

# **Oxygen Vacancy Induced Bismuth Oxyiodide with Remarkably Increased Visible-light Absorption and Superior Photocatalytic Performance**

*Yongchao Huang, Haibo Li, Muhammad-Sadeeq Balogun, Wenyue Liu, Yexiang Tong,*

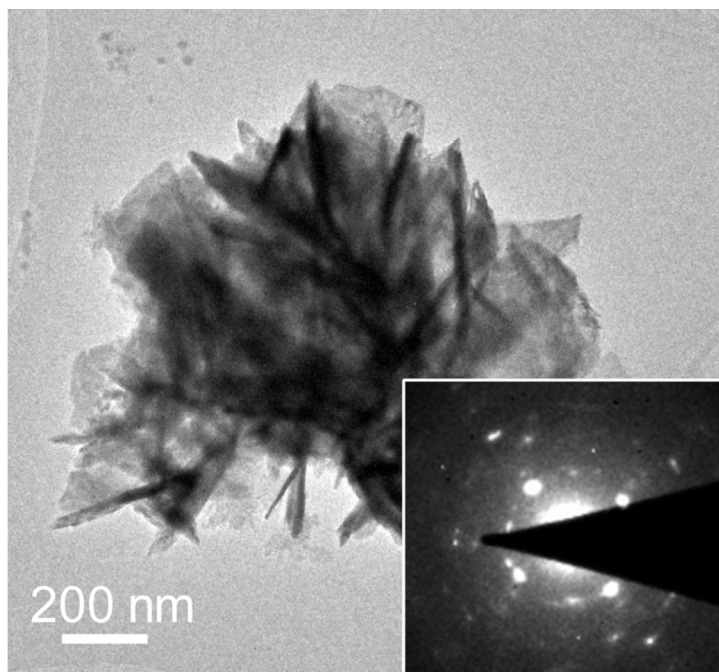
*Xihong Lu,\* and Hongbing Ji,\**

Department of Chemical Engineering, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, The Key Lab of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-Sen University,

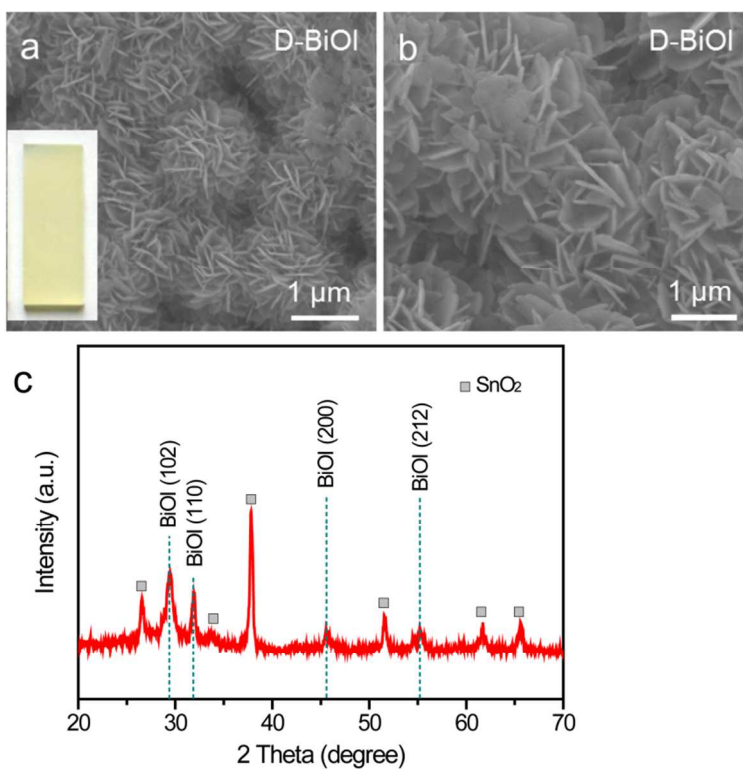
Guangzhou 510275, People's Republic of China.

Fax:(+86)2084112245

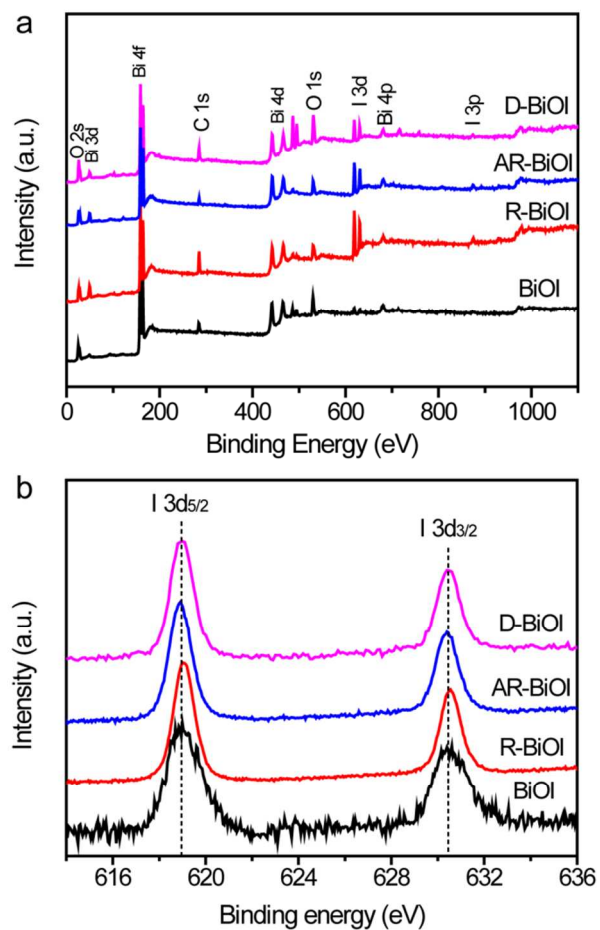
E-mail: [luxh6@mail.sysu.edu.cn](mailto:luxh6@mail.sysu.edu.cn) (X.H. Lu); [jihb@mail.sysu.edu.cn](mailto:jihb@mail.sysu.edu.cn) (H.B. Ji )



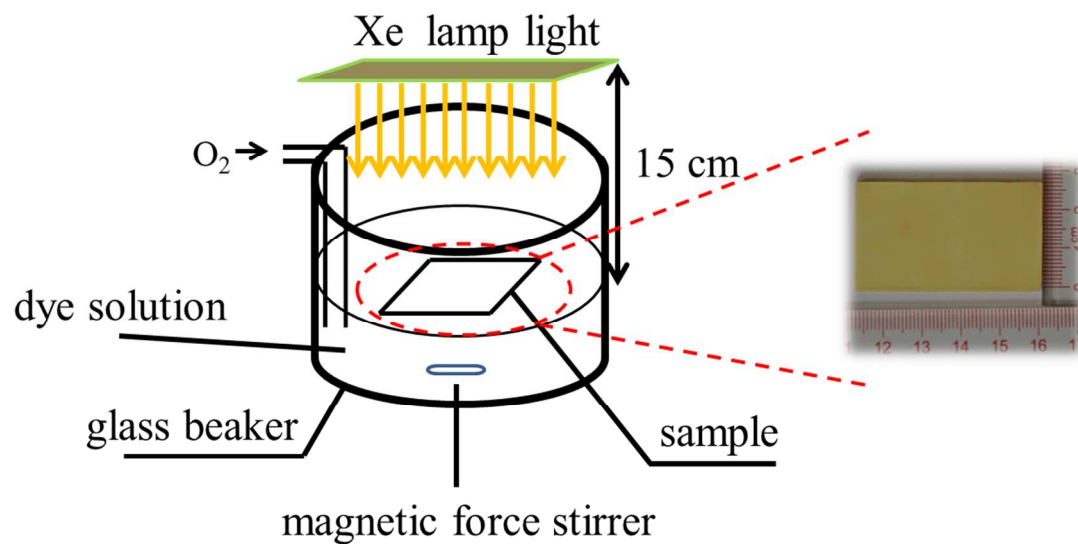
**Figure S1.** TEM image and SAED pattern of the as-prepared BiOI nanosheets.



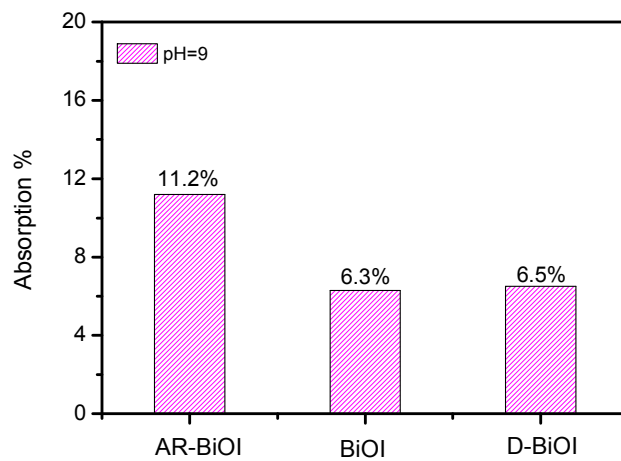
**Figure S2.** SEM images and XRD spectrum of the D-BiOI nanosheets. The inset in Figure S2a is its corresponding photograph



**Figure S3.** (a) XPS survey and (b) core level I 3d XPS spectra of the untreated BiOI, R-BiOI, AR-BiOI and D-BiOI samples.



**Figure S4.** Schematic diagram of the set up for photocatalytic dye degradation over BiOI sample.



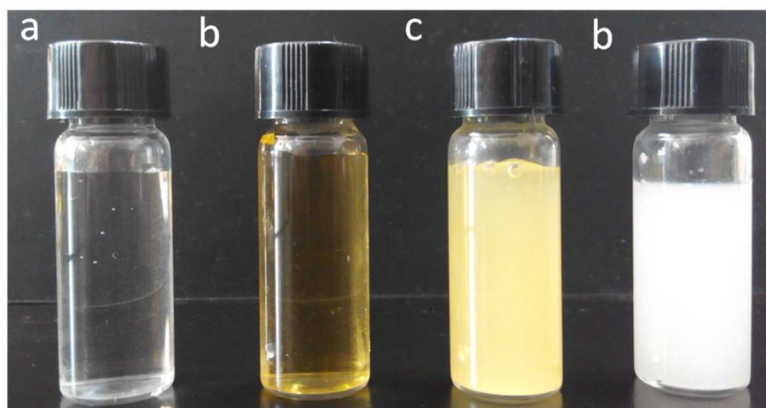
**Figure S5.** Adsorption capacity of MO over AR-BiOI solution with different pH after 60 min in the dark.

**Table S1.** Photocatalytic efficiencies of MO over BiOI-based photocatalysts under different conditions

Samples	Solution	Light source	Photocatalytic efficiency	Ref.
AR-BiOI (0.015 g)	100 mL MO (10 mg/L)	500 W Xe lamp coupled with a 420 nm cut-off filter	*T <sub>50</sub> =30 min T <sub>100</sub> =120 min	Our sample
Bi <sub>2</sub> S <sub>3</sub> /BiOI (0.10 g)	50 mL MO (10 mg/L)	500 W Xe lamp coupled with a 420 nm cut-off filter	T <sub>50</sub> =3 h T <sub>90</sub> = 5 h	<sup>1</sup>
BiOI/BiOBr (0.10 g)	50 mL MO (10 mg/L)	500 W Xe lamp coupled with a 420 nm cut-off filter	T <sub>50</sub> =18 min T <sub>90</sub> = 80 min	<sup>2</sup>
plate-like BiOI (0.1 g)	100 mL MO (10 mg/L)	500 W Xe lamp coupled with a 400 nm cut-off filter	T <sub>50</sub> =1.5 h T <sub>90</sub> =4 h	<sup>3</sup>
BiOI (0.05 g).	40 mL MO (20 mg/L)	350 W Xe lamp coupled with a 400 nm cut-off filter	T <sub>65</sub> = 2 h	<sup>4</sup>
ZnO/BiOI (0.1 g)	100 mL MO (10 mg/L)	500 W tungsten lamp with a 420 nm cut-off filter	T <sub>50</sub> =2 h T <sub>80</sub> =4 h	<sup>5</sup>
BiOCl/BiOI (0.05 g)	100 mL MO (10 mg/L)	300 W Xe lamp coupled with a 400 nm cut-off filter	T <sub>100</sub> =30 min	<sup>6</sup>
BiOI (0.1 g)	100 mL MO (10 mg/L)	500 W tungsten lamp with a 420 nm cut-off filter	T <sub>50</sub> =75 min T <sub>80</sub> =3 h	<sup>7</sup>

BiOI (0.03 g)	100 mL MO (10 mg/L)	150 W tungsten lamp with a 420 nm cut-off filter	T <sub>50</sub> =40 min T <sub>100</sub> =180 min	8
AgI/BiOI (0.1 g)	100 mL MO (10 mg/L)	300 W Xe lamp coupled with a 400 nm cut-off filter	T <sub>50</sub> =25 min T <sub>90</sub> =180 min	9
BiOI/TiO <sub>2</sub> (0.1 g)	100 mL MO (10 mg/L)	500 W tungsten lamp with a 420 nm cut-off filter	T <sub>50</sub> =1 h T <sub>100</sub> =4 h	10
Ag/BiOI (0.05 g)	50 mL MO (10 mg/L)	500 W Xe lamp coupled with a 420 nm cut-off filter	T <sub>50</sub> =60 min T <sub>80</sub> =4 h	11
BiOI/BiOBr (0.1 g)	50 mL MO (10 mg/L)	500 W Xe lamp coupled with a 420 nm cut-off filter	T <sub>50</sub> = 4.5 h T <sub>65</sub> =5 h	12
ZnWO <sub>4</sub> /BiOI (0.1 g)	100 mL MO (10 mg/L)	400 W metal halide lamp with a 420 nm cut-off filter	T <sub>50</sub> =1 h T <sub>86</sub> =4 h	13

\*T<sub>50</sub> means the time needs for photocatalytic degradation of 50% MO.



**Figure S6.** The photo image of (a) blank saturated  $\text{Ca(OH)}_2$  solution, (b) MO solution before light irradiation, (c) Saturated  $\text{Ca(OH)}_2$  after dropped 0.5 ml MO solution with light irradiation 15 min. (d) Saturated  $\text{Ca(OH)}_2$  after dropped 0.5 ml MO solution with light irradiation 90 min.

**Table S2** TOC, TC, IC, calculated generated  $\text{CO}_2$ , CO and efficiency of the MO degradation.

	TOC	TC	IC	$W_{\text{CO}_2}$	$W_{\text{CO}}$	$\eta$
AR-BiOI	1355.8	3457.3	2101.5	2012.2	3526.1	86%
Blank	6894.1	6983.4	89.3	0	--	--
DI water	0.5214	0.7528	0.2314	0	--	--

Total Organic Carbon (TOC) and Inorganic Carbon (IC) were measured with total organic carbon analyzer. One milliliter of the solution after the 90 min reaction was diluted to 50 ml

with DI water before the analysis. The TOC was calculated from Eq (1):

$$\text{TOC} = \text{TC} - \text{IC} \quad (1)$$

Where the TC is total carbon and IC is inorganic carbon. The generated  $\text{CO}_2$  would dissolve into the base solution and form carbonate which the pH was 9.0 measured by pH meter, and then IC would contain the generated  $\text{CO}_2$  and absorption of  $\text{CO}_2$ . As the IC of blank sample only can come from the absorption of  $\text{CO}_2$  in air, the generated  $\text{CO}_2$  of each samples should be calculated from Eq(2):

$$W_{\text{CO}_2} = \text{IC} - \text{IC blank} \quad (2)$$

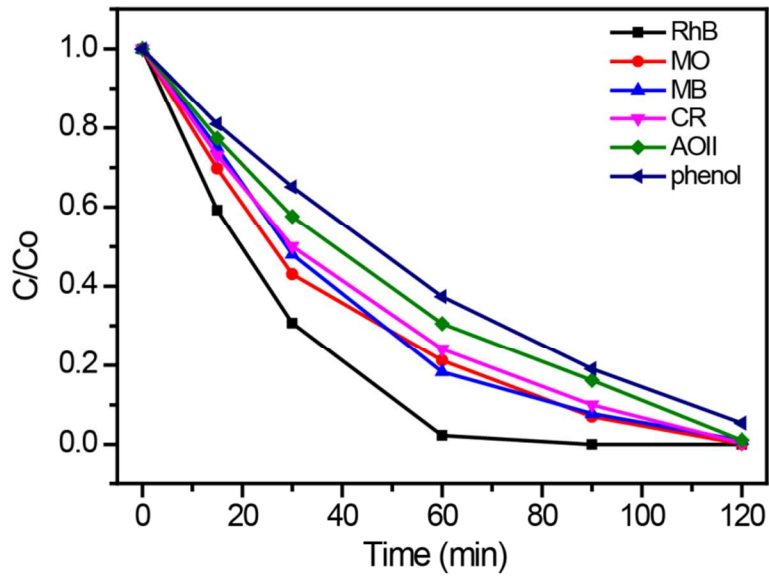
After the reaction, the carbon of the initial carbon became TOC still in the solution,  $\text{CO}_2$  transferring to carbonate and CO escaping into air. Then, we also can get the amount of the generated CO from Eq(3):

$$W_{\text{CO}} = \text{TOC blank} - \text{TOC} - W_{\text{CO}_2} \quad (3)$$

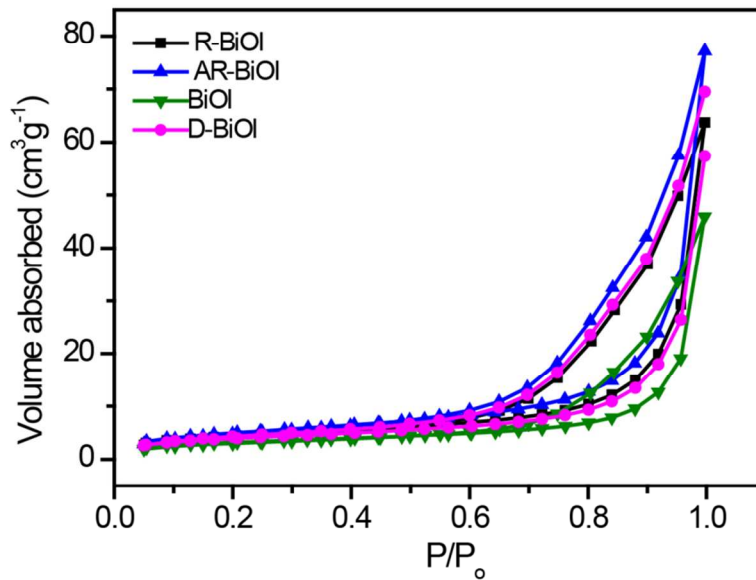
Furthermore, the efficiency of the glucose oxidation can be calculated by Eq (4):

$$\eta = [\text{W}(\text{CO}_2) + \text{W}(\text{CO})] \times 100\% / \text{W}(\text{MO}) \quad (4)$$

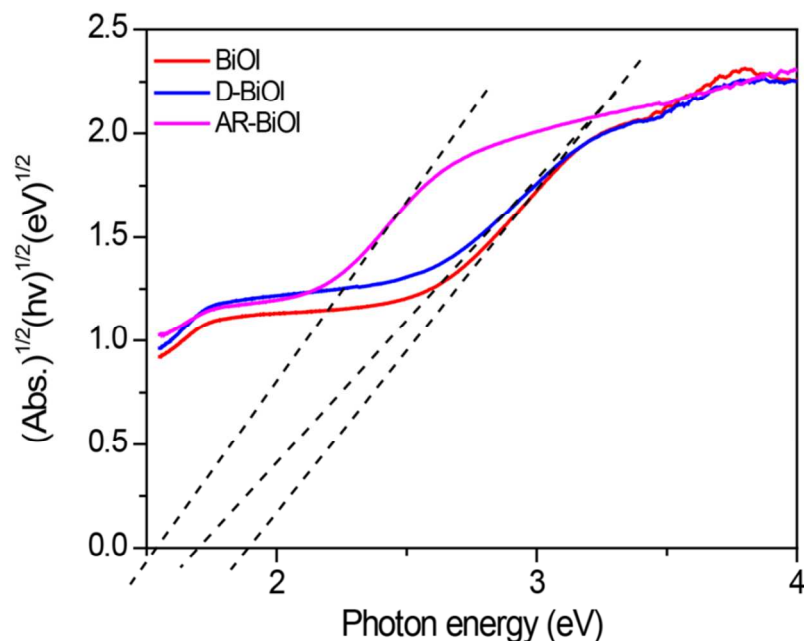




**Figure S7.** (a) Photocatalytic activity of AR-BiOI samples for degradation of different dyes under visible light irradiation



**Figure S8.** Nitrogen adsorption-desorption isotherm of untreated BiOI, R-BiOI, D-BiOI and AR-BiOI samples.



**Figure S9.** Plots of the  $(\alpha hv)^{1/2}$  vs photon energy ( $h\nu$ ) for untreated BiOI, D-BiOI and AR-BiOI samples.

- (1) Cao, J.; Xu, B.; Lin, H.; Luo, B.; Chen, S. Novel Heterostructured  $\text{Bi}_2\text{S}_3/\text{BiOI}$  Photocatalyst: Facile Preparation, Characterization and Visible Light Photocatalytic Performance. *Dalton Trans.* **2012**, *41*, 11482-11490.
- (2) Lin, H.; Ye, H.; Li, X.; Cao, J.; Chen, S. Facile Anion-Exchange Synthesis of BiOI/BiOBr Composite with Enhanced Photoelectrochemical and Photocatalytic Properties. *Ceram. Int.* **2014**, *7*, 9743-9750.
- (3) Cao, J.; Zhou, C.; Lin, H.; Xu, B.; Chen, S. Direct Hydrolysis Preparation of Plate-Like BiOI and Their Visible Light Photocatalytic Activity for Contaminant Removal. *Mate. Lett.* **2013**, *109*, 74-77.
- (4) Lei, Y.; Wang, G.; Song, S.; Fan, W.; Pang, M.; Tang, J.; Zhang, H. Room Temperature, Template-Free Synthesis of BiOI Hierarchical Structures: Visible-Light Photocatalytic and Electrochemical Hydrogen Storage Properties. *Dalton Trans.* **2010**, *39*, 3273-3278.
- (5) Jiang, J.; Zhang, X.; Sun, P.; Zhang, L. ZnO/BiOI Heterostructures: Photoinduced Charge-Transfer Property and Enhanced Visible-Light Photocatalytic Activity. *J. Physi.*

*Chem.C* **2011**, *115*, 20555-20564.

- (6) Li, T. B.; Chen, G.; Zhou, C.; Shen, Z. Y.; Jin, R. C.; Sun, J. X. New Photocatalyst BiOCl/BiOI Composites with Highly Enhanced Visible Light Photocatalytic Performances. *Dalton Trans.* **2011**, *40*, 6751-6758.
- (7) Xiao, X.; Zhang, W. D. Facile Synthesis of Nanostructured BiOI Microspheres with High Visible Light-Induced Photocatalytic Activity. *J.Mate. Chem.* **2010**, *20*, 5866-5870.
- (8) Wang, Y.; Deng, K.; Zhang, L. Visible Light Photocatalysis of BiOI and Its Photocatalytic Activity Enhancement by in Situ Ionic Liquid Modification . *J.Phys.Chem. C* **2011**, *115*, 14300-14308.
- (9) Cheng, H.; Huang, B.; Dai, Y.; Qin, X.; Zhang, X. One-Step Synthesis of the Nanostructured AgI/BiOI Composites with Highly Enhanced Visible-Light Photocatalytic Performances. *Langmuir* **2010**, *26*, 6618-6624.
- (10) Dai, G.; Yu, J.; Liu, G. Synthesis and Enhanced Visible-Light Photoelectrocatalytic Activity of p-n Junction BiOI/TiO<sub>2</sub> Nanotube Arrays *J. Phys.Chem. C* **2011**, *115*, 7339-7346.
- (11) Liu, H.; Cao, W.; Su, Y.; Wang, Y.; Wang, X. Synthesis, Characterization and Photocatalytic Performance of Novel Visible-Light-Induced Ag/BiOI. *Appl. Catal. B: Environ.* **2012**, *111*, 271-279.
- (12) Cao, J.; Xu, B.; Luo, B.; Lin, H.; Chen, S. Novel BiOI/BiOBr Heterojunction Photocatalysts with Enhanced Visible Light Photocatalytic Properties. *Cata.Comm.* **2011**, *13*, 63-68.
- (13) Li, P.; Zhao, X.; Jia, C.j.; Sun, H.; Sun, L.; Cheng, X.; Liu, L.; Fan, W. ZnWO<sub>4</sub>/BiOI Heterostructures with Highly Efficient Visible Light Photocatalytic Activity: the Case of Interface Lattice and Energy Level Match. *J.Mate.Chem. A* **2013**, *1*, 3421-3429.