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Supporting Information

Plasma modification of Poly(2-heptadecyl-4-vinylthieno[3,4-d]thiazole) low bandgap polymer and its application in solar cell

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Poly(2-heptadecyl-4-vinylthieno[3,4-d]thiazole) (PHVTT)

4,6-dibromo-2-heptadecyl-thieno[3,4-d]thiazole [1] (0.35 g, 0.650 mmol), 1-(dibutyl((E)-2-(tributylstannyl)vinylstannyl)butane (0.39 g, 0.065 mmol), and Pd(PPh_3)$_4$(0) (0.02 g, 0.025 mmol) were placed in 100-mL 3-neck round bottom flask equipped with a condenser, purged with N_2 gas and subsequently dissolved in 20 mL of toluene, from which oxygen was removed by purging with nitrogen for 1 h. The resulting mixture were stirred at 120 ^{0}C for 72 hours, after which 20 μL of 2-bromothiophene was injected as a capping agent. The reaction was stirred for 2 hr at 120 ^{0}C before 20 μL of 2-(tributyltin) thiophene was injected to complete the end-capping. The reaction mixtures were cooled and filtered to separate a blue solid as polymer. The blue polymer as product was purified by ethanol and acetone to yield a pure conducting a deep blue solid. The yield was 81%. It was soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF. Mn= 9980, Mw= 26499, PD = 2.655. ^{1}H NMR (400MHz, $CDCl_3$): δ= 7.19(m, 1H), 7.17(m, 1H), 2.92(m, 2H), 1.79(m, 2H), 1.22(m, 28H), 0.81(m, 3H) ppm ; ^{13}C NMR (400MHz, $CDCl_3$): δ= 22.71, 29.40, 29.79, 31.95, 76.68, 77.00, 77.32, 133.01, 140.97, 142.91, 170.90 ppm ; FT-IR (KBr) ν 3002, 2941, 2880,1620cm^{-1}

[1] I. T. Kim, J. H. Lee, S.W.R.L. Lee, *Bul. Korean Chem. Soc.* **2007**, *28*, 2511-2513.

Figure Captions

Fig. S1. The emission spectra of atmospheric-pressure plasma jet (APPJ) with Air as feeding gas.

Fig. S2 The emission spectra of atmospheric-pressure plasma jet (APPJ) with Ar as feeding gas.

Fig. S3 Schematic view of the γ-focused ion beam (γ-FIB) consisting of the thermal electron source, the ionization region of ions, the electrostatic single Einzel lens that focused the ion beam, and the collector and copper pad for the measurement of the secondary electron emissions from the surface of the polymer thin films.

Fig. S4 Cyclic voltammograms of the polymer films before and after plasma treatment using active electrode of carbon, reference electrode of Ag/AgNO3 and counter platinum electrode of (a) polymer, (b) polymer treated with Air plasma, (c) polymer treated with N_2 plasma and (d) polymer treated with Ar plasma.

Fig. S5 Carbon 1s spectra from (a) polymer, (b) polymer treated with Air plasma, (c) polymer treated with N_2 plasma and (d) polymer treated with Ar plasma.

Fig. S6 Oxygen 1s spectra from (a) polymer, (b) polymer treated with Air plasma, (c) polymer treated with N_2 plasma and (d) polymer treated with Ar plasma.

Fig. S7 Nitrogen 1s spectra from (a) polymer, (b) polymer treated with Air plasma, (c) polymer treated with N_2 plasma and (d) polymer treated with Ar plasma.

Fig. S8 Sulfur 2p spectra from (a) polymer, (b) polymer treated with Air plasma, (c) polymer treated with N_2 plasma and (d) polymer treated with Ar plasma.

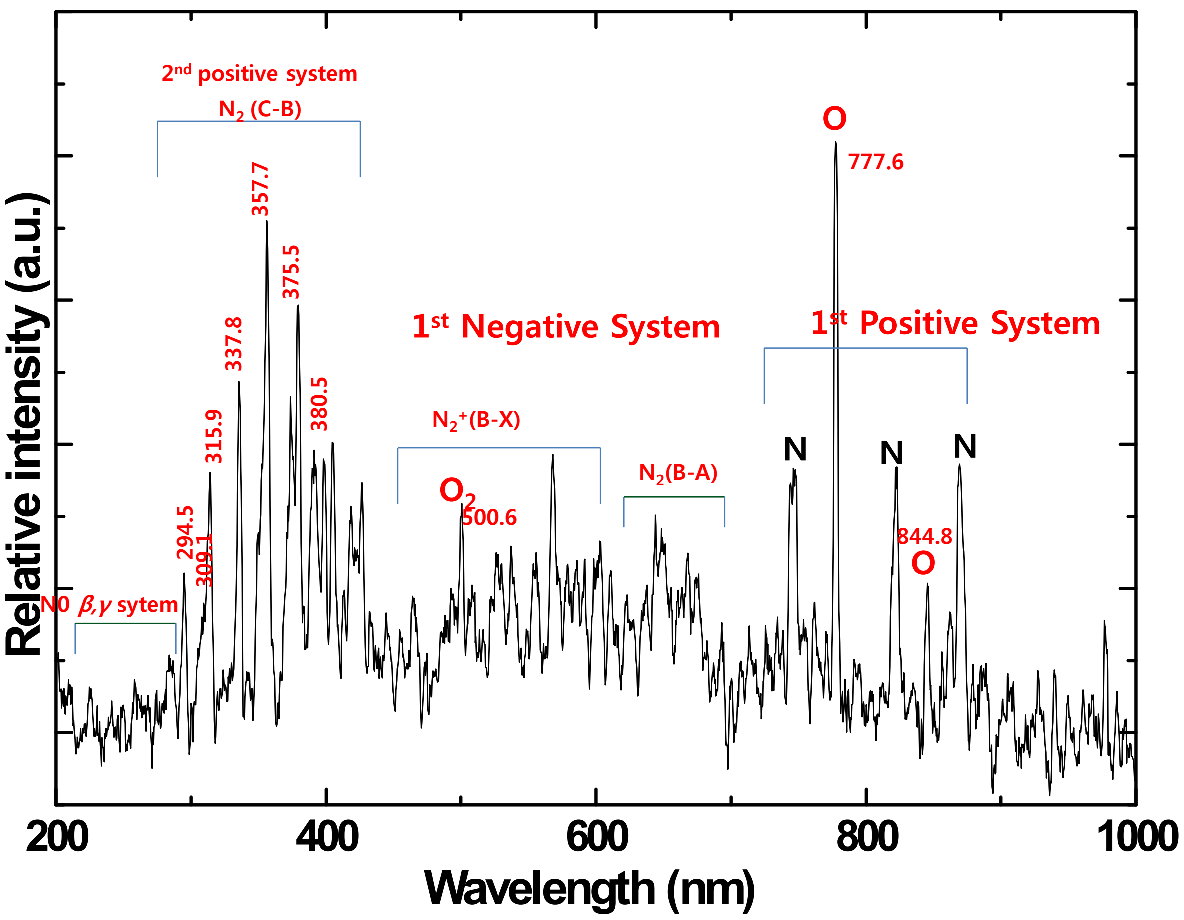
2nd positive system
N2 (C-B)
357.7
375.5
337.8
380.5
315.9
294.5
309.1
N0 β,γ sytem
1st Negative System
N2+(B-X)
O2
500.6
N2(B-A)
O
777.6
1st Positive System
N
N
N
844.8
O
Relative intensity (a.u.)
200
400
600
800
1000
Wavelength (nm)

Fig. S1.

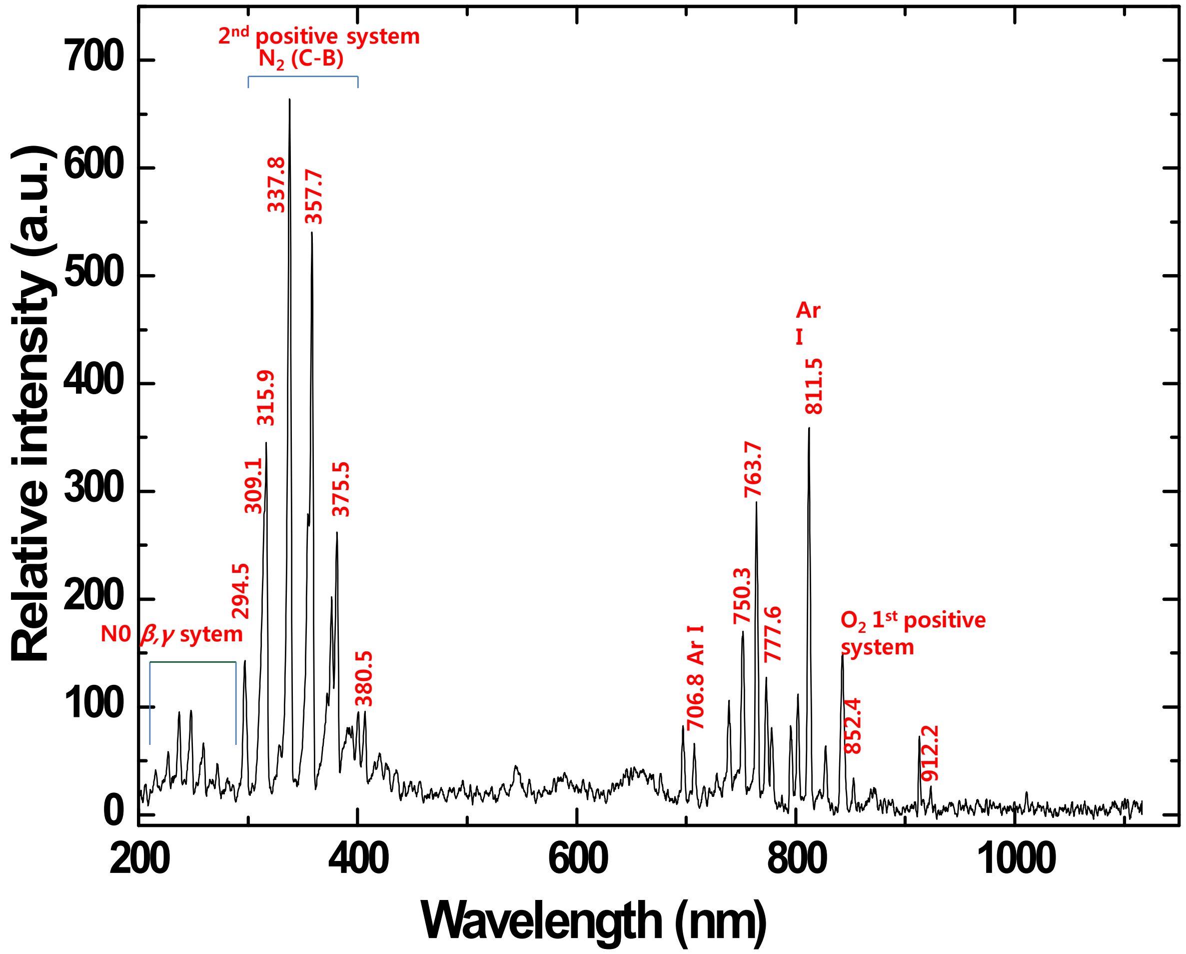
2nd positive system
N2 (C-B)
NO β,γ sytem
294.5
309.1
315.9
337.8
357.7
375.5
380.5
706.8 Ar I
750.3
763.7
777.6
Ar
I
811.5
O2 1st positive
system
852.4
912.2
Relative intensity (a.u.)
Wavelength (nm)
0
100
200
300
400
500
600
700
200
400
600
800
1000

Fig. S2.

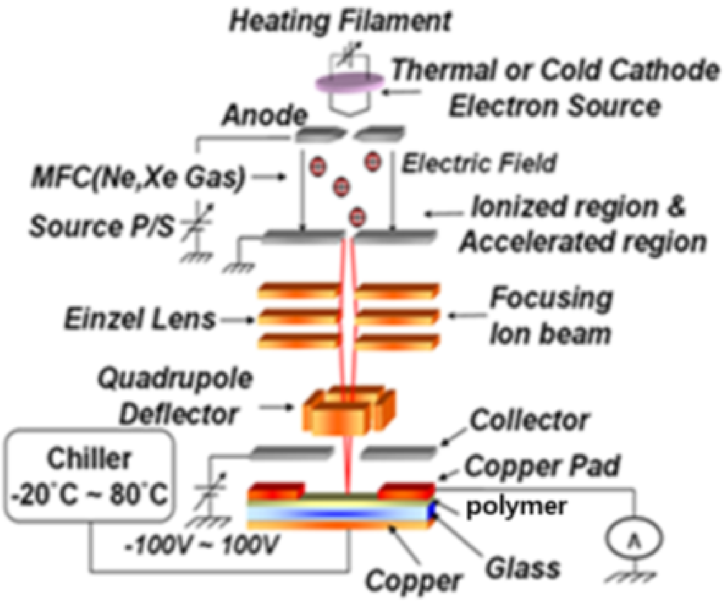
Heating Filament
Thermal or Cold Cathode Electron Source
Anode
MFC(Ne,Xe Gas)
Electric Field
Source P/S
Ionized region & Accelerated region
Einzel Lens
Focusing Ion beam
Quadrupole Deflector
Collector
Chiller -20˚C ~ 80˚C
Copper Pad
polymer
-100V ~ 100V
A
Copper
Glass

Fig.S3.

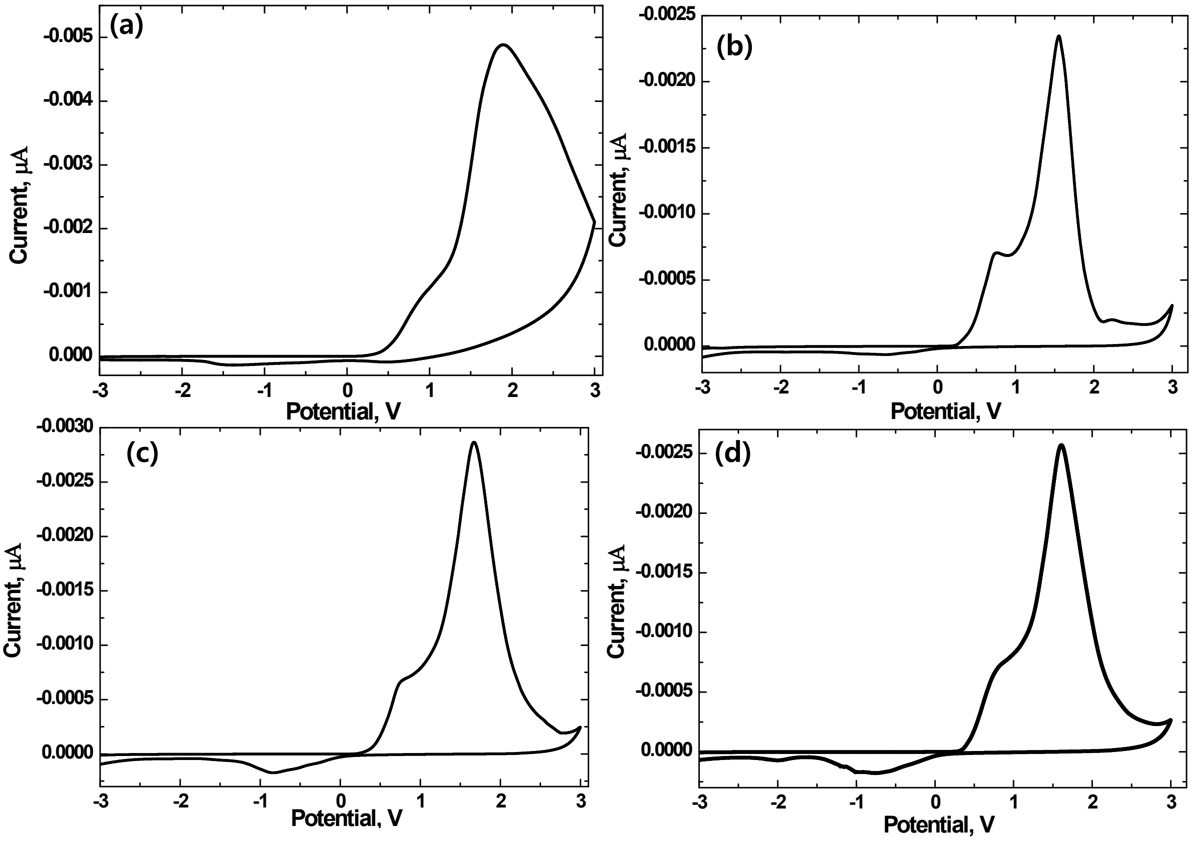
(a)
(b)
(c)
(d)
Current, μA
Potential, V
-0.005
-0.004
-0.003
-0.002
-0.001
0.000
-0.0030
-0.0025
-0.0020
-0.0015
-0.0010
-0.0005
0.0000
-3
-2
-1
0
1
2
3

Fig. S4.

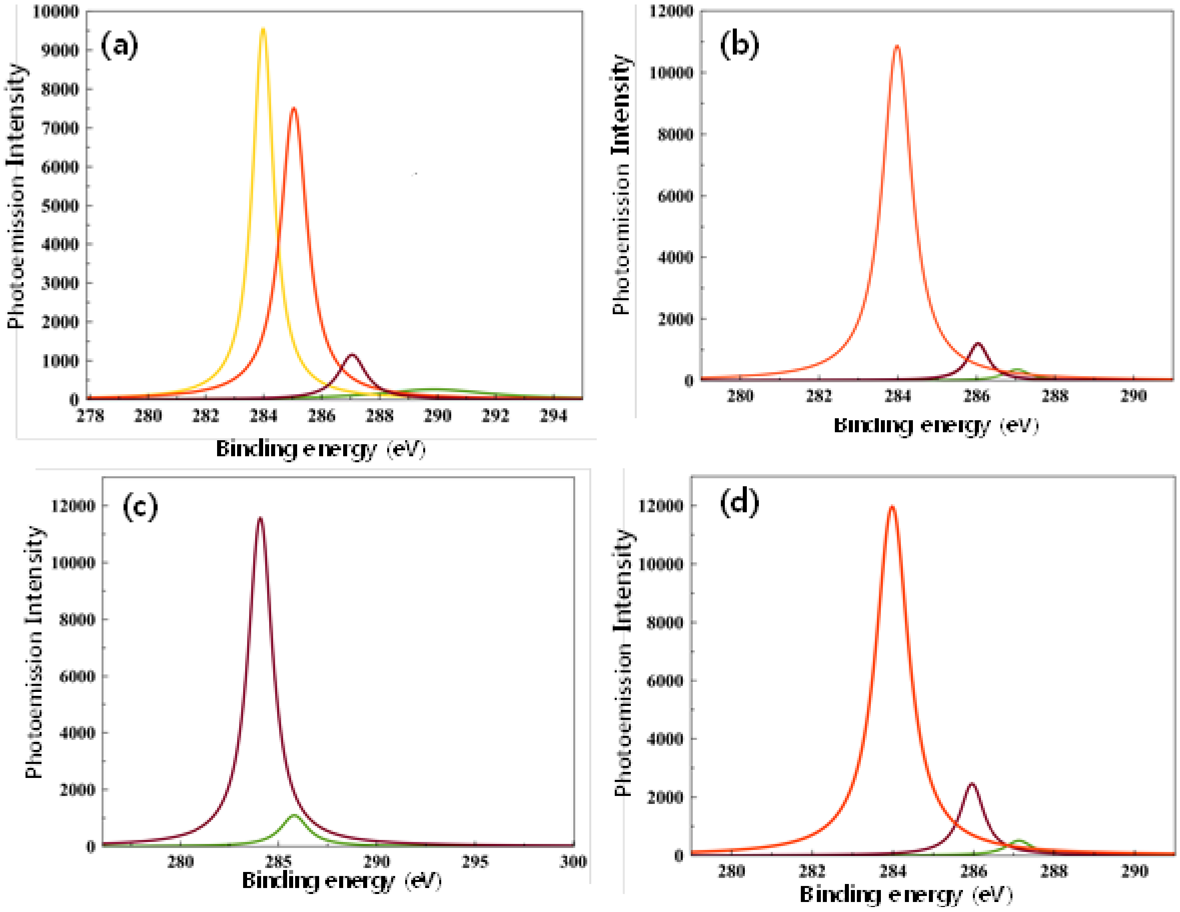
(a)
Photoemission Intensity
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
278
280
282
284
286
288
290
292
294
Binding energy (eV)
(b)
Photoemission Intensity
12000
10000
8000
6000
4000
2000
0
280
282
284
286
288
290
Binding energy (eV)
(c)
Photoemission Intensity
12000
10000
8000
6000
4000
2000
0
280
285
290
295
300
Binding energy (eV)
(d)
Photoemission Intensity
12000
10000
8000
6000
4000
2000
0
280
282
284
286
288
290
Binding energy (eV)

Fig. S5.

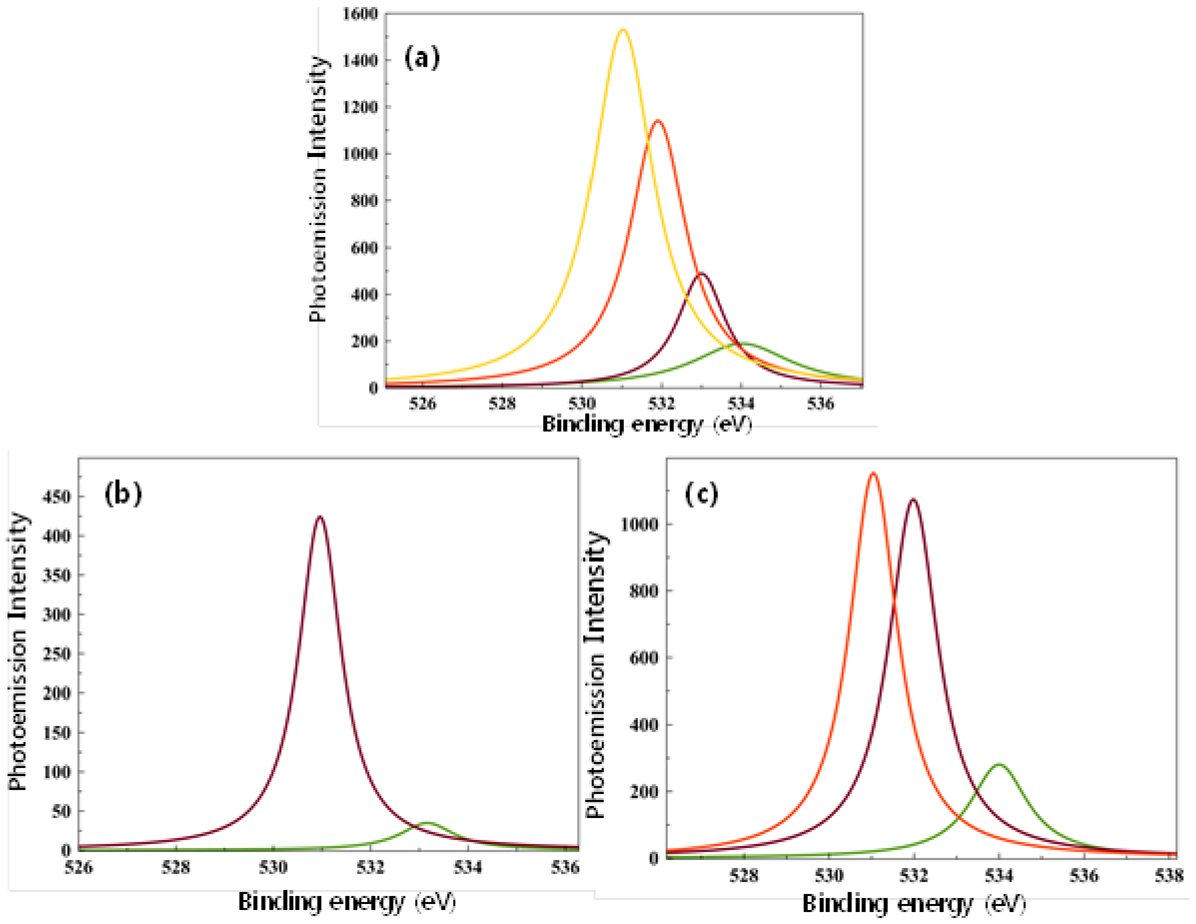
(a)
Photoemission Intensity
0
200
400
600
800
1000
1200
1400
1600
526
528
530
532
534
536
Binding energy (eV)
(b)
Photoemission Intensity
0
50
100
150
200
250
300
350
400
450
526
528
530
532
534
536
Binding energy (eV)
(c)
Photoemission Intensity
0
200
400
600
800
1000
528
530
532
534
536
538
Binding energy (eV)

Fig. S6.

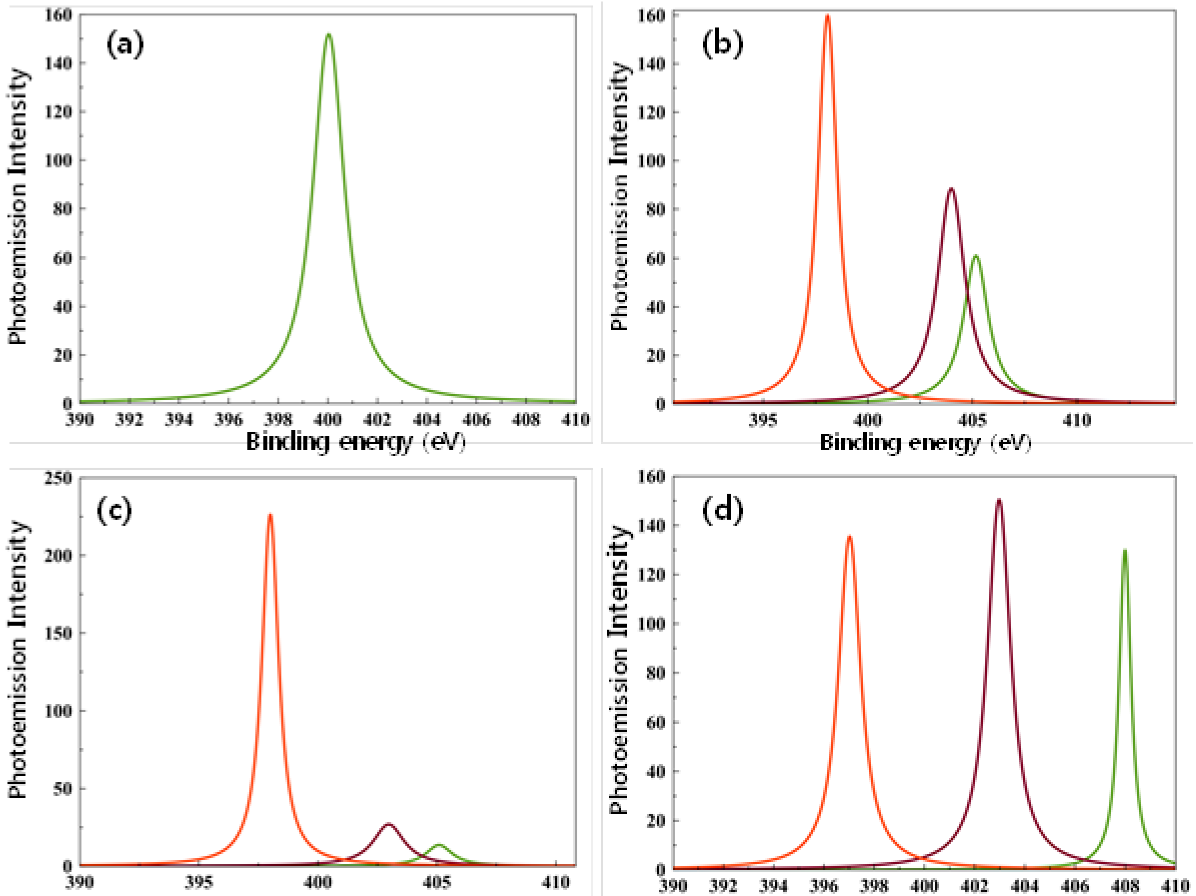
(a)
Photoemission Intensity
0
20
40
60
80
100
120
140
160
390
392
394
396
398
400
402
404
406
408
410
Binding energy (eV)
(b)
Photoemission Intensity
0
20
40
60
80
100
120
140
160
395
400
405
410
Binding energy (eV)
(c)
Photoemission Intensity
0
50
100
150
200
250
390
395
400
405
410
Binding energy (eV)
(d)
Photoemission Intensity
0
20
40
60
80
100
120
140
160
390
392
394
396
398
400
402
404
406
408
410
Binding energy (eV)

Fig. S7.

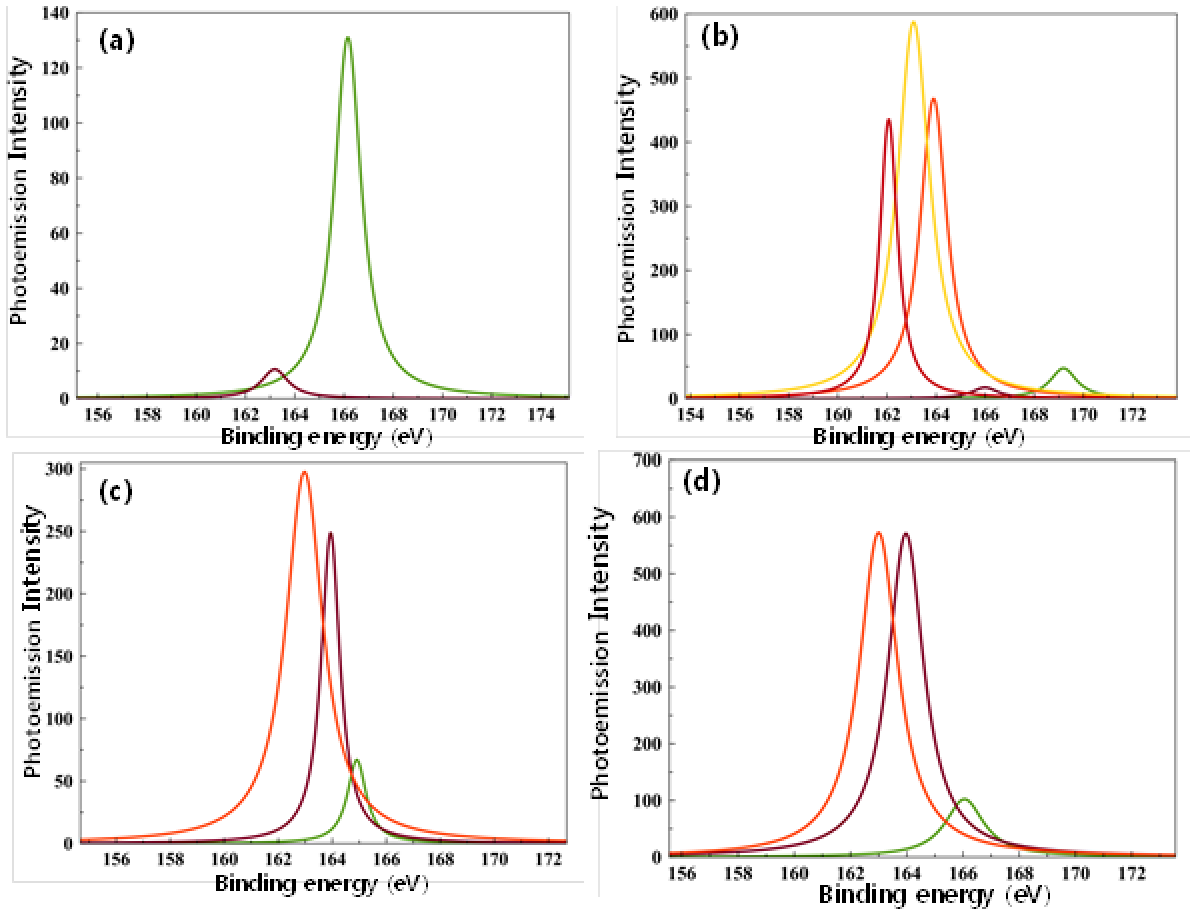
(a)
Photoemission Intensity
0
20
40
60
80
100
120
140
156
158
160
162
164
166
168
170
172
174
Binding energy (eV)
(b)
Photoemission Intensity
0
100
200
300
400
500
600
154
156
158
160
162
164
166
168
170
172
Binding energy (eV)
(c)
Photoemission Intensity
0
50
100
150
200
250
300
156
158
160
162
164
166
168
170
172
Binding energy (eV)
(d)
Photoemission Intensity
0
100
200
300
400
500
600
700
156
158
160
162
164
166
168
170
172
Binding energy (eV)

Fig. S8.