Insights into Chemical Bonds for Eliminating the Depletion Region and Accelerating the Photo-Induced Charge Efficient Separation toward Ultrasensitive Photoelectrochemical Sensing

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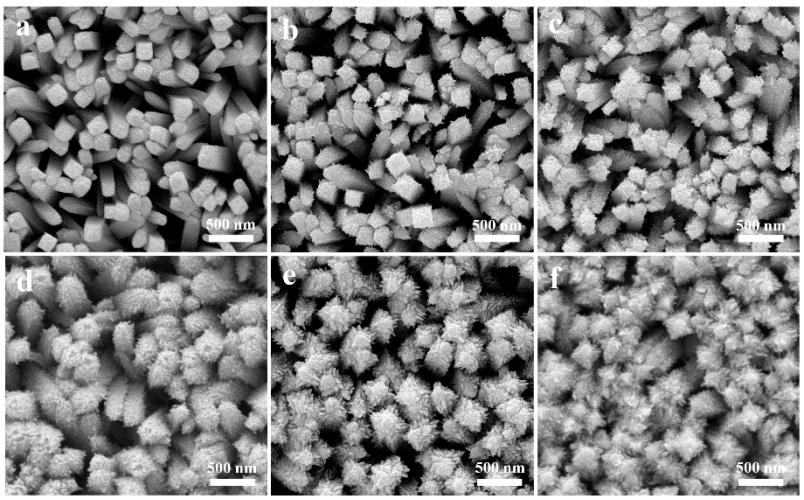

Figure S1. Time-dependent growth process of 3D HWT arrays sample. Typical SEM images of the HWT grown under the different reaction time: (a) 15 min, (b) 30 min, (c) 60 min, (d) 90 min 120 min, 150 min.

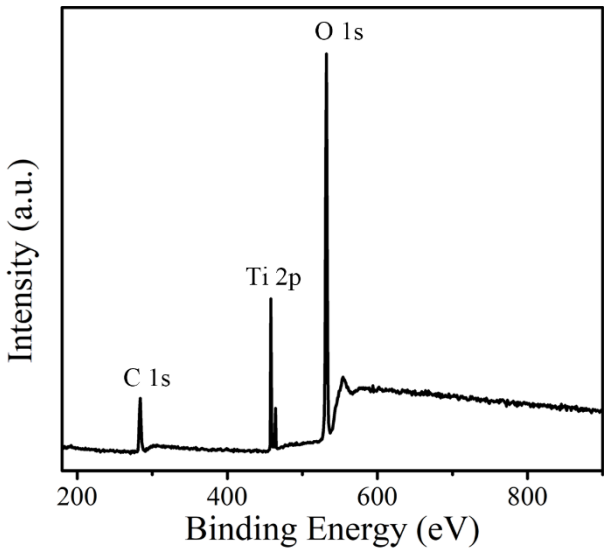

Figure S2. Full range XPS spectra of HWT-C sample.

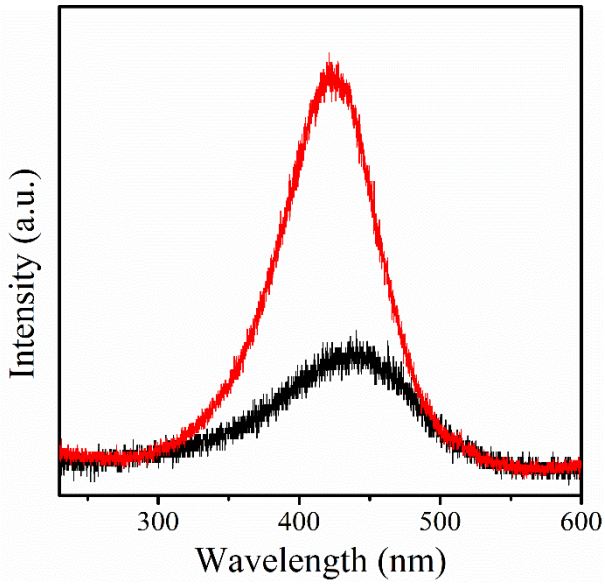

Figure S3. PL spectra of the HWT (red curve) and HWT-C (black curve) samples.

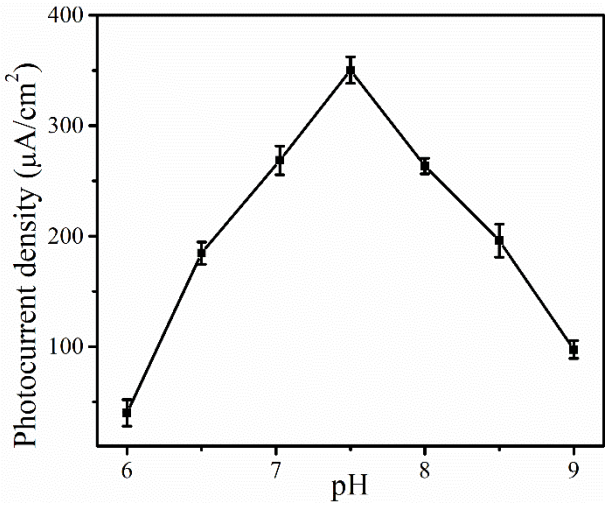

Figure S4. Effect of pH value on photocurrent responses of sensor platform with the PSA concentration of 0.6 pg/mL in PBS buffer.

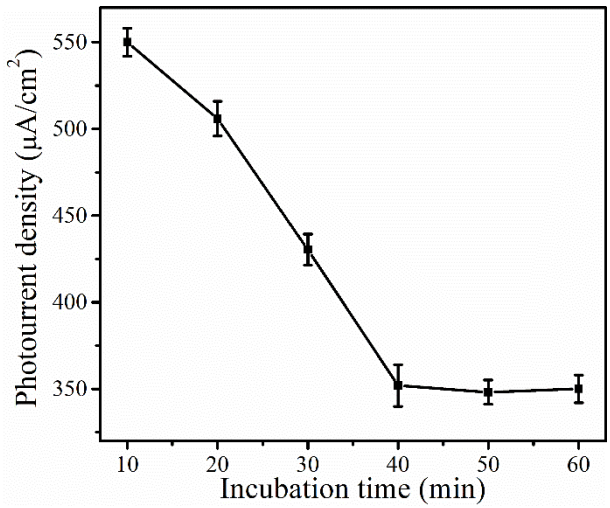

Figure S5. Effect of incubation time of antigen with antibody on photocurrent responses of sensor with the PSA concentration of 0.6 pg/mL in PBS buffer (0.01 mol/L, pH 7.4).

Table S1. Decay parameters and average lifetime according to a bi-exponential fitting model of the PL decay curves obtained from the samples.

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{ave} (ns)
HWT	9.25	6.78	2.3	1.19	8.57
HWT-C	4.33	3.68	4.6	2.12	4.14

Table S2. Comparison of previously reports methods for the detection of PSA.

Methods	Linear range	Detection limit	References
Differential pulse voltammetry	2 ng/mL-80 ng/mL	1 pg/mL	[2]
Electrochemiluminescence	1 pg/mL-10 ng/mL	0.72 pg/mL	[3]
Immunochromatography	0.5 pg/mL-200 pg/mL	2.05 pg/mL	[4]
Biofuel cell	0.3 pg/mL-7 ng/mL	0.1 pg/mL	[5]
Differential pulse voltammetry	1 pg/mL-30 ng/mL	0.78 pg/mL	[6]
PEC	0.02 pg/mL-100 ng/mL	0.007 pg/mL	This work

Table S3. Determination of PSA in human serum samples.

Number	Content of PSA (ng/mL)	Detection	Recovery (%)
1	0.02	0.021	105
2	0.1	0.098	98.0
3	1.0	0.96	96
4	10.0	10.2	102
5	50.0	49.3	98.6
6	100.0	98.5	98.5

Table S4. Comparison of previously other materials for the detection of PSA.

Materials	Linear range	Detection limit	References
Pt SA-$Zn_{0.5}Cd_{0.5}S$	0.001 ng/mL-10 ng/mL	0.22 pg/mL	[7]
PI5CA/WO_3	0.5 pg/mL-50 ng/mL	0.12 pg/mL	[8]
CdS nanorods	0.005 ng/mL-50 ng/mL	0.0018 ng/mL	[9]
PDANP	0. 05 pg/mL-50 ng/mL	0.027 pg/mL	[10]
rGO-$BiFeO_3$	10 pg/mL-100 ng/mL	0.3 pg/mL	[11]
Ag_2S/CuS/α-Fe_2O_3	0.01 pg/mL-10ng/mL	0.0033 pg/mL	[12]
ERGO-TiO_2	0.02 pg/mL-200 ng/mL	0.0068 pg/mL	[13]
3D HWT-C	0.02 pg/mL-100 ng/mL	0.007 pg/mL	This work

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