Electronic Supplementary Information (ESI) for

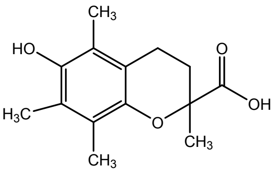
Potentiometric and UV-Vis spectrophotometric titrations for evaluation of the antioxidant capacity of chicoric acid

Haiqing Yi,[a] Yan Cheng,[a] Yu Zhang,[a] Qingji Xie*[a] and Xiaoping Yang[b]

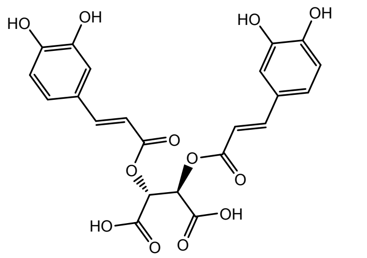
[a]Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

* E-mail: xieqj@hunnu.edu.cn (Q. Xie)

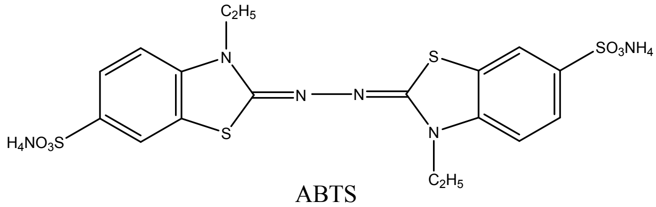
[b]Key Laboratory of Study and Discovery of Small Targeted Molecules of Hunan Province, School of Medicine, Hunan Normal University, Changsha 410013, China



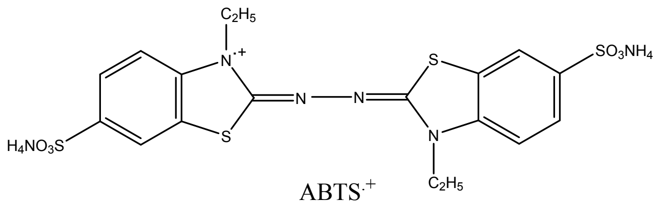
trolox



Chicoric acid

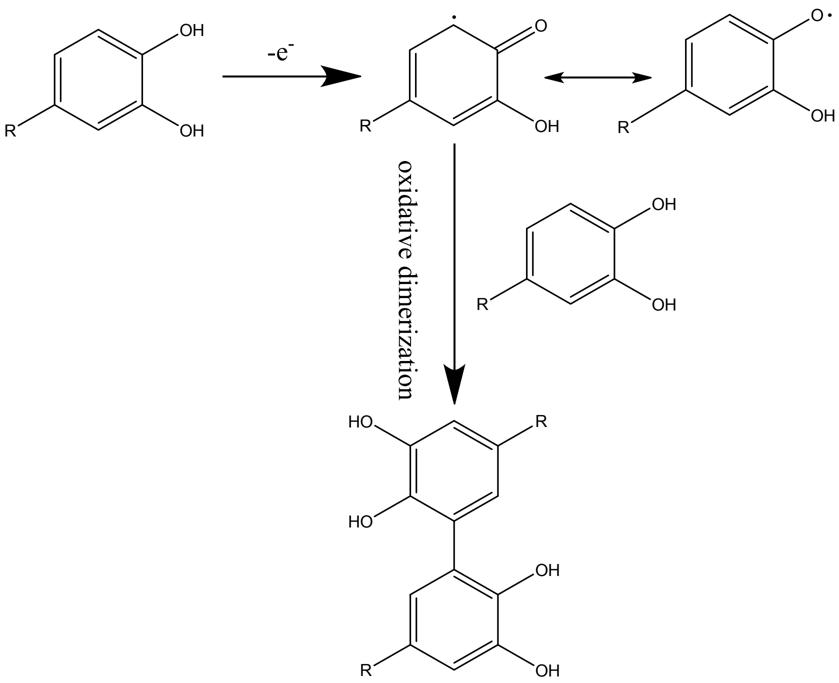


ABTS



$ABTS^{\cdot+}$

Scheme S1. The chemical structures of trolox, ChA, ABTS, and $ABTS^{\cdot+}$.



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)[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[2].

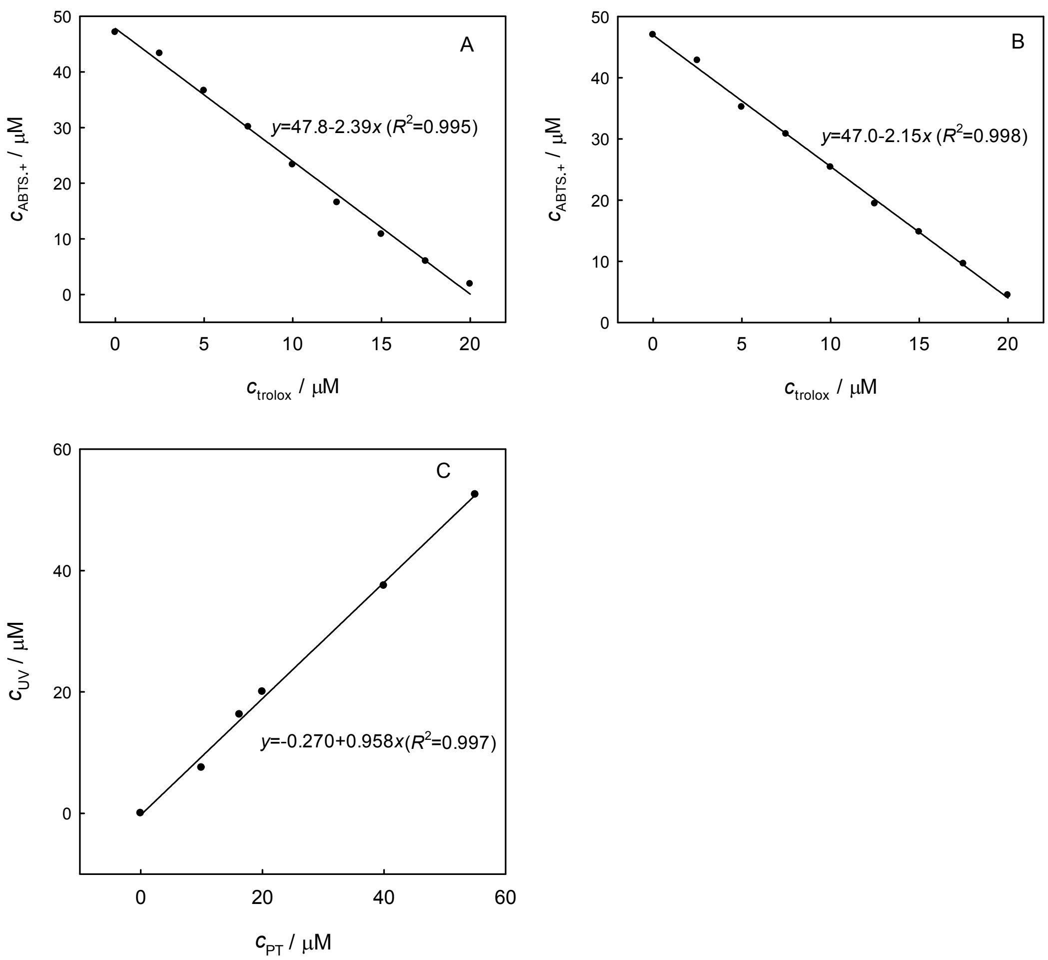


Fig. S1. Curve of trolox concentration versus $ABTS^{\cdot+}$ concentration obtained from potentiometric titration (A) or from spectrophotometric titration (B). Here, trolox was titrated into the $ABTS^{\cdot+}$ solution when the potential (A) or absorbance (B) was recorded, and the concentration of unreacted $ABTS^{\cdot+}$ 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 $ABTS^{\cdot+}$ at different concentrations (C).

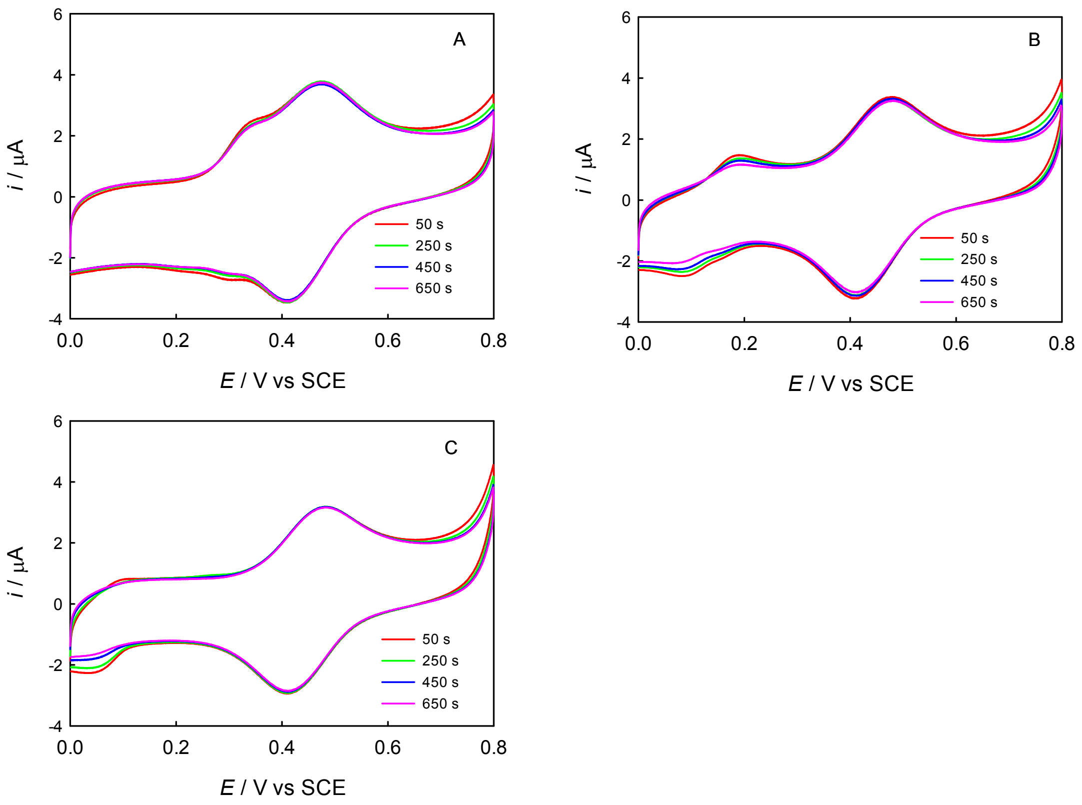


Fig. S2. CV curves on GCE at different time after titrating 25 μM ChA into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na_2SO_4, 117 μM $ABTS^{\cdot +}$ and 58.0 μM ABTS. Scan rate: 100 mV/s; initial potential: 0 V.

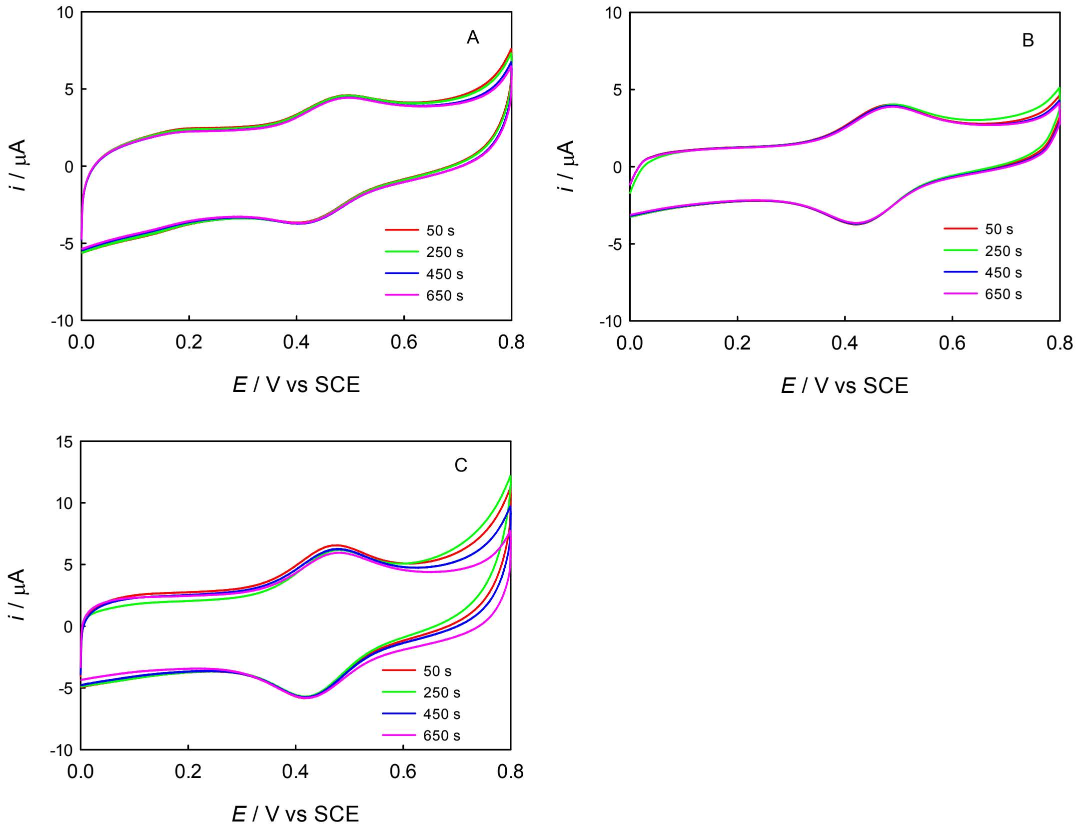


Fig. S3. CV curves on GCE at different time after titrating 50 μM trolox into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na_2SO_4, 117 μM ABTS$^{\cdot+}$ and 58.0 μM ABTS. Scan rate: 100 mV/s; initial potential: 0 V.

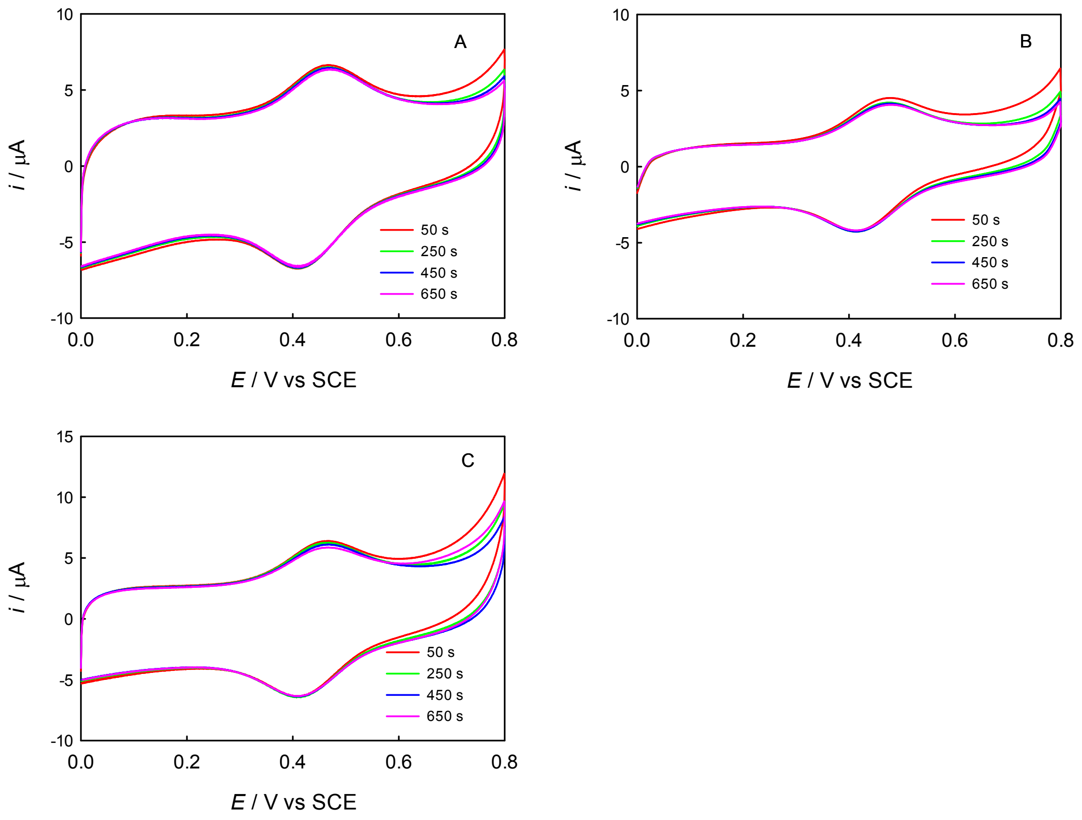


Fig. S4. CV curves on GCE at different time after adding 117 µM $ABTS^{\cdot+}$ and 58.0 µM ABTS into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na_2SO_4. Scan rate: 100 mV/s; initial potential: 0 V.

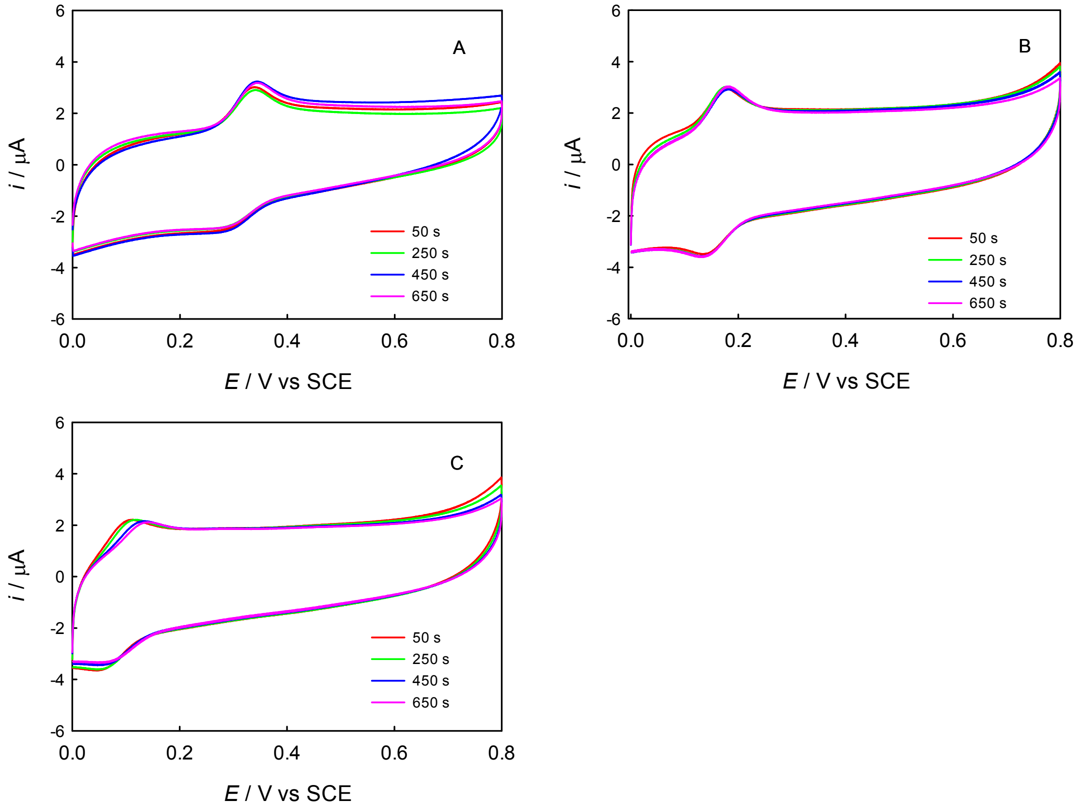


Fig. S5. CV curves on GCE at different time after adding 25 μM ChA into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na_2SO_4. Scan rate: 100 mV/s; initial potential: 0 V.

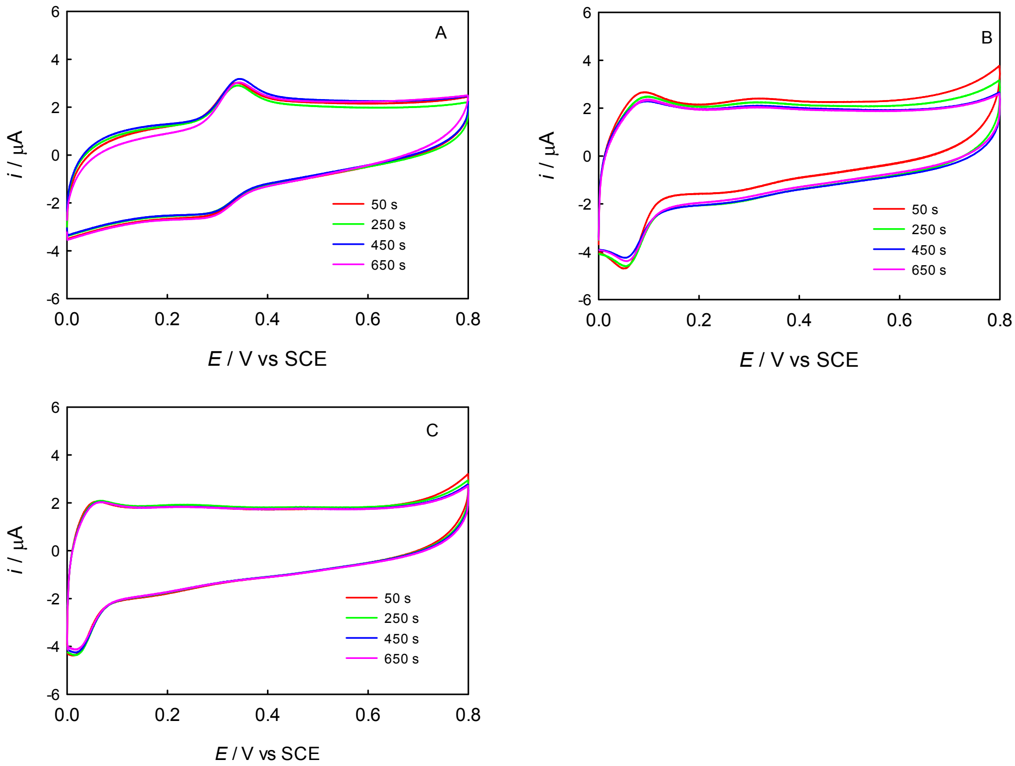


Fig. S6. CV curves on GCE at different time after adding 50 μM trolox into 0.1 M phosphate buffer at pH 5.0 (A), 7.4 (B), or 9.0 (C) containing 0.1 M Na_2SO_4. Scan rate: 100 mV/s; initial potential: 0 V.

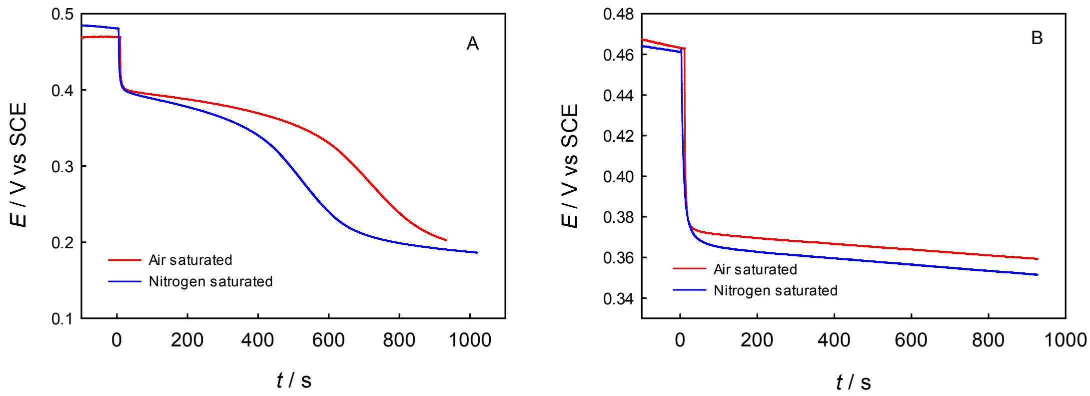


Fig. S7. Potentiometric titration kinetics curves for a single dose of 25 µM ChA (A) or 50 µM trolox (B) at 0 s into 0.1 M phosphate buffer at pH 7.4 containing 0.1 M Na_2SO_4, 117 µM $ABTS^{\cdot +}$ and 58.0 µM ABTS under nitrogen saturated and air saturated conditions.

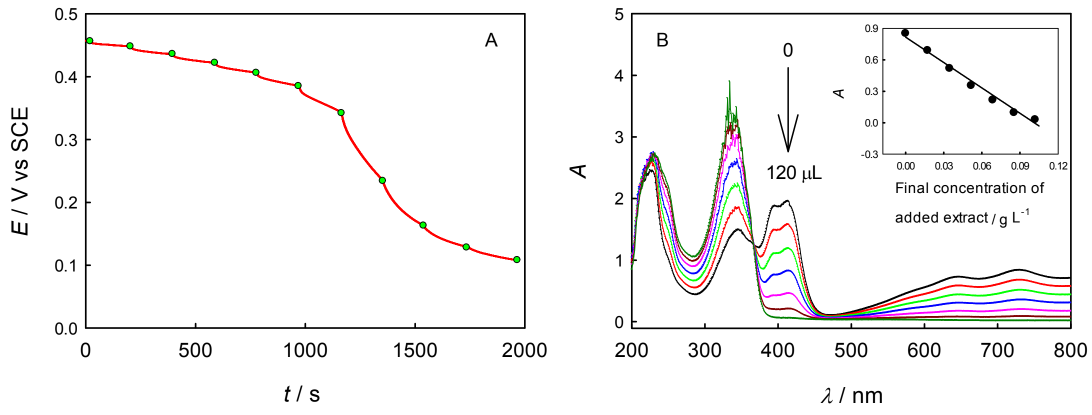


Fig. S8. (A) Potentiometric titration curves (A) on GCE for the successive additions (indicated by green spheres) of *Echinacea* extract (addition of 20.0 µL of 3.50 g/L original extract for each) into 4.0 mL of 0.1 M phosphate buffer (pH 7.4) containing 0.1 M Na_2SO_4, 33.6 µM ABTS and 53.9 µM $ABTS^{\cdot+}$. (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_2SO_4, 32.8 µM ABTS and 54.7 µM $ABTS^{\cdot+}$, 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.