Engineered Photoelectrochemical Platform for Rational Global Antioxidant Capacity Evaluation Based on Ultrasensitive Sulfonated Graphene–TiO$_2$ Nanohybrid

Lingnan Wang,$^{†,*}$ Weiguang Ma,$^{†,‡}$ Shiyu Gan,$^{†,*}$ Dongxue Han,$^{*,†}$ Qixian Zhang,$^{†}$ and Li Niu$^{‡}$

$^{†}$State Key Laboratory of Electroanalytical Chemistry, c/o Engineering Laboratory for Modern Analytical Techniques, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China
$^{‡}$University of Chinese Academy of Sciences, Beijing 100039, China

ABSTRACT: Dietary antioxidants as health promoters for human beings have attracted much attention and triggered tremendous efforts in evaluation of the antioxidant capacity. Unfortunately, no versatile detection system has been designed to date. Due to the possible synergistic effect among antioxidant components in a diversified system, to isolate and quantify an individual antioxidant via a chromatography approach limits the scope for global antioxidant activity assay. Quality inspections with a spectroscopy strategy to any colored food are far from satisfactory. Herein, a photoelectrochemical (PEC) platform with an ultrasensitive titanium dioxide decorated sulfonated graphene (SGE-TiO$_2$) based transducer was introduced for antioxidant monitoring. Under an open circuit potential (zero potential), with extraordinary response, excellent reproducibility and stability, this PEC sensor could be successfully applied for rational analysis of the global antioxidant capacity. Such a highly efficient strategy showed advantages such as simplicity, convenience, high sensitivity and universality, which were also applicable to the detection of colored system. Moreover, the PEC sensor could be employed for practical evaluation of antioxidant capacity of teas. The concerned mechanism was further proposed and adequately discussed. This straightforward yet powerful approach provides a general format for dietary antioxidant assessment in foodstuff industries.

Natural antioxidants, a specific group of secondary plant metabolites, have stimulated intense research interest due to their actions in vivo as radical scavengers or electron donors that can be related to lower incidence and mortality rates of degenerative illness, such as cancer and cardiovascular diseases.$^{1,2}$ Since it was verified that a growing body of foods and drinks possess antioxidant capability, the regular intake of natural antioxidant-rich foodstuffs has been highly recommended, which may alleviate oxidative stress in an organism, thereby maintaining homeostasis.$^{3−5}$ On account of this fact, the quest for developing simple and reliable methods to evaluate antioxidant capacity (AC) toward foodstuffs is of great importance. It is worth mentioning that among ubiquitous dietary antioxidants, tea is in close connection with antiaging, anticarcinoma and arteriosclerosis prevention, which was suggested by epidemiological studies. Such functions of tea should be derived from its high abundance of polyphenols, especially the chemical structures containing several hydroxyl substituents directly associated with an aromatic benzene ring.$^6$

Nowadays, various means have been proposed to detect antioxidants, for example, spectroscopy,$^{7−8}$ chromatography,$^{10}$ electrochemistry$^{11}$ and so forth. Nevertheless, the above-mentioned techniques involve ineluctable shortcomings arising from their instinct mechanism. More specifically, optical detection is usually troubled by color interferences, whereas most natural foodstuffs present colorful appearances. The electrochemistry method is inevitably limited by its poor reproducibility and the working electrode is apt to be fouled by the productions. As for chromatography, aside from relying on expensive instruments, it always suffers from a relatively sophisticated pretreatment and time-consuming process. In particular, during chromatographic operation, only assessment of individual antioxidant concentration instead of global capacity of foodstuffs is of great significance.$^9$ However, the detections are often troubled by complicated pretreatment and time-consuming process. In addition, the electrode fouling is hard to be avoided.$^{12}$

In light of this, it would be urgent and necessary to set up an ingenious platform to overcome these obstacles originated from all the aforementioned approaches. Therefore, a new strategy has been introduced for antioxidant monitoring. Under an open circuit potential (zero potential), with extraordinary response, excellent reproducibility and stability, this PEC sensor could be successfully applied for rational analysis of the global antioxidant capacity. Such a highly efficient strategy showed advantages such as simplicity, convenience, high sensitivity and universality, which were also applicable to the detection of colored system. Moreover, the PEC sensor could be employed for practical evaluation of antioxidant capacity of teas. The concerned mechanism was further proposed and adequately discussed. This straightforward yet powerful approach provides a general format for dietary antioxidant assessment in foodstuff industries.

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In this sense, the development of a photoelectrochemical (PEC) platform paves a new avenue for antioxidant detection owing to advantageously inheriting from both the optical and electrochemical technology. PEC sensors, which feature the greatly reduced background signals and advantage of low potential performance (even 0 V) via the total separation of excitation source (light) and detection signal (photocurrent), have been applied in a myriad of fields. Typically, semiconductor nanostructures have been considered as one of the indispensable ways for solar conversion. Notably, among a number of photoactive nanomaterials, anatase TiO2 has captured considerable attention and has had the most explosive growth, which is attributed to its abundance, photostability, environmental benignity and high charge-carrier mobility. Yet, the inherent wide band gap of TiO2 brings about a big discount of energy utilization and photocatalytic efficiency, which results in the fatal decline of PEC sensing performances. Since the expeditious development of research based on graphene concerned materials in recent years, there seems to be a consensus that this kind of 2D carbon allotrope will endow a semiconductor with the photoactivity enhancement by virtue of behaving as an electron reservoir to accept or shuttle electrons photogenerated from the semiconductor, in turn, leading to positive inhibition of the recombination of electron–hole pairs.16,27

In this paper, an ingenious PEC platform toward global capacity of antioxidant assay based on sulfonated graphene–TiO2 (SGE-TiO2) composite was successfully constructed, which is illustrated in Figure 1. Here, SGE was introduced as a potent scaffold due to its great water solubility, good adsorptivity and unique electrical properties, which played an significant role in this PEC platform that arose from the following factors: (i) SGE could enable TiO2 nanoparticles to well cover the surface of the nanosheets and thus efficiently increased the active sites of the photocatalyst; (ii) compared with pristine TiO2, the visible-light harvesting of SGE-TiO2 was drastically enhanced; (iii) coupling SGE with TiO2 could greatly facilitate the separation of photoinduced electrons and holes, which absolutely benefited the photocatalysis reactions. Investigations of such PEC platform have achieved a new train of thought on development of a facile, portable, rapid and sensitive sensor toward detecting of AC in foodstuffs.

### EXPERIMENTAL SECTION

#### Materials and Reagents.
Tianium trichloride (TiCl3), terephthalic acid (TA), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) and gallic acid (GA) were purchased from Alfa. Glucose, trollox, Folin–Ciocalteu’s reagent, (+)-catechin hydrate (CT), caffeic acid (CA), p-aminobenzenesulfonic acid and hydrazine were obtained from Sigma-Aldrich. (−)-Epicatechin gallate (ECG) and (−)-epigallocatechin (EGC) were received from Aladdin. (−)-Epigallocatechin gallate (EGCG) was gained from J&K Chemical. Graphite powder (325 mesh), sodium borohydride (NaBH4) and NaN3 were bought from Beijing Chemical Factory (Beijing, China). All chemicals were used as received without further purification. The PBS buffer was made from sodium phosphate (NaH2PO4/Na2HPO4, 81:19 (molar ratio)) and sodium chloride, which were dissolved in deionized water at final concentrations of 10 mmol L\(^{-1}\) (pH = 7.4). Four brands of tea were purchased from a local supermarket.

#### Apparatus.
Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a Tecnai G2 microscope operating at 200 kV. The X-ray diffraction (XRD) measurements were recorded in the range of 20–80° (2θ) on a D8 Focus diffractometer (Bruker) with Cu Ka radiation (\(λ = 0.154\ 05\) nm), operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) was taken on an ESCALAB-MKI250 photoelectron spectrometer with Al Ka X-ray radiation as the X-ray source for excitation. Raman spectra were measured on a Renishaw Raman system model 2000 spectrometer using a 514 nm argon ion laser and calibrating referenced to the 520 cm\(^{-1}\) line of silicon. Fourier transform infrared (FTIR) spectra were collected on a Bruker Tensor 27 spectrometer. The UV–visible diffuse reflectance spectra (DRS, taking BaSO4 as internal reference sample) were performed on the dry-pressed disk samples using a Hitachi U-3900 spectrophotometer equipped with an integrating sphere assembly. Fluorescence emission spectra were obtained from a Hitachi F-4600 fluorescence spectrophotometer with an excitation wavelength of 315 nm. All the electrochemical experiments were conducted at room temperature using a conventional three-electrode cell, comprising a glass carbon (GCE, d = 3 mm) or modified ITO electrodes, a platinum wire as an auxiliary electrode and an Ag/AgCl (3 mol L\(^{-1}\) KCl) as the reference in a CHI920C electrochemical workstation. A LED light (3 W, 420 nm) was used as the excitation source of the PEC sensor. Besides, the PBS buffer was bubbled with N2 for at least 15 min, kept over a N2 atmosphere during the experimental process. Electrochemical impedance spectroscopy (EIS) measurements were recorded on a Solartron 1255 B frequency response analyzer (Solartron Inc., UK) in a mixed solution of 1 mol L\(^{-1}\) Fe(CN)\(_6\)\(^{3−/4−}\) and 0.1 mol L\(^{-1}\) KCl aqueous solution (amplitude 10 mV, 10\(^{−2}\) to 10\(^{5}\) Hz). A Mott–Schottky plot was performed in 1 mol L\(^{-1}\) Na2SO4 with frequencies of 1000 and 2000 Hz.

#### Preparation of SGE and Reduced Graphene Oxide (RGO) Sheets.
Graphene oxide (GO) was prepared and purified by oxidizing natural graphite power based on the modified Hummers method. The raw GO suspension (75 mL, 1 mg mL\(^{-1}\); pH 9–10, adjusted by 5 wt % Na2CO3) was prereduced with NaBH4 (15 mL, 40 mg mL\(^{-1}\)) at 80 °C for 1 h, followed by rinsing repeatedly with deionized water, then the yielded...
sediment was redispersed in 75 mL of ultrapure water. Afterward, under magnetic stirring, the aryl diazonium salt obtained from mixing 46 mg of sulfanilic acid (in 5 mL of water) and 0.5 g of 1 N HCl solution with 18 mg of NaNO2 (in 5 mL of water) at 2 °C for 15 min was slowly added to the dispersion at 2 °C for 2 h. Subsequently, the dispersion was postreduced by 4 mL of hydrazine (in 5 mL of water) at 100 °C for 24 h with constant stirring. The resulting sulfonated graphene was then intensively washed with deionized water and finally dispersed in 80 mL of water for use.

In contrast, RGO was produced by the mixture of GO (pH 10, adjusted by 25 wt% ammonia solution) and hydrazine at 95 °C for 35 min under stirring, wherein the weight ratio of hydrazine to GO was about 7:10.

Preparation of SGE-TiO2 Modified Indium Tin Oxide (ITO) Electrodes. SGE-TiO2 composites were synthesized via self-assembly method according to previous work with minor modification. In brief, 4.8 mL of SGE, 0.22 mL of sodium dodecyl sulfate (SDS, 0.05 mol L⁻¹) and 68.82 mL of deionized water were mixed in the round flask, then 50 mL of TiCl3 (0.12 mol L⁻¹) was injected dropwise with modest stirring for 1 h. Immediately, 10 mL of Na2SO4 (0.6 mol L⁻¹) and 5 mL of H2O2 (1 wt%) were added, and the mixture was constantly stirred at 90 °C for 16 h. The obtained precipitates were rinsed thoroughly with water and ethanol respectively, dried at 70 °C, and calcined in nitrogen shield at 400 °C for 2 h. The obtained precipitates were mixed in the round flask, then 50 mL of TiCl3 (0.12 mol L⁻¹) was injected dropwise with modest stirring for 1 h. Immediately, 10 mL of Na2SO4 (0.6 mol L⁻¹) and 5 mL of H2O2 (1 wt%) were added, and the mixture was constantly stirred at 90 °C for 16 h. The obtained precipitates were rinsed thoroughly with water and ethanol respectively, dried at 70 °C, and calcined in nitrogen shield at 400 °C for 2 h. The obtained precipitates were mixed in the round flask, then 50 mL of TiCl3 (0.12 mol L⁻¹) was injected dropwise with modest stirring for 1 h. Immediately, 10 mL of Na2SO4 (0.6 mol L⁻¹) and 5 mL of H2O2 (1 wt%) were added, and the mixture was constantly stirred at 90 °C for 16 h. The obtained precipitates were rinsed thoroughly with water and ethanol respectively, dried at 70 °C, and calcined in nitrogen shield at 400 °C for 2 h. The obtained precipitates were rinsed thoroughly with water and ethanol respectively, dried at 70 °C, and calcined in nitrogen shield at 400 °C for 2 h.

After the ITO electrode was cleaned with NaOH (1 mol L⁻¹) and H2O2 (30%), sonicated in acetone and water and dried under ambient conditions, 100 μL of the SGE-TiO2 slurry (1 mg mL⁻¹) was cast onto the pretreated ITO glass in a defined area. Through air drying, the working electrode was further dried at 70 °C for 12 h to improve adhesion. The TiO2 or RGO-TiO2 modified ITO electrode was achieved analogously.

Antioxidant Capacity (AC) Detection. Four different varieties of tea samples were bought from the local supermarket. First, dry leaves (0.25 g) of each tea were suspended in 30 mL of boiling two-distilled water and kept infiltration for 30 min in an air atmosphere, and then the supernatant solids were collected by a normal funnel. The resultant tea soaked water extracts were stored at 4 °C until use. In comparison with the PEC methodology, DPPH and Folin-Ciocalteu (F-C) approaches were also introduced to estimate the AC of teas as control experiments.

The process of AC assay upon such PEC sensor is illustrated in Figure 1. Typically, following the onset that the sample was injected into PEC cell and the light illuminated from the back side of modified ITO, the subsequently generated photocurrent was promptly acquired by the electrochemical workstation. Note that the tea filtrates were detected without any further treatment. The PEC current was defined as follows: $I = I_{\text{blank}} - I_{\text{sample}}$ (where $I_{\text{sample}}$ and $I_{\text{blank}}$ represent the photocurrent generated in the presence and absence of sample, respectively, at the certain time after irradiation). To guarantee the reliability of data, the photocurrent was tested three rounds at the same concentration, namely, $I_{\text{sample}}$ or $I_{\text{blank}}$ was the average value of three testing currents.

DPPH radical scavenging activity was performed as described by Brandwilliams et al. with slight modifications. Briefly, to the volume of 900 μL of DPPH reagent (0.04 mg mL⁻¹, in absolute methanol), 100 μL of a various tea diluted solution or Trolox standard solution was added. Fifteen minutes later, the change of the absorbance at 514 nm of the reacted solution was monitored by UV–vis spectroscopy. The final results received from triplicate analyses were expressed as Trolox equivalents.
The F-C method was reported by Ainsworth, which regarded gallic acid (GA) as the calibration standard. In short, first 200 μL (1/10 dilution) of F-C reagent was added into 1.5 mL microtubs containing 100 μL of a various tea diluted solution or GA solution, and then 800 μL of Na2CO3 (0.7 mol L−1) was quickly injected. The mixture was shaken vigorously and then incubated at 25 °C for 2 h. The absorbance reading was measured at 765 nm against a blank sample. All the determinations were replicated three times.

## RESULTS AND DISCUSSION

### Preparation and Structural Characteristics of SGE-TiO2

Starting from single layers of fully exfoliated GO, the precursory SGE and RGO nanosheets were synthesized, which could be proved by FTIR spectra (shown in Figure S1 of the Supporting Information). As expected, the appearances of peaks at 1176, 1123 and 1033 cm−1 (C=O, C−O) exhibit three peaks at 284.6 (C−H), 286.2 (C−H), and 1603 cm−1 were quickly injected. The mixture was shaken vigorously and then incubated at 25 °C for 2 h. The absorbance reading was measured at 765 nm against a blank sample. All the determinations were replicated three times.

> **RESULTS AND DISCUSSION**

Preparation and Structural Characteristics of SGE-TiO2. Starting from single layers of fully exfoliated GO, the precursory SGE and RGO nanosheets were synthesized, which could be proved by FTIR spectra (shown in Figure S1 of the Supporting Information). As expected, the appearances of peaks at 1176, 1123 and 1033 cm−1 confirm the successful sulfonation of GO, and the in-plane bending peak for C−H at 1004 cm−1 is an evidence of p-disubstituted phenyl group. Figure 2a shows the TEM image of SGE, which exhibits a wrinkle-like ultrathin sheet appearance. It is worthwhile mentioning that the introduction of the charged −SO3 units facilitated the highly stable dispersibility of SGE, so that there was no detectable agglomeration even after more than 6 months. Benefiting from the hybridized sp2 carbon bonds and hydrophilic function groups, SGE provided an excellent platform to one-step self-assembly of TiO2 nanoparticles. As shown in Figure 2b, TiO2 nanocrystals were uniformly distributed throughout the monolayer structure other than the morphology of RGO-TiO2, (shown in Figure S2 of the Supporting Information), which was found aggregated seriously. The HRTEM image of SGE-TiO2 (shown in Figure 2c) reveals an equal interfringe spacing of 0.35 nm corresponding to (101) facets of anatase. While its selected-area electron diffraction (SAED) pattern in Figure 2d can be perfectly indexed to anatase TiO2 (JPCDS No. 21-1272), with its typical crystal plane (101), (004), (200), (211) and (204), which match well with the result of XRD spectra in Figure 2k. It indicates that no other crystalline impurities were discerned. Unquestionably, a high coverage of anatase TiO2 guaranteed the efficient optoelectronic performance, because of the fact that the anatase phase is distinctly superior for a larger surface area and faster electron transport than the rutile phase. Furthermore, HAADF-STEM and the elemental mapping (Figure 2e−j) manifest the existence of C, H, O, Ti and S in the composites, which also clearly verify that the SGE sheet was evenly and densely decorated with S−K and Ti−K elements. In this regard, it is thought that a triumphant fabrication was made in conjunction with SGE and TiO2.

Valuable insights into building components are elucidated by Raman spectroscopy (shown in Figure S3a of the Supporting Information), and it is observed that the SGE-TiO2 nanohybrid displays six characteristic bands around 147, 398, 512, 639, 1354 and 1603 cm−1, respectively. The first four are in accordance with its typical crystal plane (101), (004), (200), (211) and (204), which match well with the result of XRD spectra in Figure 2k. It indicates that no other crystalline impurities were discerned. Unquestionably, a high coverage of anatase TiO2 guaranteed the efficient optoelectronic performance, because of the fact that the anatase phase is distinctly superior for a larger surface area and faster electron transport than the rutile phase. Furthermore, HAADF-STEM and the elemental mapping (Figure 2e−j) manifest the existence of C, H, O, Ti and S in the composites, which also clearly verify that the SGE sheet was evenly and densely decorated with S−K and Ti−K elements. In this regard, it is thought that a triumphant fabrication was made in conjunction with SGE and TiO2.

Figure 3. Photocurrent responses of TiO2 (curves a0 and a1), RGO-TiO2 (curves b0 and b1) and SGE-TiO2 (curves c0 and c1) modified ITO electrode in the absence of (curves a0, b0 and c0) and presence of (curves a1, b1 and c1) 74.44 μmol L−1 GA.

merely presented a weak photocurrent of 87.2 nA (curve a0) at a potential of 0 V during the employing irradiation of 420 nm. Such a phenomenon should be ascribed to the rapid e−−h+ recombination and broad band gap, which obstruct the electron transfer. After doping with RGO or SGE, the photocurrent intensity further prominently increased to 215.38 and 326.13 nA, respectively, which were 2.47 and 3.74 times the intensity of pristine TiO2 (curves b0 and c0). In particular, upon presence of 74.44 μmol L−1 GA, the photocurrent of the SGE-TiO2 modified electrode soared to as high as 646.4 nA, severely reaching 1.51 and 5.46 times those of RGO-TiO2 and TiO2 (curves c1, b1 and a1). Whereas the electrical performance of the SGE-TiO2 modified electrode was found to be superior to that of RGO-TiO2 through photocurrent increments (defined as PEC current, I = I_{sample} − I_{blank}). It was calculated that the PEC current of RGO-TiO2 just accounted for 66% of SGE-TiO2. For comparison purpose, Figure S4 (in the Supporting Information) depicts the UV−visible diffuse reflectance spectra (DSR) of TiO2, RGO-TiO2 and SGE-TiO2. Referring to the previous research, the electron reservoir of graphene assured prolonged separation and lifetime of electron−hole pairs. Apparently, the introduction of carbon materials induced probable light absorption in the visible light region, as compared to the blank TiO2. The plot of the transformed Kubelka−Munk function versus the energy of light has been demonstrated as Figure 2m. In keeping with the outcomes of TEM, incorporated SGE allowed a favorable morphology and accessible active sites, which greatly altered the light absorption feature and shortened electron-transfer pathway than RGO. To shed light on the interface properties of...
electrodes, electrochemical impedance spectroscopy (ESI) was utilized to characterize the charge carrier migration of samples. Figure S5 (in the Supporting Information) shows that the resistance $R_{\text{ct}}$ of SGE-TiO$_2$ distinctly declined with respect to TiO$_2$ and RGO-TiO$_2$. Although the semiconductive properties of TiO$_2$ impeded electron transfer, the successful assembling with SGE partially offset the hindrance effect and finally insulating effect.

It is well-known that the operating potential plays a crucial role in a PEC procedure because it has an immense influence on current intensity or charge measurement. Figure S6 (in the Supporting Information) depicts that PEC current enhanced along with varying potential from $-0.2$ to $0.3$ V. It should be stressed that although PEC current at 0 V took up 58% of that at 0.3 V, it already showed enough sensitivity for photocurrent signal detection under such condition. Moreover, in consideration of elimination of coexisted interference in the practical detection circumstance, such as polysaccharides, amino acids, etc., the applied potential of 0 V seemed to be a suitable choice for the PEC sensor.

GA, CA, CT, EGC, EGCG and ECG are known as major polyphenol antioxidants ingredients in tea. Figure 4 represents the photocurrent versus time tests for polyphenol reagents including six standard antioxidants to successive additions at 0 V. Under optimal conditions, the photocurrent responses mainly displayed linear increases and then trended toward a plateau, accompanied by increments of antioxidant concentrations. Taking GA for instance, the inset of Figure 3a reports a linear range from 24.94 to 867.58 $\mu$mol L$^{-1}$ with the detection limit of 12.17 $\mu$mol L$^{-1}$. Likewise, the other antioxidants also present linear dependences of PEC current on antioxidant concentrations. As listed below, the linear relationships were calculated to be in the range of 123.46 to 2156.9 $\mu$mol L$^{-1}$ for CA, 12.46 to 433.79 $\mu$mol L$^{-1}$ for CT, 2.49 to 130.02 $\mu$mol L$^{-1}$ for EGC and 2.49 to 71.77 $\mu$mol L$^{-1}$ for EGCG and ECG. In light of better response for the main components of tea polyphenols, a conceptual strategy was proposed to use GA as the reference. That is to say, first, the calibration curve of GA was collected via a SGE-TiO$_2$ ITO electrode; second, the same electrode was then applied to detect the tea extract; third, antioxidant capacity (AC) was expressed as GA equivalents. Clearly, PEC transducers

**Figure 4.** Photocurrent responses of SGE-TiO$_2$ modified ITO electrode upon different concentration of (a) GA, (b) CT, (c) CA, (d) EGC, (e) EGCG and (f) ECG, respectively. The inset in each graph is the corresponding liner calibration curve. The photoelectrochemical sensors were applied at 0 V under 420 nm light excitation in 0.1 mol L$^{-1}$ PBS (pH = 7.4).
turned out to offer timely response to the sum of tea polyphenols, which could be adequately applied to realize AC assessment in comprehensive antioxidant status. Since the synergistic effect among each antioxidant should not be ignored, the concentration of an individual antioxidant composition is not able to rationally reveal the global antioxidants contributions. It is noticeable that five electrodes prepared independently at the identical circumstance suggested satisfactory reproducibility with relative standard deviation (RSD) of 2.54% upon a 123.46 μmol L⁻¹ GA solution. Moreover, after 27 times of repeated on–off measurements upon a 123.46 μmol L⁻¹ GA solution, the photocurrent of three electrodes almost had no distinct influence over time, which indicated that the electrode fouling effect did not show a significant impact on such PEC systems. (shown in Figure S7 of the Supporting Information). When two electrodes were stored at room temperature in darkness, 5 weeks later, the PEC current could still perceive at least 93.85% of the initial intensity, which showed acceptable long-term stability.

Actually, the concomitant components frequently appear in tea including polysaccharides, amino acids and organic acids, hence, the interferents on PEC biosensing response were inspected. Figure 5 justifies that no obvious signal decay was observed when each concentration of L-malic acid and L-citric acid were 20-fold that of GA. Similarly, the interference of 50 times of L-lysine (Lys), 200 times of L-threonine (Thr), and 500 times of fructose, glucose, ethanol, methanol, L-glycine, L-proline, L-histidine in 0.1 mol L⁻¹ PBS (pH = 7.4) containing 77.78 μmol L⁻¹ GA at 0 V under 420 nm light excitation.

Table 1. Detection of Antioxidant Capacity by Three Different Methods

<table>
<thead>
<tr>
<th>tea</th>
<th>PEC sensor, GA (mg g⁻¹)</th>
<th>F-C method, GA (mg g⁻¹)</th>
<th>DPPH method, trolox (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>brand 1</td>
<td>38.55 ± 2.71</td>
<td>28.78 ± 1.82</td>
<td>67.98 ± 8.22</td>
</tr>
<tr>
<td>brand 2</td>
<td>79.46 ± 6.59</td>
<td>67.33 ± 4.36</td>
<td>126.39 ± 12.73</td>
</tr>
<tr>
<td>brand 3</td>
<td>103.95 ± 5.29</td>
<td>94.95 ± 14.37</td>
<td>160.27 ± 8.36</td>
</tr>
<tr>
<td>brand 4</td>
<td>17.03 ± 3.48</td>
<td>14.39 ± 0.31</td>
<td>50.30 ± 6.61</td>
</tr>
</tbody>
</table>

Date are expressed mean of samples analyzed ± standard deviations (n = 3).

Table 1 roughly classified as hydrogen atom transfer (HAT) and electron transfer (ET) reaction mechanisms. DPPH is a stable nitrogen radical, which can be applied to investigate the electron donating potency of antioxidants. Depending on the chemical reaction involved, the DPPH assay may be grouped into a HAT/ET reaction, and uses trolox as the calibration standard. However, DPPH serves as both radical probe and oxidant, which leads to reacting with all the relatively reducing substances. Hence, this method would always exaggerate the sample’s reducing capacity. F-C assay is a common means to colorimetrically quantify total phenolic content, which has been frequently employed in dietary supplement analysis. Thus, for its principle, quality inspections with this strategy for any colored foods are far from satisfactory. In fact, F-C and PEC assays are considered as an ET-based reaction, and both take GA as an equivalent to express results. Additionally, the redox potential of Folin reagent lies in the range of E° = 0.6–0.7 V, which is much lower than the VB of SGE-TiO₂ (Figure 6c). In this respect, more antioxidants may be reacted in the PEC method than the F-C method. The detection data for tea as obtained by F-C assay is smaller than that of our PEC measurement. Despite all that, Table 1 outlines that both DPPH and F-C methods demonstrated an identical tendency of AC assessment with our

Figure 5. Photocurrent responses of SGE-TiO₂ modified ITO electrode upon the addition of 1.56 mmol L⁻¹ each of L-malic acid, L-citric acid, or 3.89 mmol L⁻¹ of L-lysine, or 15.56 mmol L⁻¹ L-threonine, or 38.89 mmol L⁻¹ of fructose, glucose, ethanol, methanol, L-glycine, L-proline, L-histidine in 0.1 mol L⁻¹ PBS (pH = 7.4) containing 77.78 μmol L⁻¹ GA at 0 V under 420 nm light excitation.

Figure 6. (a) Fluorescence emission of 0.5 mmol L⁻¹ terephthalic acid in 0.1 mol L⁻¹ PBS (pH = 7.4) with light of 0, 30 s, 1, 2 and 3 min. (b) Mott–Scottky plot of SGE-TiO₂ modified ITO electrode in 0.1 mol L⁻¹ PBS (pH = 7.4) with frequencies of 1000 and 2000 Hz. The x-axis intercept is equal to the flat band potential Eₜₐ₉ which is the approximate value of CB. (c) Schematic illustration of the charge separation and transfer in the SGE-TiO₂ system under 420 nm.

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PEC system upon the real samples analysis. It indicated that such a PEC platform was able to provide a powerful tool for global AC detection, which also fully embodied the synergistic effect among antioxidants. To uncover this fact, synergy between GA and EGC was explored and the results are shown in Figure S9 (in the Supporting Information). Definitely, an about 18% higher response signal was obtained when GA coexisted with EGC, as compared with the sum signal of individual GA and EGC.

Based on the above results, the PEC sensor had an advisable accuracy for practical application in AC evaluation of foodstuff.

Hypothesis of PEC Mechanism. As reported in the previous literatures, there are two possible processes for TiO2 photocatalytic oxidation: (i) hydroxyl (•OH) radicals can generate by oxidation of water molecules with the aid of photogenerated holes; (ii) direct reaction with the trapped holes.48 As for validation of the mechanism, fluorescence spectroscopy was utilized through chemical interaction between •OH radicals and terephthalic acid (TA), which is shown in Figure 6a. Once •OH radicals generate, the fluorescence response rises with the increasing of illumination time.49 Quite interestingly, no distinct change was discovered even after 3 min. It seems that in this PEC sensor, antioxidants should react directly with the trapped holes. On the basis of the above discussion, a tentative mechanism of the PEC sensor can be inferred as the following (Figure 6c). TiO2 contrives to absorb visible light because carbon doped might sufficiently narrow the band gap (Figure 2m), which will induce electron transition from valence band (VB) to conduction band (CB) and produce the band gap (Figure 2m), which will induce electron transition from visible light because carbon doped might sufficiently narrow the band gap.

CONCLUSIONS

In summary, a truly economical, valid and innovative PEC sensor was established for global antioxidant capacity detection via an ultrasensitive bicomponent SGE-TiO2 nanohybrid. Unlike conventional spectrophotometric methods, the PEC platform translated visible-light driven energy into remarkable photocurrent output at zero potential, which could greatly avoid interferences. Obviously, as a result of the prompt communication among tea polyphenols, TiO2, SGE and ITO electrode, the proposed transducer underlined an eminent analytical performance toward rationally estimating AC of tea, such as simplicity, convenience, high sensitivity and universality. By the same token, the integrated PEC system opens a novel perspective for a general format in the broad applications, progressively miniaturization detection in food and pharmaceutical industries.

REFERENCES


AUTHOR INFORMATION

Corresponding Author
D. Han. E-mail: dxhan@ciac.ac.cn. Fax: +86-431-85262425.

Notes
The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information
FTIR spectra of SGE and RGO, TEM image of RGO-TiO2, Raman spectra of powdery SGE, TiO2 and SGE-TiO2, C 1s, Ti 2p, and S 2p XPS spectrum of SGE-TiO2, UV–vis DRS of TiO2, RGO-TiO2, and SGE-TiO2, EIS images of TiO2, RGO-TiO2, and SGE-TiO2, effects of applied potential on photocurrent response of SGE-TiO2, modified ITO electrode in 0.1 mol L–1 PBS (pH = 7.4) containing 243.90 μmol L–1 GA under 420 nm light excitation, photocurrent responses of three different electrodes, cyclic voltammograms of 1.25 mmol L–1 GA, CA, CT, ECG, EGC, EGCG, glucose, and l-glycine, electrochemical characteristics of the first anodic peak of 1.25 mmol L–1 glucose, l-glycine, and six antioxidants using a 3 mm glassy carbon electrode at 0.1 V/s in 0.1 mol L–1 PBS (pH = 7.4), and photocurrent responses of the same SGE-TiO2 modified ITO electrode without and with 50 μmol L–1 GA, or 62.5 μmol L–1 EGCG, or the mixture of 50 μmol L–1 GA and 62.5 μmol L–1 EGCG. This material is available free of charge via the Internet at http://pubs.acs.org.

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