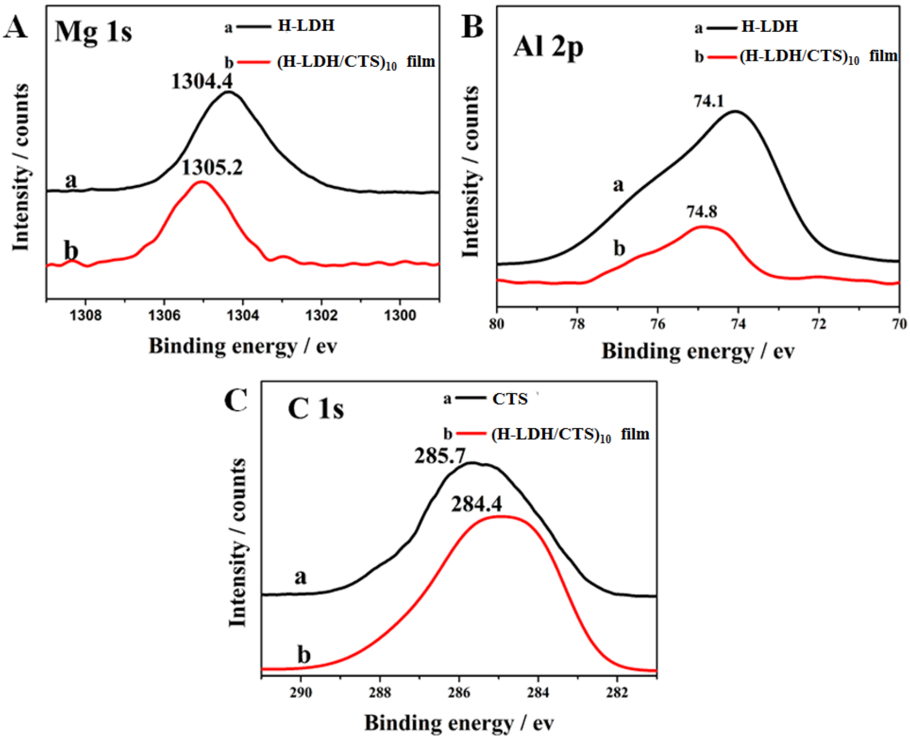

Fig. S2 (A) Mg 1s, (B) Al 2p XPS spectra for (a) H-LDH and (b) (H-LDH/CTS)$_{10}$ film, (C) C 1s XPS spectra for (a) CTS and (b) (H-LDH/CTS)$_{10}$ film.

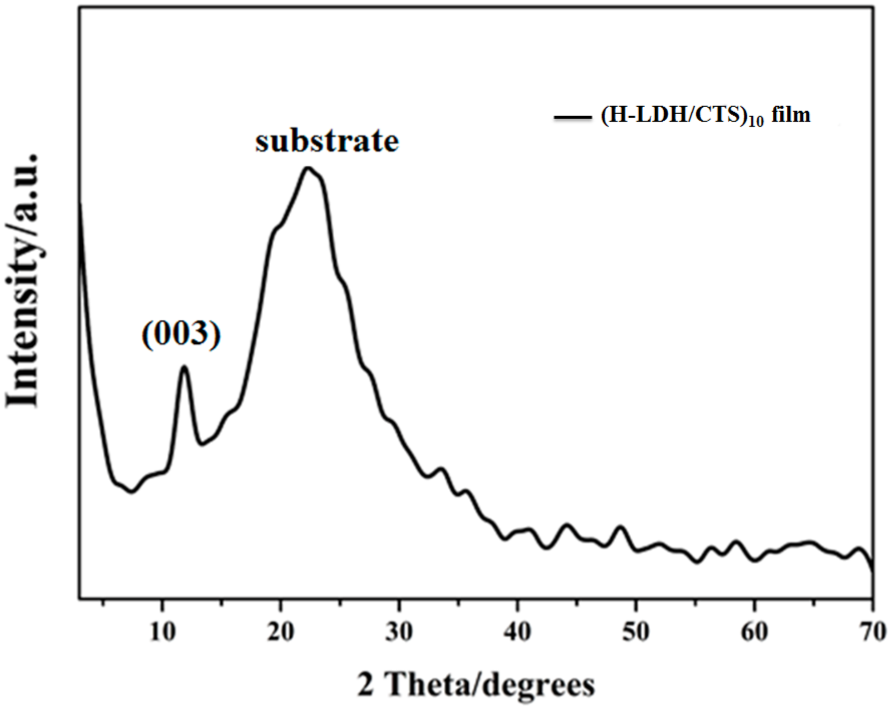

Fig. S3 XRD pattern of (H-LDH/CTS)$_{10}$ film.

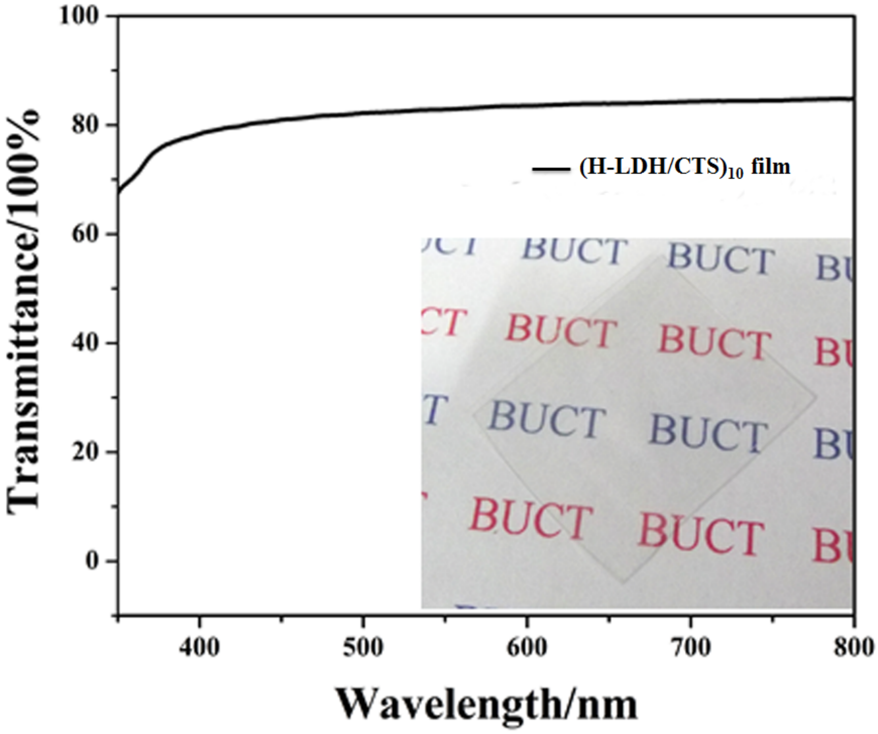

Fig. S4 UV-vis transmittance spectrum (inset: photograph) of the $(\text{H-LDH/CTS})_{10}$ film.

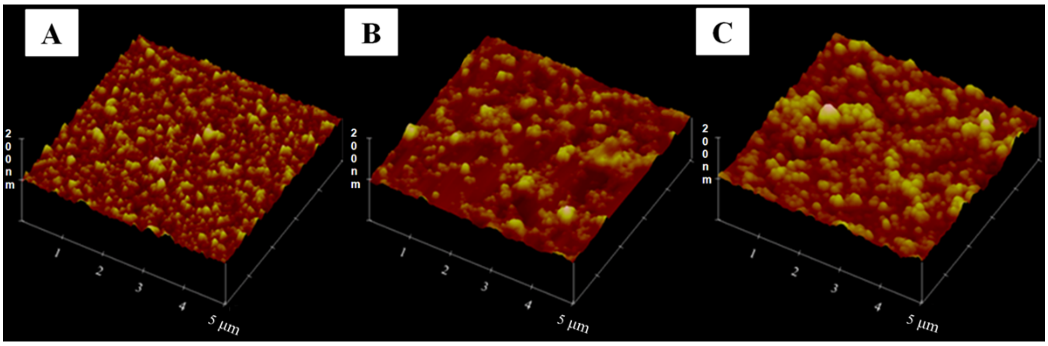

Fig. S5 AFM images of the $(\text{H-LDH/CTS})_n$ (n = 3, 6, 10) films.

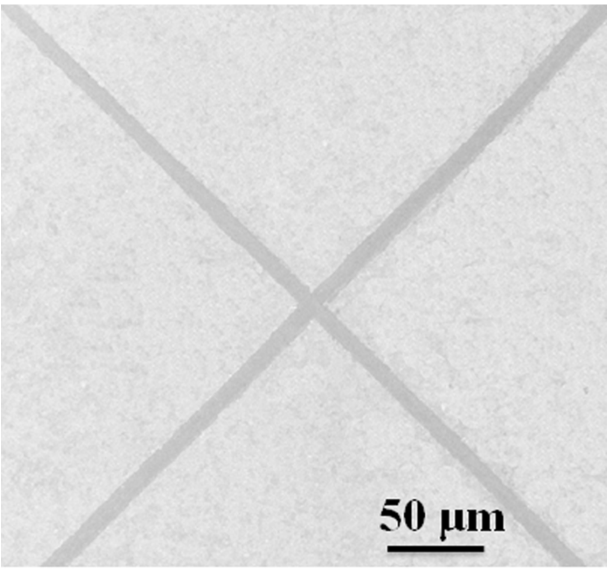

Fig. S6 SEM image of the (H-LDH/CTS)$_{10}$ film on PET substrate after scratching on its surface.

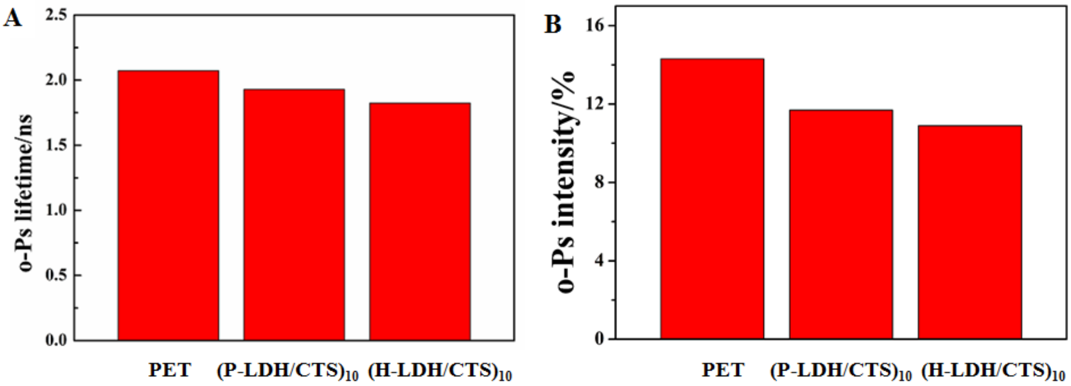

Fig. S7 (A) O-Ps lifetime and (B) intensity of PET, (P-LDH/CTS)$_{10}$ and (H-LDH/CTS)$_{10}$ films, respectively.

The positron annihilation lifetime spectroscopy (PALS) technique has been widely applied to determine the free volume properties of polymer materials based on an infinitive potential spherical model originally proposed by Tao et al in 1972.[1] The free volume fraction (F_V) is calculated from the following equation:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+0.166}\right)\right]^{-1} \qquad (1)$$

$$F_{\mathrm{V}} = C\left(\frac{4\pi}{3}R^3\right)I_3 \qquad (2)$$

Where τ_3 is the o-Ps lifetime; I_3 is o-Ps intensity, R is free volume size.

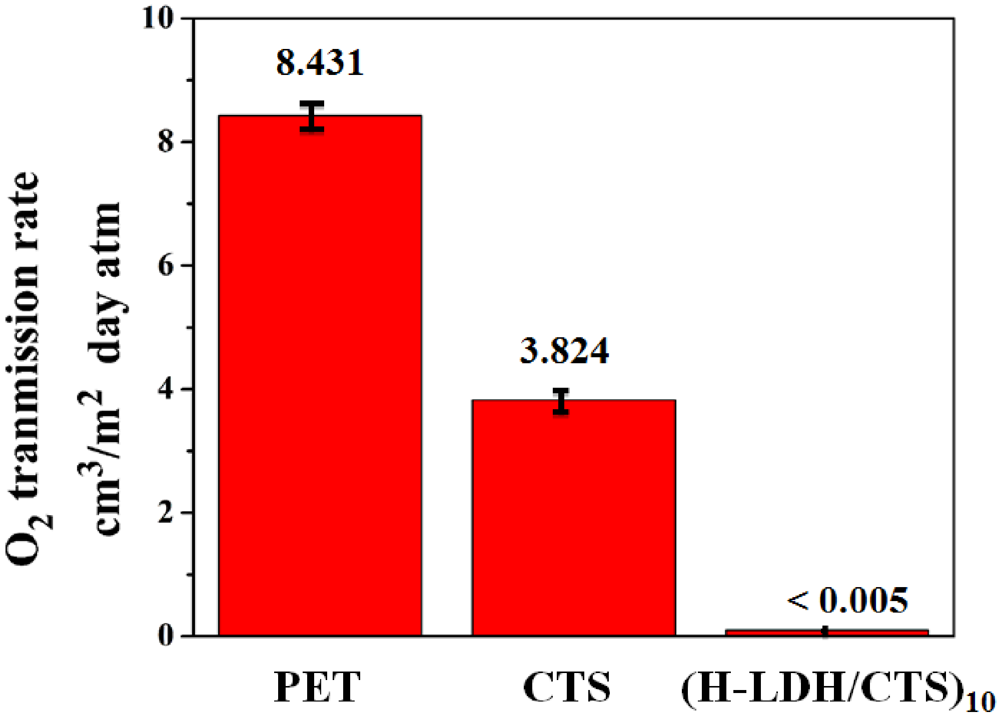

Fig. S8 Oxygen transmission rate values for PET, CTS and $(H\text{-}LDH/CTS)_{10}$ films, respectively.

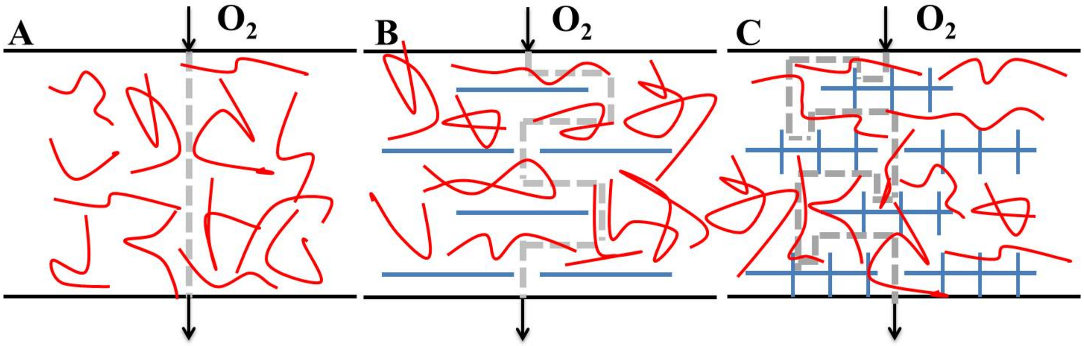

Fig. S9 Schematic representation showing the possible oxygen barrier mechanism for (A) CTS polymer, (B) $(P\text{-}LDH/CTS)_n$ and (C) $(H\text{-}LDH/CTS)_n$ films, respectively.

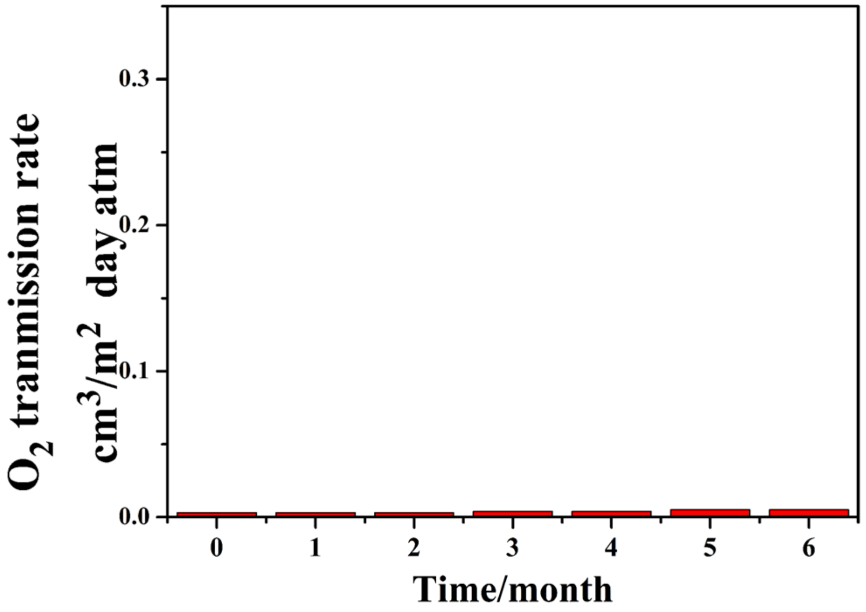

Fig. S10 OTR values for (H-LDH/CTS)$_{10}$ film (stored at room temperature) recorded monthly for 6 months.

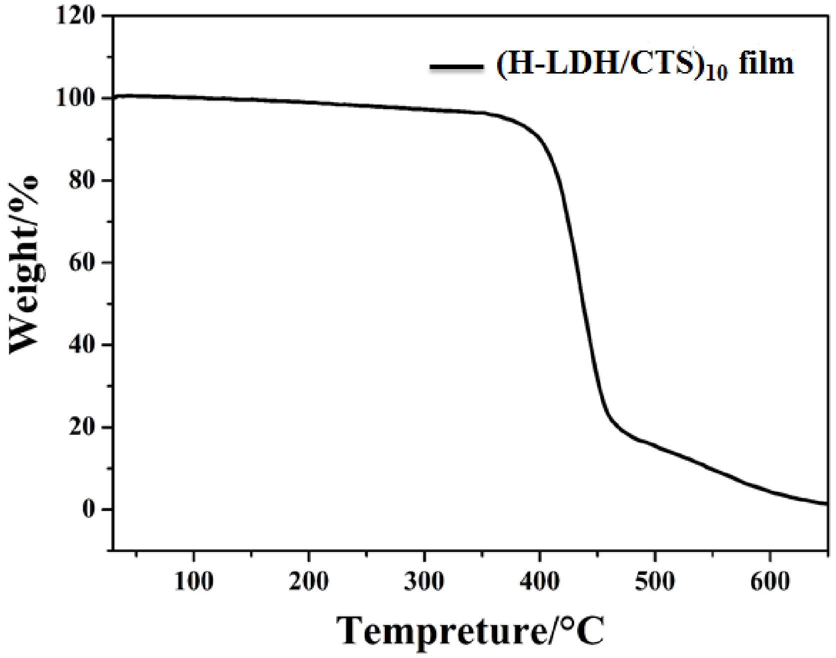

Fig. S11 Thermogravimetric curve for (H-LDH/CTS)$_{10}$ film.

2. Theoretical calculations

2.1 Models construction

The bulk MgAl-CO_3-LDH with molar ratio of Mg/Al=3:1 was built with the space group of $p\bar{3}m1$. The lattice parameters (*a*, *b*, and *c*) were obtained by the powder X-ray diffraction observation. The lattice parameters of the unit cell were set as follows: $a = b = 3.02$ Å, $c = 8.67$ Å (obtained from XRD results), $\alpha = \beta = 90°$, $\gamma = 120°$. The supercell of MgAl-CO_3-LDH is 4 × 4 × 1 in the *a*-, *b*- and *c*- directions, respectively. Two carbonate ions were put in the interlayer region randomly to keep the model neutral.

After geometric optimization, the P-LDH model with one bilayer of LDH nanosheet and one layer of carbonate was constructed by cleaving the (003) surface of P-LDH. The thickness of vacuum layer is 15 Å. The H-LDH model was built by deleting one hydroxyl of P-LDH model.

The H-LDH and P-LDH models were enlarged 5 × 2 × 1 in the *a*-, *b*- and *c*- directions, respectively. Therefore, *a* of the cell is as big as 60.4 Å, meaning the sizes of H-LDH and P-LDH are big enough to represent the materials. After that, four chains of $(CTS)_{12}$ were added into these two models randomly. The final models were named as H-LDH/CTS and P-LDH/CTS systems, which were used for density functional theory (DFT) calculations of adsorption energy and binding energy.

2.2 Computational method

For models of bulk MgAl-CO_3-LDH, P-LDH and H-LDH, the calculations were performed with the CASTEP code in the Materials Studio version 6.1 software package (Accelrys software inc.: San Diego, CA).[2] The density functional theory (DFT) calculations are carried out using a plane wave implementation[3] at the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) level.[4] The DFT dispersion correction is dealt with Tkatchenko-Scheffler method to better describe the noncovalent forces, such as hydrogen bonding and Van der Waals interactions. The ionic cores are described by ultrasoft pseudopotentials, which improve transferability and reduce the number of plane waves required in the expansion of the Kohn-Sham orbitals.[5] The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm is used to search the potential energy surface during optimization.[6] The structure optimizations are based on the following points: (1) an energy tolerance of 1×10^{-5} eV per atom; (2) a maximum force tolerance of 0.03 eV/Å; (3) a maximum displacement tolerance of 1×10^{-3} Å. A Fermi smearing of 0.1 eV and Pulay mixing are used to ensure the fast convergence of the self-consistent electron density.[7]

For H-LDH/CTS and P-LDH/CTS systems, the molecular dynamics (MD) simulations are performed using force field of LDHFF[8] developed by our group in isothermal-isobaric (*NPT*) ensemble. The temperature is set to be 298 K and the pressure to be 0.1 MPa. Temperature and pressure control are performed using the Andersen method[9] and the Berendsen method,[10] respectively. The long-range coulombic interactions are computed by the Ewald summation technique[11] and Van der Waals interactions are calculated using a “spline-cutoff” method. The time step is set to be 1 fs. All the molecular dynamics simulations are carried out using the Forcite module in the Materials Studio version 6.1 software package (Accelrys Software Inc.: San Diego, CA). For H-LDH/CTS, molecular dynamics simulations of 1000 ps are performed. The binding energy (E_B) between H-LDH and CTS is calculated as equation 1.

$$E_{\mathrm{B}} = E_{\mathrm{H-LDH/CTS}} - (E_{\mathrm{H-LDH}} + E_{\mathrm{CTS}}) \quad (1)$$

References:

1. S. J. Tao, *J. Chem. Phys.*, 1972, **56**, 5499.

2. (*a*) M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, M. C. Clark and M. C. Payne, *J. Phys.*, 2002, **14**, 2717; (*b*) M. Segall, M. Probert, C. Pickard, P. Hasnip, S. Clark, K. Refson and M. Payne, *CASTEP Module*, *MS Modeling*, version 2.2; Accelrys Inc.: San, Diego, CA, 2003.

3. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys*., 1992, **64**, 1045.

4. J. P Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865.

5. (*a*) M. Bajdich, M. Garcia-Mota, A. Vojvodic, J. K. Norskov and A. T. Bell, *J. Am. Chem. Soc*., 2013, **135**, 13521; (*b*) M. Garcia-Mota, M. Bajdich, V. Viswanathan, A. Vojvodic, A. T. Bell and J. K. Norskov, *J. Phys. Chem. C*, 2012, **116**, 21077.

6. P. L. Liao, J. A. Keith and E. A. Carter, *J. Am. Chem. Soc*., 2012, **134**, 13296.

7. A. Valdes, Z. W. Qu, G. J. Kroes, J. Rossmeisl and J. K. Norskov, *J. Phys. Chem. C*, 2008, **112**, 9872.

8. S. T. Zhang, H. Yan, M. Wei, D. G. Evans and X. Duan, *J. Phys. Chem. C*, 2012, **116**, 3421.

9. H. C. Andersen, *J. Chem. Phys.*, 1980, **72**, 2384.

10. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola and J. R. Haak, J.

Chem. Phys., 1984, **81**, 3684.

11. M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids; Clarendon: Oxford, U. K., 1987.