

Supporting Information

**Enhanced sodium storage by hetero-interface effect in
BiOCl/TiO₂ p-n junctions**

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Experiment

A series of BiOCl/TiO₂ p-n junctions with different mass ratio were synthesized via a facile sol-gel method and followed by heat treatment. Certain amount of BiCl₃ was dissolved into 25 mL glycol to form a uniform yellowish solution. 2.5 g titanium butoxide was added dropwise to the solution under magnetic stirring. After that, the gel was dried at 180 °C to remove the solvent and then calcined at 500 °C for 2 h in air. The product was washed by water and ethanol for several times and dried at 60 °C. Pure-phased TiO₂ and BiOCl were also synthesized for comparison according to similar procedure. BiOCl/TiO₂ p-n junctions are named as 7%-BiOCl/TiO₂, 14%-BiOCl/TiO₂ and 28%-BiOCl/TiO₂ based on mass ratio of BiCl₃ (0.175 g, 0.35 g, 0.7 g) and titanium butoxide (2.5 g).

X-ray diffraction (XRD) was measured using Rigaku MiniFlex600. Transmission electron microscopy (TEM) was performed on JEOL JEM2100F. X-ray absorption spectroscopy (XAS) was carried out in Photoelectron Spectroscopy Station (4B9B, Beijing Synchrotron Radiation Facility). Ultraviolet-visible spectroscopy (UV-Vis) was obtained utilizing U-3900 (Hitachi). X-ray photoelectron spectroscopy (XPS) was recorded by Escalab 250Xi (Thermo Fisher Scientific). N₂ adsorption-desorption isotherms were conducted by BeiShiDe (3H-2000 PS2).

The electrodes were prepared in a conventional way by mixing the active materials with Super P and a sodium alginate binder and then tested in coin cell. The electrolyte was consisted of 1 M NaClO₄ in ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1 and 5% fluorinated ethylene carbonate (FEC) as an

electrolyte additive. The discharge-charge measurements were collected on a battery tester (Land CT2001A, China) in the voltage range between 0.01 V and 3 V. The CV curves of the TiO₂, 14%-BiOCl/TiO₂ and BiOCl electrodes were recorded between 0.01 V and 3 V at different scan rates from 0.1 mV s⁻¹ to 1.0 mV s⁻¹ on CHI1000C electrochemical workstation. Electrochemical impedance spectra (EIS) were analyzed on an electrochemical workstation (CHI660E, China), collecting by 5.0 mV amplitude over the range from 10⁻¹ Hz to 10⁵ Hz.

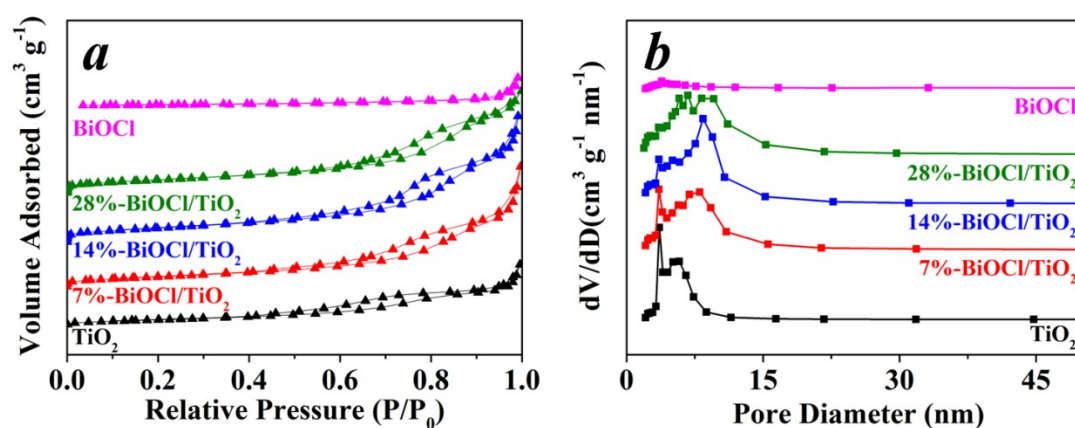


Fig. S1 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of BiOCl/TiO₂ p-n junctions, pure TiO₂ and pure BiOCl

| samples | BET surface area (m ² g ⁻¹) | pore volume (ml g ⁻¹) | average pore diameter (nm) |
|----------------------------|--|-----------------------------------|----------------------------|
| TiO ₂ | 30.0219 | 0.1165 | 8.15 |
| 7%-BiOCl/TiO ₂ | 48.3393 | 0.2158 | 11.24 |
| 14%-BiOCl/TiO ₂ | 59.7670 | 0.2256 | 10.06 |
| 28%-BiOCl/TiO ₂ | 53.7416 | 0.1813 | 9.09 |
| BiOCl | 4.1618 | 0.0479 | 20.25 |

Table.1 BET surface area, pore volume and average pore diameter of BiOCl/TiO₂ p-n junctions, pure TiO₂ and pure BiOCl

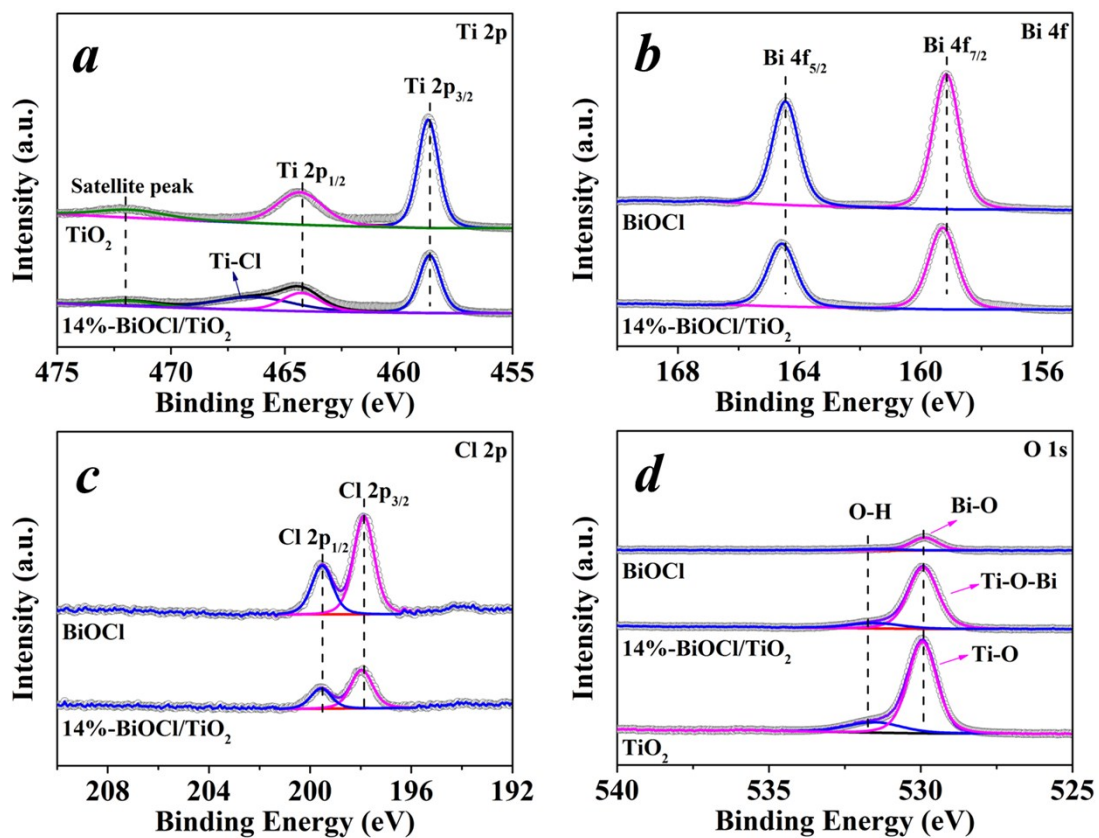


Fig. S2 XPS spectra of 14%-BiOCl/TiO₂, pure TiO₂ and pure BiOCl

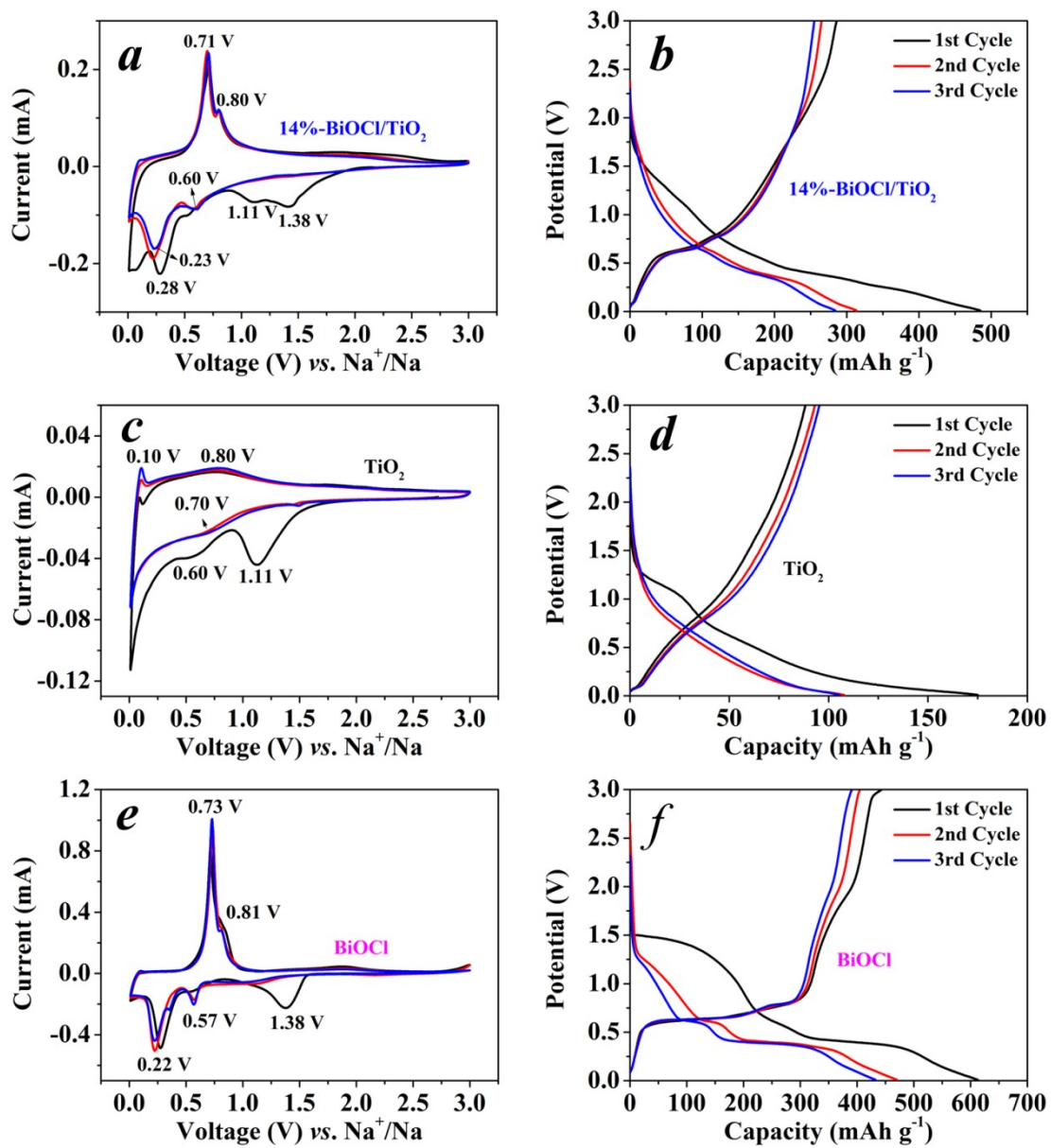


Fig. S3 CV and charge-discharge curves of 14%-BiOCl/TiO₂, pure TiO₂ and pure BiOCl

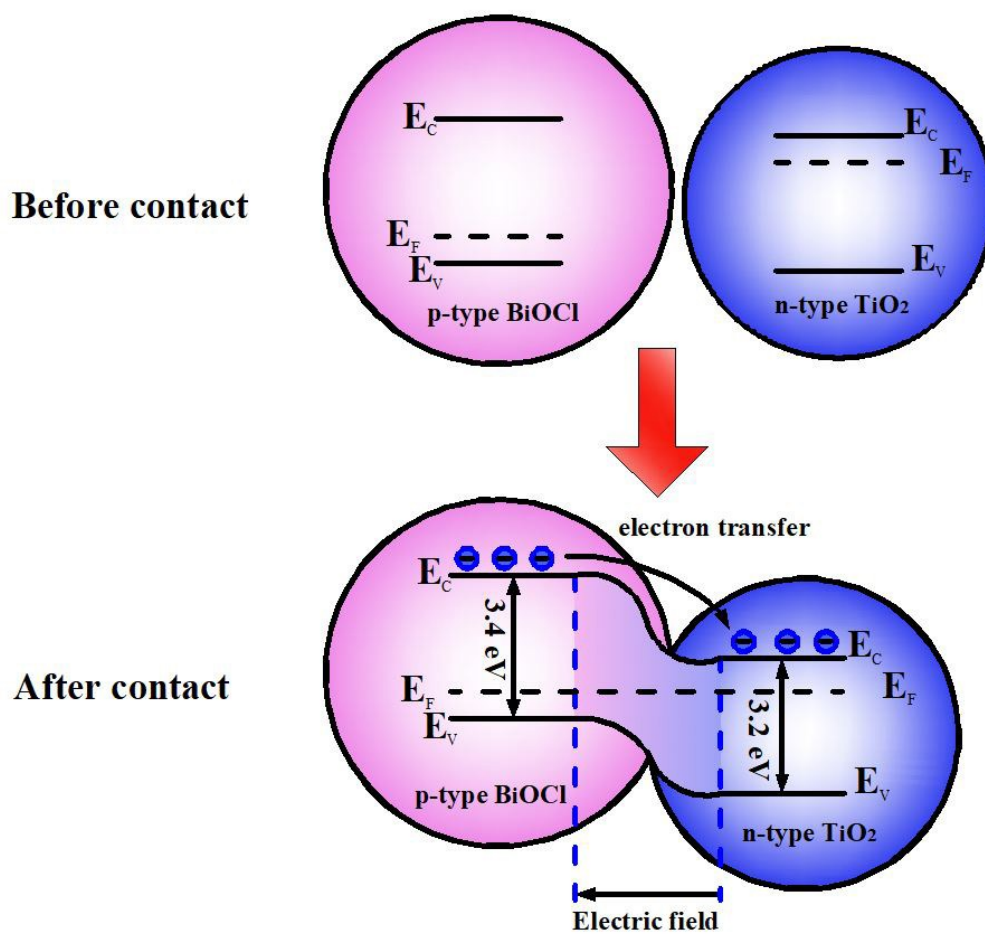


Fig. S4 the formation scheme of BiOCl/TiO₂ p-n junctions

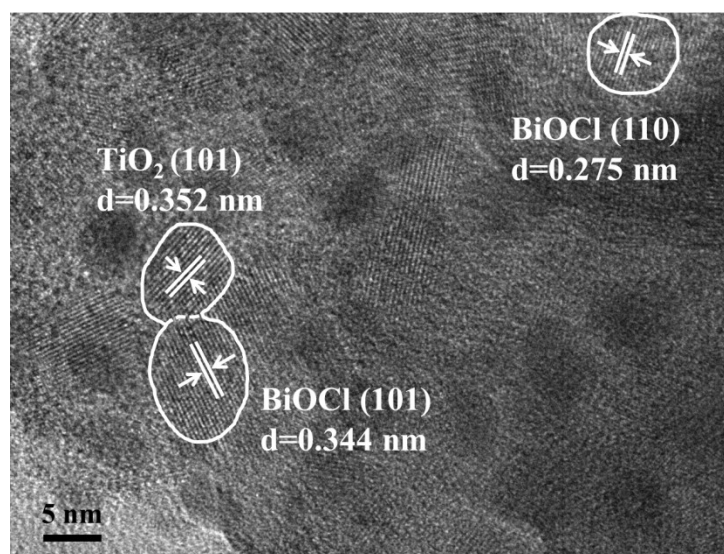


Fig. S5 HRTEM image of 14%-BiOCl/TiO₂ electrode after 100 cycles

| materials | Rate performance | Reference |
|--|--|-----------|
| 14%-BiOCl/TiO ₂ | 154 mAh g ⁻¹ at 1 A g ⁻¹ 124 mAh g ⁻¹ at 2 A g ⁻¹ | this work |
| Oxygen Deficient Anatase TiO ₂ | 124.6 mAh g ⁻¹ at 1 A g ⁻¹ | 1 |
| Niobium-doped anatase TiO ₂ | 108.8 mAh g ⁻¹ at 5 C (1 C=330 mA g ⁻¹) | 2 |
| N/S co-doped TiO ₂ nanoparticles | 75 mAh g ⁻¹ at 1 A g ⁻¹ | 3 |
| pinecone-like carbon- coupled TiO ₂ | 139.7 mAh g ⁻¹ at 5 C (1 C=336 mA g ⁻¹) | 4 |
| TiO ₂ /C nanopowders | 93 mAh g ⁻¹ at 2 A g ⁻¹ | 5 |
| Anatase TiO ₂ @C composites | 111.1 mAh g ⁻¹ at 1 A g ⁻¹ | 6 |
| Carbon coated anatase TiO ₂ mesocrystals | 113.3 mAh g ⁻¹ at 10 C (1 C=168 mA g ⁻¹) | 7 |
| Carbon-coated rutile titanium dioxide | 86.8 mAh g ⁻¹ at 10 C (1 C=168 mA g ⁻¹) | 8 |
| TiO ₂ @N-doped graphene | 140 mAh g ⁻¹ at 5 C (1 C=335 mA g ⁻¹) | 9 |

Table. 2 Comparison of rate performance for 14%-BiOCl/TiO₂ with some TiO₂-based anodes modified by carbon coating and heteroatoms doping

Reference

- 1 W. Wang, M. Wu, P. Han, Y. Liu, L. He, Q. Huang, J. Wang, W. Yan, L. Fu, and Y. Wu, *ACS Appl. Mater. Interfaces*, 2018, **11**, 3061.
- 2 F. Zhao, B. Wang, Y. Tang, H. Ge, Z. Huang and H. Liu, *J. Mater. Chem. A*, 2015, **3**, 22969.
- 3 W. Song, H. Zhao, L. Wang, S. Liu, and Z. Li, *ChemElectroChem*, 2018, **5**, 316.
- 4 J. Chen, G. Zou, H. Hou, Y. Zhang, Z. Huang and X. Ji, *J. Mater. Chem. A*, 2016, **4**, 12591.
- 5 C. Ding, T. Nohira and R. Hagiwara, *J. Mater. Chem. A.*, 2015, **3**, 20767.
- 6 X. Shi, Z. Zhang, K. Du, Y. Lai, J. Fang and J. Li, *J. Power Sources*, 2016, **330**, 2.
- 7 W. Zhang, T. Lan, T. Ding, N. Wu and M. Wei, *J. Power Sources*, 2017, **359**, 64.
- 8 G. Zou, J. Chen, Y. Zhang, C. Wang, Z. Huang, S. Li, H. Liao, J. Wang and X. Ji, *J. Power Sources*, 2016, **325**, 25.
- 9 B. Li, B. Xi, Z. Feng, Y. Lin, J. Liu, J. Feng and Y. Qian, *Adv. Mater.*, 2018, **1705788**, 1.