Electronic Supplementary Information (ESI) for

Potentiometric and UV-Vis spectrophotometric titrations for evaluation of the antioxidant capacity of chicoric acid

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**Scheme S1.** The chemical structures of trolox, ChA, ABTS, and ABTS$^+$. 
Scheme S2. Possible mechanism of the oxidation and dimerization of a catechol structure at high pH (the dimerization at other available phenyl carbon atoms is also possible. R is an appropriate substituent group)\textsuperscript{1}. Moreover, the pH-dependent nucleophilic attack of one hydroxyl group of catechol structure to the available phenyl carbon atoms of the \(o\)-benzoquinone structure is also possible, like the oxidation of dopamine\textsuperscript{2}.
**Fig. S1.** Curve of trolox concentration versus ABTS$^+$ concentration obtained from potentiometric titration (A) or from spectrophotometric titration (B). Here, trolox was titrated into the ABTS$^+$ solution when the potential (A) or absorbance (B) was recorded, and the concentration of unreacted ABTS$^+$ corresponding to each added trolox concentration can be worked out by the Nernst equation (A) or by Lambert-Beer's law (B). Relationship between the ChA concentrations consumed at end points by spectrophotometric ($c_{UV}$) and potentiometric ($c_{PT}$) titrations of ChA into ABTS$^+$ at different concentrations (C).
**Fig. S2.** CV curves on GCE at different time after titrating 25 μM ChA into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na$_2$SO$_4$, 117 μM ABTS$^+$ and 58.0 μM ABTS. Scan rate: 100 mV/s; initial potential: 0 V.
**Fig. S3.** CV curves on GCE at different time after titrating 50 μM trolox into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na$_2$SO$_4$, 117 μM ABTS$^+$ and 58.0 μM ABTS. Scan rate: 100 mV/s; initial potential: 0 V.
Fig. S4. CV curves on GCE at different time after adding 117 μM ABTS$^+$ and 58.0 μM ABTS into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na$_2$SO$_4$. Scan rate: 100 mV/s; initial potential: 0 V.
**Fig. S5.** CV curves on GCE at different time after adding 25 μM ChA into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na₂SO₄. Scan rate: 100 mV/s; initial potential: 0 V.
**Fig. S6.** CV curves on GCE at different time after adding 50 μM trolox into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na$_2$SO$_4$. Scan rate: 100 mV/s; initial potential: 0 V.
**Fig. S7.** Potentiometric titration kinetics curves for a single dose of 25 μM ChA (A) or 50 μM trolox (B) at 0 s into 0.1 M phosphate buffer at pH 7.4 containing 0.1 M Na₂SO₄, 117 μM ABTS⁺ and 58.0 μM ABTS under nitrogen saturated and air saturated conditions.
Fig. S8. (A) Potentiometric titration curves (A) on GCE for the successive additions (indicated by green spheres) of *Echinacea* extract (addition of 20.0 µL of 3.50 g/L original extract for each) into 4.0 mL of 0.1 M phosphate buffer (pH 7.4) containing 0.1 M Na$_2$SO$_4$, 33.6 µM ABTS and 53.9 µM ABTS$^+$. (B) Spectrophotometric titration of *Echinacea* extract (addition of 20.0 µL of 3.50 g/L original extract for each) into 4.0 mL of 0.1 M phosphate buffer (pH 7.4) containing 0.1 M Na$_2$SO$_4$, 32.8 µM ABTS and 54.7 µM ABTS$^+$, and the relationship of the peak absorbance at 734 nm versus final concentration of added extract (inset).
References (The numbering here is valid only for the Supporting Information)

1 E. F. Newair, R. Abdel-Hamid and P. A. Kilmartin, *Electroanalysis*, 2017, **29**, 850-860.

2 Y. L. Li, M. L. Liu, C. H. Xiang, Q. J. Xie and S. Z. Yao, *Thin Solid Films*, 2006, **497**, 270-278.