Electronic Supplementary Information for

Highly Active, Stable Oxidized Platinum Clusters as Electrocatalysts forthe Hydrogen Evolution Reaction

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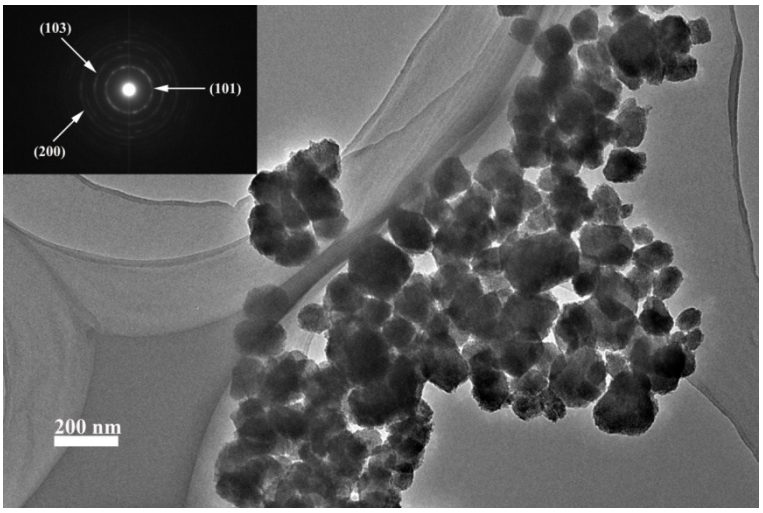

Figure S1a.TEM images of PtO_x/TiO_2. Scale bar 200 nm; insert: SAED of PtO_x/TiO_2.

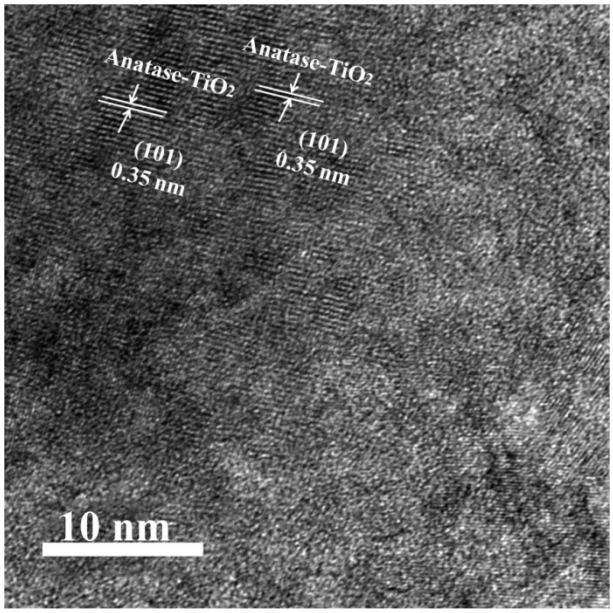

Figure S1b. TEM images of PtO_x/TiO_2. Scale bar 10 nm.

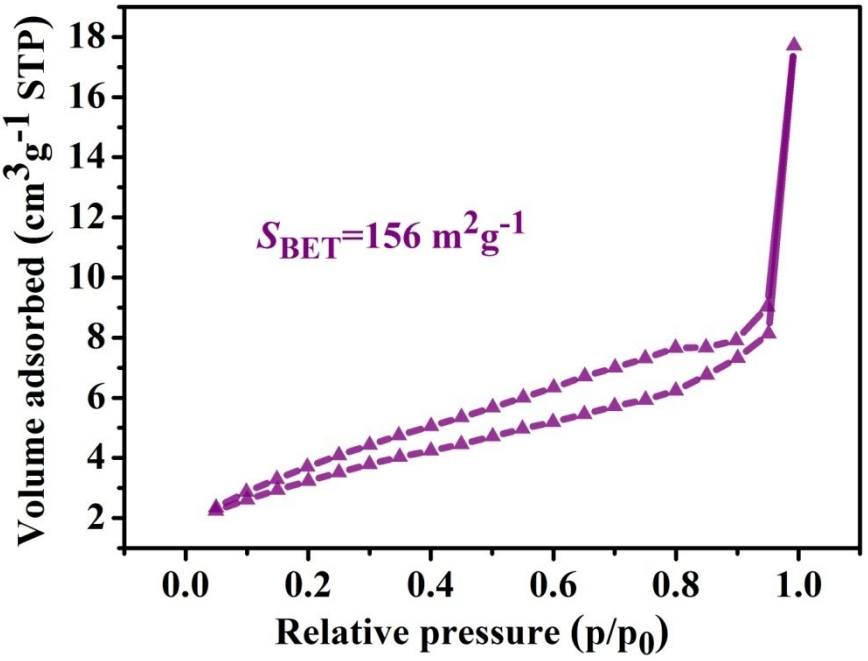

Figure S2a. N_2 absorption and desorption isotherms plots of PtO_x/TiO_2.

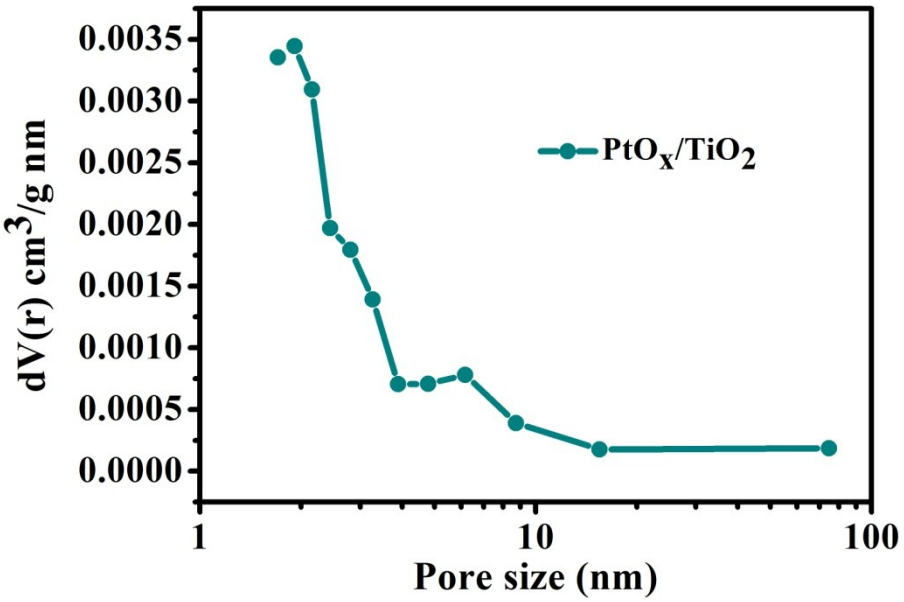

Figure S2b. BJH pore size distribution for PtO_x/TiO_2.

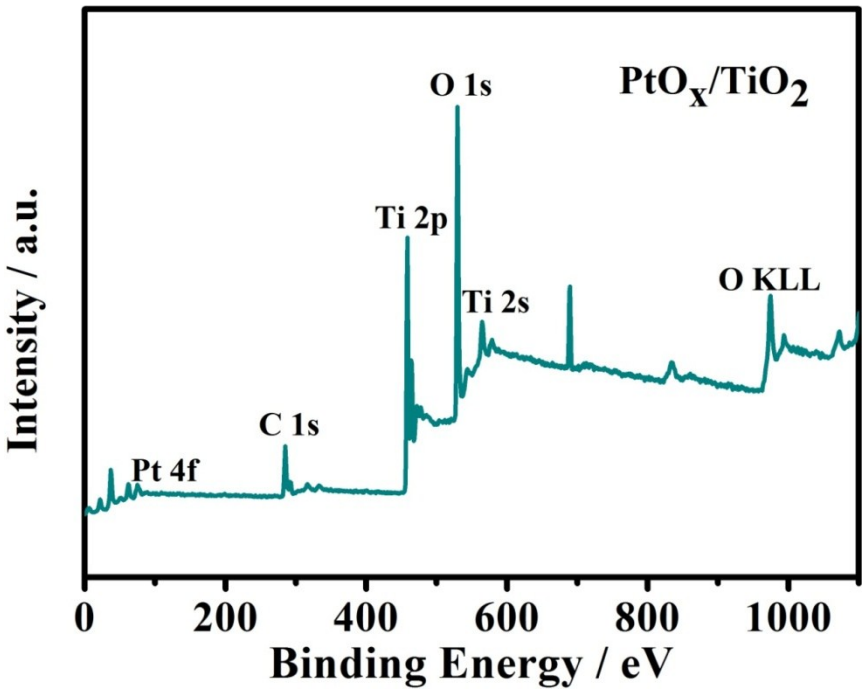

Figure S3a.XPS survey spectrumfor PtO_x/TiO_2 catalyst.

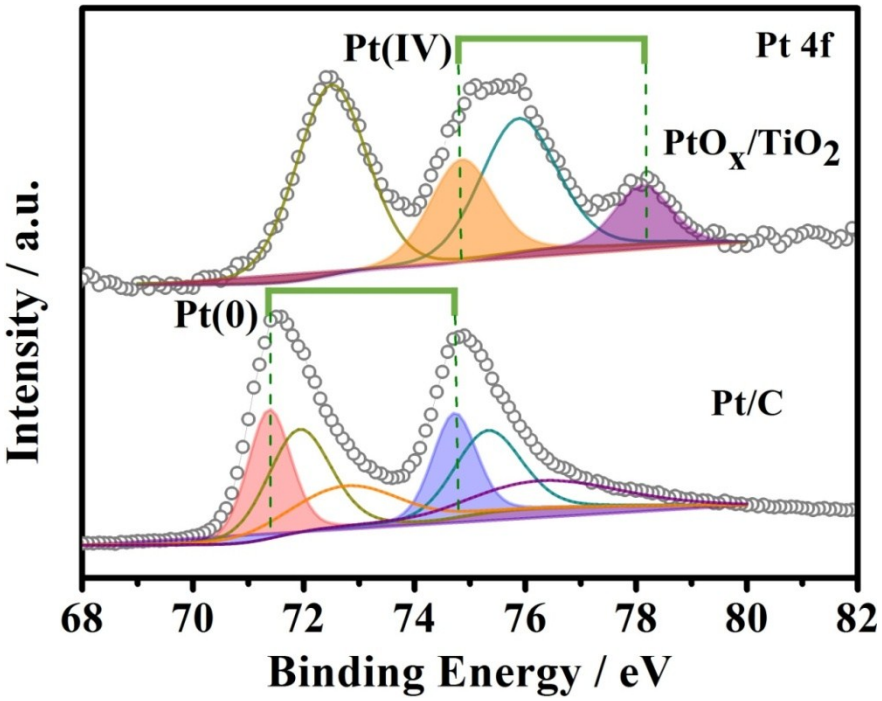

Figure S3b. High-resolution XPS spectra of Pt 4*f* in the PtO_x/TiO_2 and the Pt/C catalysts.

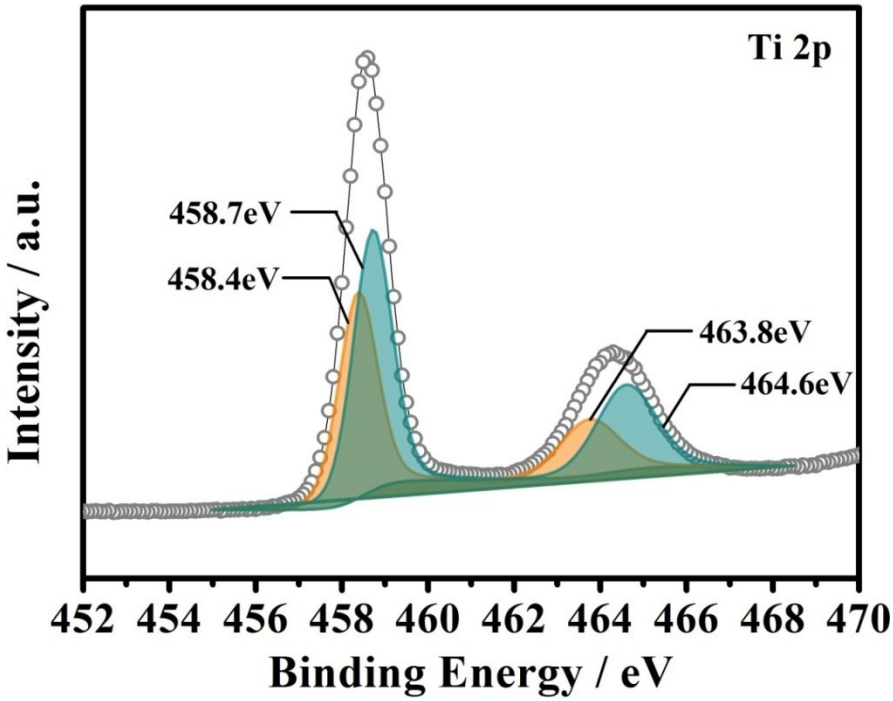

Figure S3c. High-resolution XPS spectrum of Ti2*p* in the PtO_x/TiO_2 catalyst.

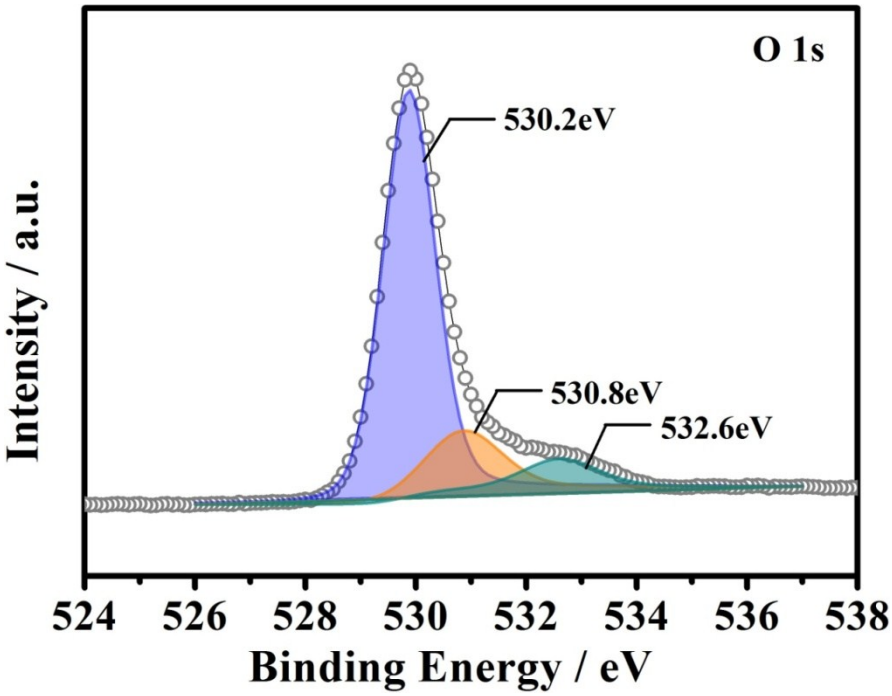

Figure S3d. High-resolution XPS spectrum of O 1*s* in the PtO_x/TiO_2 catalyst.

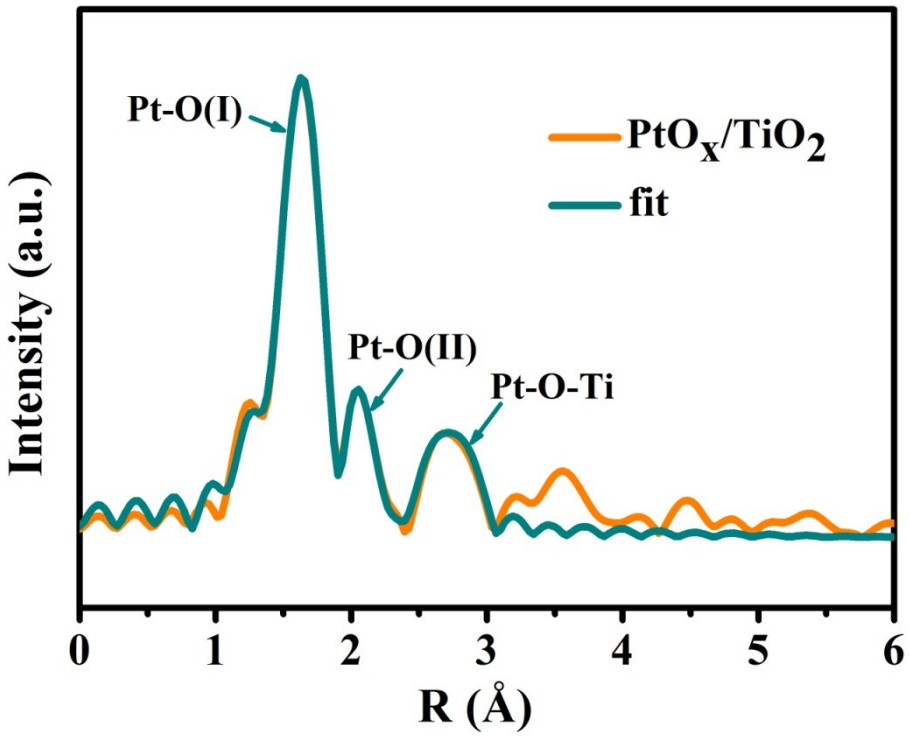

Figure S4.K^3-weighted Fourier transform spectra from EXAFS and fitted spectraof fresh PtO$_x$/TiO$_2$.

EXAFS fitting parameters at the Pt L_{III}-edge forthe fresh PtO$_x$/TiO$_2$						
Sample	**Shell**	***N*^{a}**	***R*(Å)^b**	**σ^2(Å^2·10^3)^c**	**ΔE_0(eV)^d**	***R* factor (%)**
PtO$_x$/TiO$_2$	Pt-O(I)	4.3	1.99	2.2	10.9	0.53
	Pt-O(II)	2.5	2.43	4.1		
	Pt-O-Ti	1.8	3.07	6.0	5.7	

Table S1. EXAFS fitting parameters at the Pt L_{III}-edge for the fresh PtO$_x$/TiO$_2$. ^{a}*N*: coordination number; ^{b}*R*: bond distance; $^c\sigma^2$: Debye-Waller factor; $^d\Delta E_0$: inner potential correction.

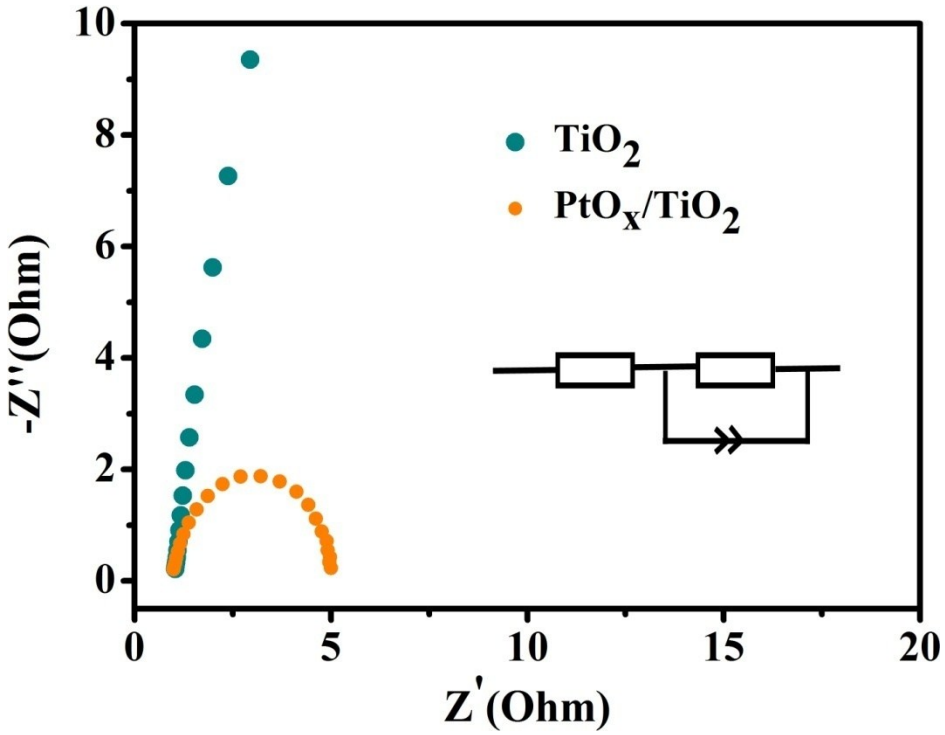

Figure S5. Electrochemical impedance spectroscopy (EIS) (Nyquist plots) of PtO_x/TiO_2 and TiO_2 in 0.5 M H_2SO_4 solution.

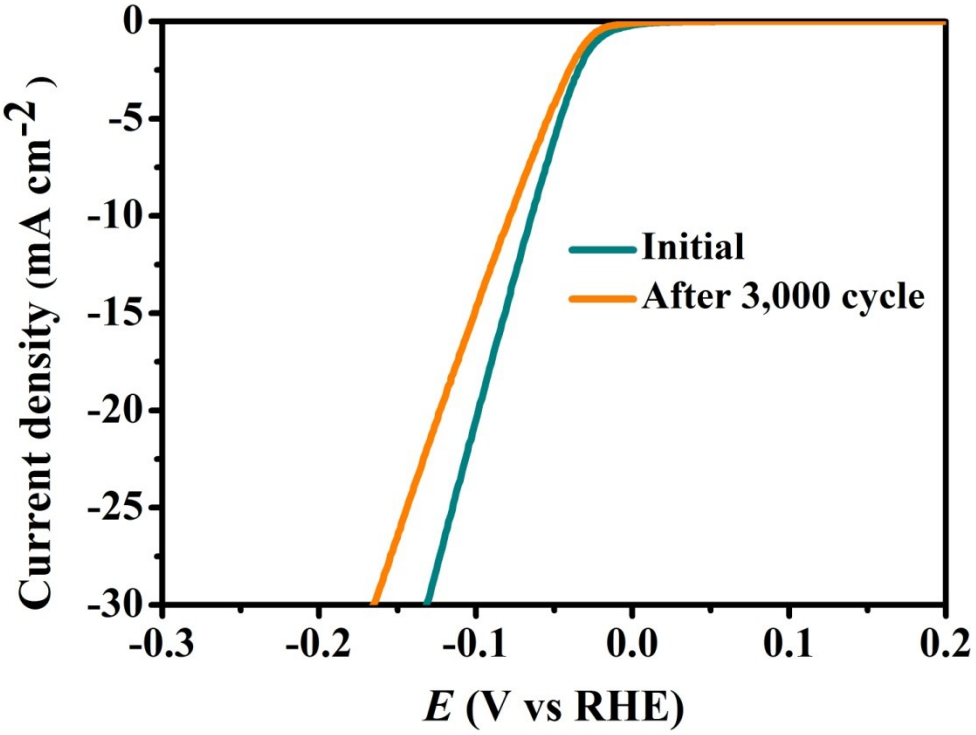

Figure S6. Polarizations curves of Pt/Cbefore and after CV between -0.15~0.4 V vs. RHE at 100mVs^{-1} for 3,000 cycles.

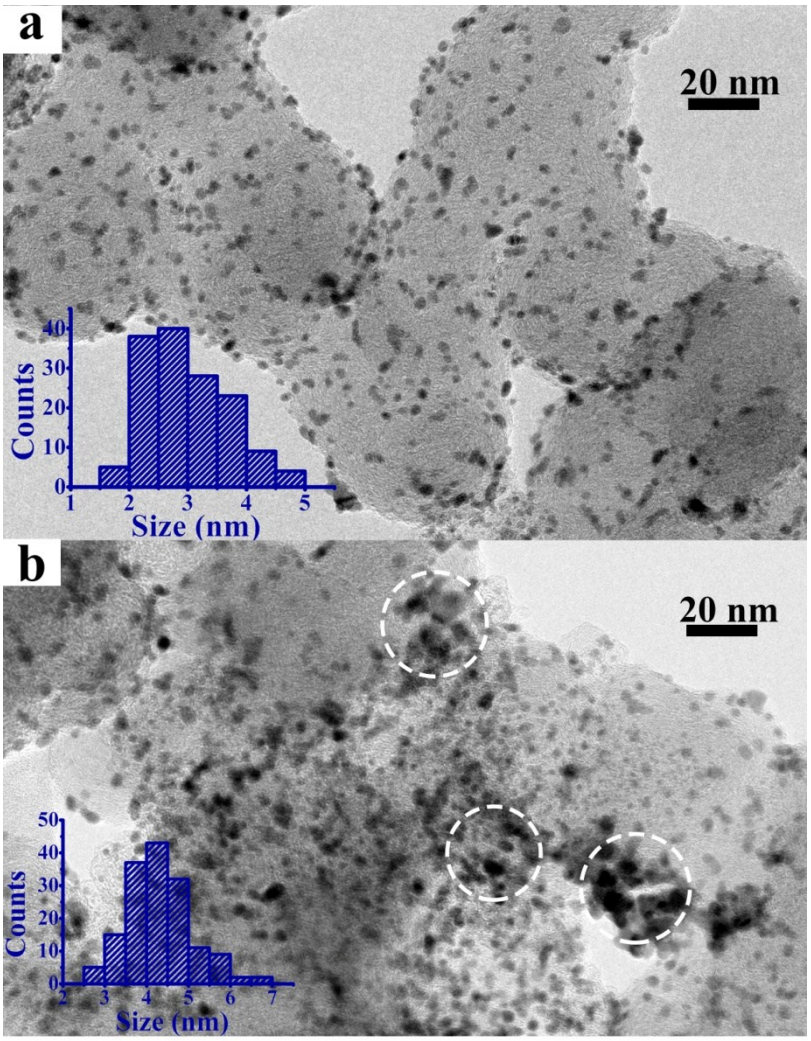

Figure S7.TEM images of Pt/C catalyst (a) before and (b) after ADT.

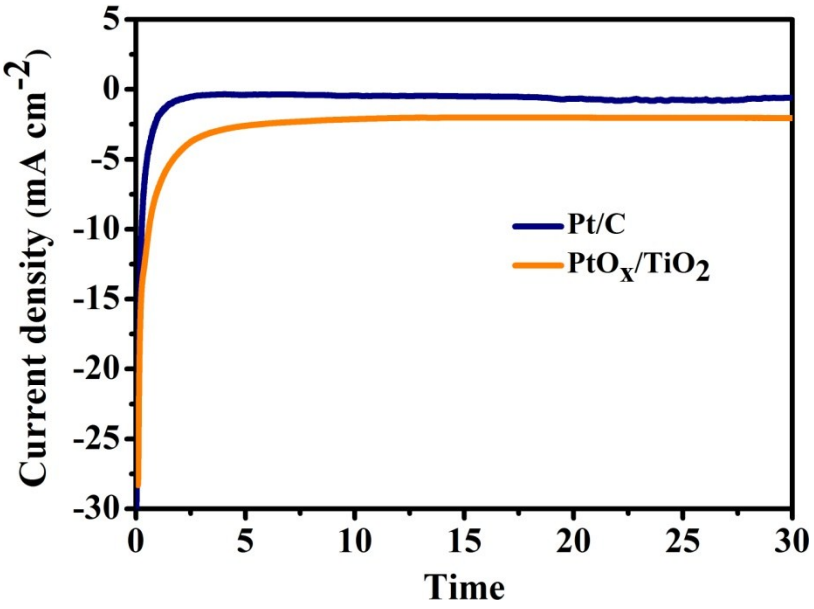

Figure S8. The long term stability of the PtO_x/TiO_2 and Pt/C catalysts for the HER at -0.2V (vs.RHE) for 30 hours.

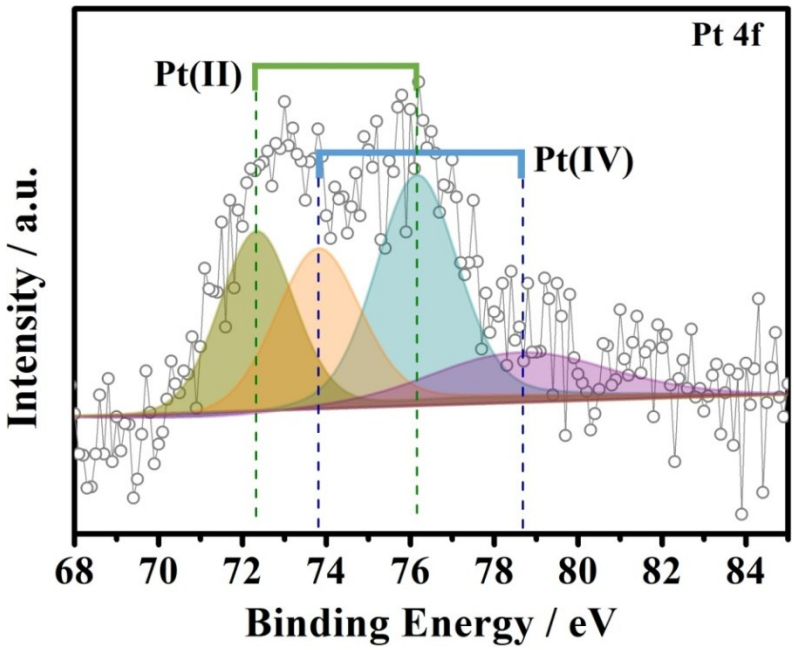

Figure S9. High-resolution XPS spectra of Pt 4*f* in the PtO_x/TiO_2 catalyst. (after 30 hours ofelectrolysis).

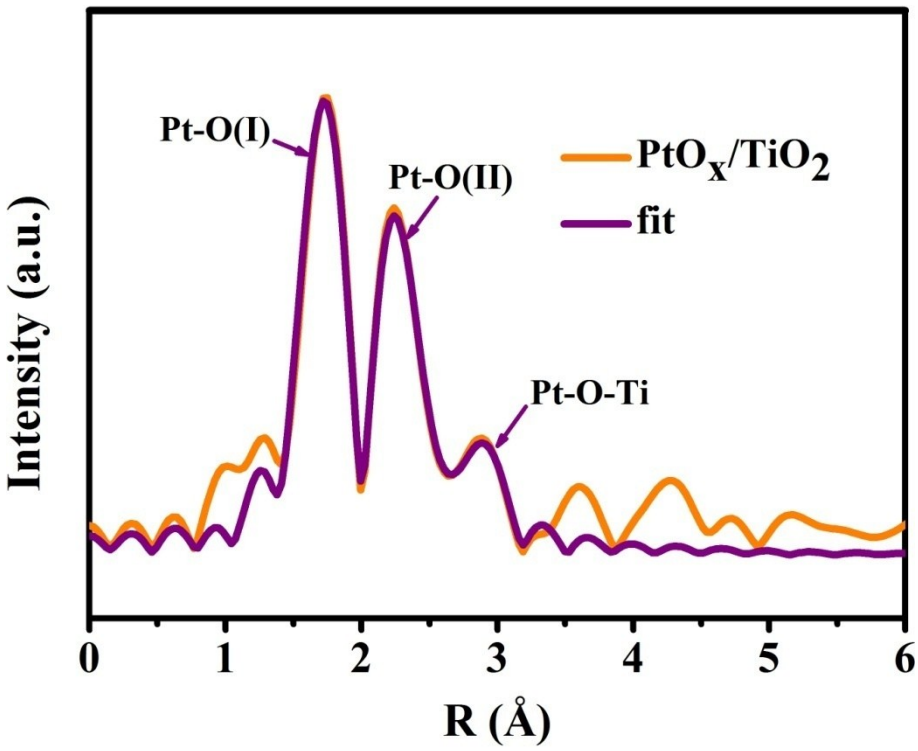

Figure S10.K^3-weighted Fourier transform spectra from EXAFS and fitted spectraof PtO_x/TiO_2.（after 30hours ofelectrolysis）.

EXAFS fitting parameters at the Pt L_{III}-edge forthe PtO_x/TiO_2						
Sample	**Shell**	***N*[a]**	***R*(Å)[b]**	**σ^2(Å$^2\cdot10^3$)[c]**	**ΔE_0(eV)[d]**	***R* factor (%)**
PtO_x/TiO_2	Pt-O(I)	1.2	2.04	1.5	13.8	0.64
	Pt-O(II)	1.6	2.61	2.0		
	Pt-O-Ti	0.6	3.28	5.2	15.3	

Table S2. EXAFS fitting parameters at the Pt L_{III}-edge for the PtO_x/TiO_2 after 30hours of stability measurements. [a]*N*: coordination number; [b]*R*: bond distance; [c]σ^2: Debye-Waller factor; [d]ΔE_0: inner potential correction.

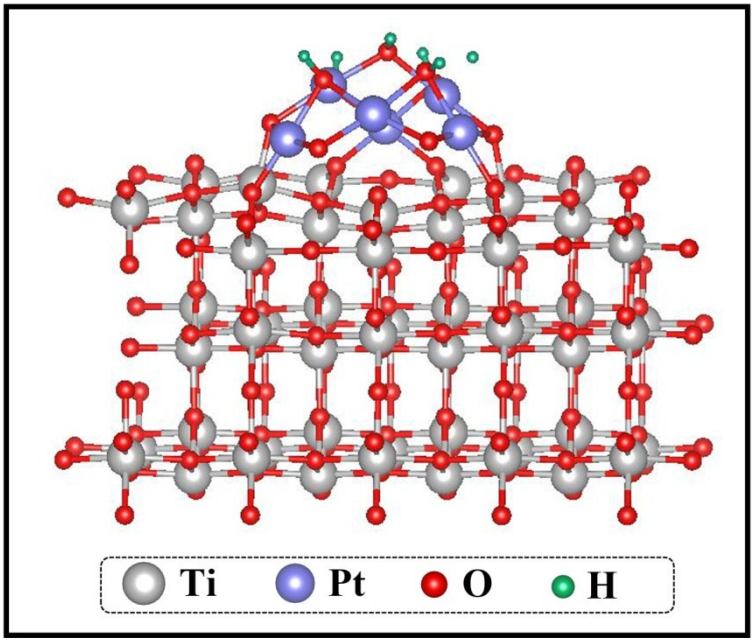

Figure S11. Geometry structure ofH*absorbed on Pt^{4+} site after O^{2-} sites occupied byH*.

Bader charges of TiO_2(anatase)-(101) surface and PtO_x cluster				
	Before loading		**After loading**	
	TiO_2(anatase)-(101) surface	PtO_x cluster	TiO_2(anatase)-(101) surface	PtO_x cluster
Badercharge (a.u.)	767.89	113.91	767.88	113.99

Table S3. Bader charges of TiO_2(anatase)-(101) surface and PtO_x cluster before and after loading.