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). 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.
**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 Na₂SO₄, 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 Na₂SO₄, 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 Na₂SO₄. 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 Na₂SO₄, 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 Na₂SO₄, 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)
