Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Pd Nanocrystals on WC as a Synergistic Electrocatalyst for Hydrogen Oxidation Reactions

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Determination of exchange current

The exchange current density was calculated form a current-potential profile of Butler-Volmer equation,

$$I = i_0[\exp(-\alpha\eta F/RT) - \exp((1-\alpha)\eta F/RT)]$$

where, η is overpotential and T is temperature.

For small overpotential, the equation becomes,

$$i = i_0\eta F/RT$$

Thus, we can obtain the exchange current, i_0, form the $i_k RT/(F\eta)$.

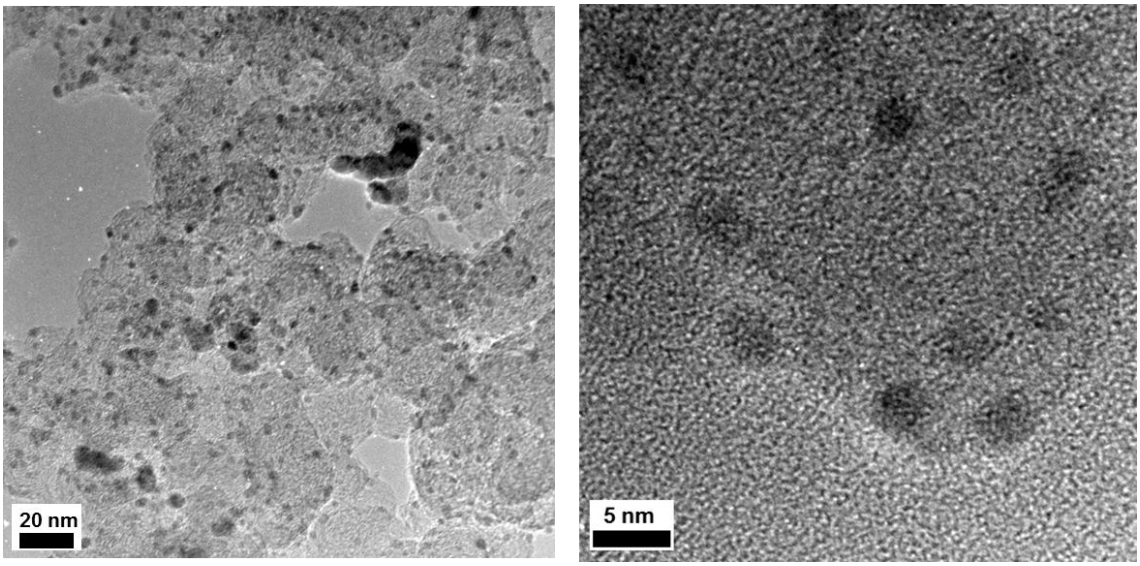

Figure S1. TEM image of Pd/C-200.

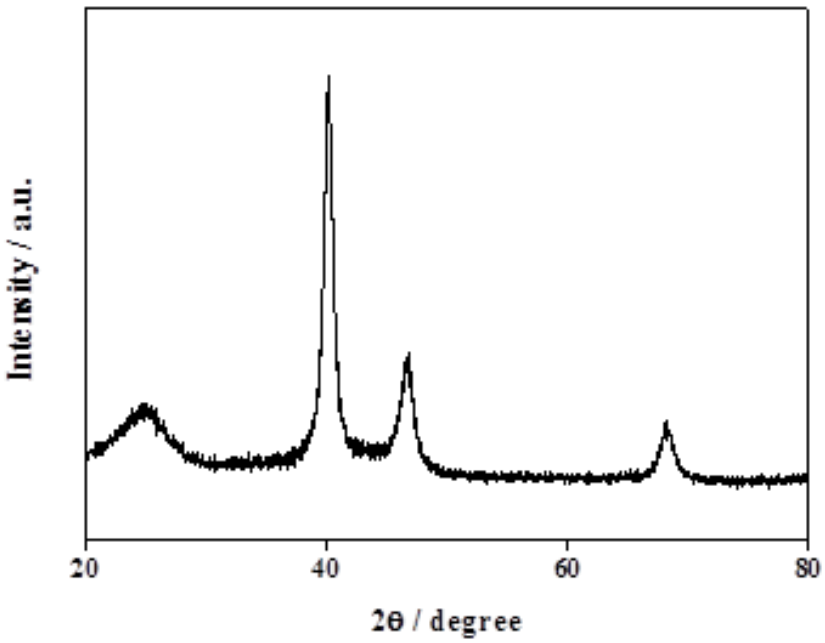

Figure S2. X-ray diffraction of Pd/C-200.

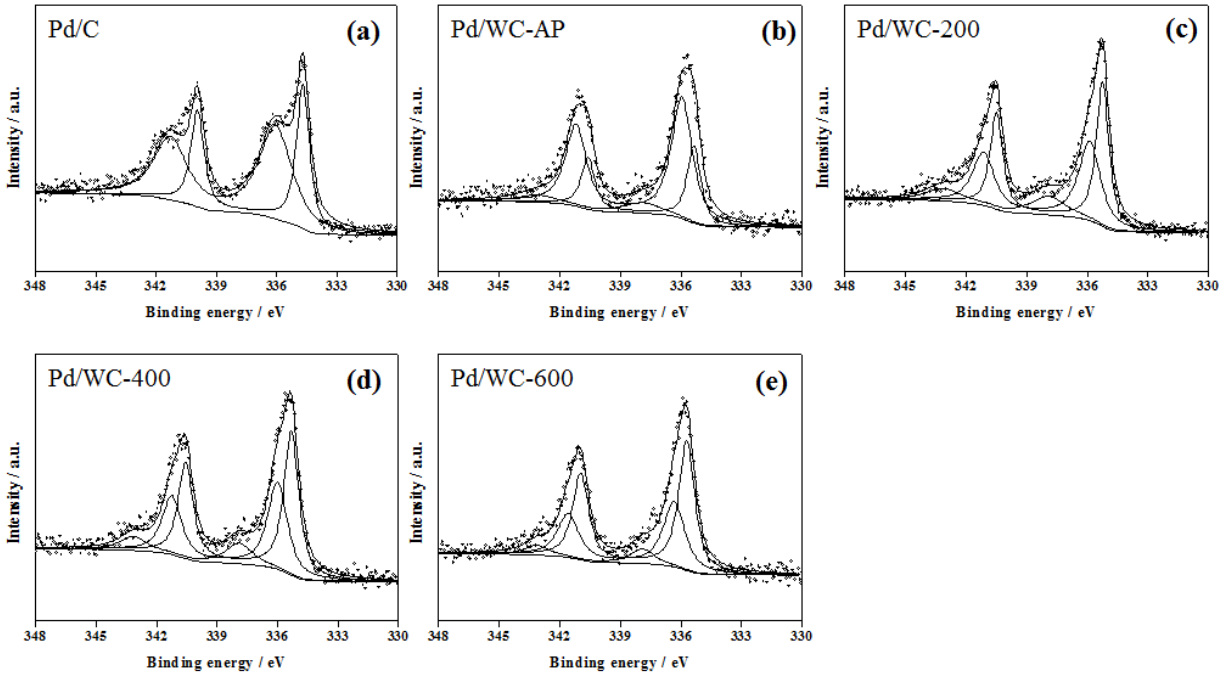

Figure S3. The Pd 3d XPS spectra of (a) Pd/C, (b) Pd/WC-AP, (c) Pd/WC-200, (d) Pd/WC-400, and (e) Pd/WC-600.

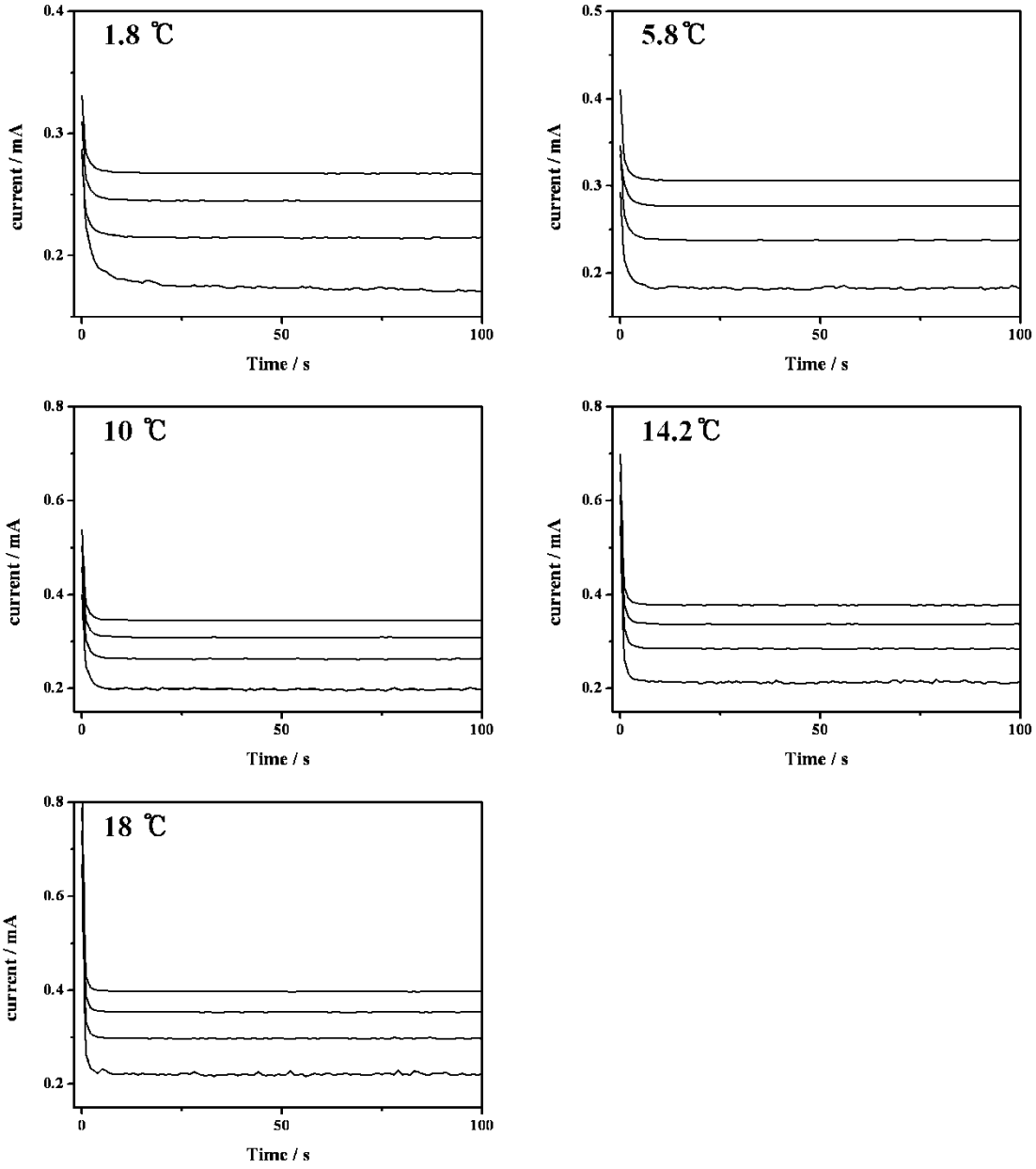

Figure S4. Current-time profiles of HOR on Pd/WC-AP. Reaction temperatures were denoted in the graph. At each temperature, the current-time profiles represent that of 2000 rpm, 1500 rpm, 1000 rpm and 500 rpm, in turn from top to bottom, respectively.

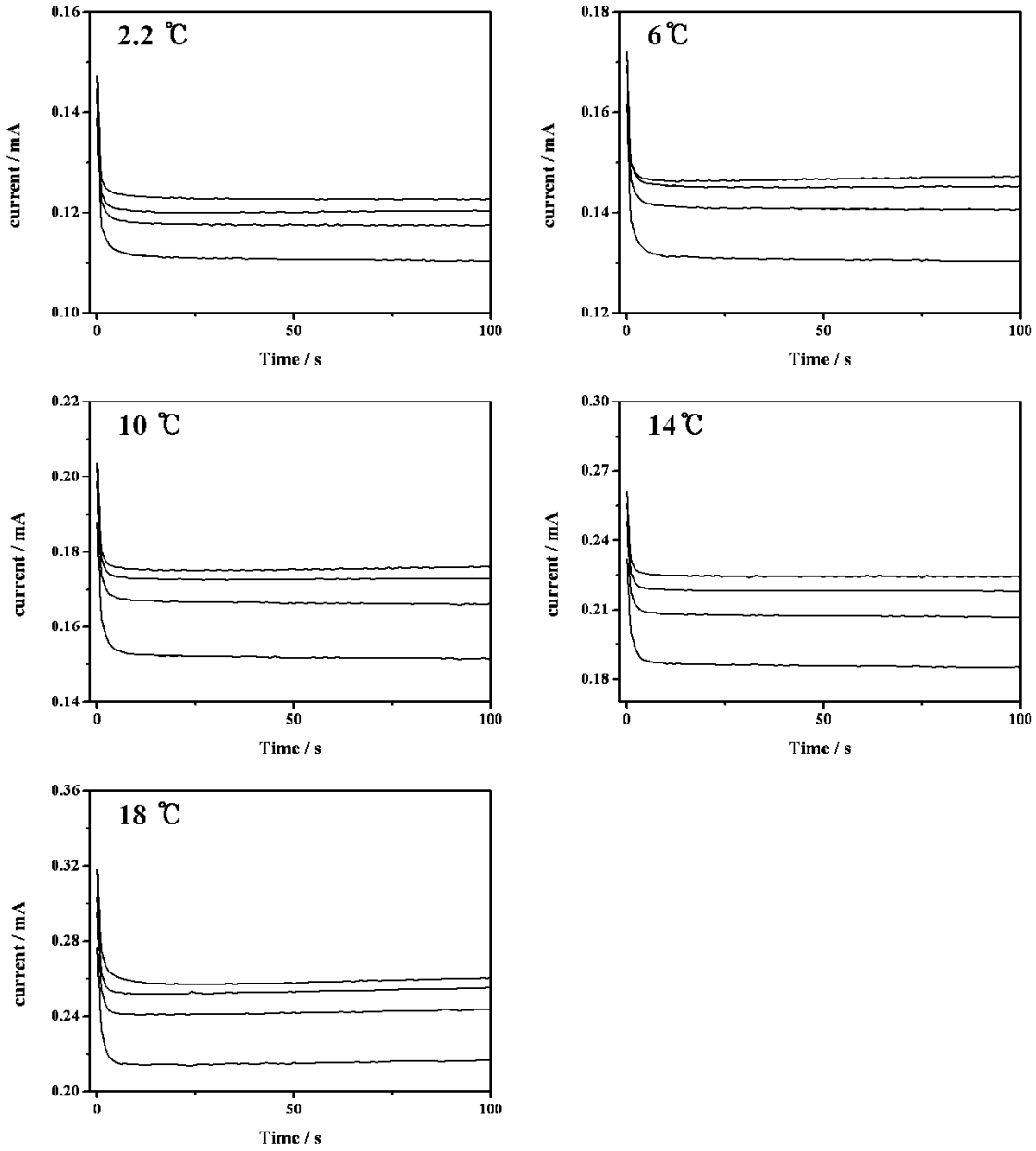

Figure S5. Current-time profiles of HOR on Pd/C-200. Reaction temperatures were denoted in the graph. At each temperature, the current-time profiles represent that of 2000 rpm, 1500 rpm, 1000 rpm and 500 rpm, in turn from top to bottom, respectively.

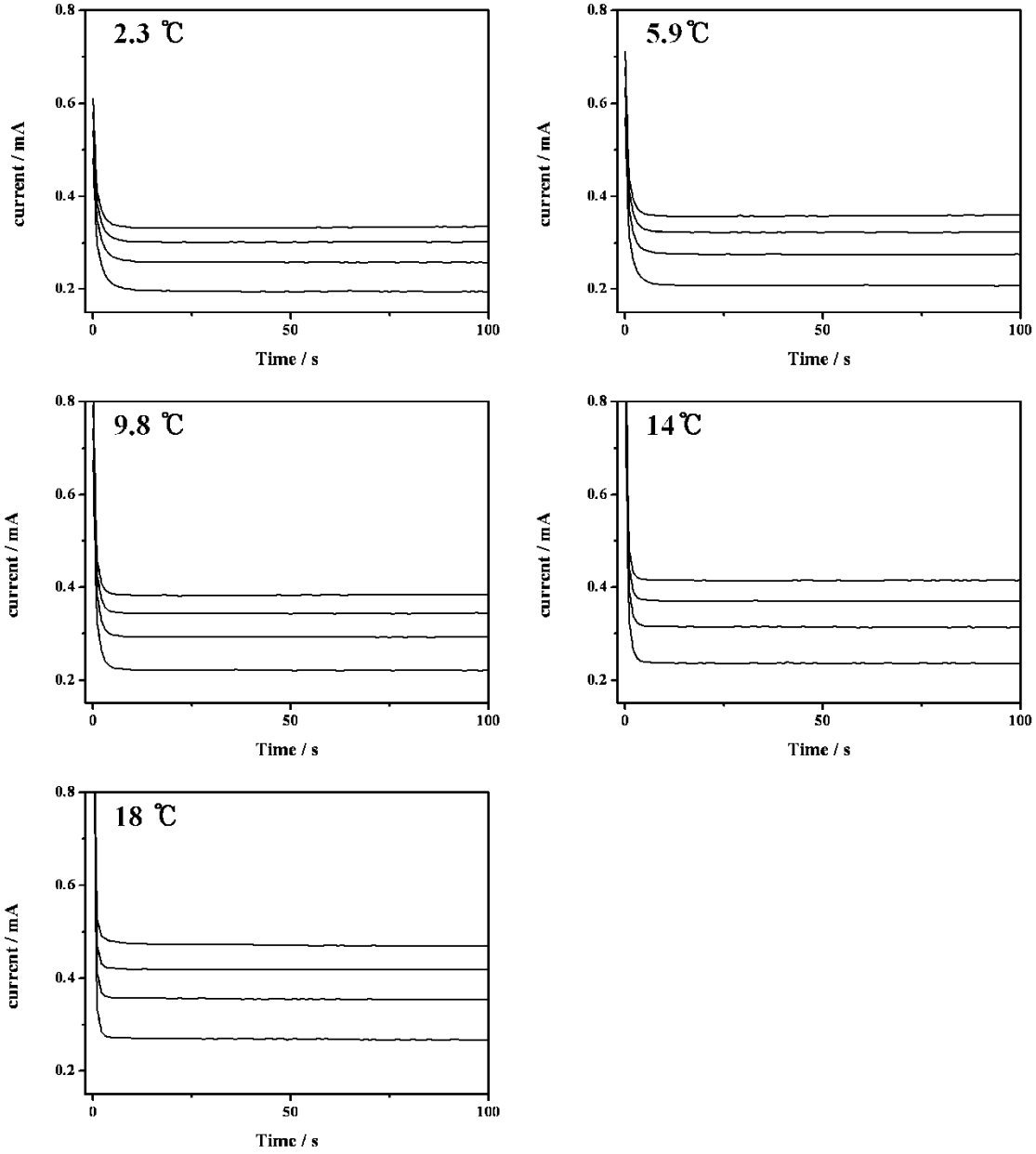

Figure S6. Current-time profiles of HOR on Pd/WC-200. Reaction temperatures were denoted in the graph. At each temperature, the current-time profiles represent that of 2000 rpm, 1500 rpm, 1000 rpm and 500 rpm, in turn from top to bottom, respectively.

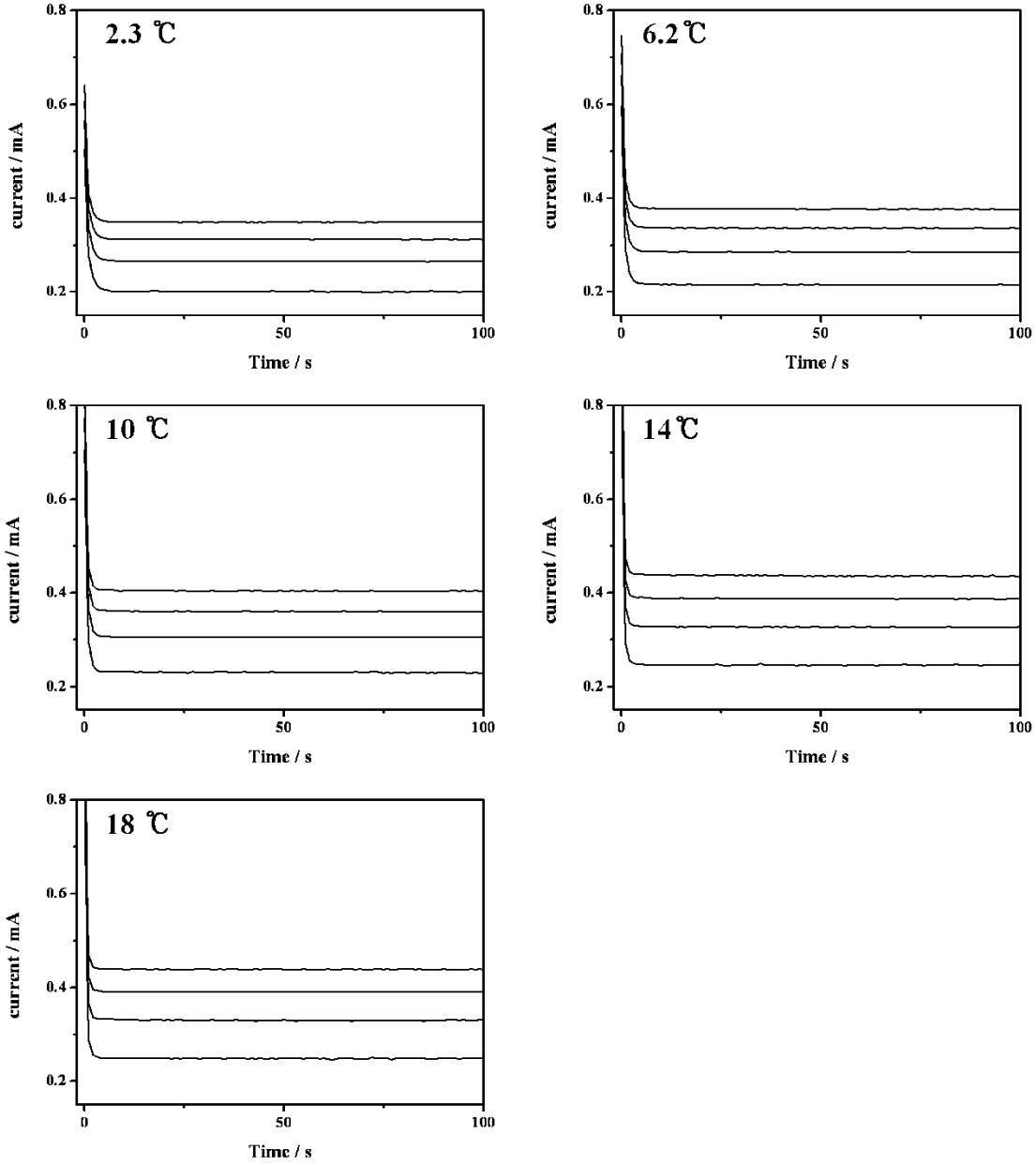

Figure S7. Current-time profiles of HOR on Pd/WC-400. Reaction temperatures were denoted in the graph. At each temperature, the current-time profiles represent that of 2000 rpm, 1500 rpm, 1000 rpm and 500 rpm, in turn from top to bottom, respectively.

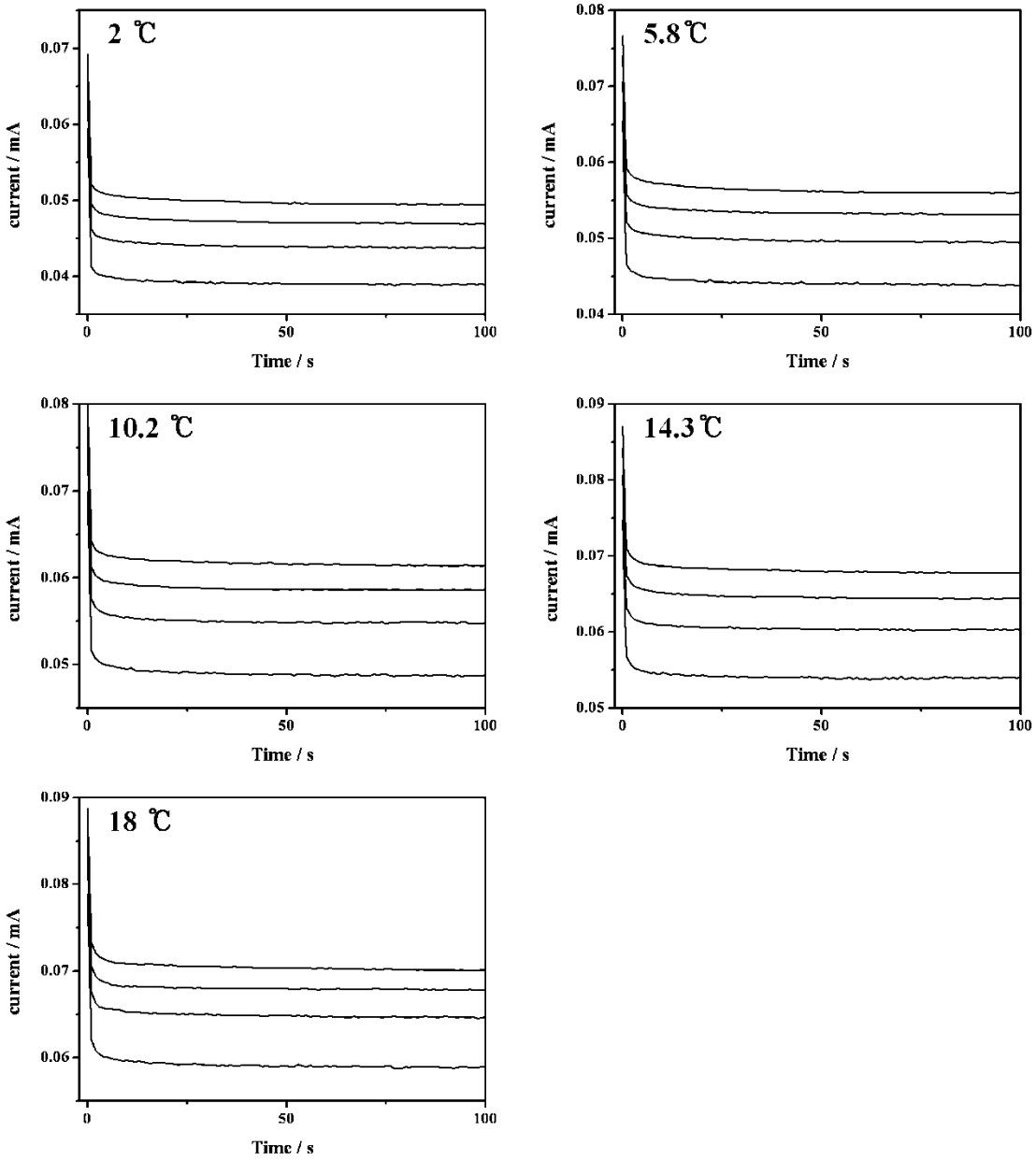

Figure S8. Current-time profiles of HOR on Pd/WC-600. Reaction temperatures were denoted in the graph. At each temperature, the current-time profiles represent that of 2000 rpm, 1500 rpm, 1000 rpm and 500 rpm, in turn from top to bottom, respectively.

Table S1. The Pd 3d XPS data of Pd/C-200, Pd/WC-AP, Pd/WC-200, Pd/WC-400, and Pd/WC-600.

Samples	BE (eV) of Pd(0)	XPS area ratio (%)		
		Pd(0)	Pd(II)	Pd(IV)
Pd/C-200	335.2	37.9	62.1	0
Pd/WC-AP	335.2	31.3	51.7	17.0
Pd/WC-200	335.3	47.6	37.1	15.3
Pd/WC-400	335.4	55.3	28.5	16.2
Pd/WC-600	335.8	60.7	12.4	26.9

Table S2. W 5f XPS spectra in fresh WC, WC mixing with DI water for 12 hrs, WC mixing with Pd salt for 12 hrs, and WC mixing with Pd salt + $NaBH_4$ for 12 hrs.

Samples	BE (eV)			XPS area ratio (%)		
	W(0)	W(IV)	W(VI)	W(0)	W(IV)	W(VI)
Fresh WC	29.9	30.6	33.6	55.3	25.4	19.3
WC + water	29.9	30.6	33.7	58.2	23.7	18.1
WC + water + Pd salt	29.7	30.3	33.5	46.2	21.8	31.9
WC + water + Pd salt + $NaBH_4$	29.9	30.5	34.0	36.2	17.7	46.1

Table S3. Area ratios of W 5f XPS spectra in (a) fresh WC (b) mixing with DI water for 12 hrs (c) mixing with Pd salt and stirred for 12 hrs (d) Pd/WC-AP

samples	**(a)**	**(b)**	**(c)**	**(d)**
$[W(IV)+W(VI)]/W_{total}$	**0.44**	**0.42**	**0.54**	**0.64**