基于s-p杂化理论开发新型太阳能转化材料

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Outline

- **Introduction: *sp* hybridization**

Four stories

Symmetry

- **$Bi_{24}O_{31}Br_{10}/Bi_{24}O_{31}Cl_{10}$**
- **$Ag_{10}Si_4O_{13}$**

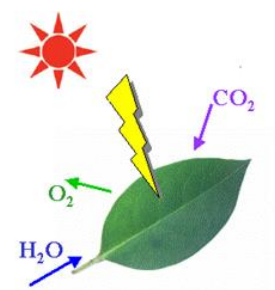
Symmetry Breaking

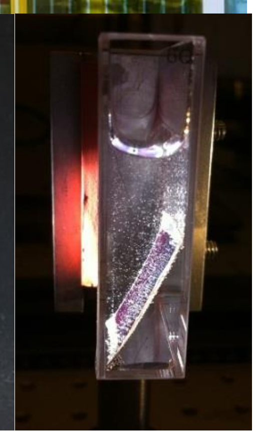
- **Vacancy Engineering – Blank TiO_2**
- **Strain engineering – BiOBr**

太阳能转化和利用：国家重大战略需求、国际学术前沿

Solar Energy-Heat
(Radiation, Concentrating
Solar Power(CSP)）

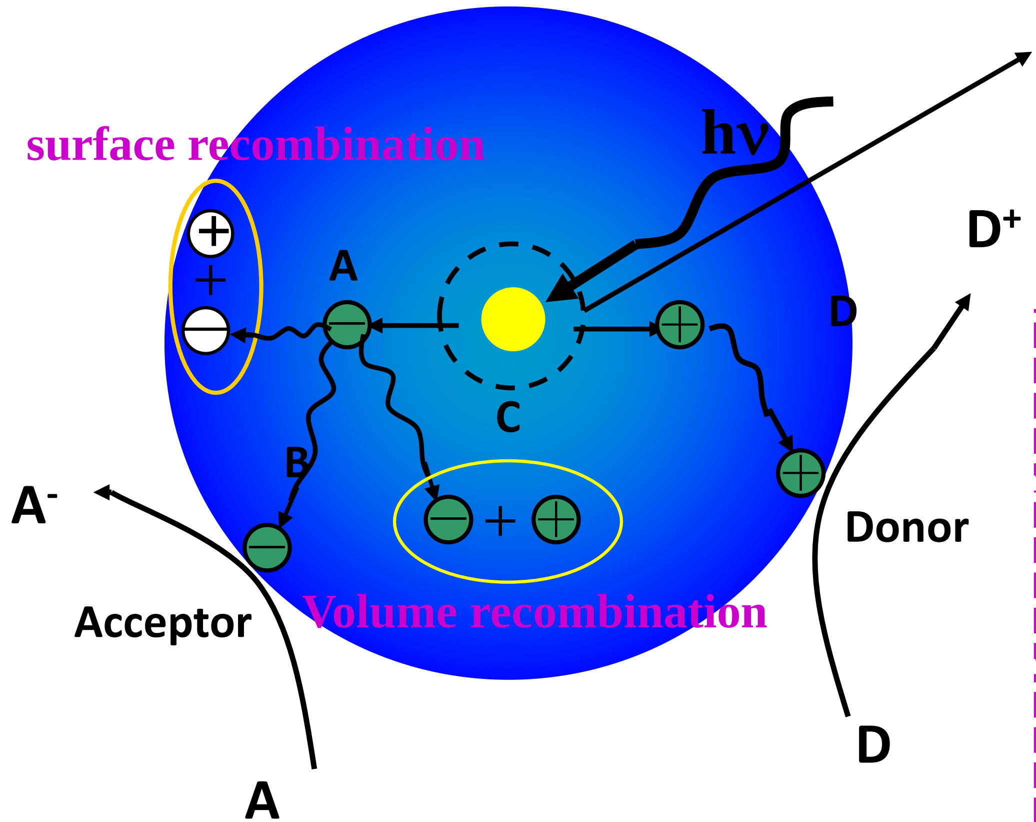
Solar Energy-Electrical Energy



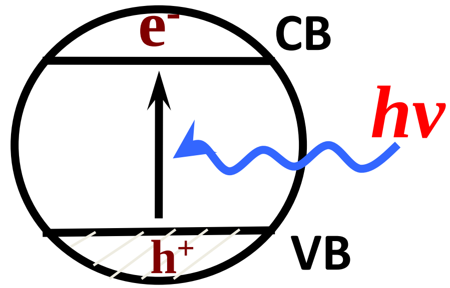


Solar Energy-Chemical Energy

Semiconductor Photocatalysis



Main processes in photocatalytic reaction



Redox reaction

$H^+ + 2e^- \rightarrow H_2$

$H_2O + 2h \rightarrow 2H^+ + 1/2O_2$

$h^+ + H_2O \rightarrow \cdot OH + H^+$

$h^+ + OH^- \rightarrow \cdot OH$

$O_2 + e^- \rightarrow \cdot O^{2-}$

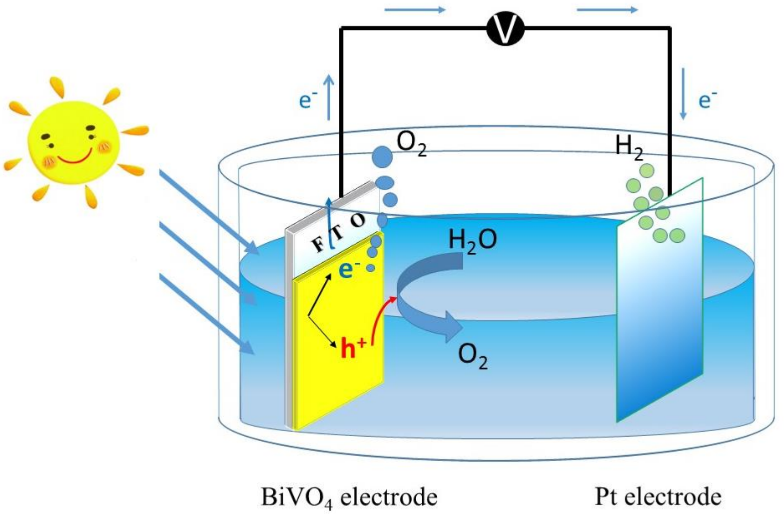
$\cdot O^{2-} + H_2O \rightarrow \cdot OOH + OH^-$

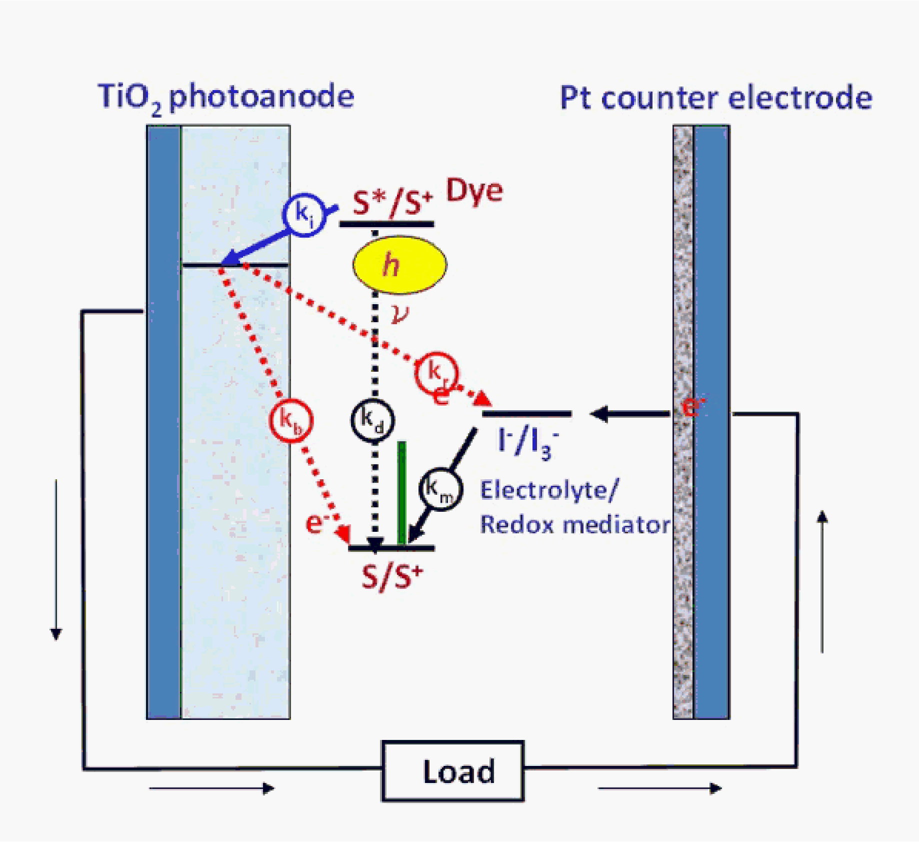
$2 \cdot OOH \rightarrow O_2 + H_2O_2$

$\cdot OOH + H_2O + e^- \rightarrow H_2O_2 + OH^-$

$H_2O_2 + e^- \rightarrow \cdot OH + OH^-$

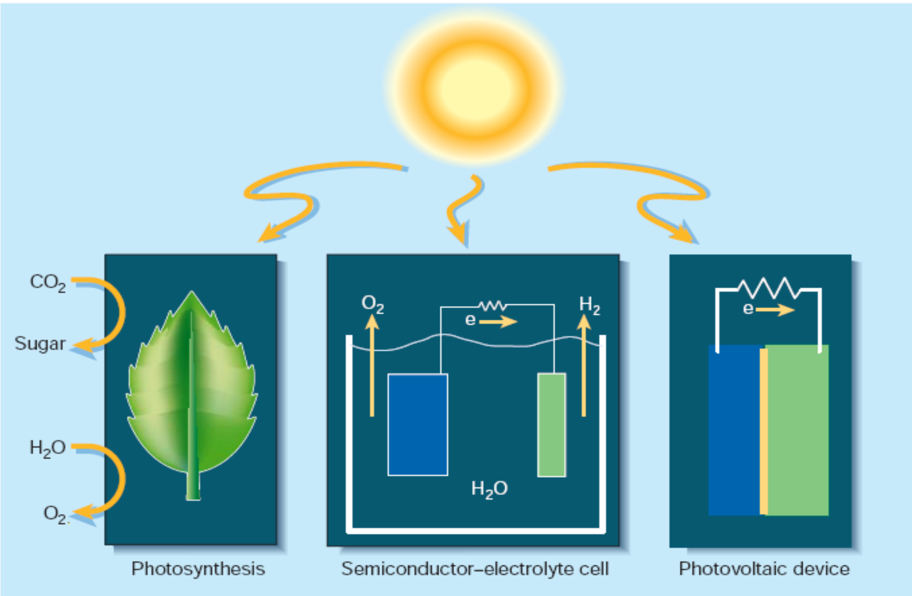
Solar Cell





Photoelectrochemical cell **Dye-sensitized solar cell**

关键科学问题



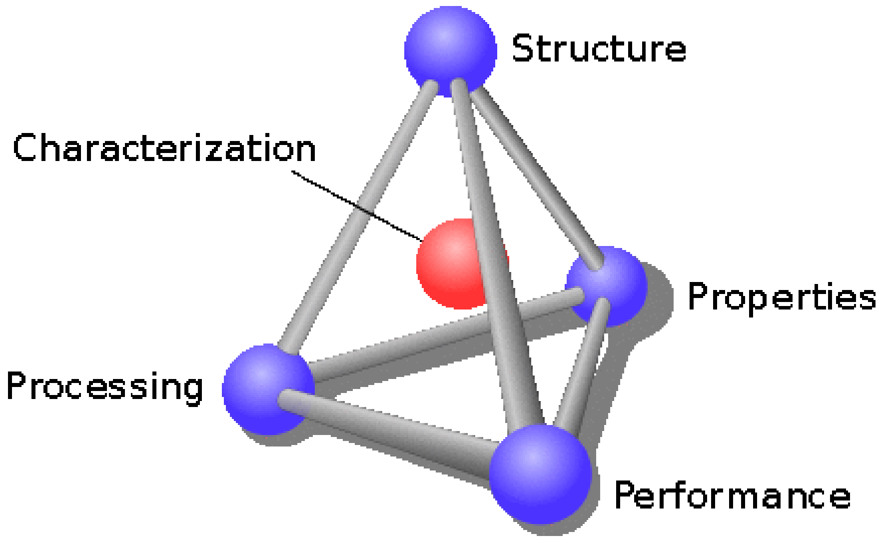
- Solar absorption η_A
- Charge separation η_S
- Energy conversion η_C

- 光与物质相互作用的本质与规律
- 半导体材料中光生载流子产生、输运与能量转化物理机制

$$\eta = \eta_A \times \eta_S \times \eta_C$$

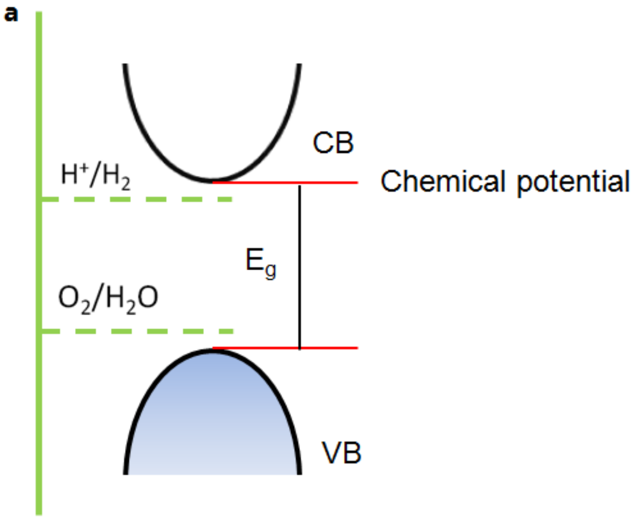
Fundamental scientific issues

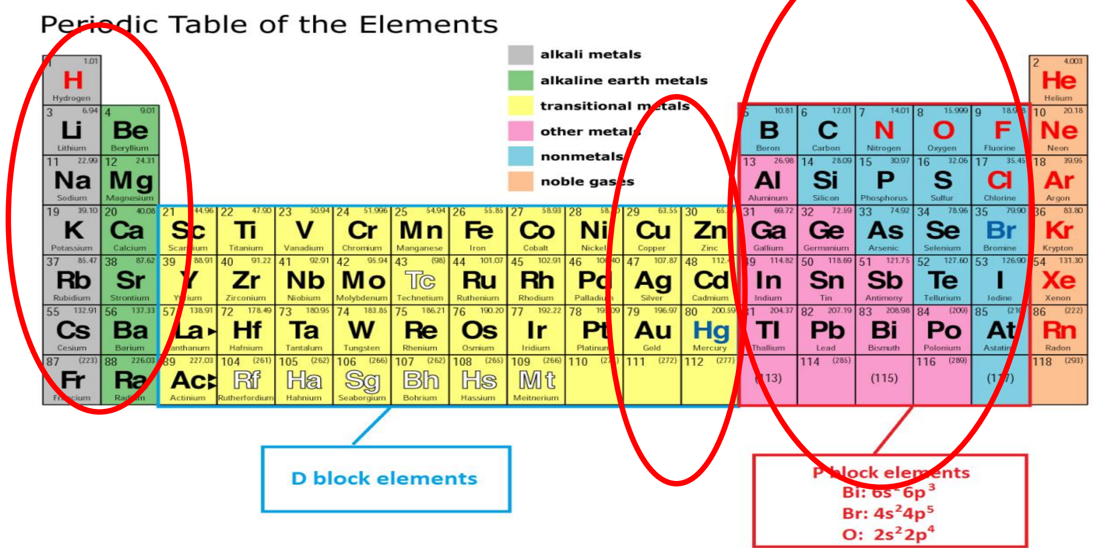
- Elements
- Crystalline structure (symmetry), Defects, Surface state
- Internal Stress, Internal electric fields
- Electronic Structure
- Properties



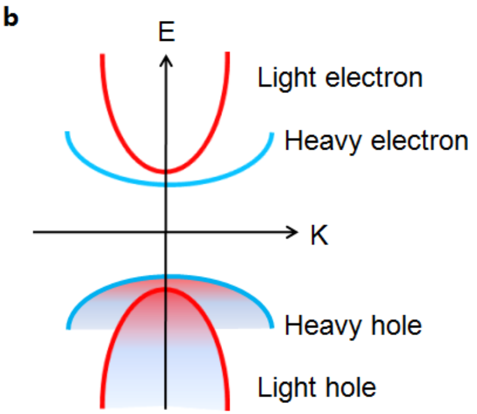
提出了新的物理路线：基于sp杂化寻找新型光能转化材料

a





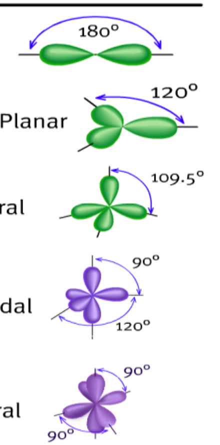
b



sp hybridization
Anisotropy orbital
Dispersive band

$$m^* = \frac{1}{\frac{1}{\hbar^2}\frac{d^2E}{dk^2}}$$

Pure atomic orbitals of central atom	Hybridization of the central atom	Number of hybrid orbitals	Shape of hybrid orbitals
s,p	sp	2	Linear
s,p,p	sp^2	3	Trigonal Planar
s,p,p,p	sp^3	4	Tetrahedral
s,p,p,p,d	sp^3d	5	Trigonal Bipyramidal
s,p,p,p,d,d	sp^3d^2	6	Octahedral



Metal: Na K Mg Ca Sr Ba In Sn Sb Bi Cu Zn Ag
Nonmetal: O S X (X=F, Cl, Br, I) B C N P
Nothing is Impossible

Orbital overlapping

$$\hat{H}\Psi(x) = E\Psi(x)$$

$$E_n(\vec{k}) = E_n^a + A_n + J_n \sum_{r_{near}} e^{i\vec{k}\cdot\vec{r}_{near}}$$

E_n^a Atomic energy level

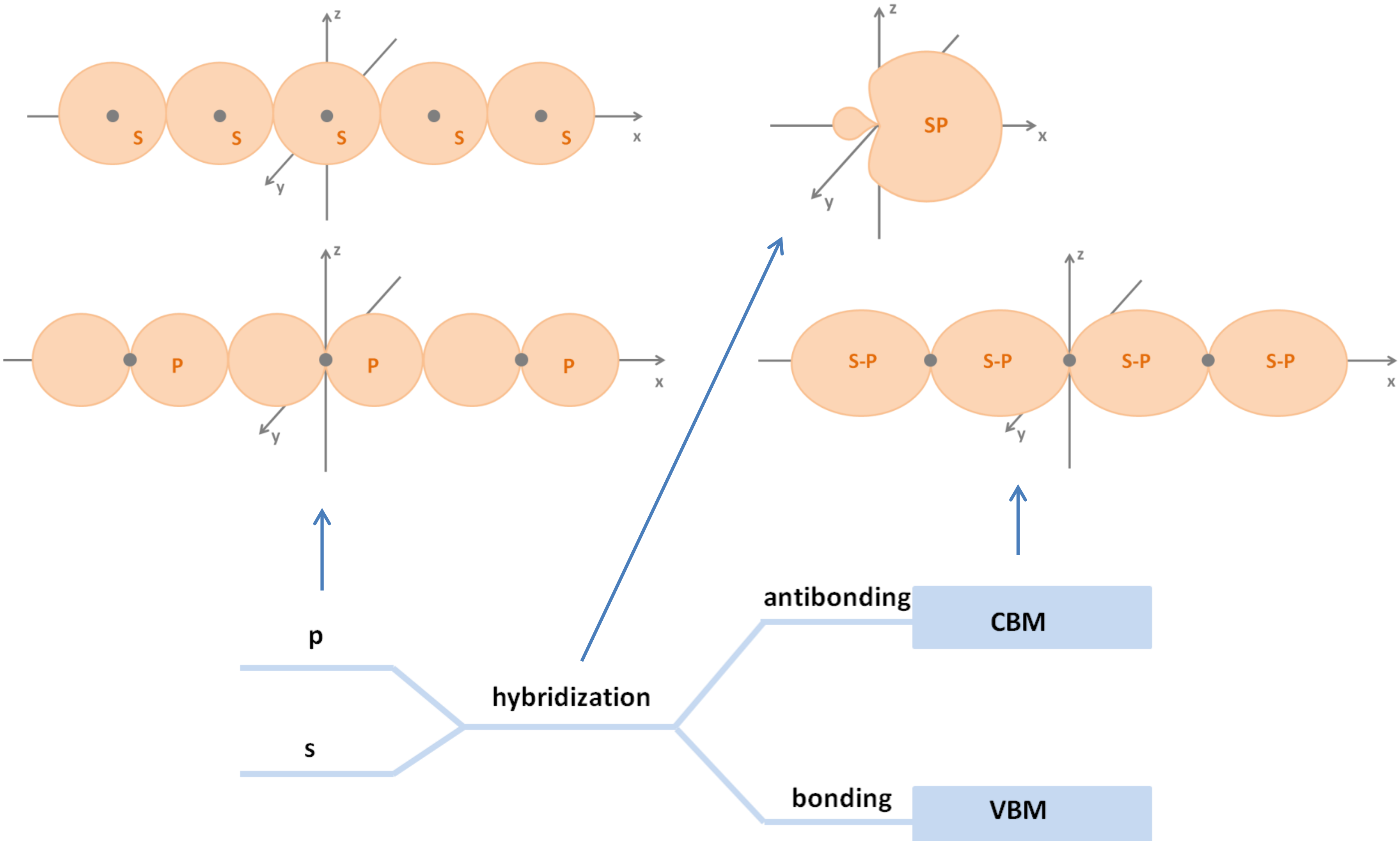
A_n The influence on the movement of the Atomic energy level

J_n The overlap integral of the atom with its nearest neighbors

Band width is proportional to the degree of the orbital overlap

Larger overlap, wider Band, more dispersive band

Energy level and energy band



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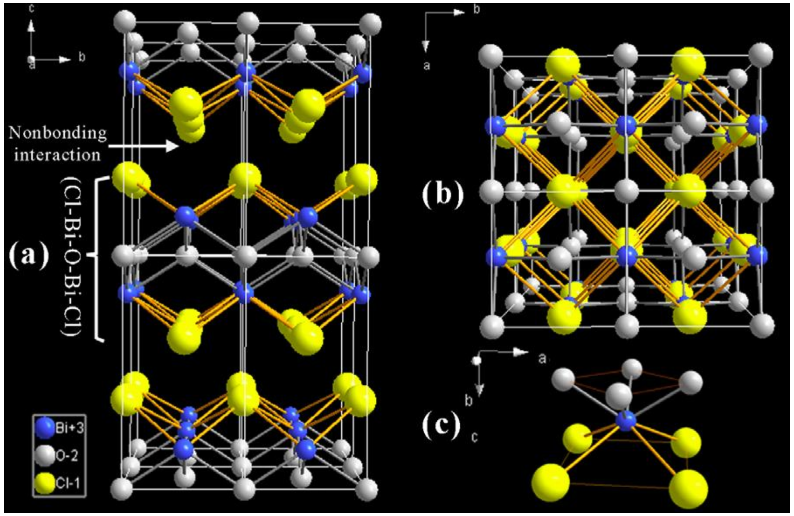
Interesting Bismuth Compounds

- Bismuth is a kind of green heavy metal element
- Solidification: volume expansion like water (3 %)
- Melting point 271 ^{o}C, boiling point 1560 ^{o}C
- the de Haas-van Alphen (dHvA) effect
- Bi^{3+} with $5d^{10}6s^{2}6p^{0}$ electronic configuration results in lone pairs of electron
- The strong internal static electric field between perpendicular to the [Xm] layer and the [Bi_2O_2] layer is advantages to the photoinduced electron−hole pairs

Ind Lubr Tribol, 2002, 54, 153

Mini-Rev Org Chem, 2009, 6, 241

Novel Photocatlyst： BiOX(X=Cl, Br, I)



Typical layer crystal structure

Huang FQ, Wang WD, Appl. Catal. B 68 (2006) 125–129 **BiOCl**

Zhang LZ,J. Phys. Chem. C 112, 747-753 (2008). **BiOCl**

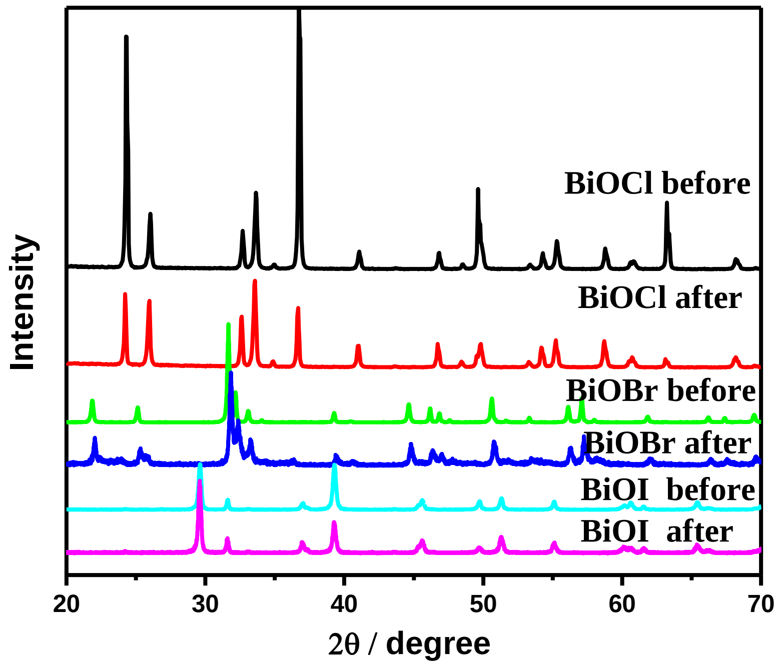
Wang C, Wang TM, Rare Metals 27, 243-250 (2008)

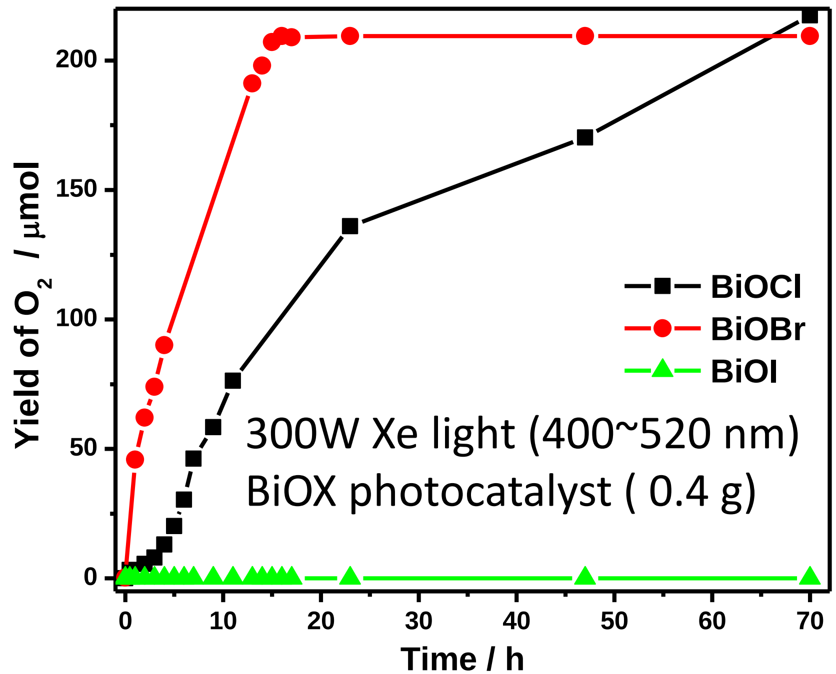
June 18th, 2007. BiOX(X=Cl, Br,I)

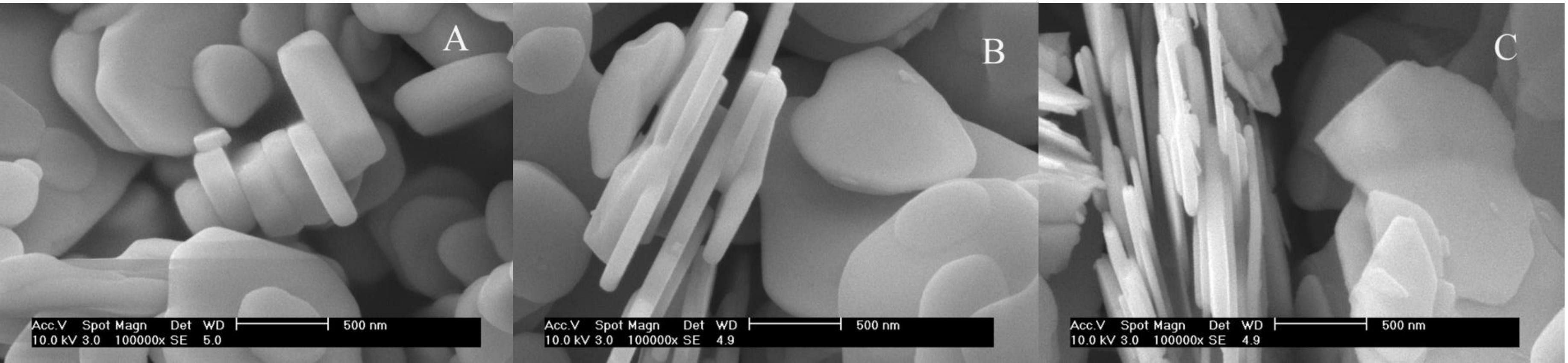
The photocatalytic activity BiOX was discovered by chance

In order to get $CaBi_2O_4$, we use HCl instead of HNO_3 reported in reference， and then we get a novel visible light photocatalyst-BiOCl.

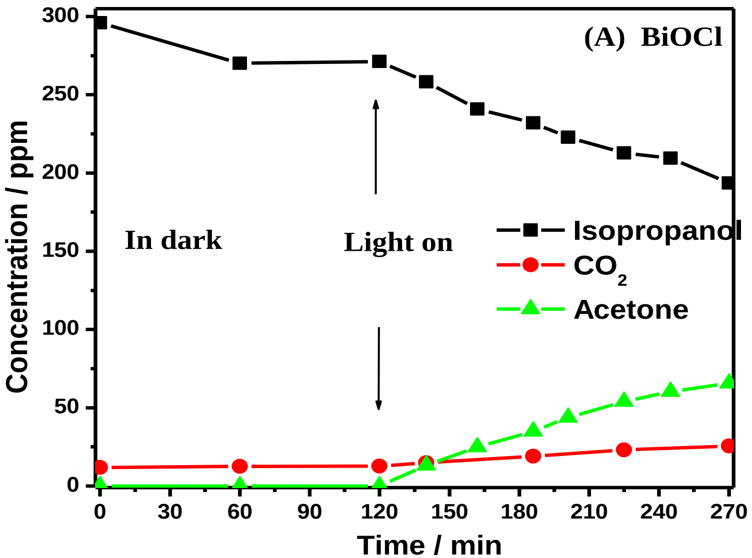
Oxygen Evolution vs. Irradiation Time

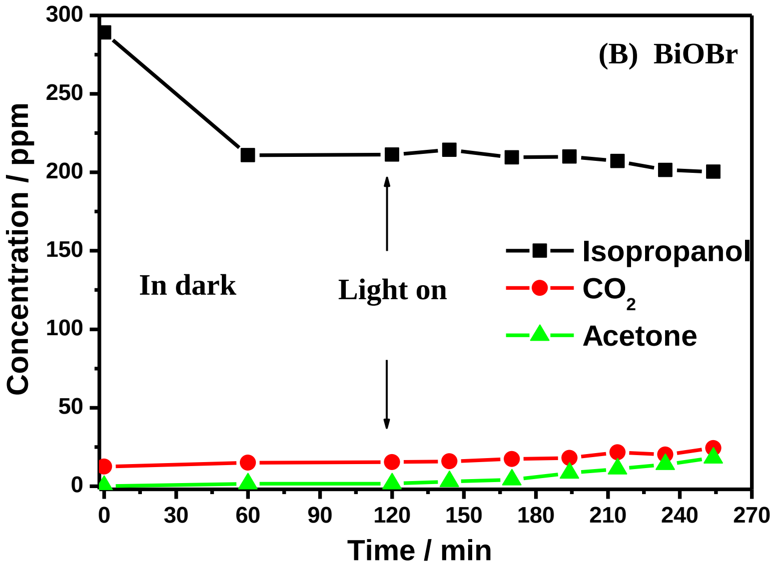


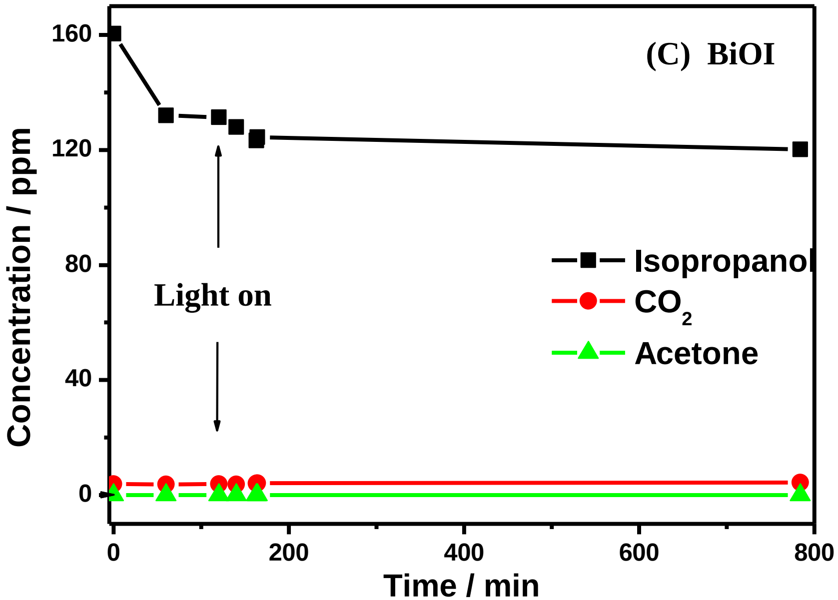




Photodegradation of isopropanol (IPA)





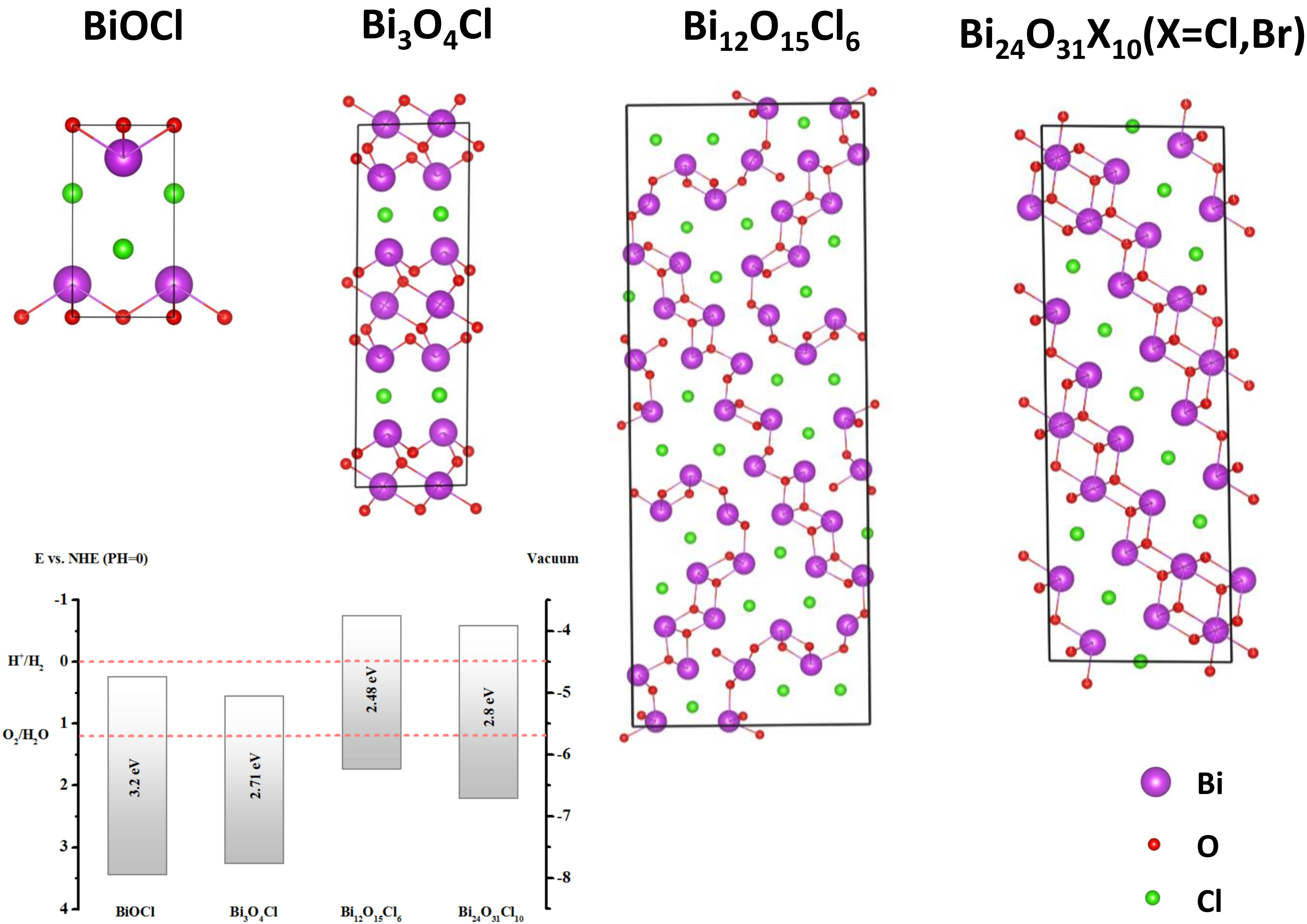


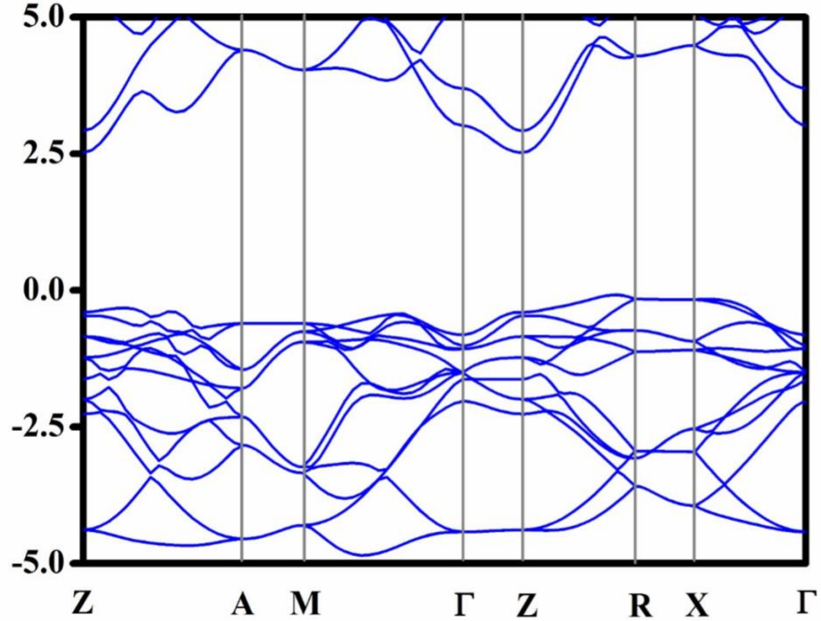
IPA (20 mL)

300W Xe light (400 nm~520 nm)

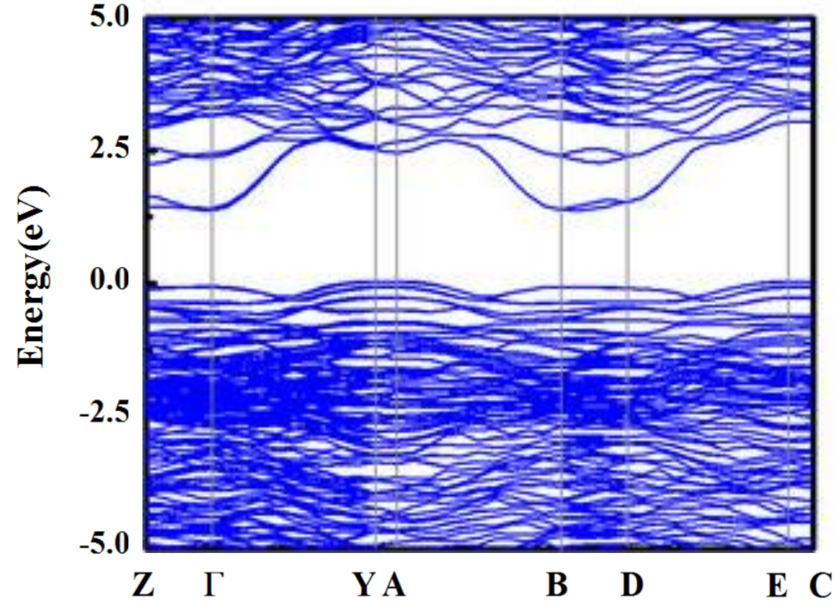
BiOX photocatalyst (0.4 g)

Rare Metal , 2008, 27, 243-250

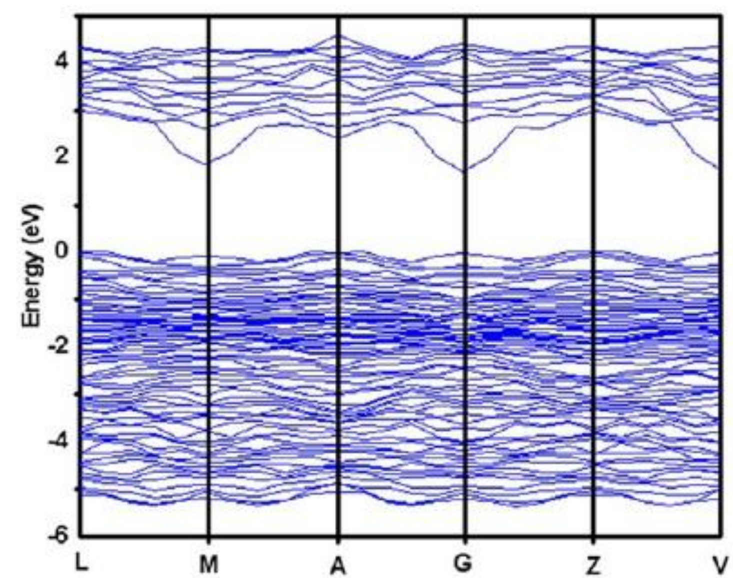

BiOCl
Bi_3O_4Cl
$Bi_{12}O_{15}Cl_6$
$Bi_{24}O_{31}X_{10}$(X=Cl,Br)
E vs. NHE (PH=0)
Vacuum
-1
0
1
2
3
4
-4
-5
-6
-7
-8
H^+/H_2
O_2/H_2O
3.2 eV
2.71 eV
2.48 eV
2.8 eV
BiOCl
Bi_3O_4Cl
$Bi_{12}O_{15}Cl_6$
$Bi_{24}O_{31}Cl_{10}$
Bi
O
Cl



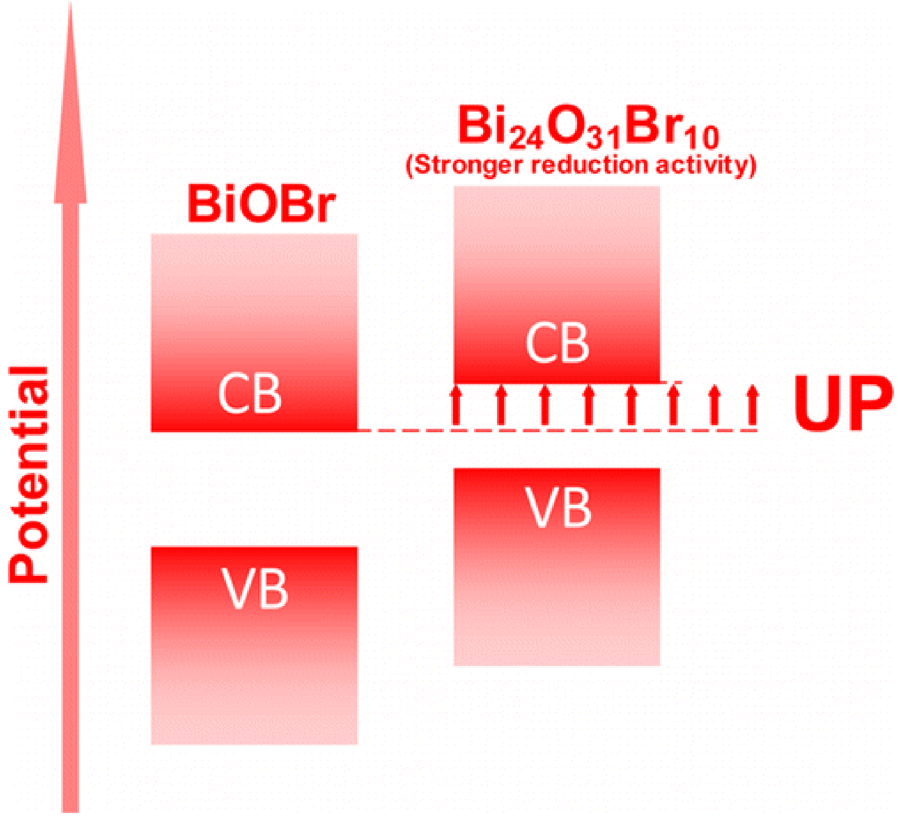
BiOCl



$Bi_{24}O_{31}Cl_{10}$



$Bi_{24}O_{31}Br_{10}$



$Bi_{24}O_{31}Br_{10}$

$Bi_{2.4}O_{3.1}Br_{1}$

E_c=0.30 eV

BiOBr

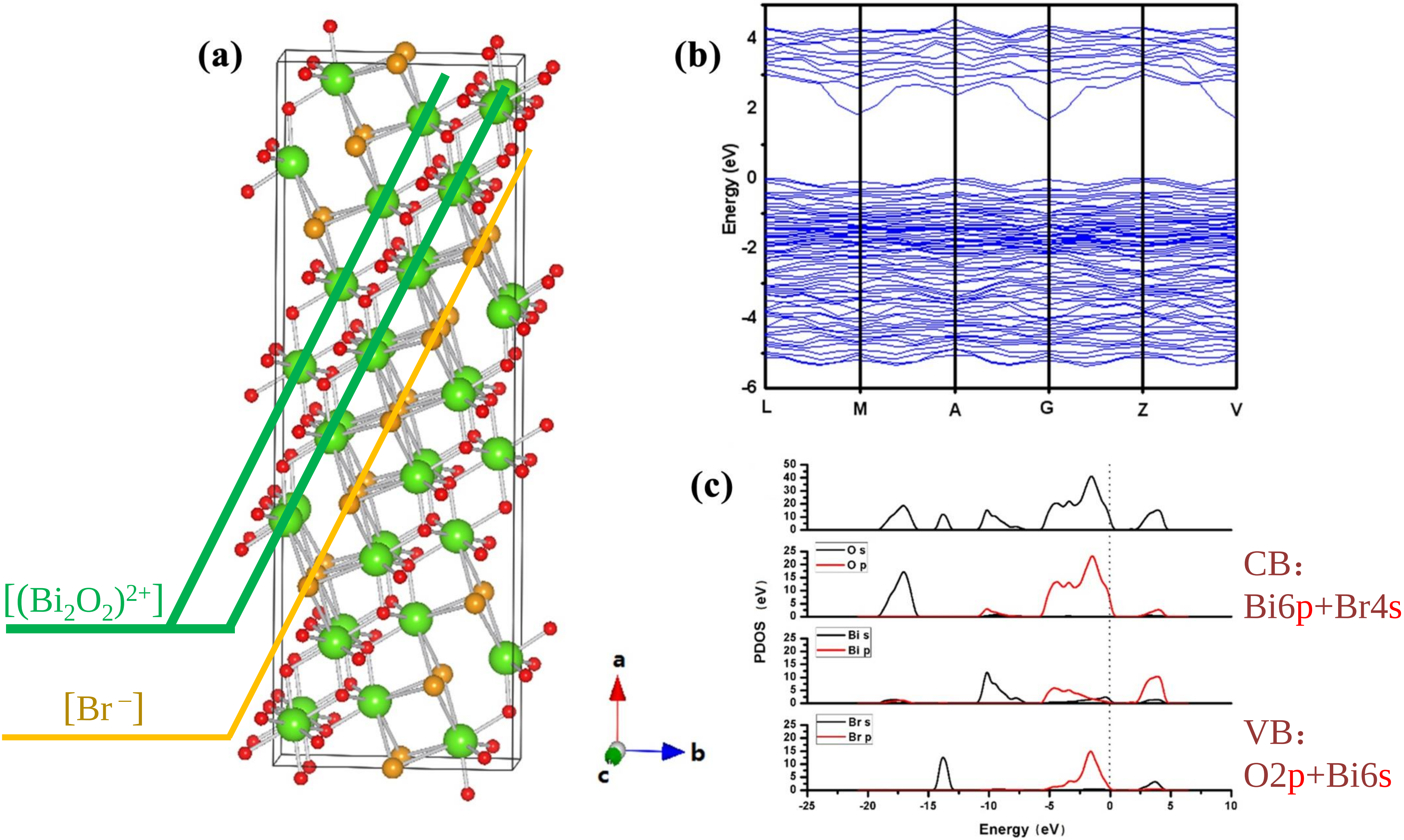
E_c=0.56 eV

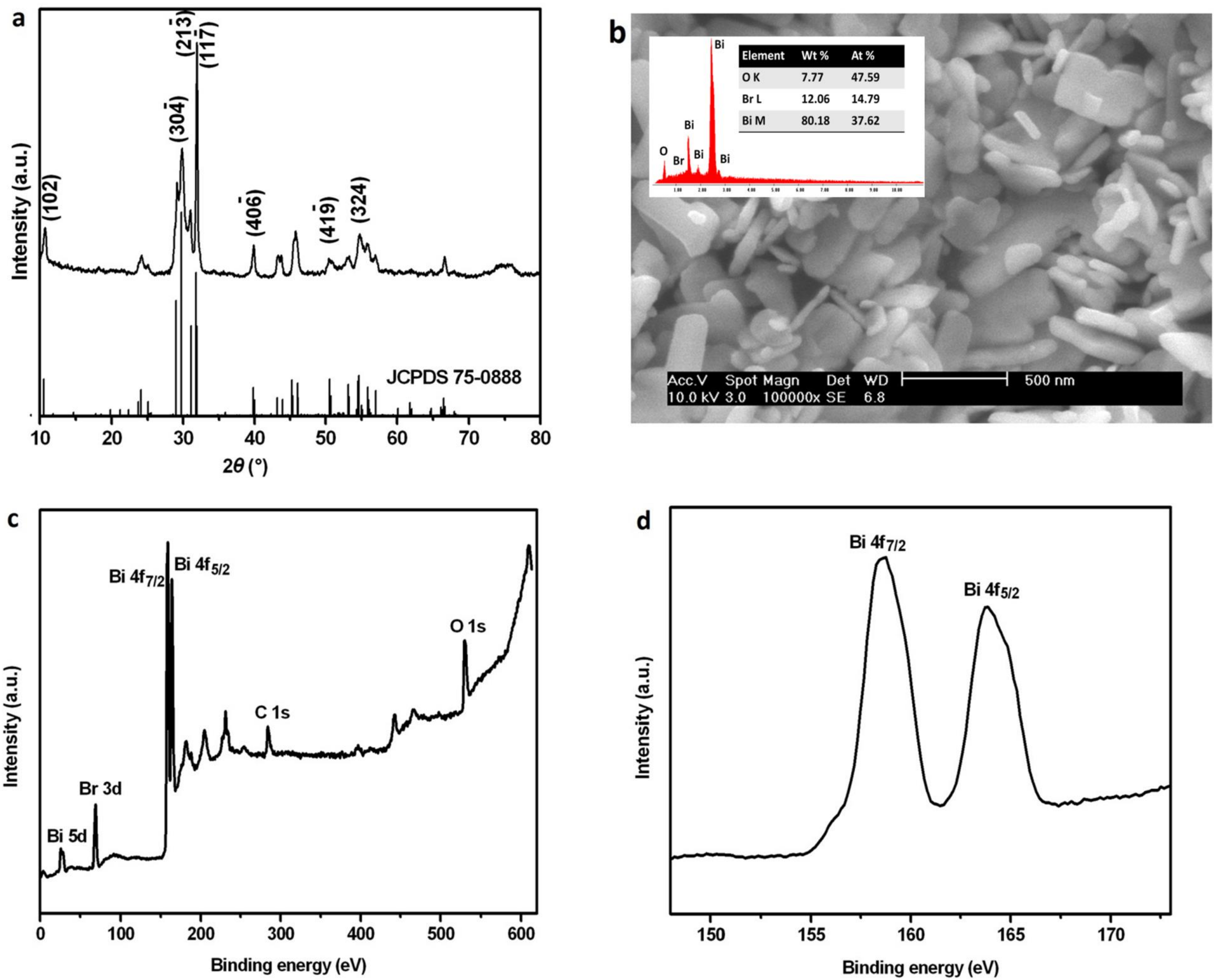
Empirical formula

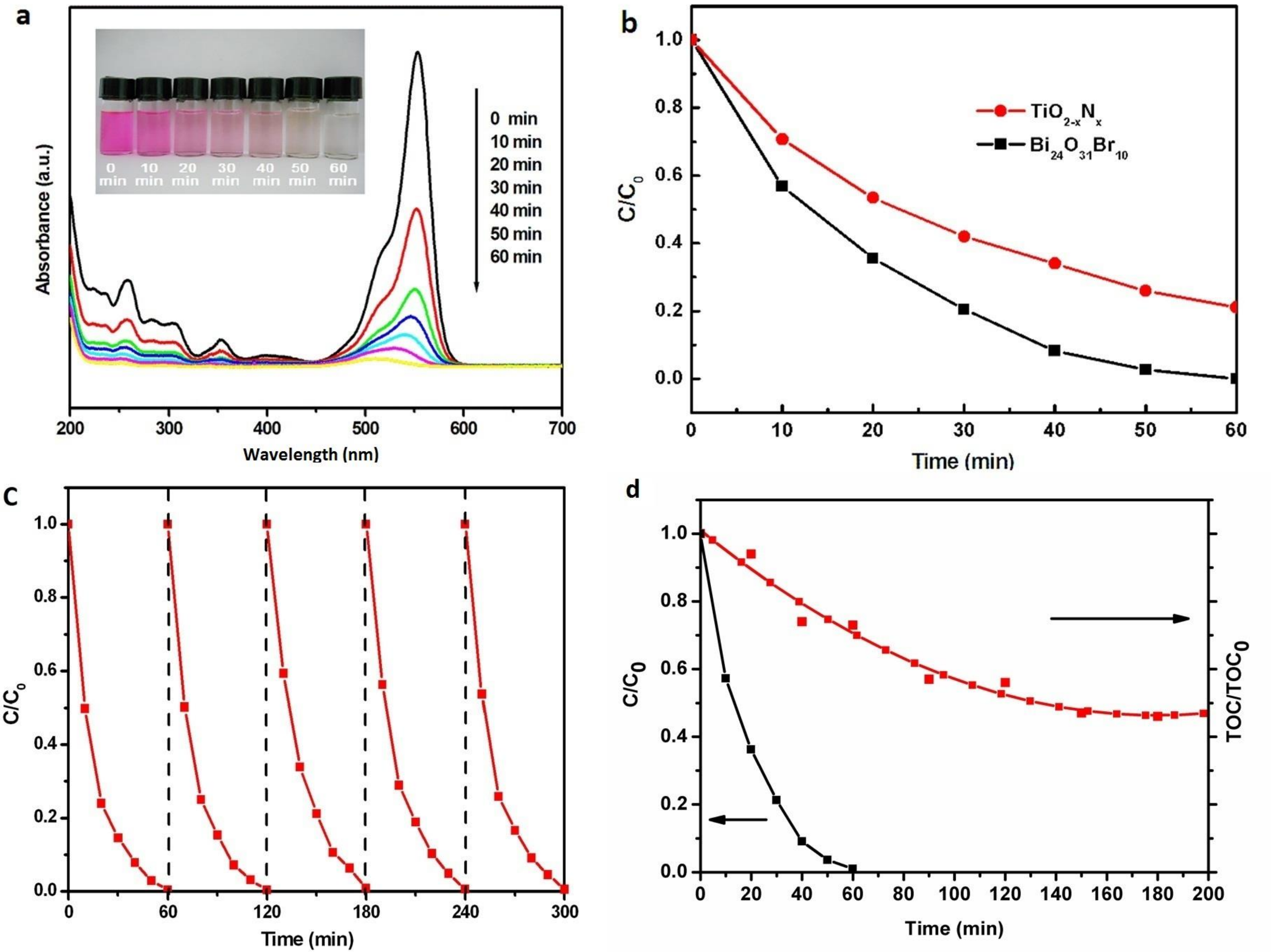
$$E_c = \chi - 0.5\, E_g + E_0$$

E_g is band gap, E_0 is scale factor relating the reference electrode redox level to the absolute vacuum scale (E_0=−4.5 eV for normal hydrogen electrode), and χ is absolute electronegativity of semiconductor

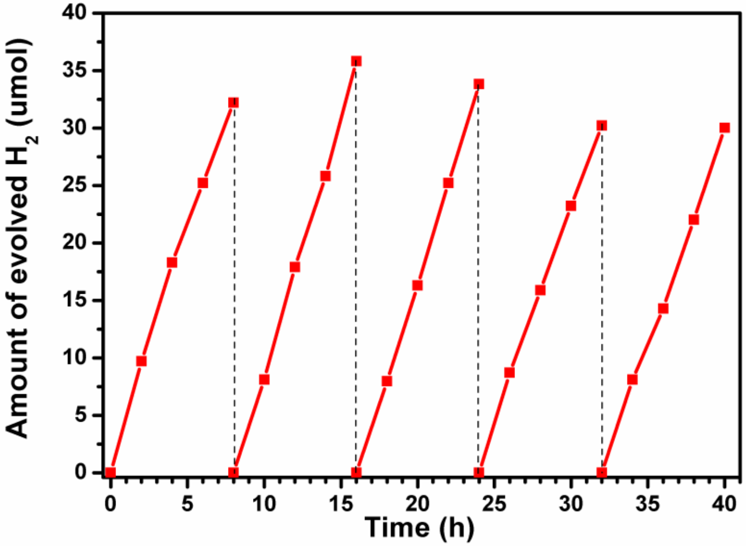
Xu, Y. ; Schoonen, M. A.A. ***Am. Mineral***.2000,*85*, 543-556.


(a)
[(Bi2O2)2+]
[Br−]
a
b
c
(b)
Energy (eV)
4
2
0
-2
-4
-6
L
M
A
G
Z
V
(c)
PDOS (eV)
O s
O p
Bi s
Bi p
Br s
Br p
Energy (eV)
-25
-20
-15
-10
-5
0
5
10
CB：
Bi6p+Br4s
VB：
O2p+Bi6s

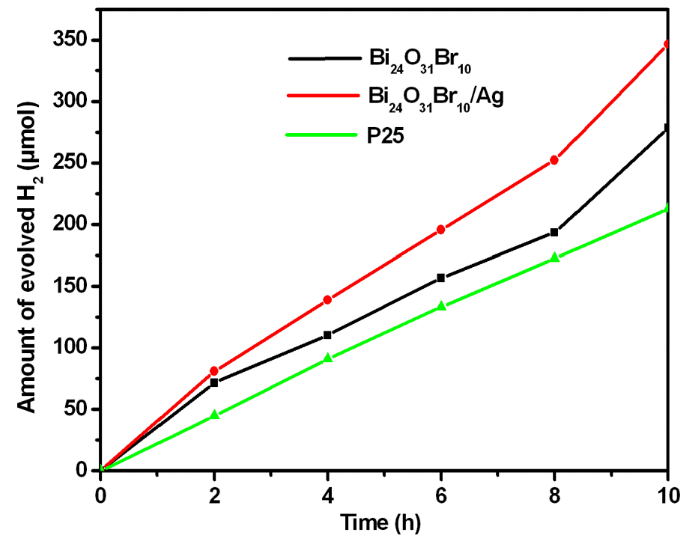

a
Intensity (a.u.)
(102)
(30$\bar{4}$)
(21$\bar{3}$)
(11$\bar{7}$)
(40$\bar{6}$)
(41$\bar{9}$)
(324)
JCPDS 75-0888
10 20 30 40 50 60 70 80
2θ (°)
b
Bi
O
Br
Element Wt % At %
O K 7.77 47.59
Br L 12.06 14.79
Bi M 80.18 37.62
Acc.V Spot Magn Det WD 500 nm
10.0 kV 3.0 100000x SE 6.8
c
Intensity (a.u.)
Bi $4f_{7/2}$
Bi $4f_{5/2}$
O 1s
C 1s
Br 3d
Bi 5d
0 100 200 300 400 500 600
Binding energy (eV)
d
Intensity (a.u.)
Bi $4f_{7/2}$
Bi $4f_{5/2}$
150 155 160 165 170
Binding energy (eV)



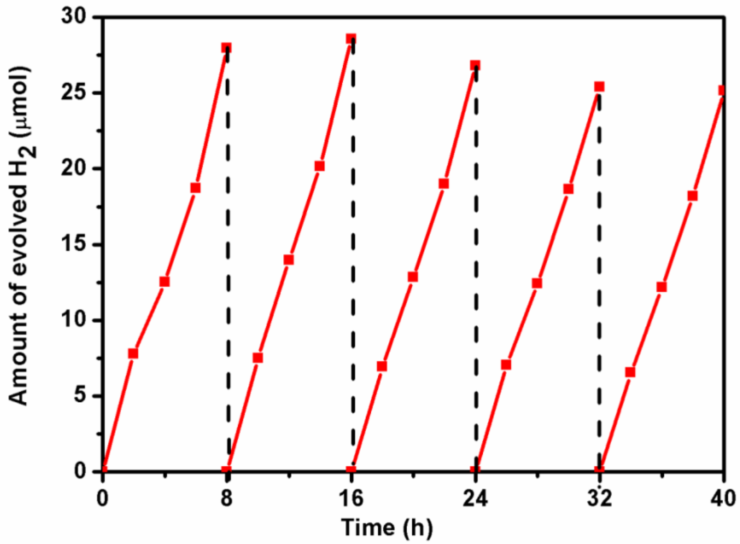
a
0 min
10 min
20 min
30 min
40 min
50 min
60 min
Absorbance (a.u.)
Wavelength (nm)
b
$TiO_{2-x}N_x$
$Bi_{24}O_{31}Br_{10}$
C/C_0
Time (min)
c
C/C_0
Time (min)
d
C/C_0
TOC/TOC_0
Time (min)



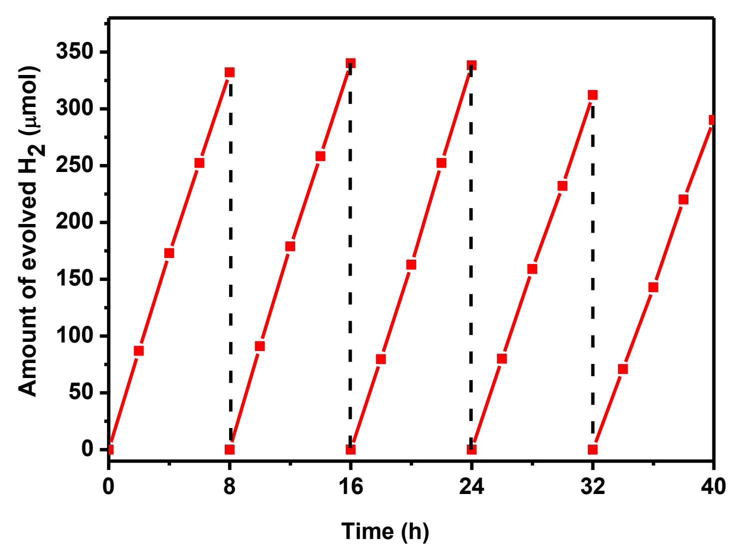
Visible light (NaS/Na_2SO_3)



UV-Vis (NaS/Na_2SO_3)

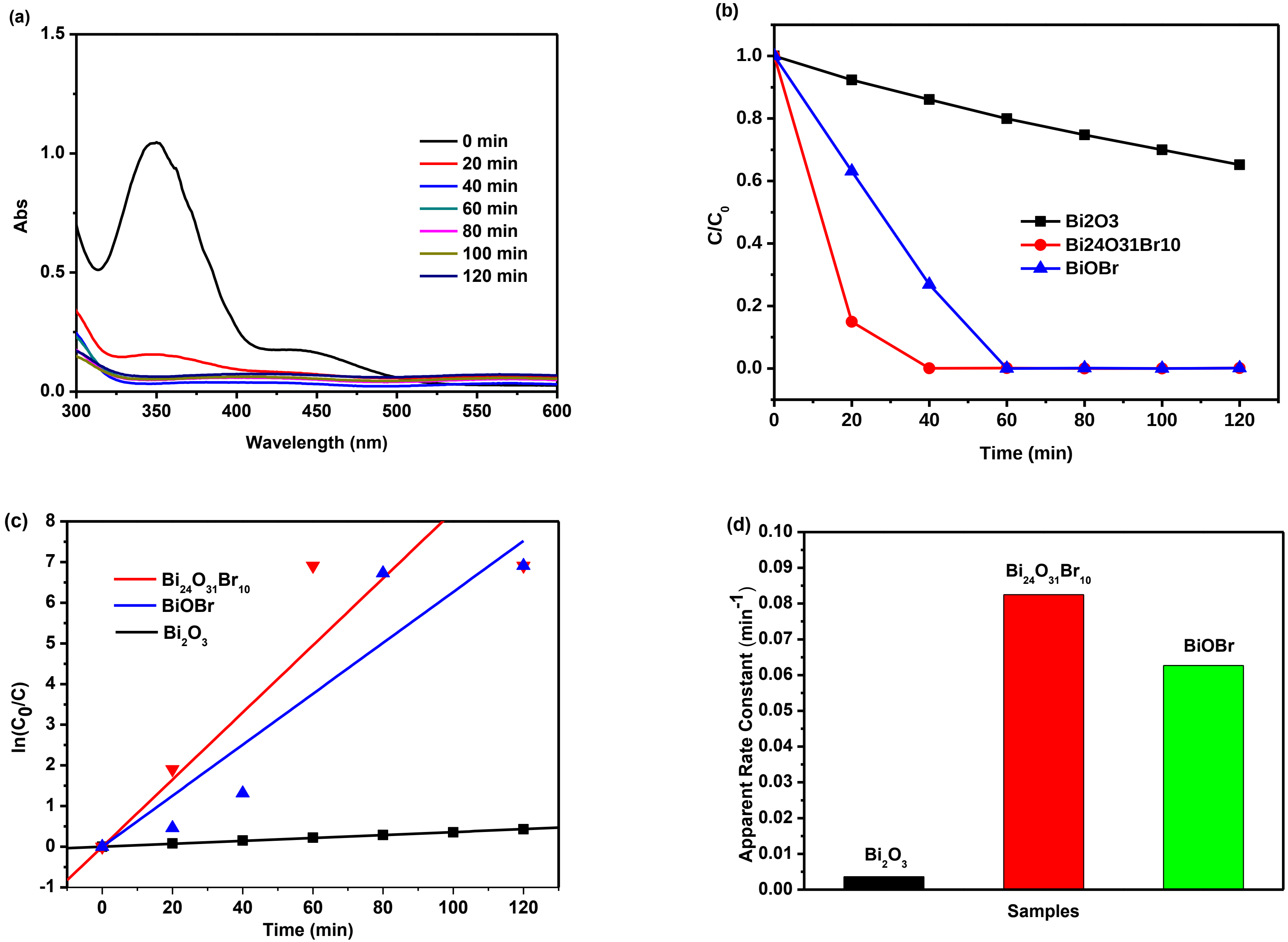


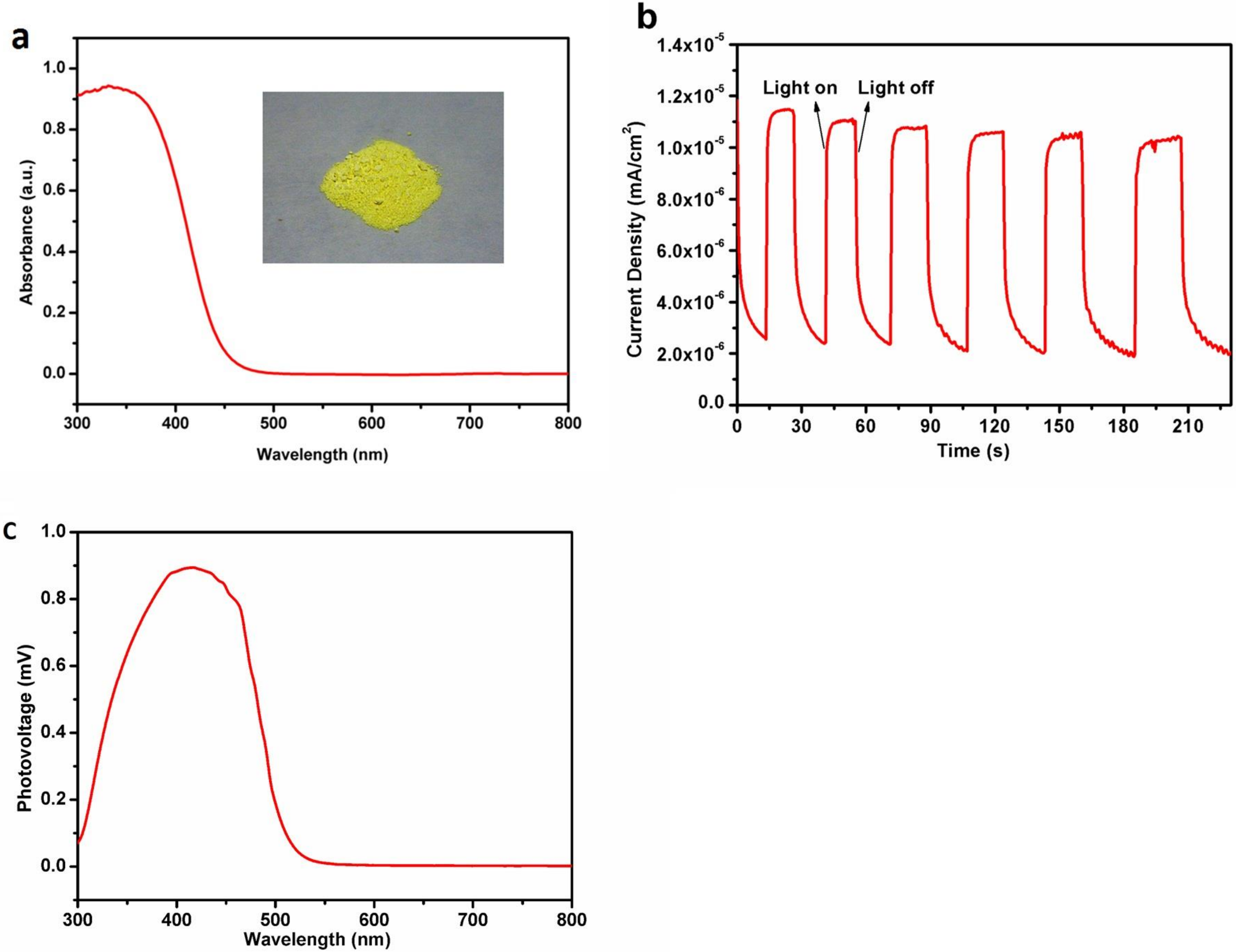
Visible light (ethanol)

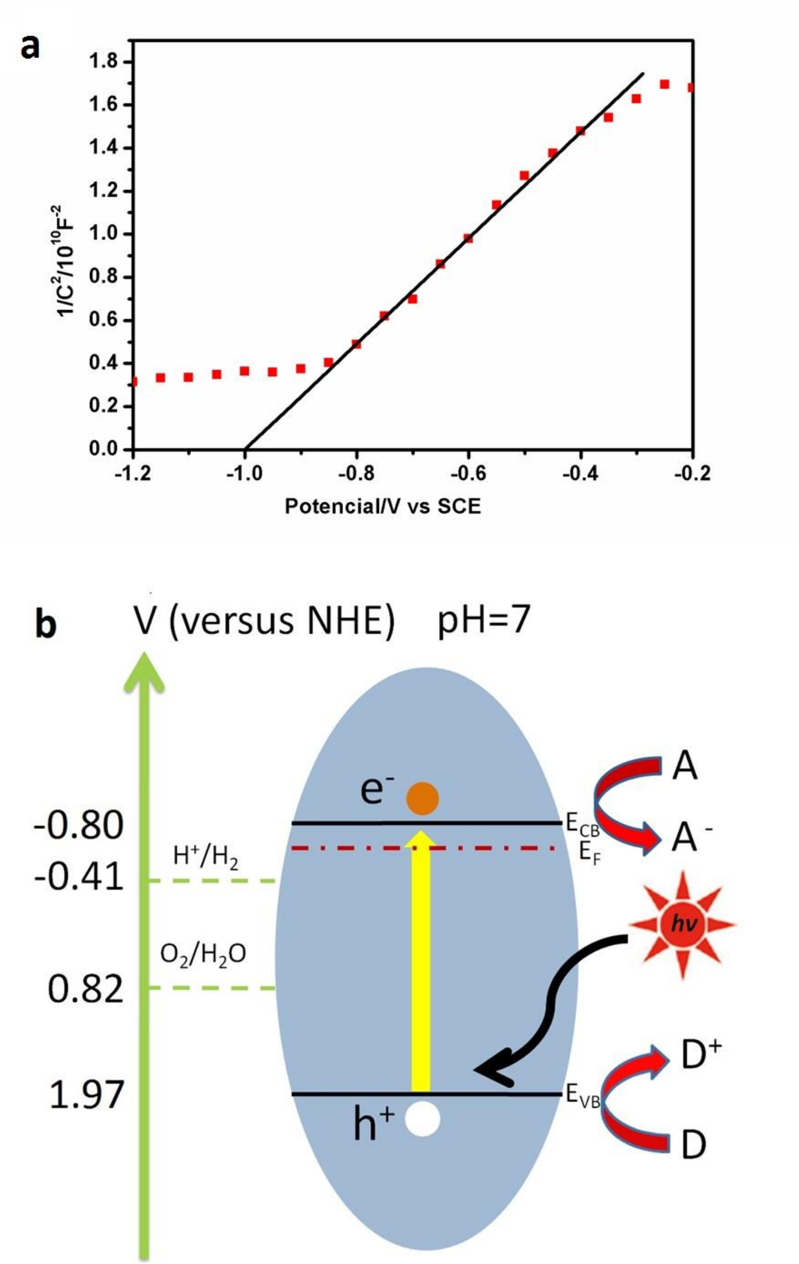


Uv-Vis (ethanol)

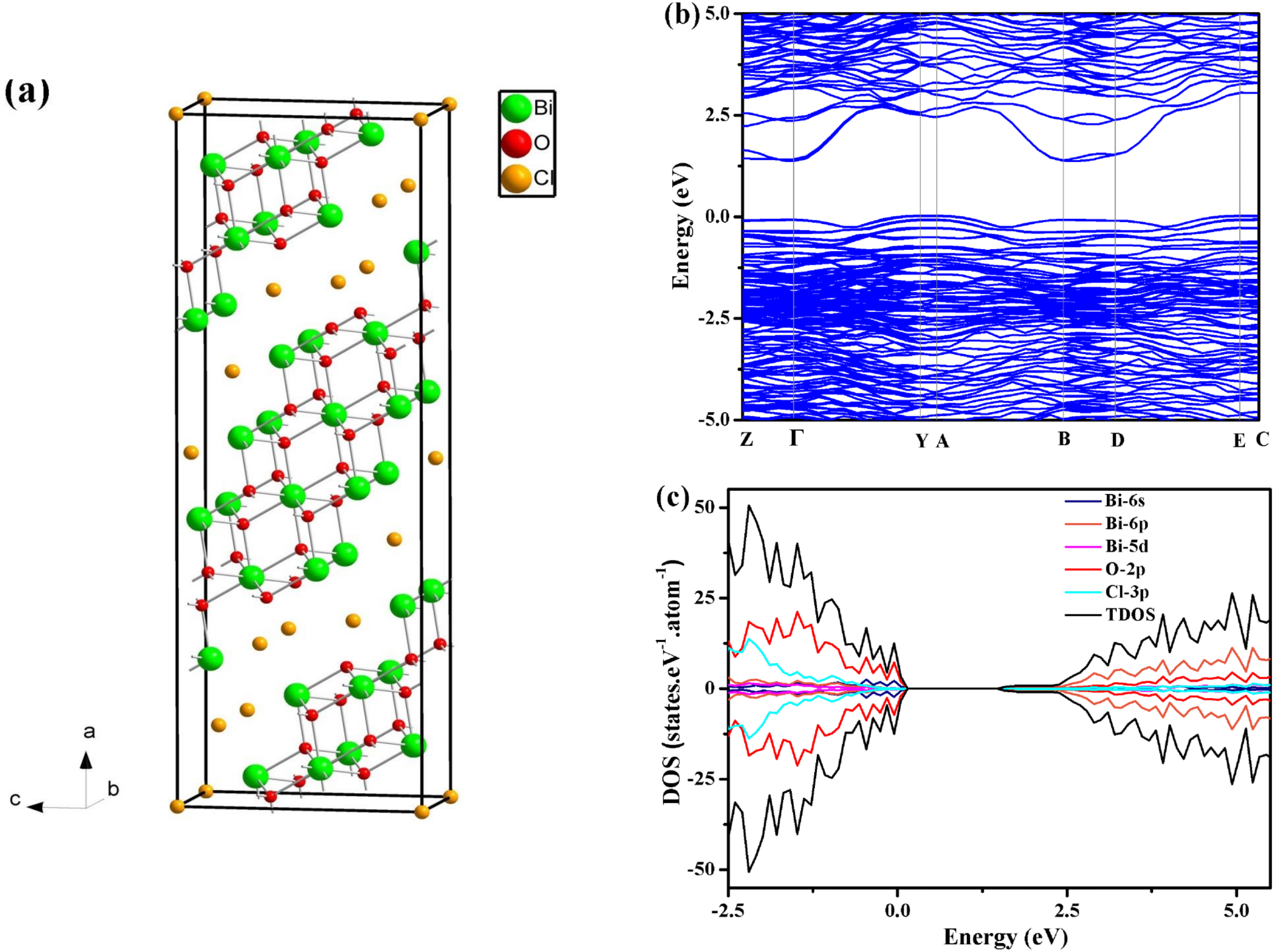
Hexavalent Chromium reduction



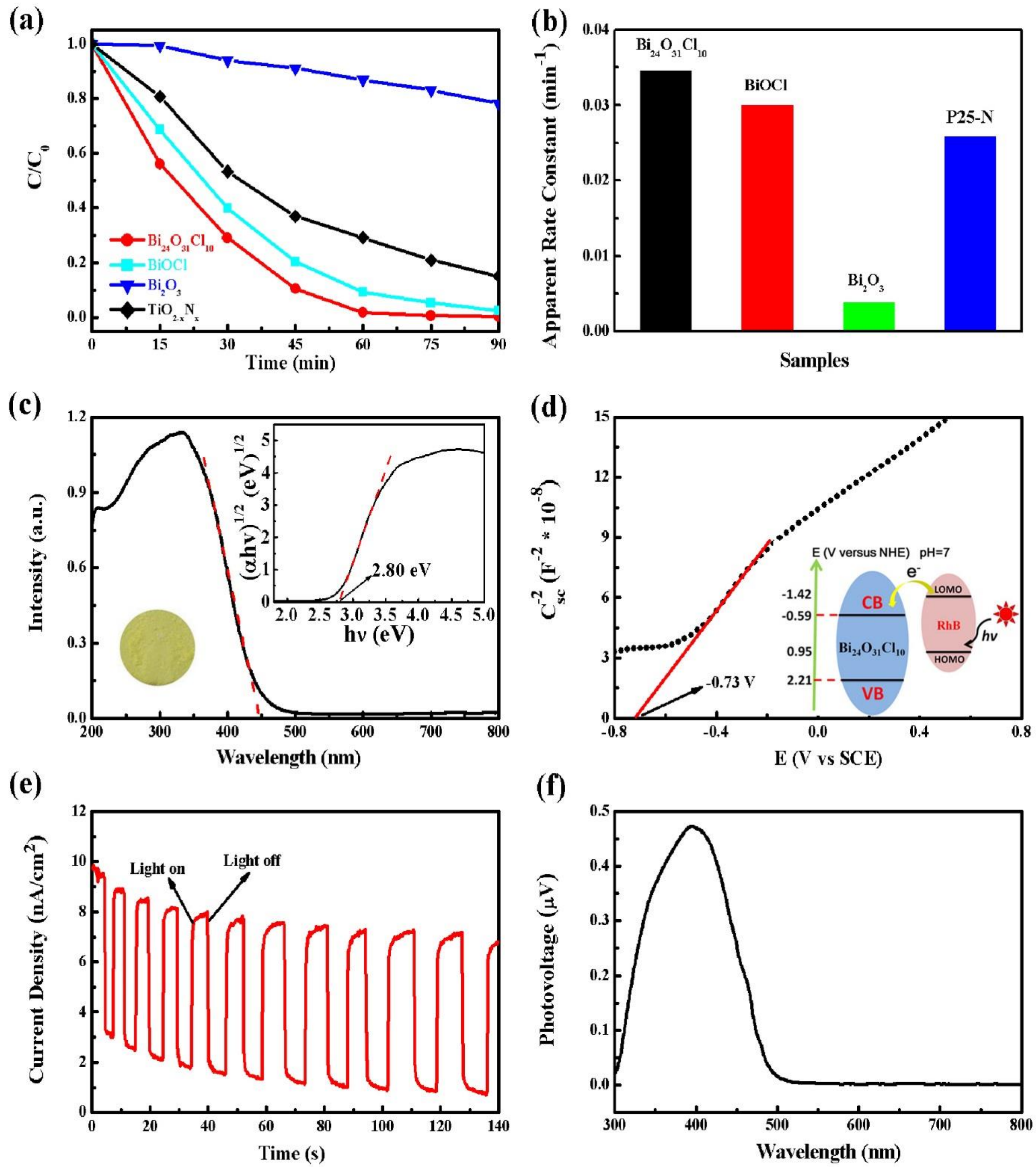

a
Absorbance (a.u.)
Wavelength (nm)
b
Light on
Light off
Current Density (mA/cm^2)
Time (s)
c
Photovoltage (mV)
Wavelength (nm)



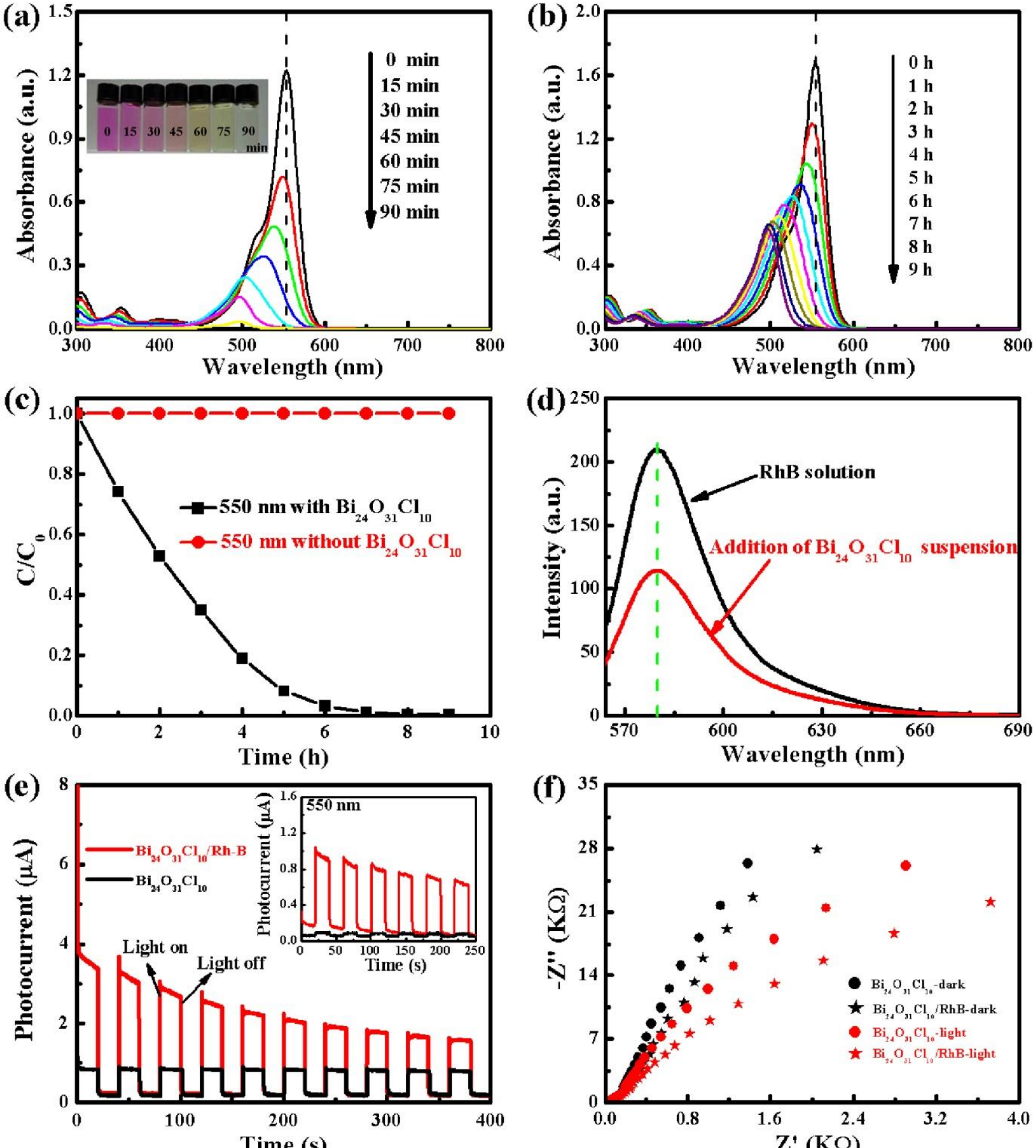
ACS Catal. 2014, 4: 954

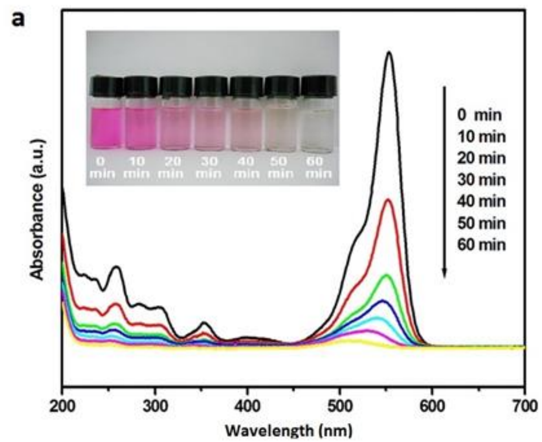


(a)
Bi
O
Cl
a
b
c
(b)
Energy (eV)
5.0
2.5
0.0
-2.5
-5.0
Z Γ Y A B D E C
(c)
Bi-6s
Bi-6p
Bi-5d
O-2p
Cl-3p
TDOS
DOS (states.eV^{-1}.atom^{-1})
50
25
0
-25
-50
-2.5
0.0
2.5
5.0
Energy (eV)



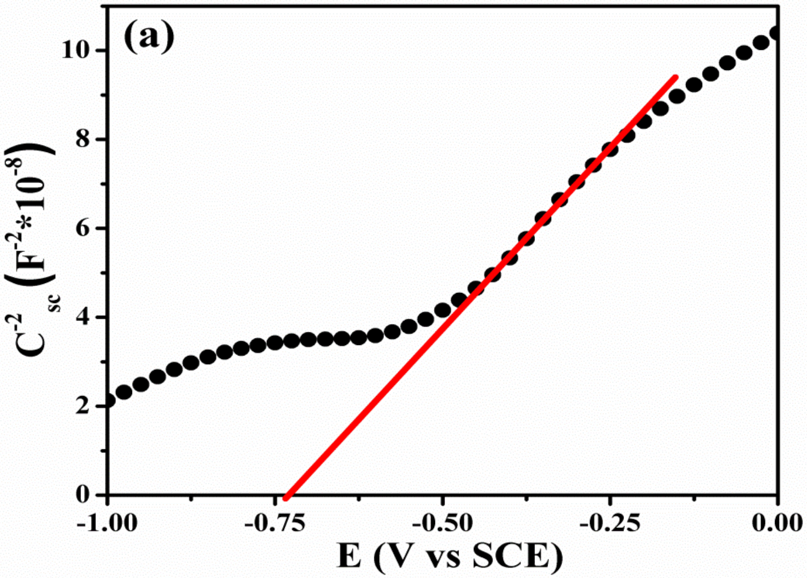
(a)
C/C0
Time (min)
Bi24O31Cl10
BiOCl
Bi2O3
TiO2-xNx
(b)
Apparent Rate Constant (min-1)
Bi24O31Cl10
BiOCl
Bi2O3
P25-N
Samples
(c)
Intensity (a.u.)
Wavelength (nm)
(αhν)1/2 (eV)1/2
2.80 eV
hν (eV)
(d)
C-2sc (F-2 * 10-8)
E (V vs SCE)
-0.73 V
E (V versus NHE) pH=7
e-
-1.42
-0.59
0.95
2.21
CB
VB
Bi24O31Cl10
LOMO
RhB
HOMO
hv
(e)
Current Density (nA/cm2)
Time (s)
Light on
Light off
(f)
Photovoltage (μV)
Wavelength (nm)



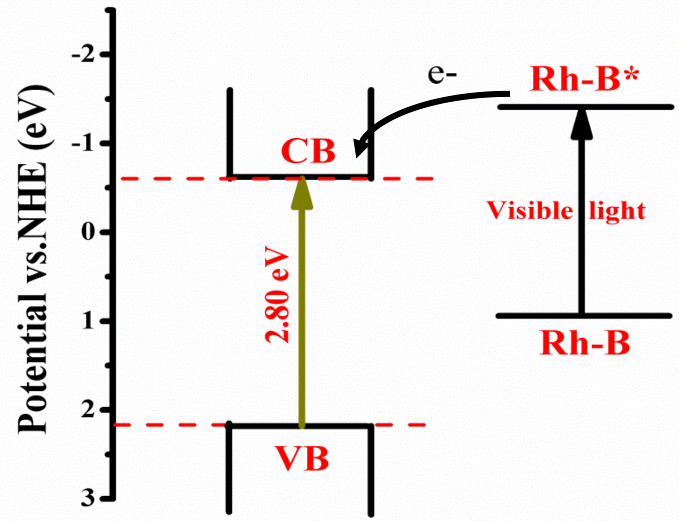


$Bi_{24}O_{31}Br_{10}$

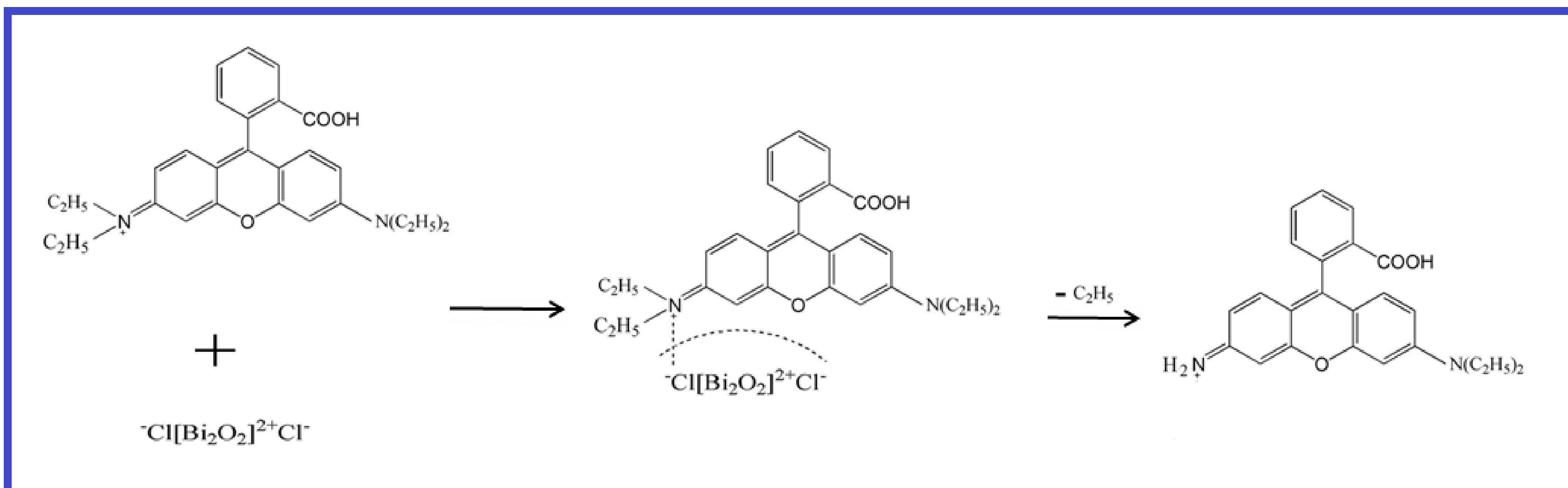
$Bi_{24}O_{31}Cl_{10}$



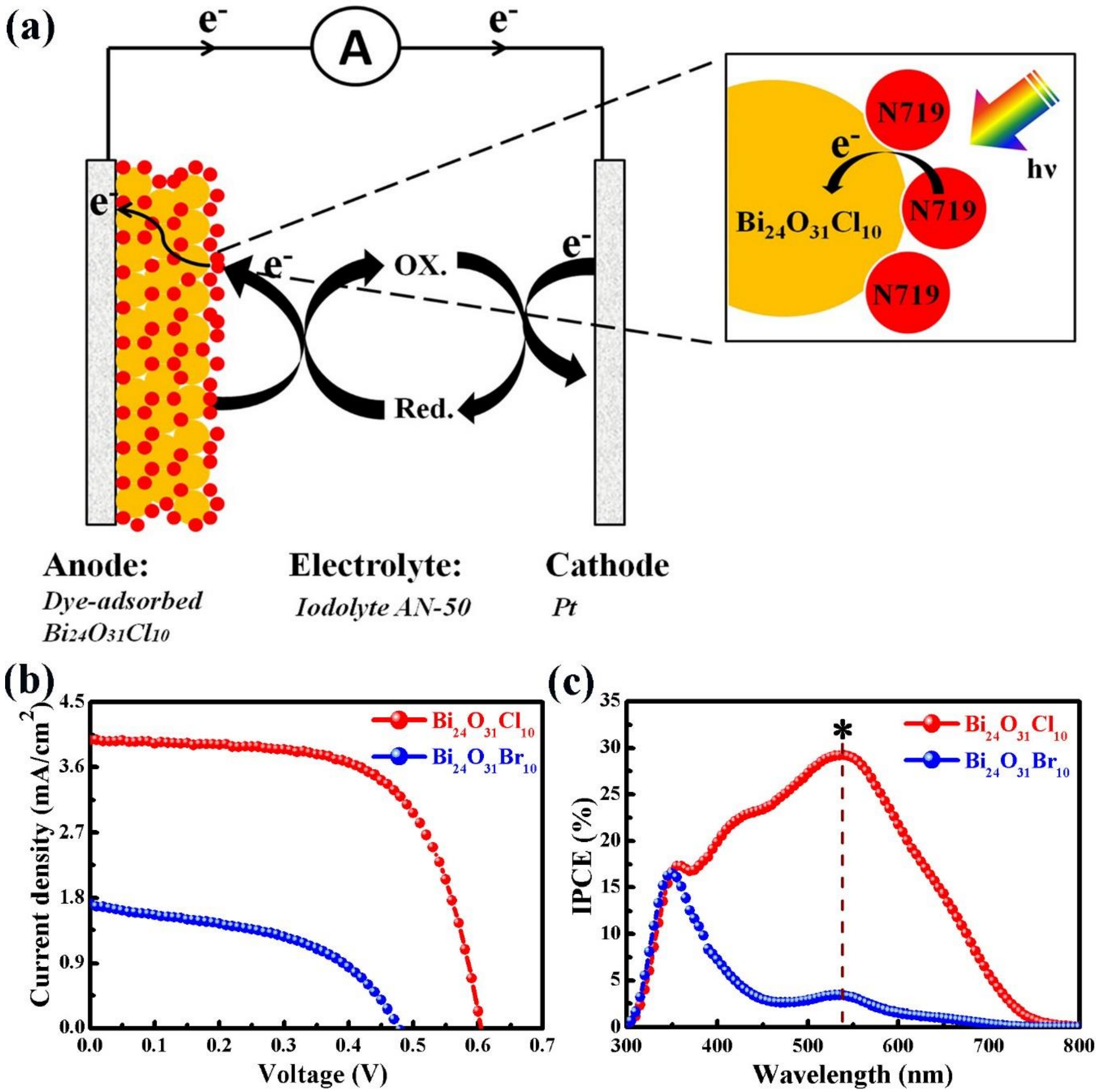
(a)
C^{-2}_{sc} (F^{-2}*10^{-8})
10
8
6
4
2
0
-1.00
-0.75
-0.50
-0.25
0.00
E (V vs SCE)

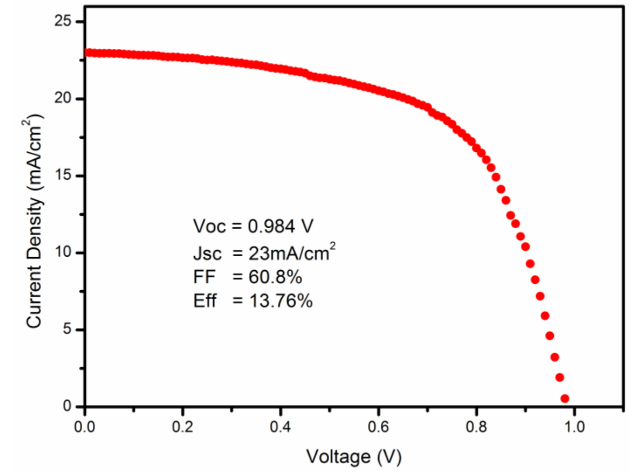


Potential vs.NHE (eV)
-2
-1
0
1
2
3
CB
VB
2.80 eV
e-
Rh-B*
Rh-B
Visible light



COOH
C_2H_5
C_2H_5
N
$N(C_2H_5)_2$
O
+
$^{-}Cl[Bi_2O_2]^{2+}Cl^{-}$
COOH
C_2H_5
C_2H_5
N
$N(C_2H_5)_2$
O
$^{-}Cl[Bi_2O_2]^{2+}Cl^{-}$
- C_2H_5
COOH
H_2N
O
$N(C_2H_5)_2$





Scientific Reports 2014,4:7384

电池	填充因子 (FF)	短路电流密度 ($Jsc/mA\ cm^{-2}$)	开路电压 (Voc/V)	电池效率 (η)
$Bi_{24}O_{31}Cl_{10}$	75.05 %	3.98	0.61	1.50 %
$Bi_{24}O_{31}Br_{10}$	50.90%	1.72	0.48	0.4 %

Outline

- Introduction: *sp* hybridization

Four stories

Symmetry

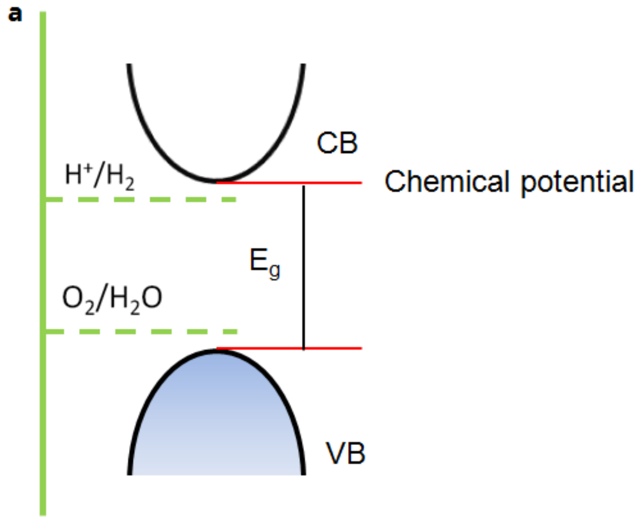
- $Bi_{24}O_{31}Br_{10}/Bi_{24}O_{31}Cl_{10}$
- $Ag_{10}Si_4O_{13}$

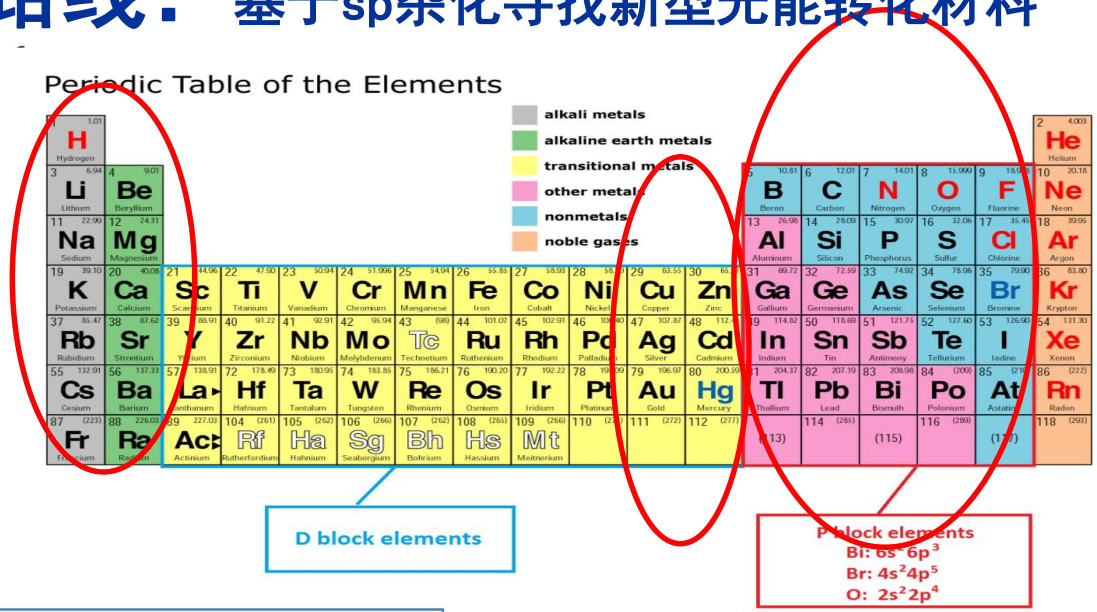
Symmetry Breaking

- Vacancy Engineering – Blank TiO2
- Strain engineering – BiOBr

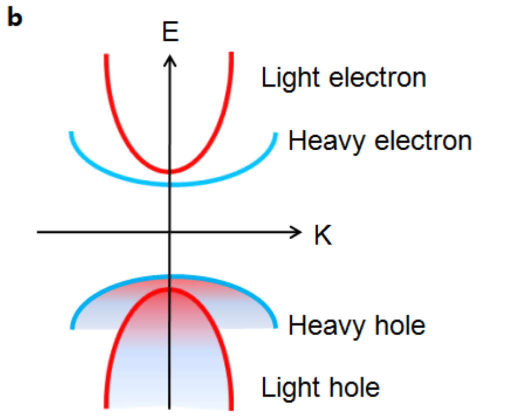
提出了新的物理路线： 基于sp杂化寻找新型光能转化材料

a





b



sp hybridization
Anisotropy orbital
Dispersive band

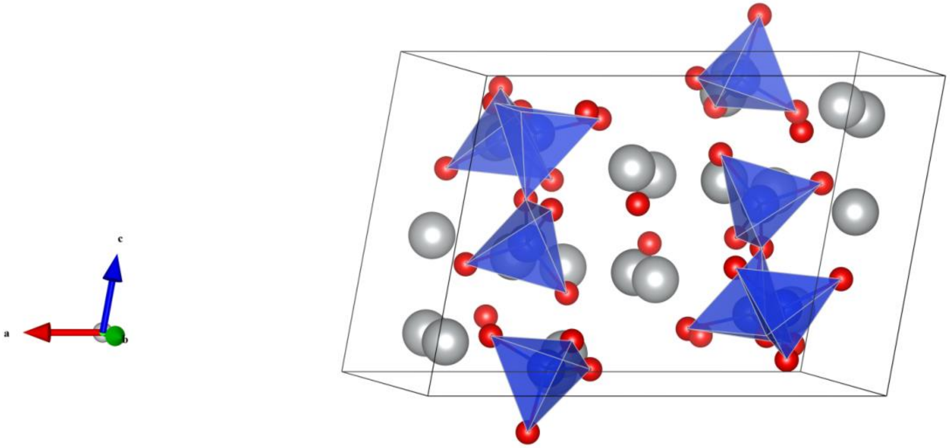
$$m^* = \frac{1}{\frac{1}{\hbar^2}\frac{d^2E}{dk^2}}$$

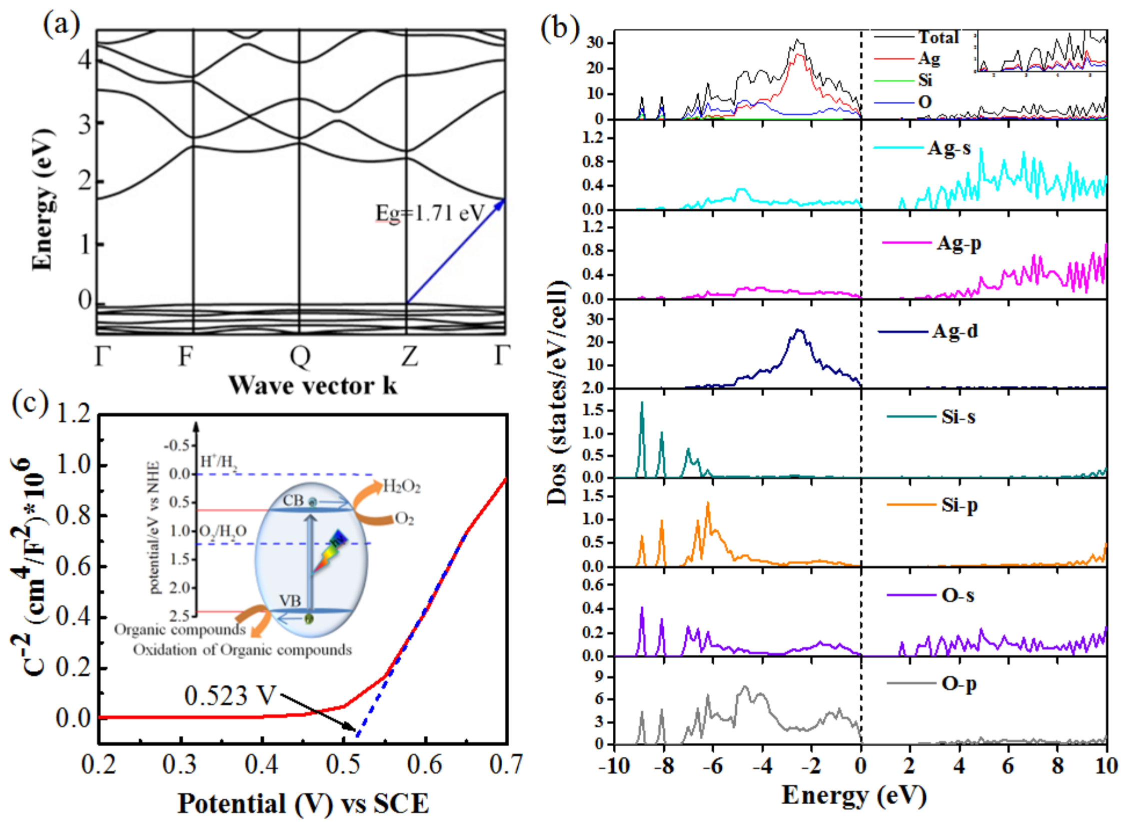
Pure atomic orbitals of central atom	Hybridization of the central atom	Number of hybrid orbitals	Shape of hybrid orbitals
s,p	sp	2	Linear 180°
s,p,p	sp^2	3	Trigonal Planar 120°
s,p,p,p	sp^3	4	Tetrahedral 109.5°
s,p,p,p,d	sp^3d	5	Trigonal Bipyramidal 90° 120°
s,p,p,p,d,d	sp^3d^2	6	Octahedral 90° 90°

Metal: Na K Mg Ca Sr Ba In Sn Sb Bi Cu Zn Ag

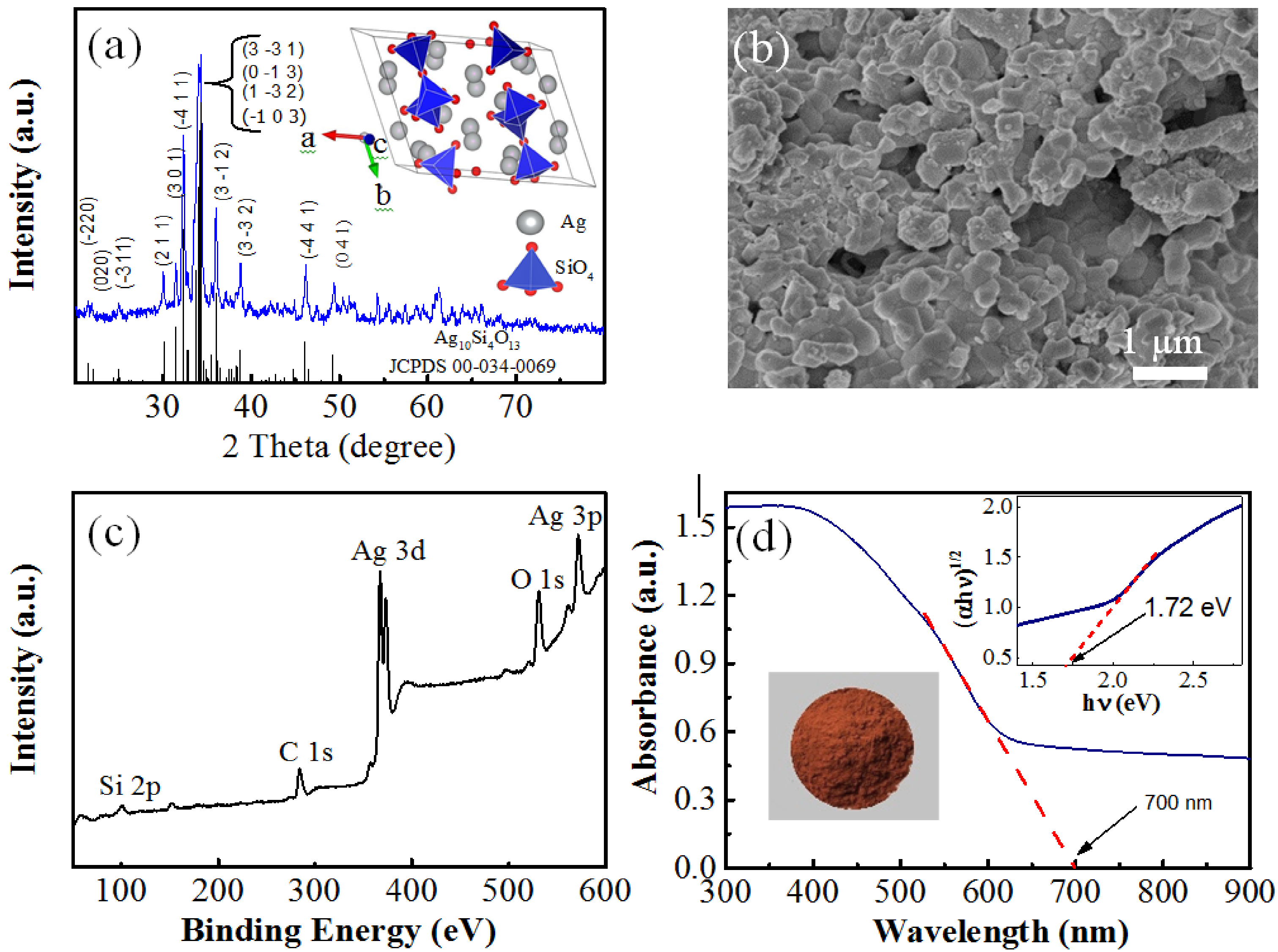
Nonmetal: O S X (X=F, Cl, Br, I) B C N P

Nothing is Impossible

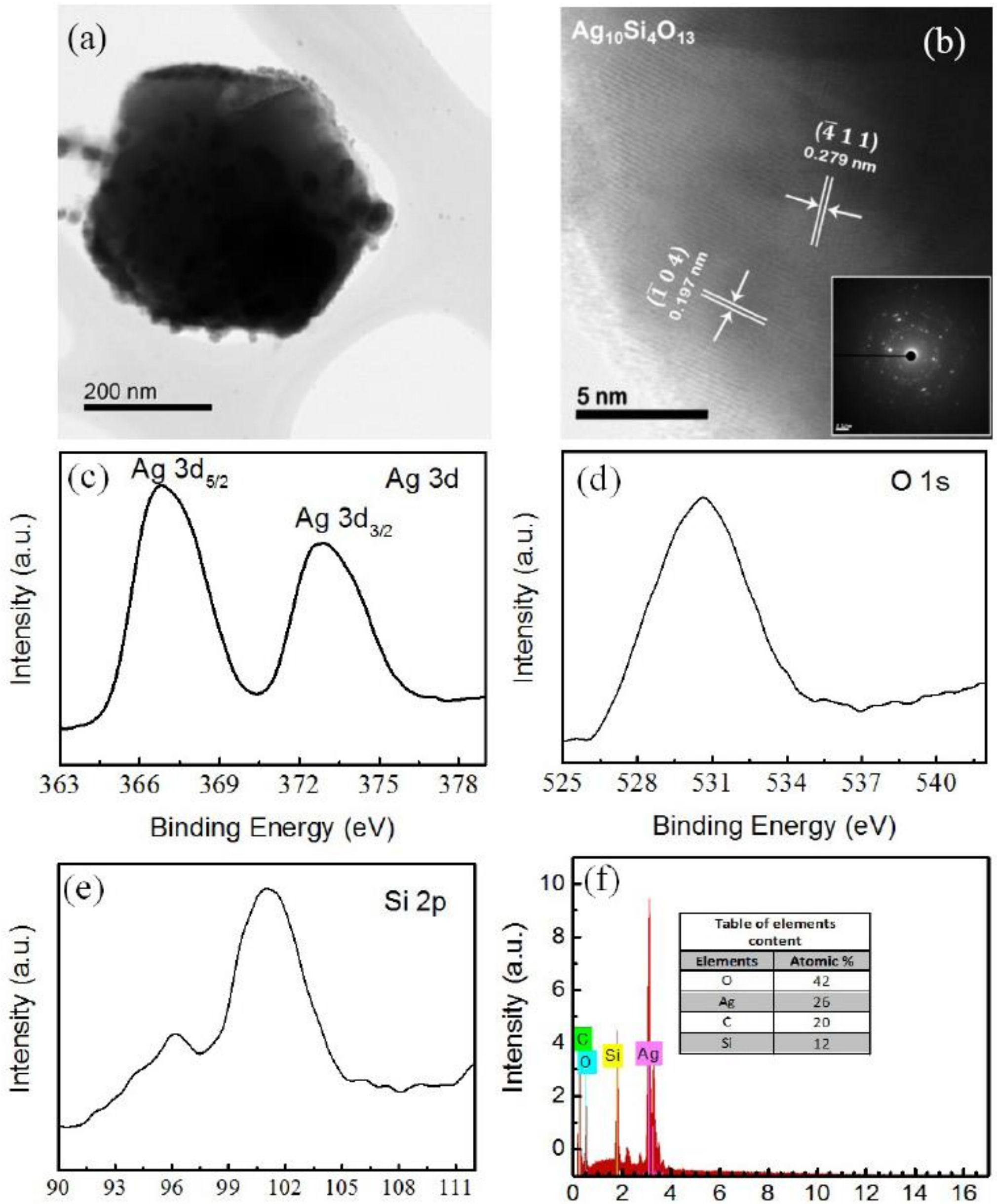


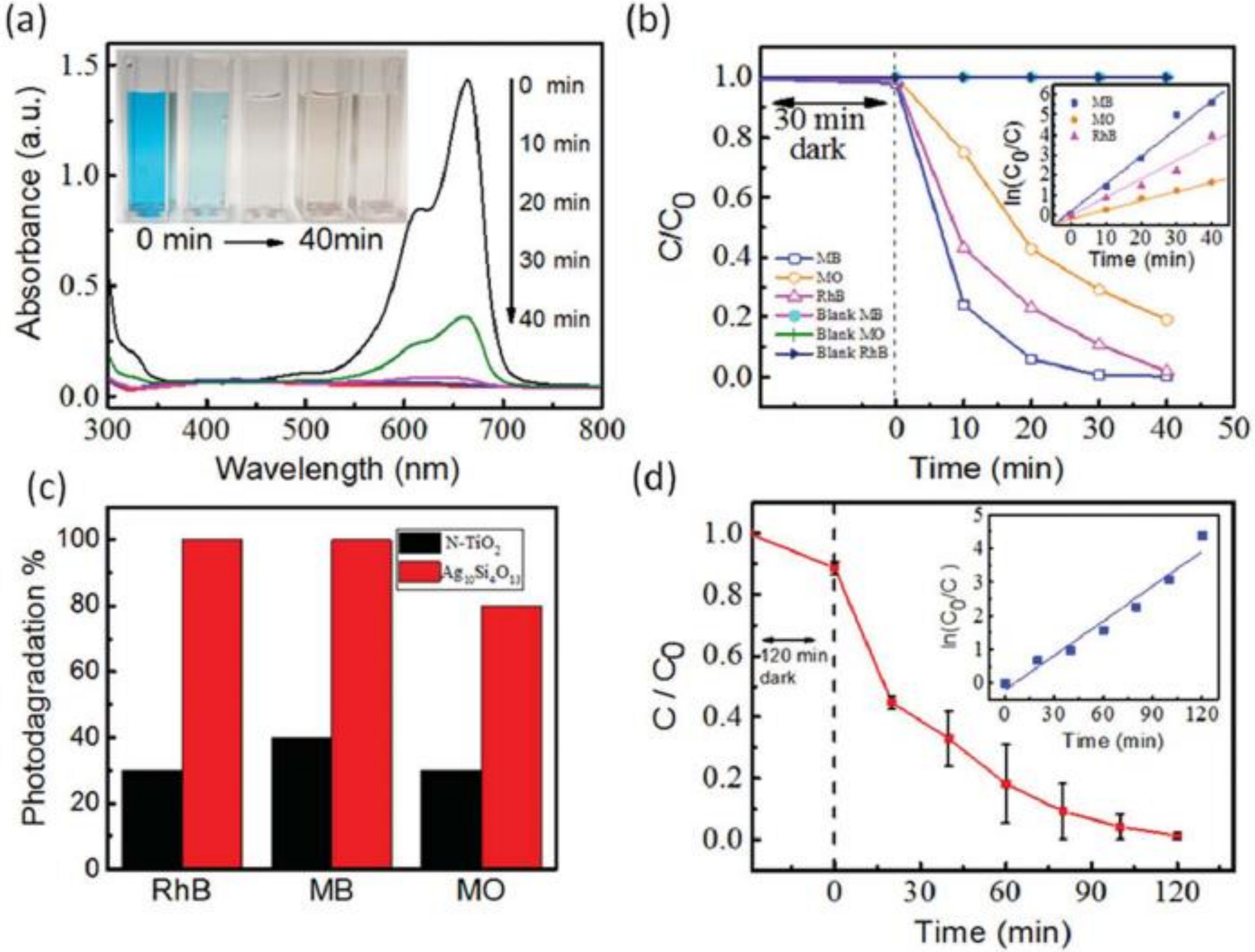


J. Mater. Chem. A 2016, 4: 10992

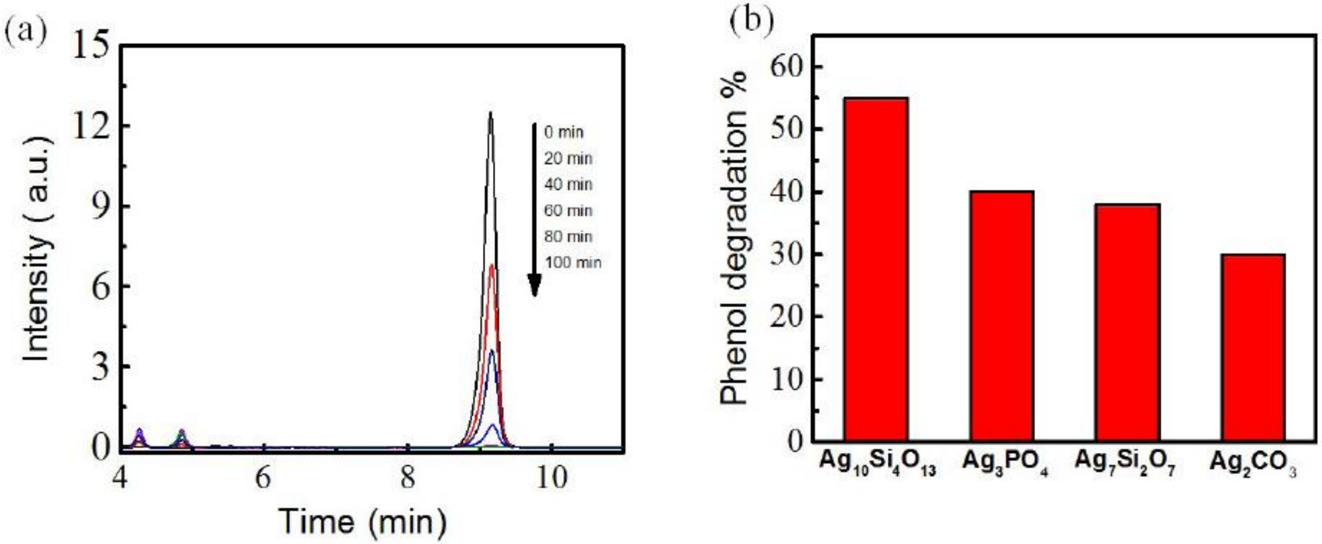


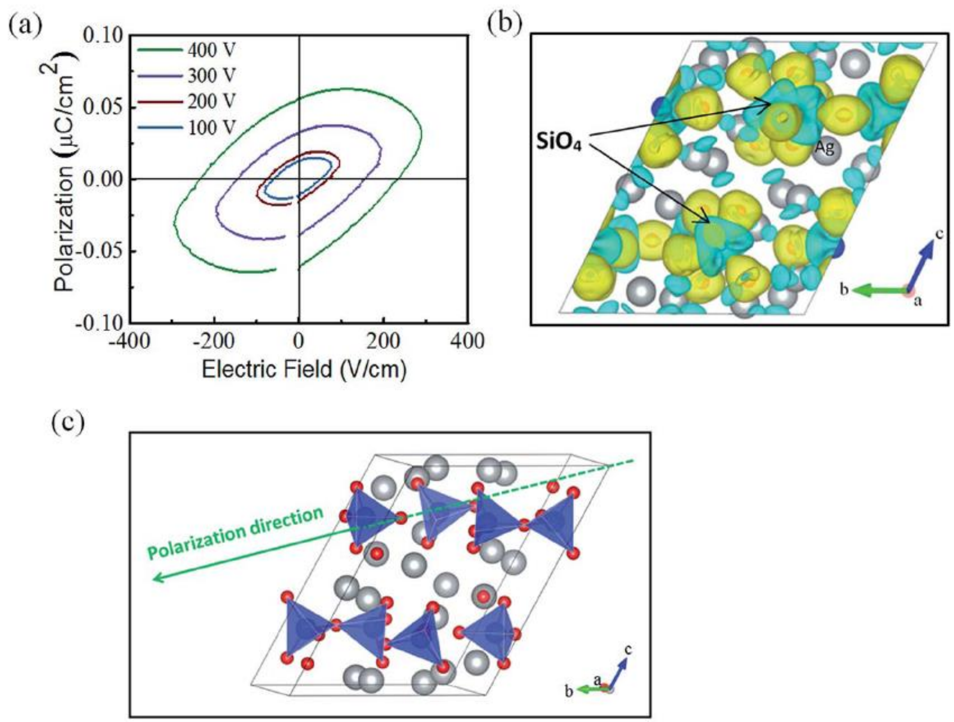
(a)
(3 -3 1)
(0 -1 3)
(1 -3 2)
(-1 0 3)
(-220)
(020)
(-311)
(2 1 1)
(3 0 1)
(-4 1 1)
(3 -1 2)
(3 -3 2)
(-4 4 1)
(0 4 1)
a
b
c
Ag
SiO_4
$Ag_{10}Si_4O_{13}$
JCPDS 00-034-0069
Intensity (a.u.)
2 Theta (degree)
(b)
1 μm
(c)
Si 2p
C 1s
Ag 3d
O 1s
Ag 3p
Intensity (a.u.)
Binding Energy (eV)
(d)
Absorbance (a.u.)
Wavelength (nm)
700 nm
$(\alpha h\nu)^{1/2}$
1.72 eV
hν (eV)


(a)
200 nm
Ag10Si4O13
(b)
(4̄ 1 1)
0.279 nm
(1̄ 0 4)
0.197 nm
5 nm
(c)
Ag 3d5/2
Ag 3d3/2
Ag 3d
Intensity (a.u.)
363 366 369 372 375 378
Binding Energy (eV)
(d)
O 1s
Intensity (a.u.)
525 528 531 534 537 540
Binding Energy (eV)
(e)
Si 2p
Intensity (a.u.)
90 93 96 99 102 105 108 111
(f)
Intensity (a.u.)
0 2 4 6 8 10
0 2 4 6 8 10 12 14 16
C
O
Si
Ag
Table of elements content
Elements Atomic %
O 42
Ag 26
C 20
Si 12



(a)
Absorbance (a.u.)
Wavelength (nm)
0 min → 40min
0 min
10 min
20 min
30 min
40 min
(b)
C/C0
Time (min)
30 min dark
MB
MO
RhB
Blank MB
Blank MO
Blank RhB
ln(C0/C)
(c)
Photodagradation %
N-TiO2
Ag10Si4O13
RhB
MB
MO
(d)
C / C0
Time (min)
120 min dark
ln(C0/C)


(a)
Intensity (a.u.)
Time (min)
0 min
20 min
40 min
60 min
80 min
100 min
(b)
Phenol degradation %
$Ag_{10}Si_4O_{13}$
Ag_3PO_4
$Ag_7Si_2O_7$
Ag_2CO_3

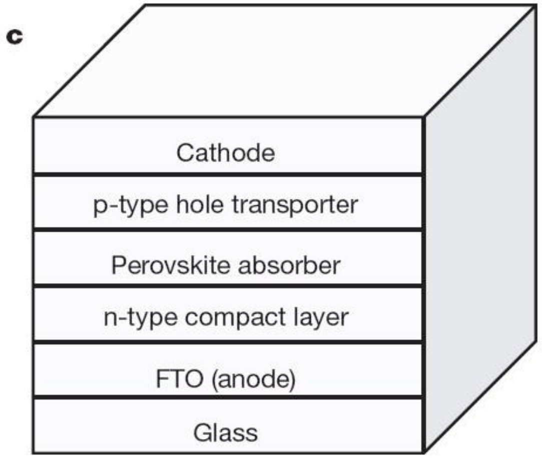

(a)
Polarization ($\mu C/cm^2$)
Electric Field (V/cm)
400 V
300 V
200 V
100 V
(b)
SiO_4
Ag
(c)
Polarization direction

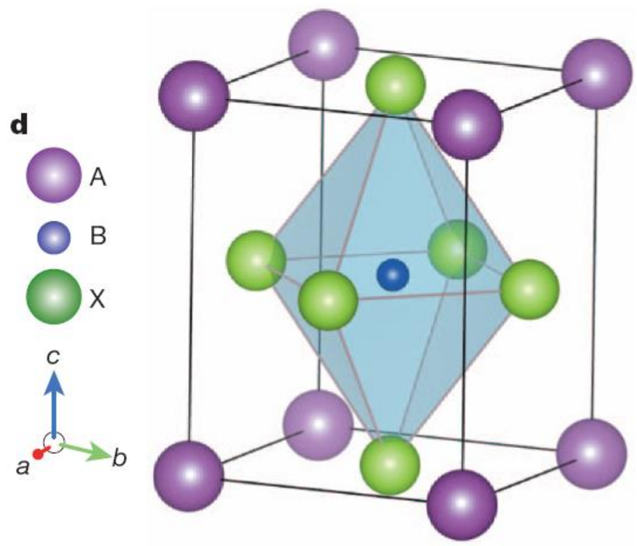
新型光能转化材料

新材料	文章发表	他引	性能
BiOX(X=Cl, Br, I)	Rare Metals 2008, 27：243	165	分解水产氢
$Bi_{24}O_{31}Br_{10}$	ACS Catal. 2014, 4: 954	80	分解水产氢 Cr^{6+}还原
$Bi_{24}O_{31}Cl_{10}$	Scientific Reports 2014, 4: 7384	24	染料敏化太阳能电池
$Ag_{10}Si_4O_{13}$	J. Mater. Chem. A 2016, 4: 10992	5	有机污染物氧化
BiSiO	Dalton Transactions2017 DOI: 10.1039/C7DT03193A		有机污染物氧化

发展了3类6种新型光能转化材料，受到了广泛的关注

Perovskite as absorber

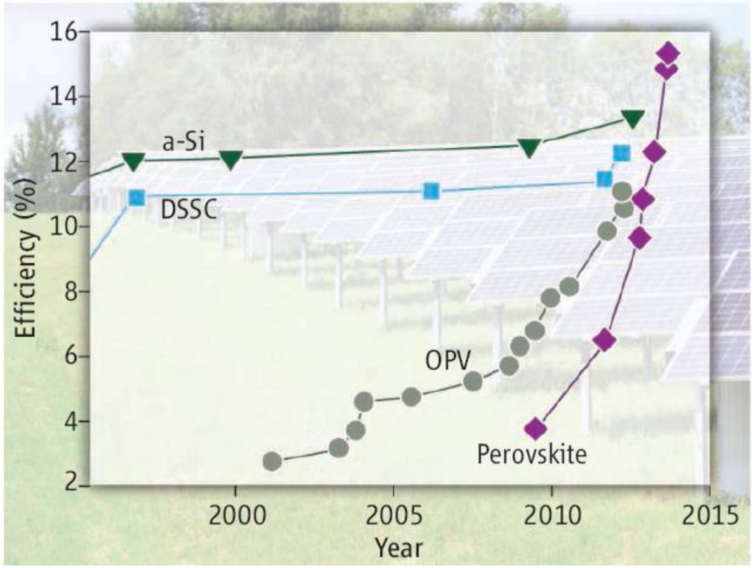




2013 Years Material

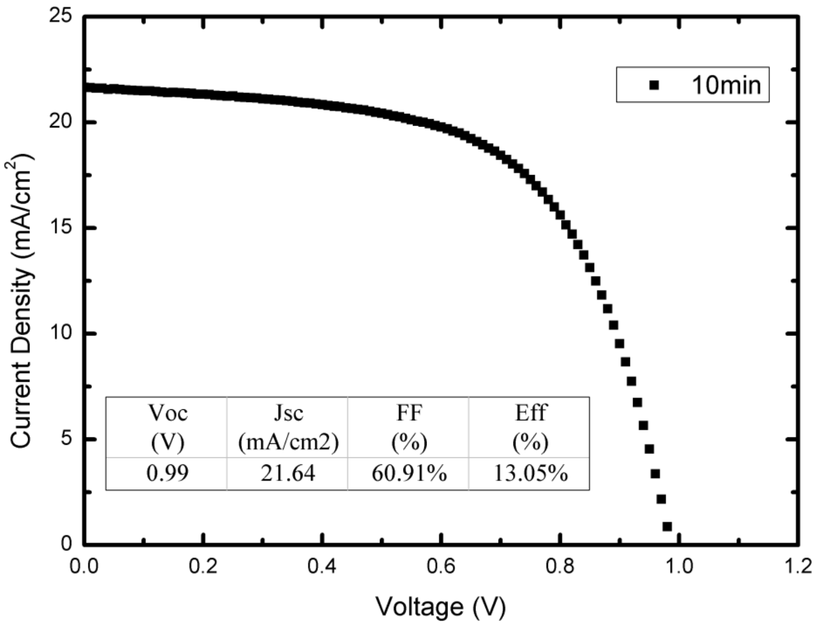
$CH_3NH_3PbI_3$

Ethylammonium

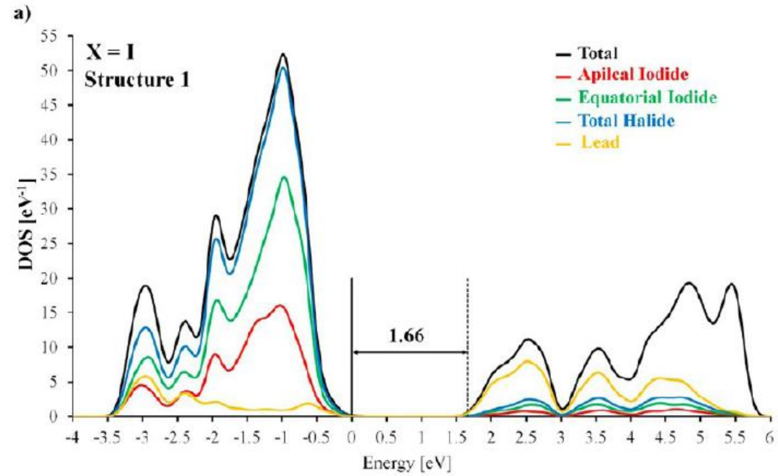


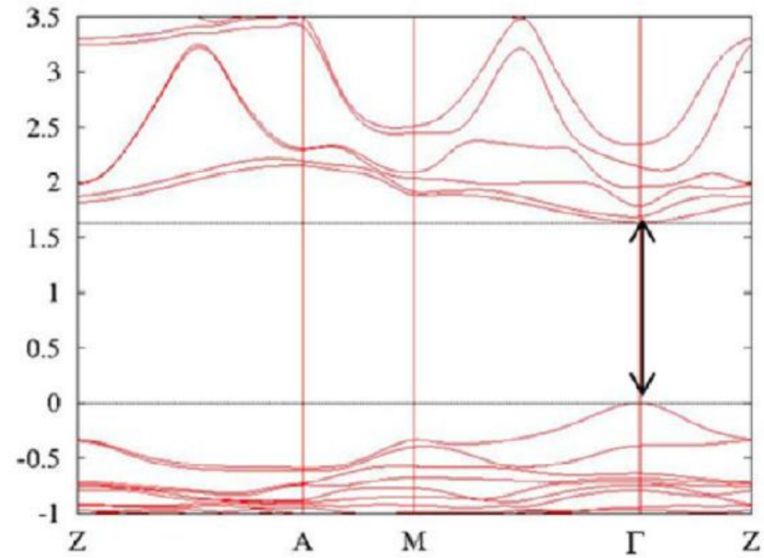
The cumulative world PV installations reached around 100 GWp (gigawatts) by the end of 2012. Some 85% use crystalline Si, with the rest being polycrystalline thin film cells, mostly cadmium telluride/cadmium sulfide ones.

Nature, 2013,501,323; Nature, 2013,342,344; Nature,2013, 501,396; Nature, 2013, 499, 316



Voc (V)	Jsc (mA/cm2)	FF (%)	Eff (%)
0.99	21.64	60.91%	13.05%



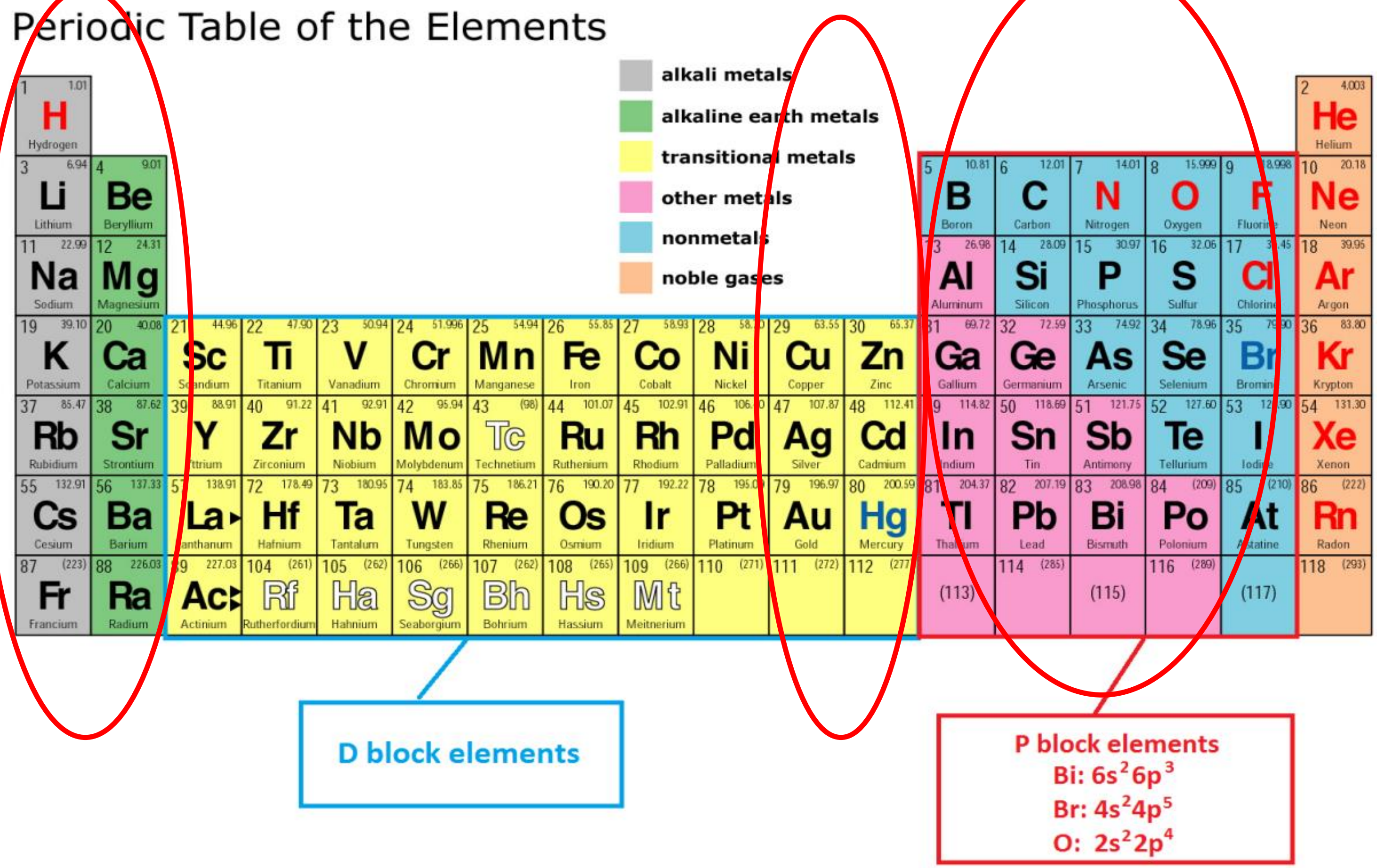


What is next one ?

Layer structure bismuth materials??

J. Phys. Chem. C 2013, 117, 13909

c



Metal: Na K Mg Ca Sr Ba In Sn Sb Bi Cu Zn Ag

Nonmetal: O S X (X=F, Cl, Br, I) B C N P

Nothing is Impossible！！！

Outline

- **Introduction: *sp* hybridization**

Four stories

Symmetry

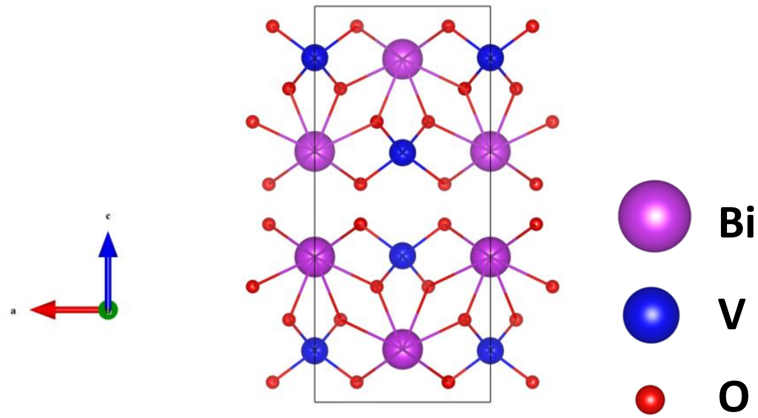
- $Bi_{24}O_{31}Br_{10}/Bi_{24}O_{31}Cl_{10}$
- $Ag_{10}Si_4O_{13}$

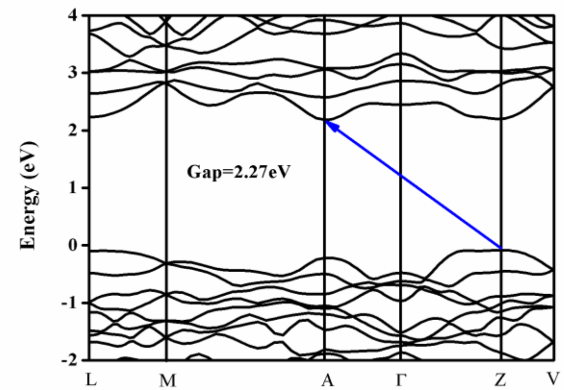
Symmetry Breaking

- Vacancy Engineering – Blank TiO_2
- Strain engineering – BiOBr

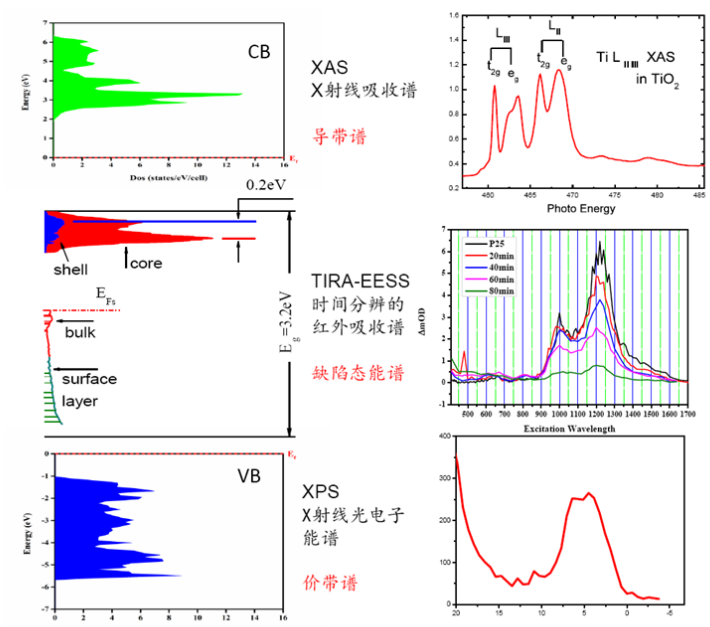
- **对称性决定基本电子结构**

$$\hat{H}\Psi(x) = E\Psi(x)$$





- **对称破却决定光电转化效率**



对称性减少！！

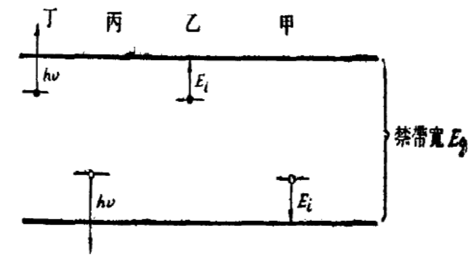


图 49.7

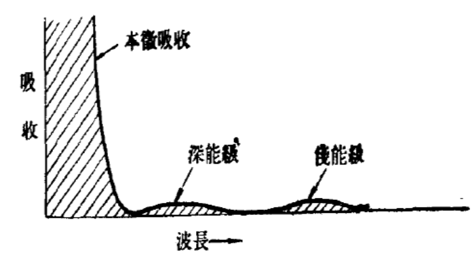
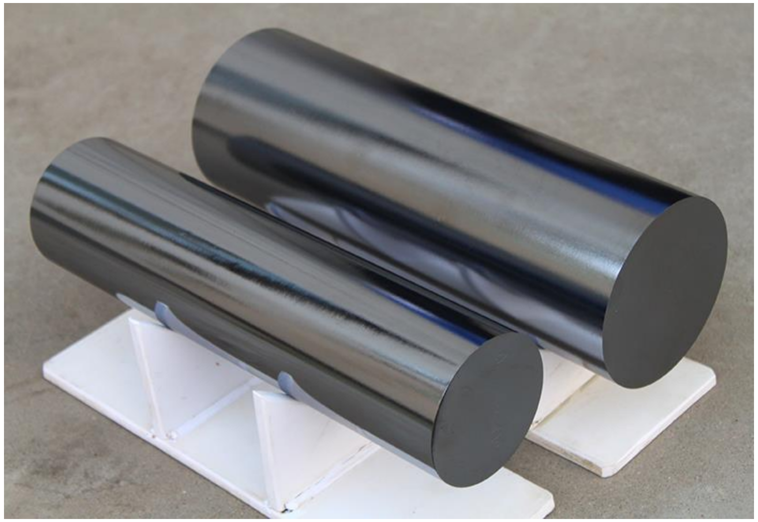
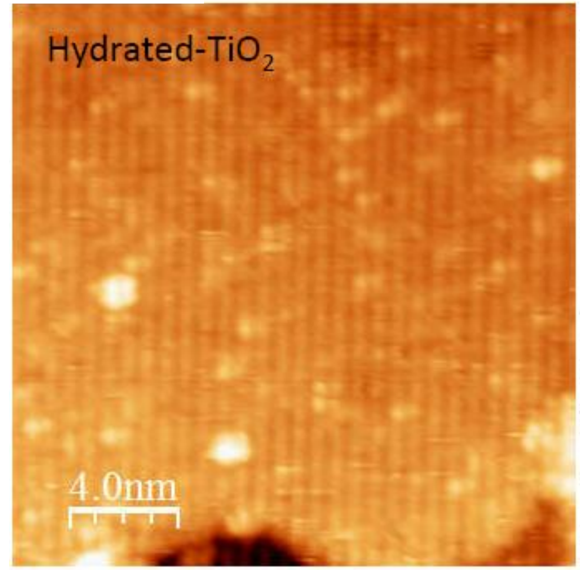


图 49.8

黄昆、谢希德，《半导体物理学 》p308

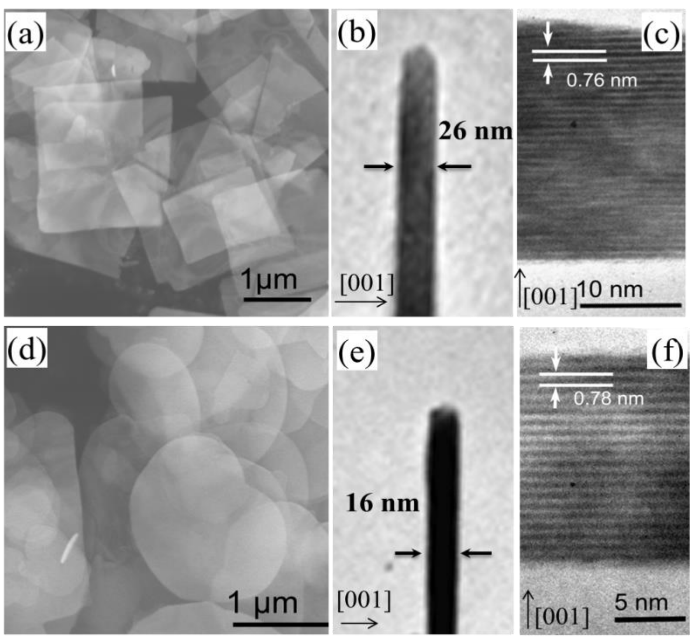
对称性破不同决定了大家的差异！！！

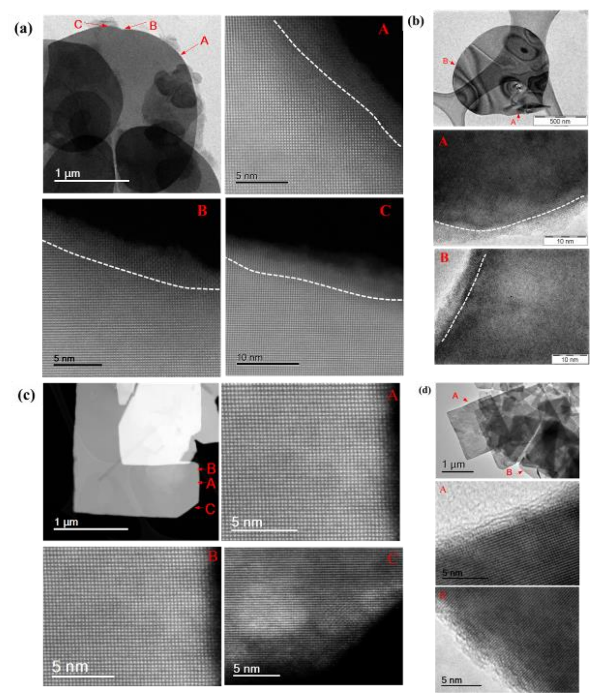




The **water** comes from **residual water molecular** in the HUV chamber.

The $\mathbf{V_O}$ on the surface of r-TiO_2 can only survive for **several hours** in HUV.





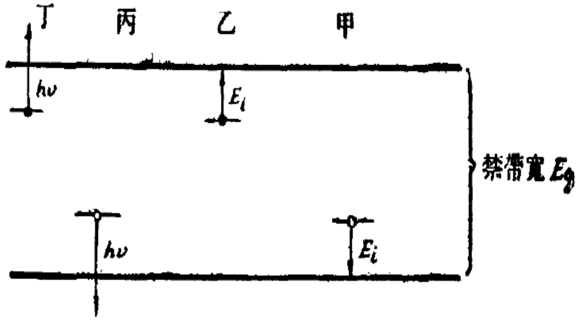


图 49.7

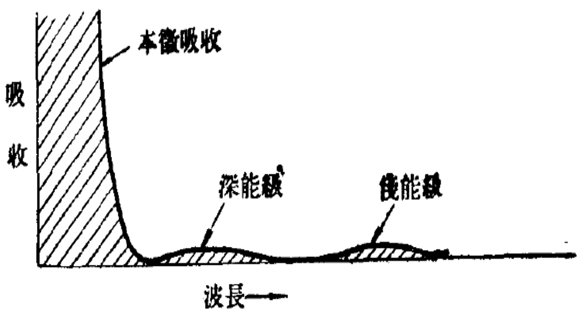
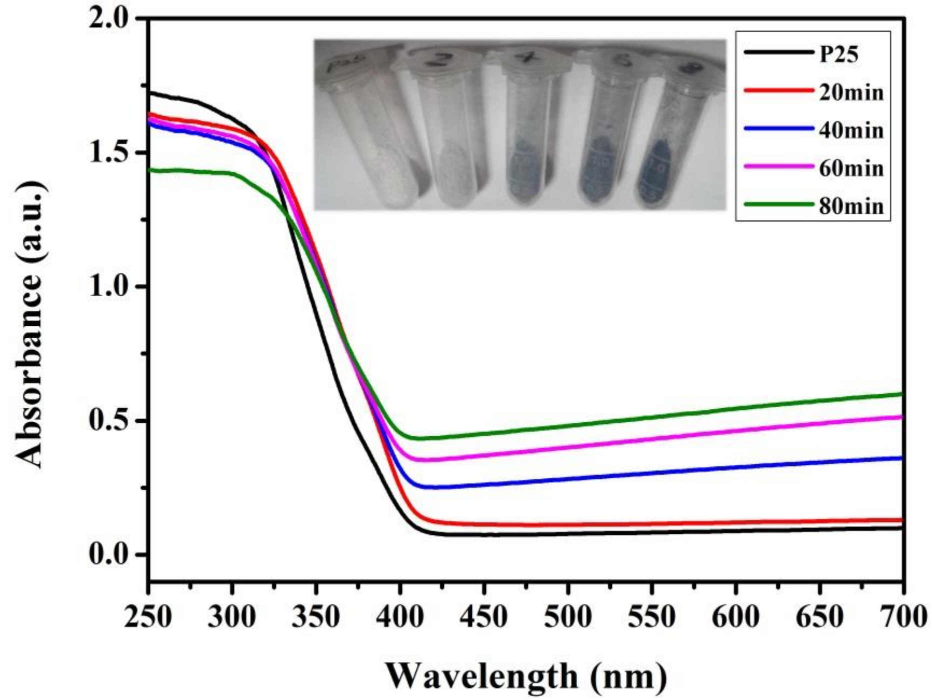
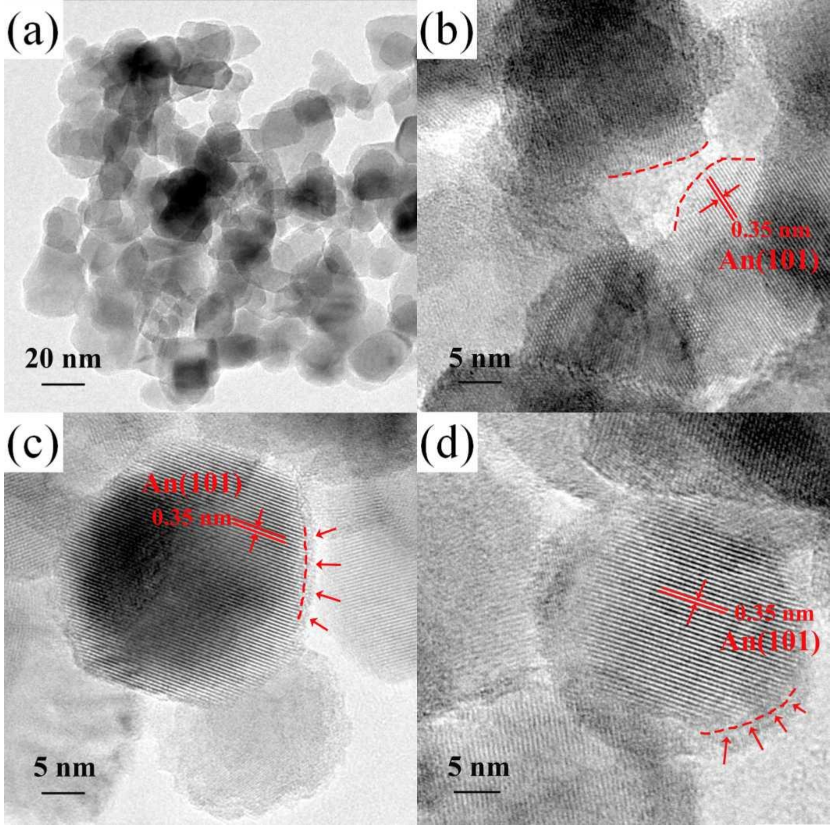


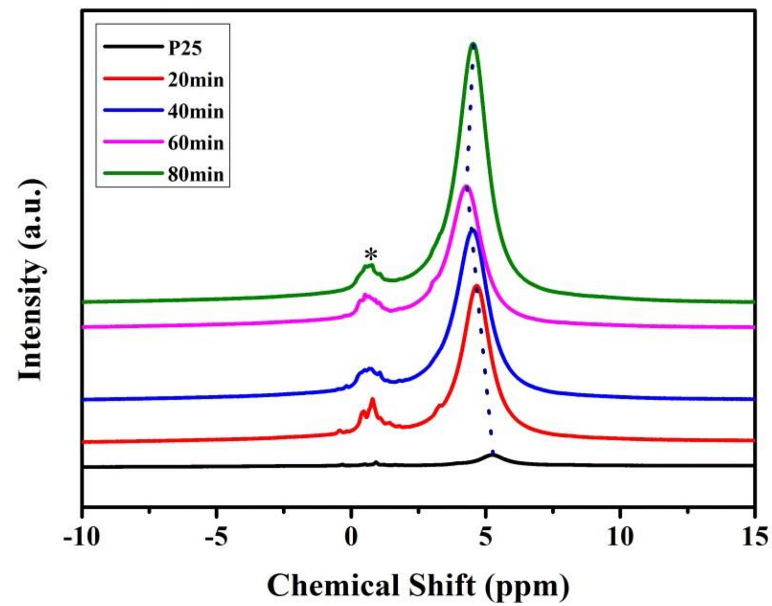
图 49.8



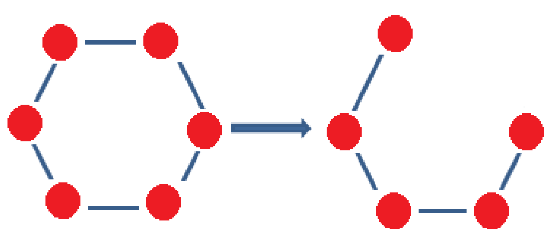
- 本征吸收
- 激子吸收
- 自由载流子吸收
- 杂质吸收
- 晶格吸收

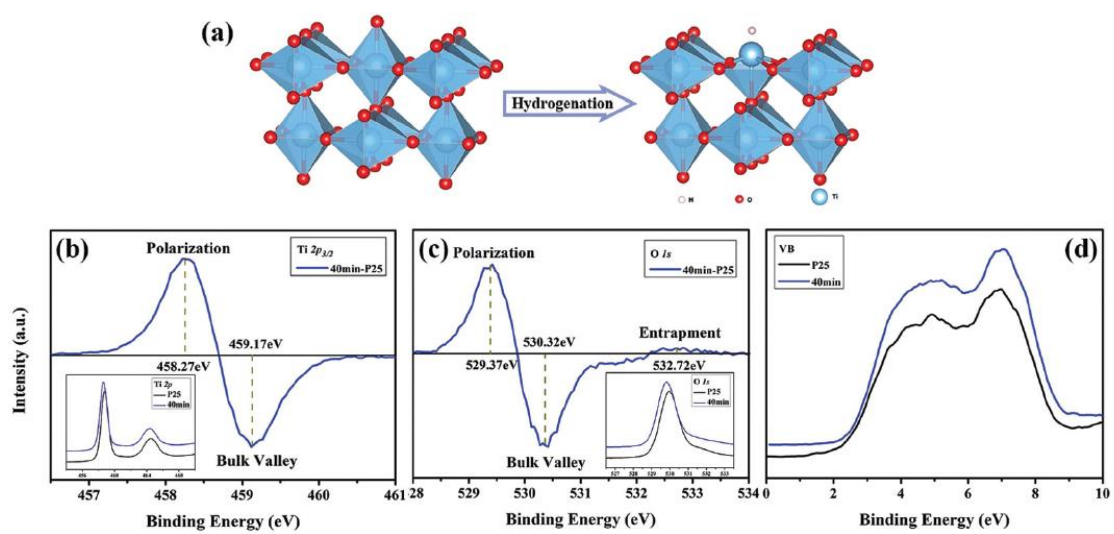
黄昆、谢希德，《半导体物理学 》p308

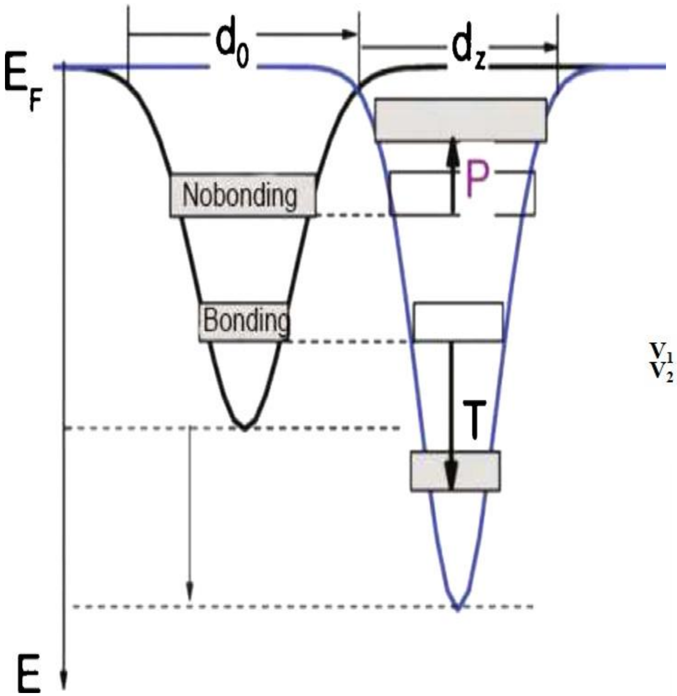


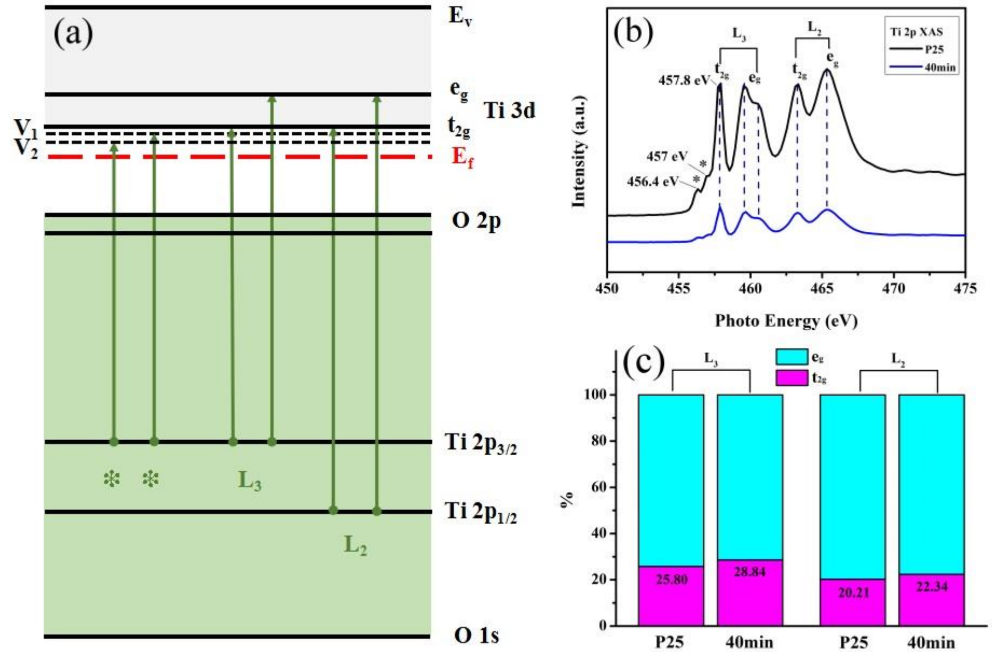


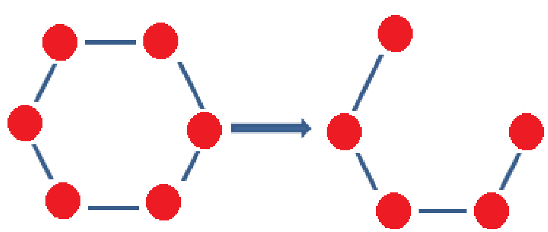
Polarization VS Trap state?









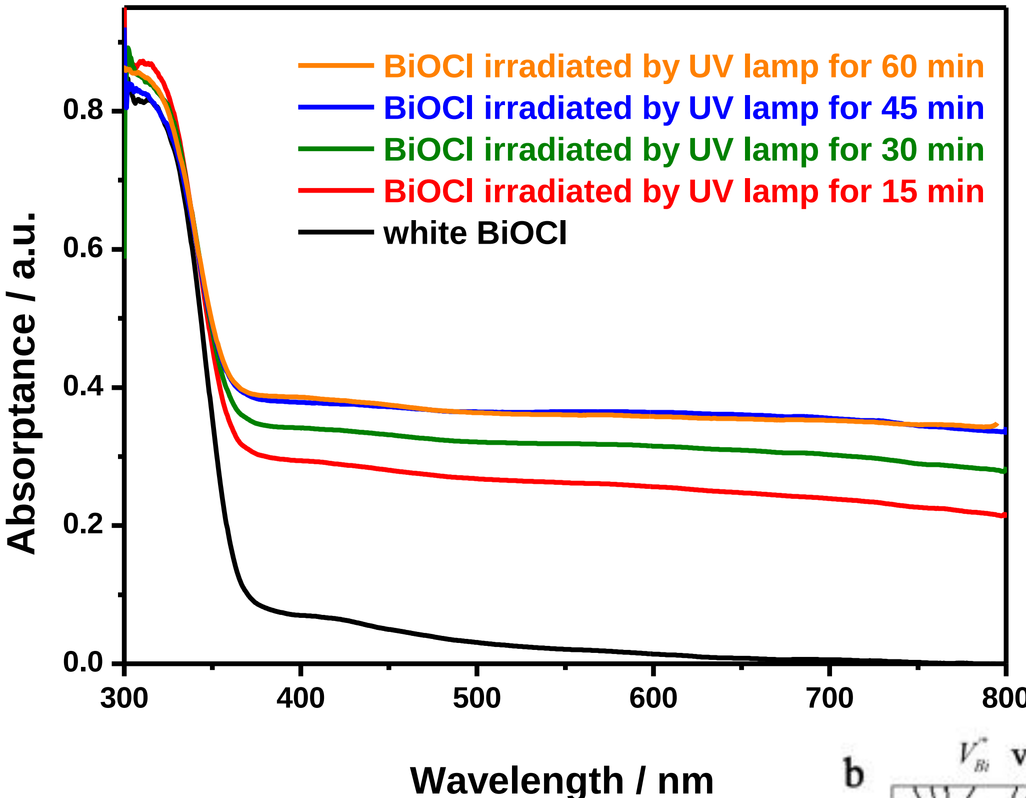


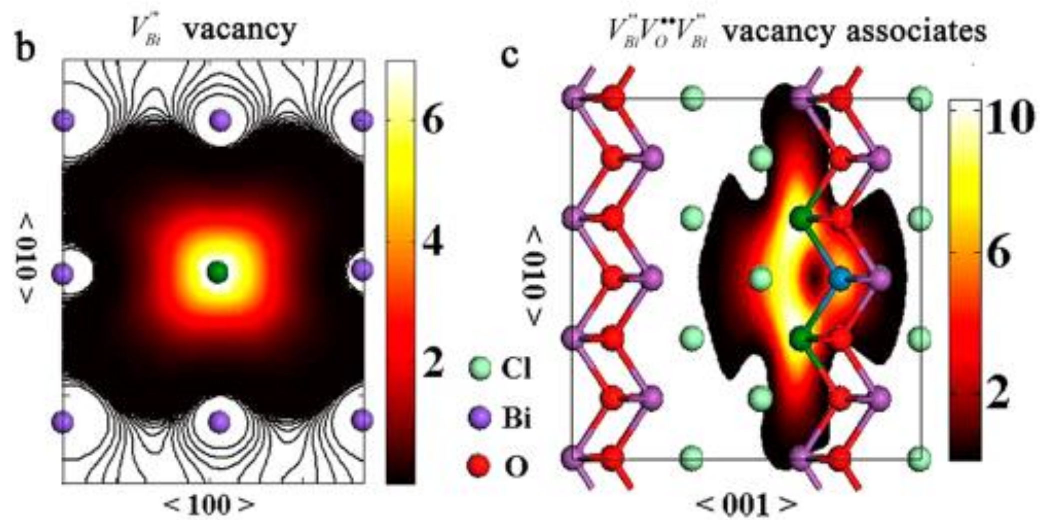
Polarization VS Trap state?

Surface state

Defects state

Dalton Transactions 2017, 46: 10694





Y Xie, J. Am. Chem. Soc. 2013, 135, 10411

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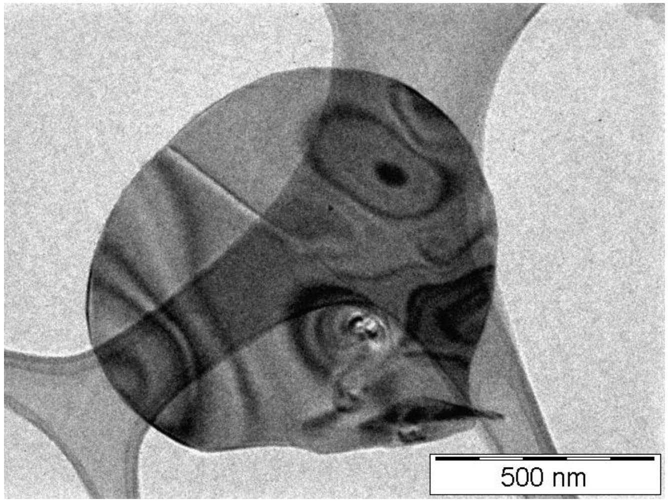
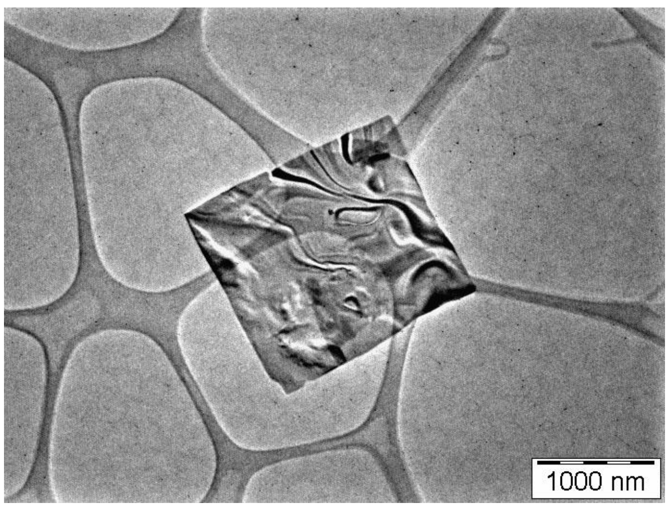
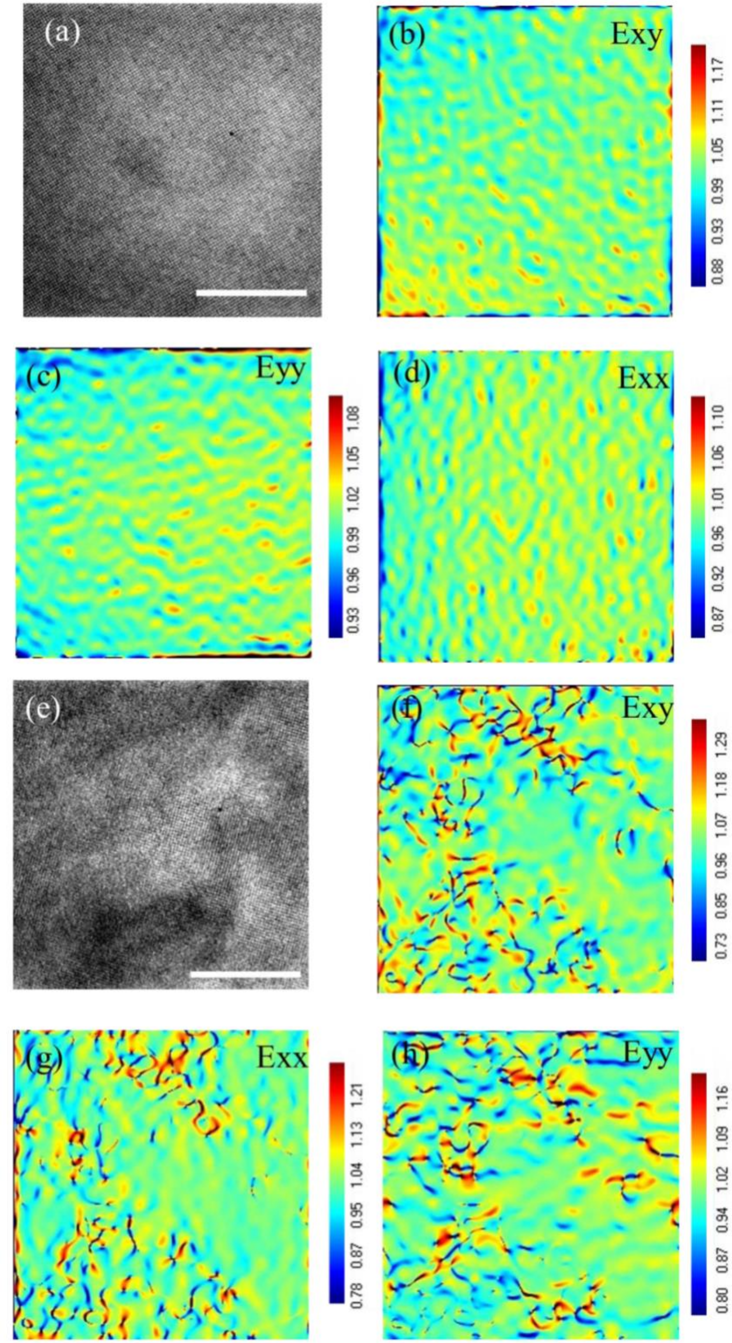
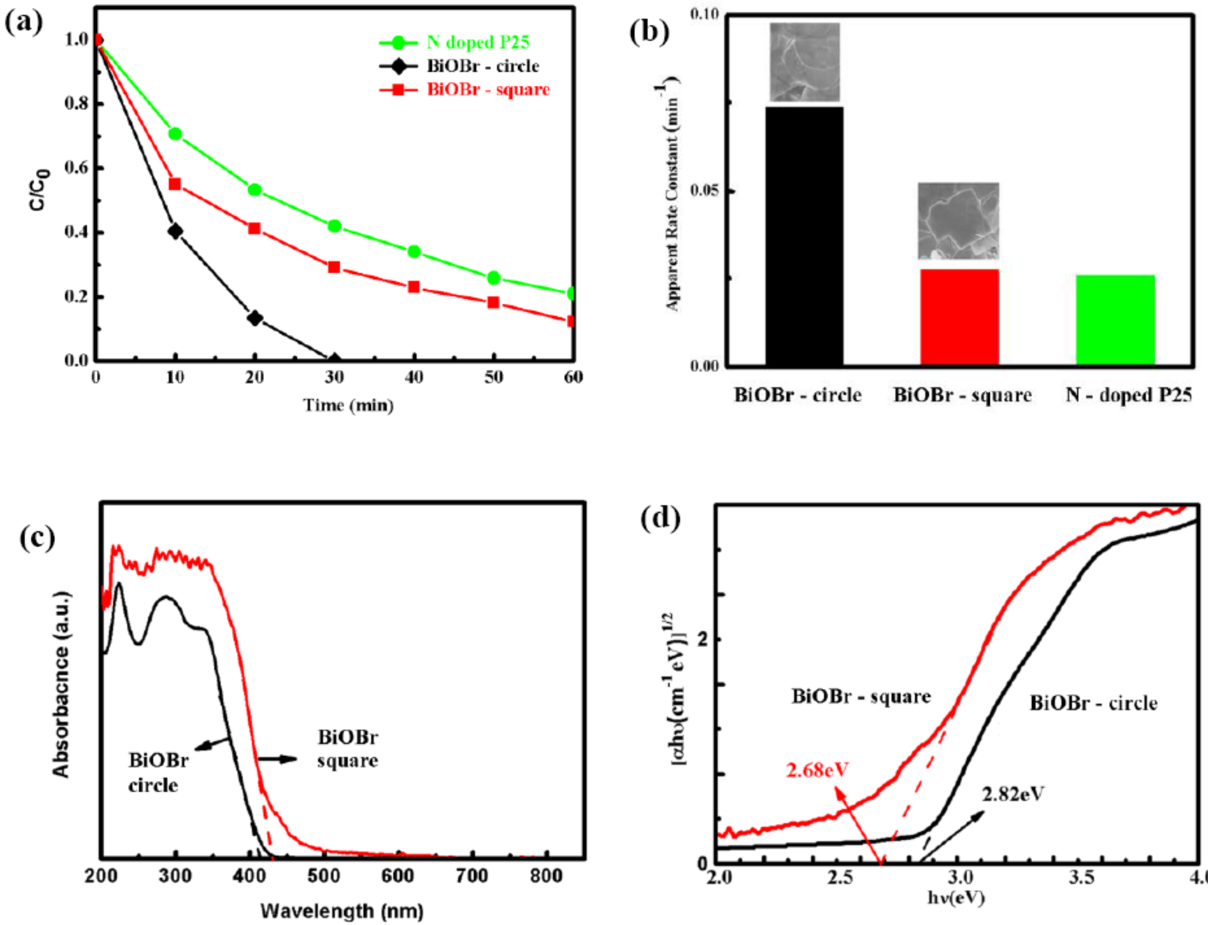
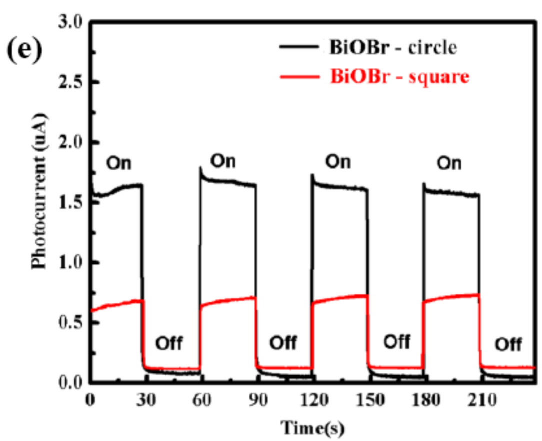






ACS Appl. Mater. Interface 2015, 7: 27592

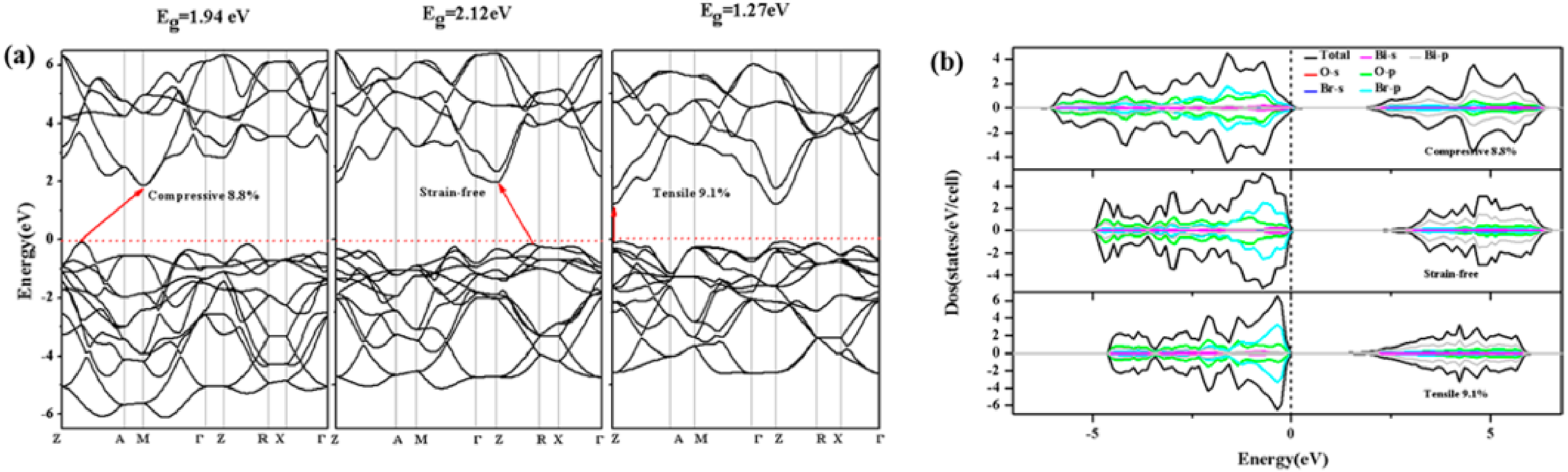


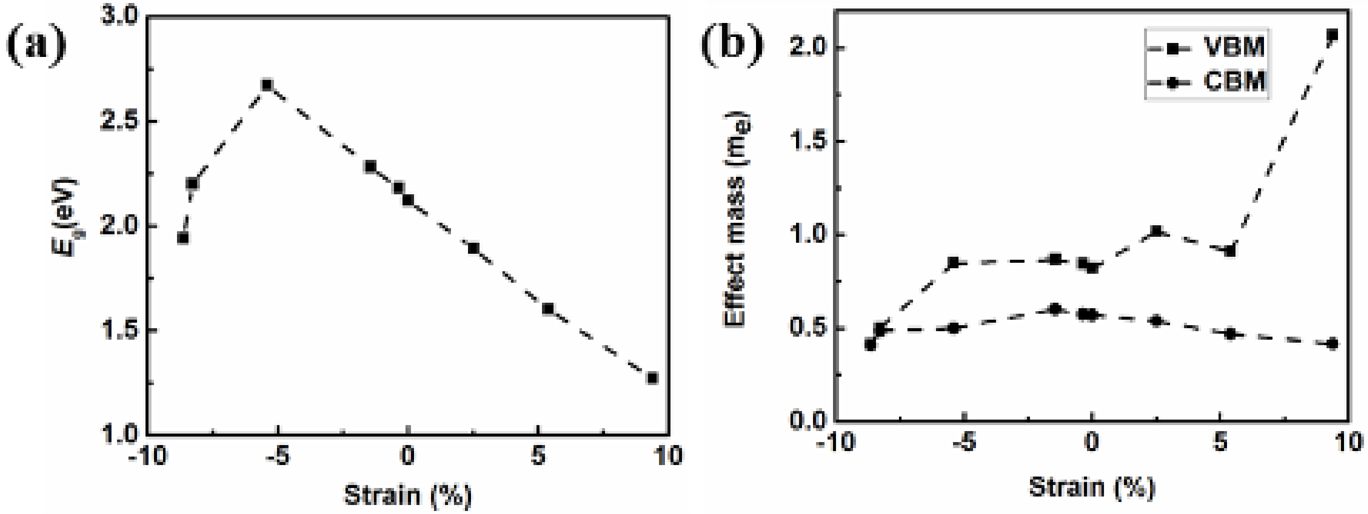


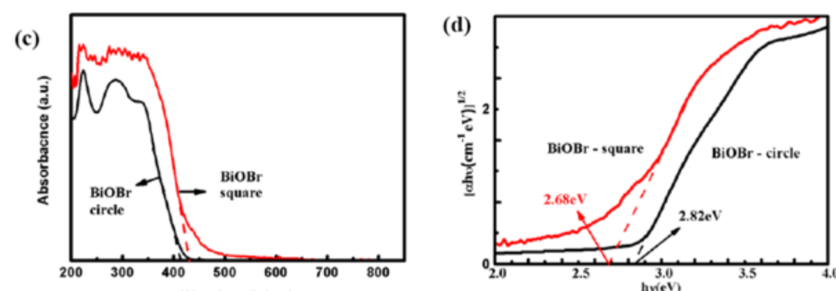
BET measurements

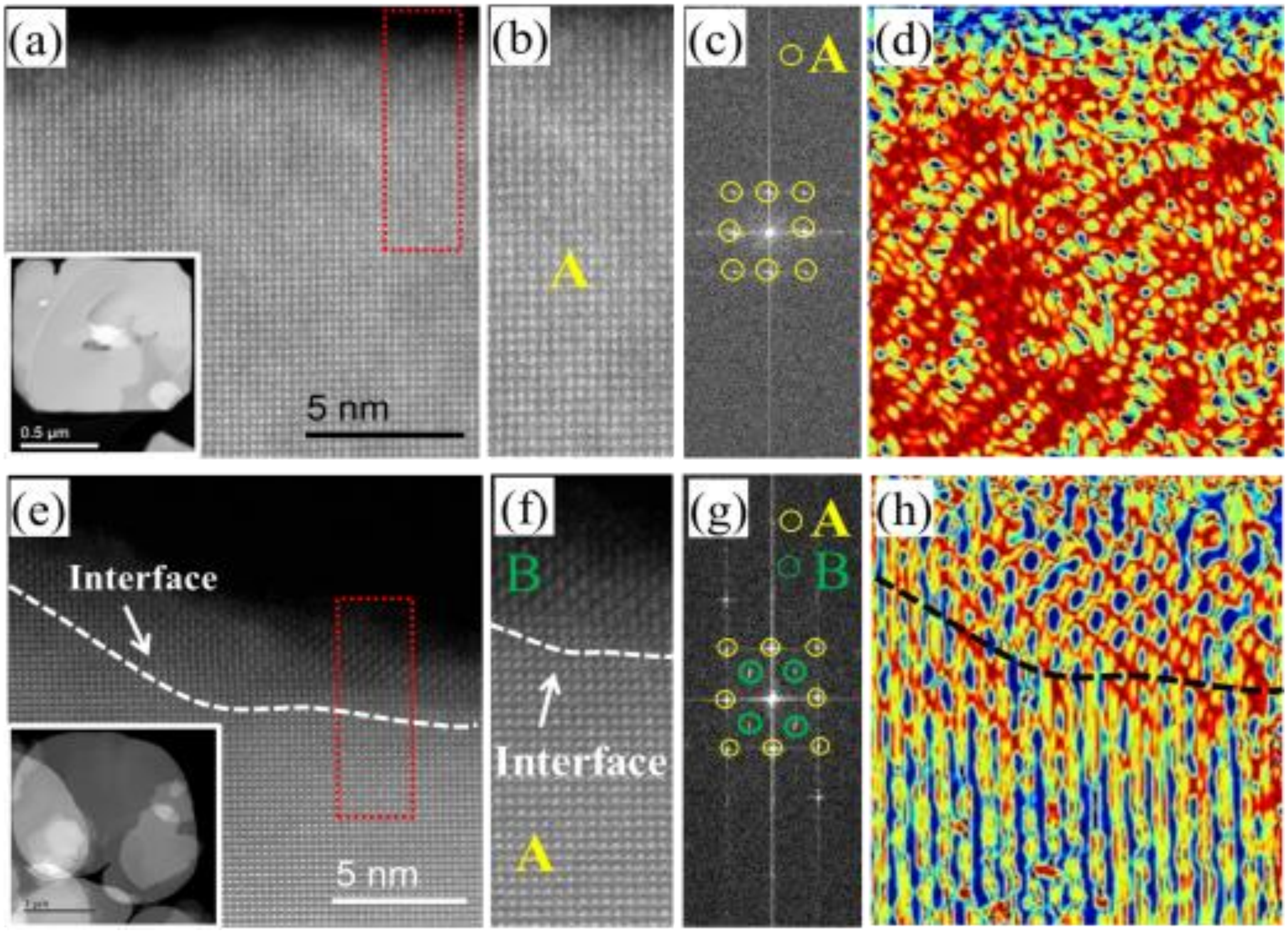
BiOBr-circle 4.49 m_3/g

BiOBr-square 7.03 m_3/g

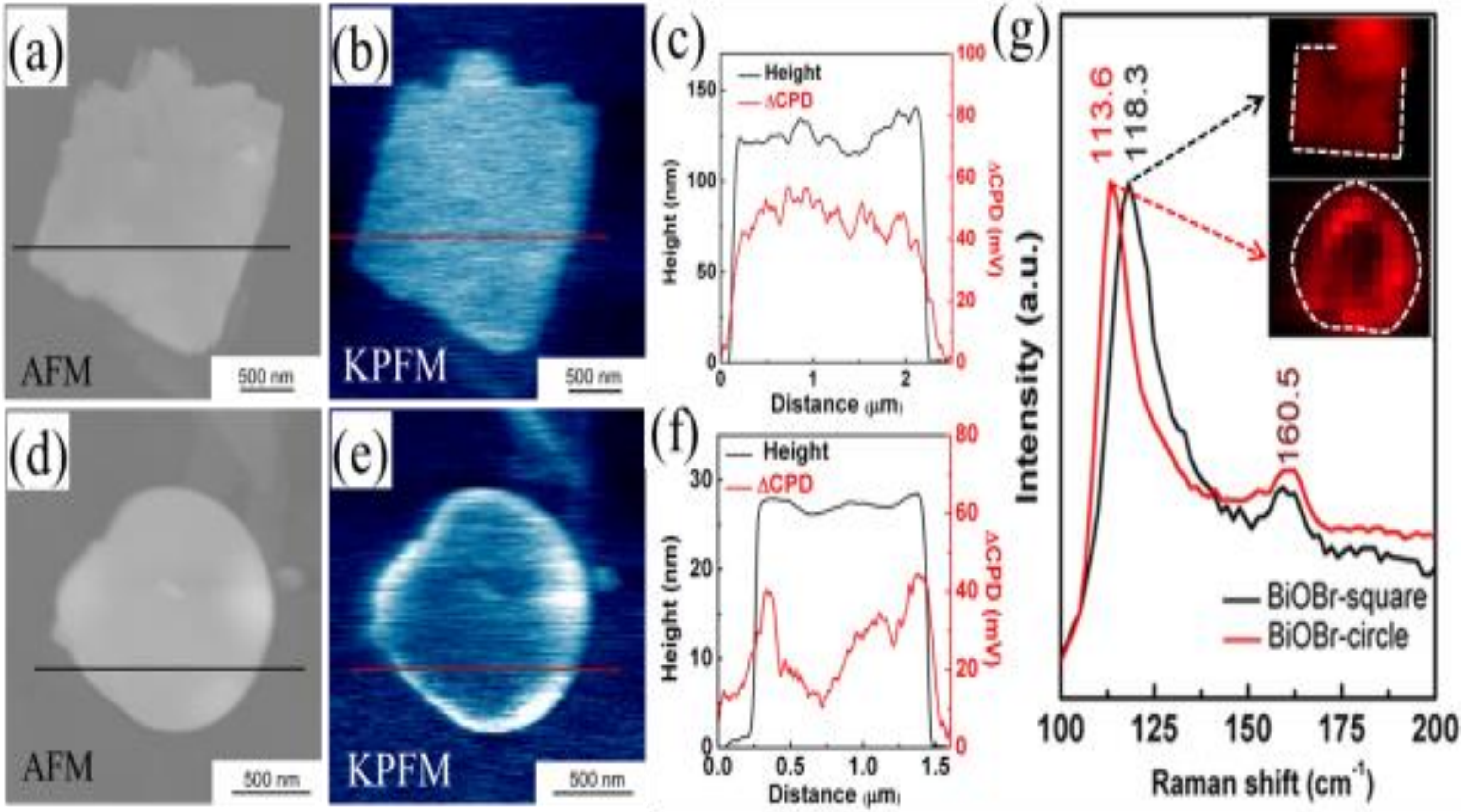

Eg=1.94 eV
Eg=2.12eV
Eg=1.27eV
(a)
Energy(eV)
Compressive 8.8%
Strain-free
Tensile 9.1%
Z A M Γ Z R X Γ
(b)
Total
Bi-s
Bi-p
O-s
O-p
Br-s
Br-p
Dos(states/eV/cell)
Energy(eV)

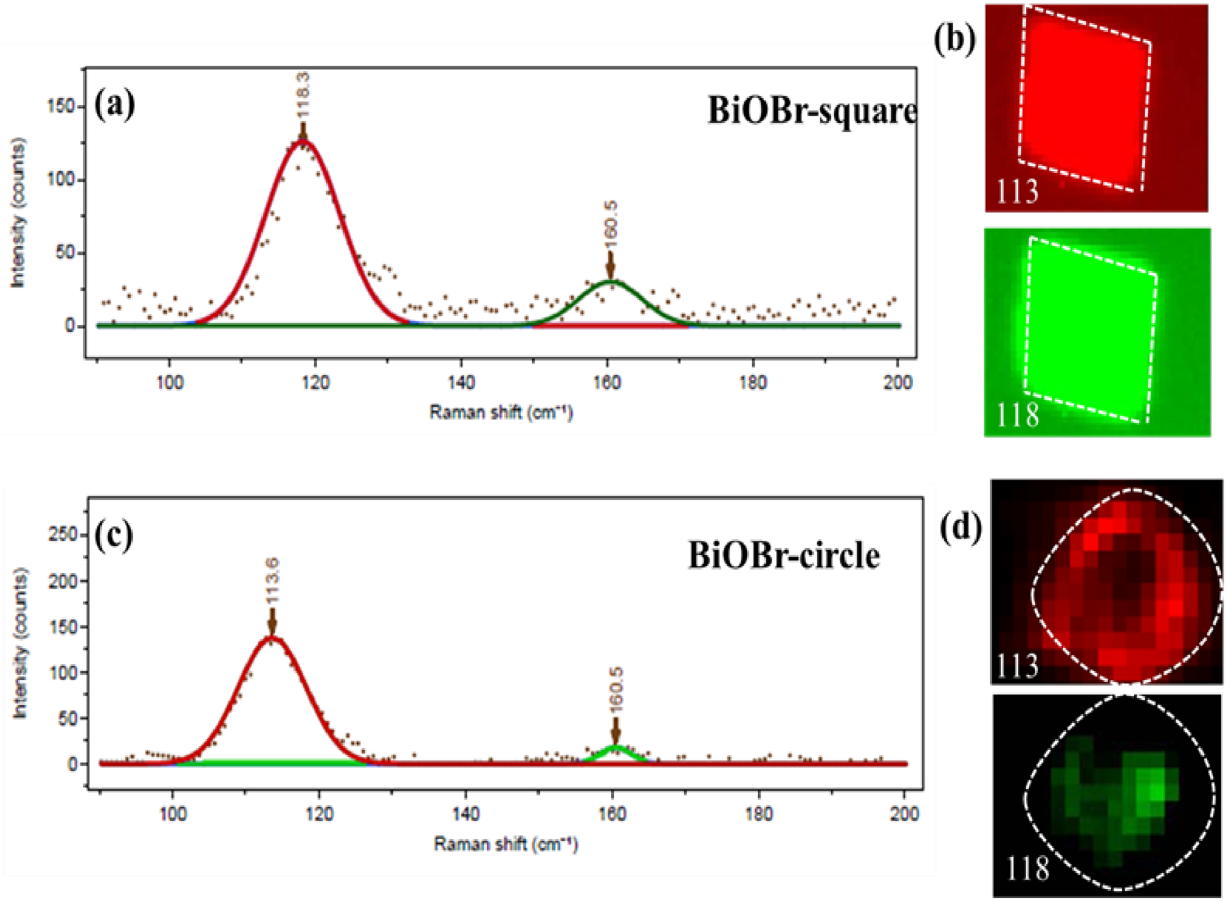

(a)
Eg(eV)
Strain (%)
(b)
VBM
CBM
Effect mass (me)
Strain (%)

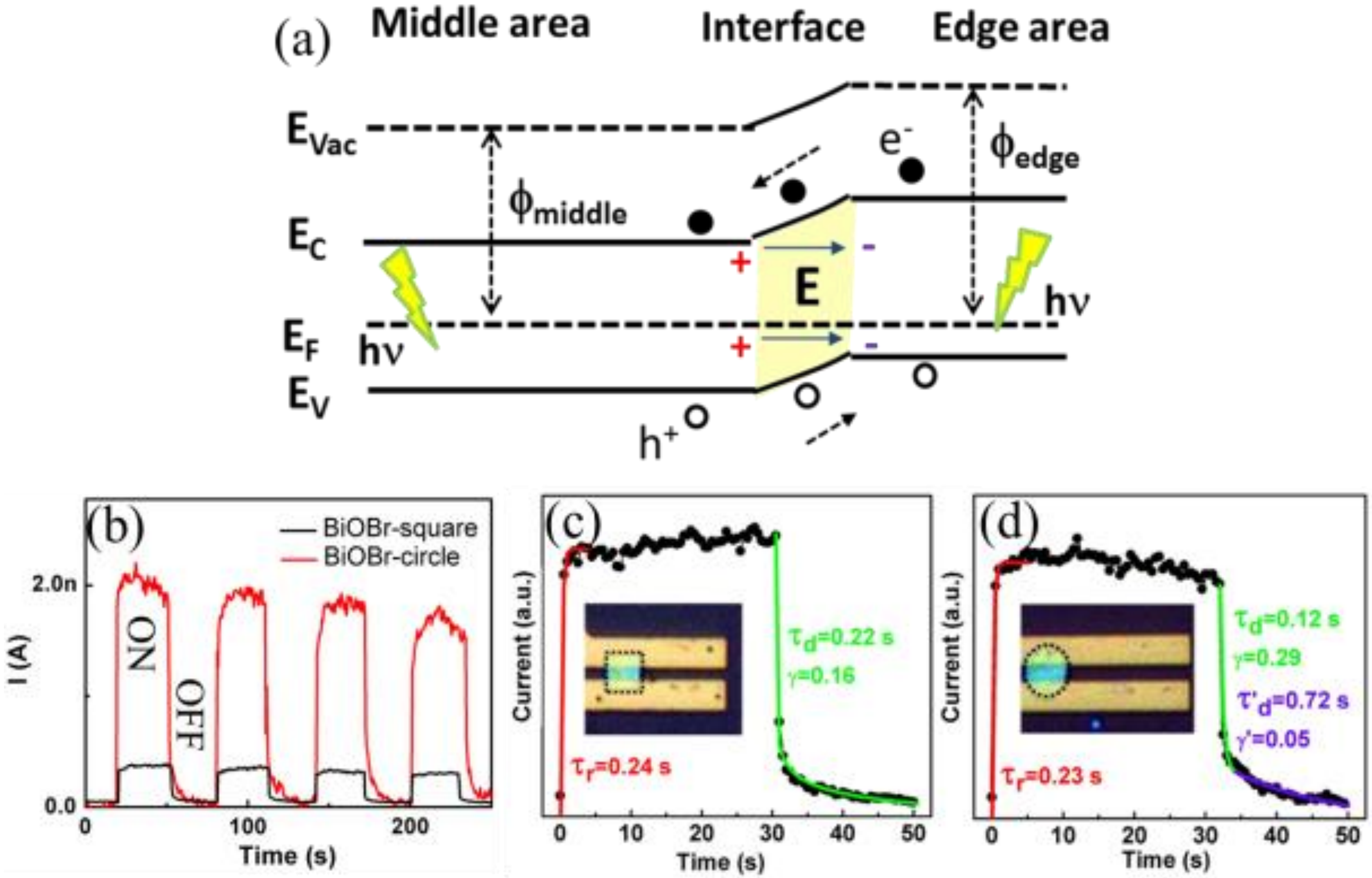

(c)
Absorbacnce (a.u.)
BiOBr circle
BiOBr square
Wavelength (nm)
(d)
BiOBr - square
BiOBr - circle
2.68eV
2.82eV
hv(eV)



2D Mater. 2017, 4: 025102


(a)
AFM
500 nm
(b)
KPFM
500 nm
(c)
Height
ΔCPD
Height (nm)
ΔCPD (mV)
Distance (μm)
(d)
AFM
500 nm
(e)
KPFM
500 nm
(f)
Height
ΔCPD
Height (nm)
ΔCPD (mV)
Distance (μm)
(g)
113.6
118.3
160.5
Intensity (a.u.)
BiOBr-square
BiOBr-circle
Raman shift (cm-1)


(a)
BiOBr-square
118.3
160.5
Intensity (counts)
Raman shift (cm⁻¹)
(b)
113
118
(c)
BiOBr-circle
113.6
160.5
Intensity (counts)
Raman shift (cm⁻¹)
(d)
113
118



(a)
Middle area
Interface
Edge area
E_{Vac}
E_C
E_F
E_V
ϕ_{middle}
ϕ_{edge}
e^-
h^+
$h\nu$
E
(b)
BiOBr-square
BiOBr-circle
ON
OFF
I (A)
Time (s)
(c)
τ_d=0.22 s
γ=0.16
τ_r=0.24 s
Current (a.u.)
Time (s)
(d)
τ_d=0.12 s
γ=0.29
τ'_d=0.72 s
γ'=0.05
τ_r=0.23 s
Current (a.u.)
Time (s)

Publication

[1] ***Curr. Opin. Green Sustain. Chem.*** 2017,6: 93-100
[2] ***2D Mater.*** 2017, 4: 025102
[3] ***ACS Catal.*** 2014, 4: 954
[4] ***ACS Appl. Mater. Interface*** 2015, 7: 27592
[5] ***J. Mater. Chem. A*** 2016, 4: 10992
[6] ***Energy Environ. Sci.*** 2015, 8:1231
[7] ***Scientific Reports*** 2014, 4: 7384
[8] ***J. Phys. Chem. C*** 2016, 120: 8589
[9] ***J. Phys. Chem. C*** 2015, 119: 14094
[10] ***J. Phys. Chem. C*** 2012, 116: 1251

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Thank You!

祝大家一切顺利！

UOW

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NSFC（Nos. 51672018, 51472016，51272015）

ARC（ DP140102581，DP170101467）

Thank You!