Design of two electrode system for detection of antioxidant capacity with photoelectrochemical platform

Dongxue Han\textsuperscript{a}, Weiguang Ma\textsuperscript{a,b,*}, Lingnan Wang\textsuperscript{a}, Shuang Ni\textsuperscript{c}, Nan Zhang\textsuperscript{a}, Wei Wang\textsuperscript{a}, Xiandui Dong\textsuperscript{a}, Li Niu\textsuperscript{a,\texttt{**}}

\textsuperscript{a} 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

\textsuperscript{b} Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

\textsuperscript{c} Shenyang Agricultural University, Shenyang 110161, China

\textsuperscript{*} Corresponding author at: 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

\textsuperscript{**} Corresponding author.

E-mail addresses: wgma@ciac.ac.cn (W. Ma), lniu@ciac.ac.cn (L. Niu).

\textsuperscript{nn} Available online 3 September 2015

\textsuperscript{nn} © 2015 Elsevier B.V. All rights reserved.

\section*{A R T I C L E   I N F O}

Article history:
Received 10 June 2015
Received in revised form 21 August 2015
Accepted 28 August 2015
Available online 3 September 2015

Keywords:
Antioxidant capacity
Photoelectrochemistry
Two electrode technique

\section*{A B S T R A C T}

Recently, a flow photoelectrochemical cell has been first developed and applied to assay global antioxidant capacity in our group. Yet, shortcomings of liquid reference electrode such as sample contaminations from the leaking of the reference solution, mechanically fragile, temperature and light sensitivity, etc. are significant restrictions for integration and miniaturization of photoelectrochemical sensing instruments, which have greatly limited their practical applications. Bearing these problems, in this work a novel two electrode flow photoelectrochemical system (two-EPCS) has been developed for detection of antioxidant capacity. It is noteworthy that the electrochemical modulation-free mode (detection at the potential of 0.0 V) is performed, which has greatly simplified the analysis process and will result in significant simplifications of the instrument integrations. During the sample analysis, both standard antioxidants and commercial beverages were detected. Results evaluated from the two-EPCS are well agreed with those of the traditional three-EPCS at low potentials. By unloading of the reference electrode, it is of great convenience to design a novel photoelectrochemical microfluidic chip based on the two-EPCS, which has also been successfully applied for antioxidant capacity assay. It is satisfactory that comparable detection concentration range and sensitivity were accomplished by applying the microfluidic chip technique. Moreover, the two-EPCS is verified to be a universal platform which does not depend on selected optoelectronic materials but pervasive for general photocatalysts. Such a two-EPCS should be considered as a feasible alternative to the three-EPCS, which will become a promising candidate for industrial and commercial photoelectrochemical sensing instrument integrations in the future.

\section*{1. Introduction}

Photoelectrochemical technique has attracted tremendous attentions since it combined merits of both optical and electrochemical methods, which has been applied as efficient strategy to develop DNA sensor (Liang and Guo, 2007; Li et al., 2014; L. Wang et al., 2014; W. Wang et al., 2014), cytosensing (Qian et al., 2010; W.-W. Zhao et al., 2012a, 2012b; X. Zhao et al., 2012), enzymatic analysis (Yildiz et al., 2008), immunoassay (Zhao et al., 2012a, 2012b, 2012c; W.-W. Zhao et al., 2012a, 2012b; X. Zhao et al., 2012) and many other small molecules sensing (Long et al., 2011; Golub et al., 2009; Pardo-Yissar et al., 2003; Tu et al., 2010) etc. However, just as the traditional electrochemical approach, during the photoelectrochemical detections, the work electrode is easily fouled by the productions, which will result in the gradually attenuation of the detection signal. In order to improve the recyclability of the work electrode, a flow photoelectrochemical cell with thin layer structure has been developed to assay global antioxidant capacity in our previous study (Ma et al., 2014). Yet, intrinsic shortcomings of the liquid reference electrode exhibited quite a few restrictions to flourish the flow photoelectrochemical cell system into industrial applications as well as the corresponding commercial instruments. As is known that, sample contaminations from the leaking of the reference solution (Peters, 1997; Zhang et al., 2012), mechanically fragile, temperatures sensitivity (Oijerholm et al., 2009) and light sensitivity (Ansuini and Dimond, 1994), etc. are typical inevitable drawbacks of the liquid reference electrode. In addition, another serious defect should be the unavailability of a reliable miniature liquid reference electrode (Suzuki et al., 1998; Vonau et al., 2010; Suzuki et al., 1999), which has significantly

http://dx.doi.org/10.1016/j.bios.2015.08.066

0956-5663/© 2015 Elsevier B.V. All rights reserved.
restricted the design of high throughput integration of electrode array and their biomedical applications. In response to these problems, amount of methods have been developed by researchers, e.g., utilizing of all solid state reference electrode (Vonau et al., 2010; F.-X. Rius-Ruiz et al., 2011; Ex. Rius-Ruiz et al., 2011; Michalska, 2012), introducing of screen printed electrode (F.-X. Rius-Ruiz et al., 2011, Ex. Rius-Ruiz et al., 2011; Liao and Chou, 2006) and bipolar electrodes (Mavre et al., 2010; Zhu et al., 2014) etc. Although great progress were achieved, there are still many problems need to be urgently solved upon the practical applications of the photoelectrochemical technique.  

In this research, to face these challenges, a novel two electrode flow photoelectrochemical system (two-EPCS) has been designed for detection of global antioxidant capacity without employment of the reference electrode. It is gratified that results of such a two-EPCS are well agreed with that of the traditional three electrode flow photoelectrochemical system (three-EPCS) at low potentials. Based on this, the technique of the two-EPCS photoelectrochemical microfluidic chips have been designed and successfully applied for antioxidant capacity assay. In addition, several optoelectronic materials were performed to construct the two-EPCS, all of which showed favorable responses. Therefore, the advisable universality of the two-EPCS should make itself a general strategy for miniaturization of photoelectrochemical sensing instruments in industrial and biomedical application.

2. Experimental section

2.1. Reagent

Caffeic acid (CA), (+)-catechin hydrate (CT), α-cysteine (Cys), glucose, and Folin–Ciocalteu (F–C) reagent (10%) were received from Sigma-Aldrich. Titanium trichloride (TiCl3), Gallic acid (GA), Zinc acetate dehydrate (Zn (AC)2 2H2O) and cadmium acetate dehydrate (Cd(AC)2 2H2O) were purchased from Alfa. (-)-Epigallocatechin gallate (EGCG) was gained from J&K Chemical. The measurement process of the two-EPCS was illustrated in Scheme 1.

2.2. Instruments

All electrochemical experiments were performed with a CHI660A Electrochemical Workstation (CHI). A thin layer three-EPCS, comprising ITO or modified ITO as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode (3 mol L⁻¹ KCl) as reference electrode was used in the photoelectrochemical measurement. The structure of the two-EPCS is similar with that of the three-EPCS except without an Ag/AgCl electrode. 0.1 mol L⁻¹ PBS solution containing 10 mmol L⁻¹ NaCl was applied as supporting electrolyte and bubbled with N2 for 15 min before each experiment. LED light (420 nm or 545 nm, Beijing Perfectlight Technology) was employed as light source for photoelectrochemical sensor: the peristaltic pump was bought as assistant of the modified ITO electrode (LED, 420 nm), which can effectively prevent interference from the colored samples. Each sample was detected for three times and the average value was recorded. The photoelectrocurrent was collected following the principle: I = I＼n– I＼nblank (I＼nblank: the photoelectrochemical current with sample, I＼n: the photoelectrochemical current without sample). In addition, CdS modified ITO electrode was irradiated by the 545 nm LED. Other conditions

First, ultrathin graphic carbon nitride (utg-C3N4)/TiO2 were synthesized by our previous method (Ma et al., 2014). To prepare ZnO/utg-C3N4 directly from utg-C3N4, utg-C3N4 (40 mg) and Zn (AC)2 2H2O (87.3 mg) were dispersed in DMSO (40 mL). After vigorous stirring, the solution was transferred into a Teflon-lined stainless steel autoclave (50 mL) and reacted under 180 °C for 12 h. The obtained solution was then washed extensively with acetone and alcohol in a sonication washer to remove non-reacted reactants. Finally, the product was centrifuged at 5000 rpm, and dried in a vacuum drier at 60 °C. To obtain CdS nanoparticles, 106 mg Cd (AC)2 2H2O was dissolved in 40 mL DMSO and then transferred into a Teflon-lined stainless steel autoclave (50 mL) and reacted under 180 °C for 12 h. Other steps are similar with the synthesis of ZnO/utg-C3N4. The evidences for the structural properties of the ZnO/utg-C3N4 and CdS nanoparticles composites from XPS were presented in Fig. S1 (in Supporting information).

2.4. Preparation of the work electrode

After an ITO electrode was cleaned with NaOH (1 mol L⁻¹) and H2O2 (30%), washed with acetone and twice-distilled water and dried at room temperature, a certain amount of photocatalyst suspension, for example 100 μL of utg-C3N4/TiO2 (1 mg mL⁻¹), was cast onto the ITO electrode and dried at room temperature to obtain the photocatalyst modified ITO electrode. Then, the working electrode was ultra-dried at 70 °C for 12 h to improve the adhesion. The utg-C3N4/ZnO or CdS modified ITO electrode was prepared analogously.

2.5. Assay of antioxidant capacity

The measurement process of the two-EPCS was illustrated in Scheme 1. After the two-EPCS was successfully fixed, the buffer or sample solution was injected into the flow cell with assistant of the peristaltic pump at 2 rev min⁻¹. During the detections, the light irritated from the backside of the modified ITO electrode (LED, 420 nm), which can effectively prevent interference from the colored samples. Each sample was detected for three times and the average value was recorded. The photoelectrocurrent was collected following the principle: I = I＼n– I＼nblank (I＼nblank: the photoelectrochemical current with sample, I＼n: the photoelectrochemical current without sample). In addition, CdS modified ITO electrode was irradiated by the 545 nm LED. Other conditions
are similar with that of the utg-C3N4/TiO2 modified electrode. Eleven brands of drinking obtained from the local supermarket were detected without special pretreatment. The results were expressed in GA equivalents.

2.6. Investigation of interference, stability, repeatability, and reproducibility studies

The procedure of interference evaluation is similar to that of sample detections. 25 μmol L\(^{-1}\) GA and interference species with a certain concentration were added into 0.1 mol L\(^{-1}\) PBS (pH = 7.4), and then mixed homogeneously. The mixture was subsequently detected immediately. The final calculated concentrations of interference are 25 mmol L\(^{-1}\) for each of \(\alpha\)-histidine, ethanol, methanol, 12.5 mmol L\(^{-1}\) for each of \(\alpha\)-proline, \(\alpha\)-glycine, glucose, \(\alpha\)-citric acid, \(\alpha\)-malic acid and 5 mmol L\(^{-1}\) for \(\alpha\)-threonine and fructose. The stability and repeatability were evaluated as following: a certain concentration of GA was injected into the two-EPCS, and then the photocurrent was collected for about 1200 s. For reproducibility study, the modified electrode was kept in a desiccator for 2 weeks under room temperature without light for the next detection. Then, the two results were compared with each other.

2.7. Reference method

Folin–Ciocalteu (F–C) approach was operated as following. 100 μL of each sample was added to 2-ml microtubers; then, 200 μL of F–C reagent (10%, v/v, Sigma) was introduced with a thorough vortex; at last, 800 μL of Na\(_2\)CO\(_3\) (0.7 mol L\(^{-1}\)) was added to the above solution and the mixture was incubated at 20 °C for 2 h. The reacted solution was detected by UV–visible spectrophotometer. The absorbance was recorded at 765 nm.

3. Results and discussions

At present, chronoamperometry method is one of the most frequently applied strategies in the photoelectrochemical measurement (L. Wang et al., 2014; W. Wang et al., 2014; Qian et al., 2010; W.-W. Zhao et al., 2012a, 2012b, X. Zhao et al., 2012; Wu et al., 2013). Concerned on such a technique, the essential requirement should be the accurate potential control as well as the favorable photocurrent response stability at every applied potential. Our previous research showed that the three-EPCS can well meet these criterions during the assay of antioxidant capacity (Ma et al., 2014; Ma et al., 2013; L. Wang et al., 2014; W. Wang et al., 2014). In order to achieve equivalent consequences in the photoelectrochemical measurement, the two-EPCS should also meet these approvals.

3.1. Effective potential control

In a photoelectrochemical system, when n-type semiconductor is employed as the optoelectronic material, with the increasing of applied potential, the photoelectrons apt to be driven to the electrode and thus results in a much higher photocurrent response. Taking utg-C3N4/TiO2 composite as the case study, as shown in Fig. 1a, with the applied potential elevated from −0.05 to 0.4 V, the photocurrent of the traditional three-EPCS shows a gradual ascending response. Here, the utilizing of Ag/AgCl reference electrode is capable to accurately control the potential. While in the two-EPCS (Fig. 1b), analogous phenomenon is observed, which indicates that such a reference electrode free system can also effectively accomplish the chronoamperometric analysis in a certain potential range. As is known that, for most of the photoelectrochemical measurements (Tu et al., 2010; Wu et al., 2013), the applied potential always hovers in the relatively low range, since low potential could avoid quite a few interferences from reductive species to a large extent. Therefore, according to the appreciated performance of the present two-EPCS, it is considered to act as a considerable candidate for voltammetric analysis.

3.2. Stability of photocurrent response

Since photoelectrochemical sensing is essentially based on the relationship between photocurrent and the concentration of analyte, the stability of photocurrent is of significant importance at the setting potential. Taking the detection sample of 109.89 μmol L\(^{-1}\) GA as the model, for the routine three-EPCS, when the applied potential performed at −0.05, 0.0, 0.1, 0.2, 0.3 and 0.4 V, the corresponding photocurrent responses are recorded respectively for more than 1200 s. As shown in Fig. 2a, during six parallel tests, pleasurable stability were observed for all the defined potentials. Similarly, the two-EPCS is also employed for this detection model and favorable photocurrent stabilities have been achieved upon all these applied potentials (Fig. 2b). The variation amplitude of both the three-EPCS and two-EPCS are calculated and summarized as Fig. 2e. It reveals that compared with the three-EPCS, slight expanded photocurrent fluctuations of the two-EPCS occur but is still acceptable. Such phenomena should be ascribed to different electrochemical potential modulation mode of the three-electrode and two-electrode electrochemical systems, which is shown in Fig. S2 (Supporting information). It seems that at low potential range, the two-EPCS exhibits enough stability which can fulfill the requirement for photoelectrochemical sensing.

Considering the comprehensive affections of both the photocurrent sensitivity and coexist species interference originated from the applied potential, 0.0 V is thus selected for the investigations.

![Fig. 1](https://example.com/figure1.png)  
*Fig. 1. The relations between photocurrent and potential applied on the three-EPCS (a) and two-EPCS (b). (The concentration of GA is 109.89 μmol L\(^{-1}\)).*
of photocurrent stability. As is known that the intensity of photocurrent will extremely relate to the concentration of analyte, chronoamperometric assay of several different concentration of GA were performed based on both the three-EPCS (Fig. 2c) and two-EPCS (Fig. 2d) at 0.0 V. It is observed that both the two systems show satisfactory photocurrent stability at all the GA concentrations (Fig. 2f). For example, the photocurrent of the two-EPCS is about 270 nA at a low concentration of GA (22.7 μmol L⁻¹), which only decreases 1.0% after more than 1200 s scanning (red curve). Such excellent photocurrent stability should guarantee the accurate detection of antioxidant capacity at the two-EPCS.

Fig. 3 presents the novel designed two-EPCS device and the detailed inner structure. As discussed above, this fixed two-EPCS exhibits equivalent features to the typical three-EPCS, especially in the low potential range. These outstanding performances should essentially be attributed to the innovation of the counter electrode. Compared with the platinum wire which is usually used as the counter electrode in the traditional three-EPCS, a platinum plate (56.52 mm²) was employed here as the count electrode, which is also endowed the function of reference electrode. The large surface area of Pt plate can efficiently decrease the current density on the counter electrode. Low current density of the counter electrode is beneficial to exactly control potential on the working electrode (Janle and Cregor, 1996). This principle can be further proved by the controlled experiment. By applying the same two-EPCS device, when the counter electrode is replaced by Pt plate with a smaller area (15.42 mm²), a diminishing photocurrent response is recorded (Fig. S3 in supporting information), which implies a distinct deficiency of current stability.

![Diagram](image-url)
3.3. Detection of antioxidant capacity

Evaluation of global antioxidant capacity with photoelectrochemical technique is first developed and introduced by our group (Ma et al., 2014). In comparison with traditional methods, photoelectrochemical way shows considerable advantages including high stability, outstanding reproducibility as well as excellent anti-interference, especially for the colored analytes. Photoelectrochemical platform is proved as the efficient, prompt, convenient and cost-effective method for antioxidant capacity evaluation till now. Yet, inherent shortcomings of reference electrode significantly restrict the further application as well as development and integration of commercial instruments. To meet the industrial approval, such a reference electrode free two-EPCS is designed.

As classic antioxidants, antioxidant capacity of GA, EGCG, CA, and CT were assayed by applying this two-EPCS. As is observed in Fig. 4, it performed desirable feasibility that all these standard antioxidants demonstrate favorable linearity according to certain of concentration range. The relationships between photocurrent and concentrations of these four antioxidants are $11.10 \pm 0.02, 332.18 \pm 0.01$, $343.35 \pm 0.02$, and $555 \pm 0.01$ $\mu$mol L$^{-1}$ respectively. These excellent performances indicates that the two-EPCS exhibits sufficient availability for the antioxidant capacity assay applications. It is well known that some interference species such as amino acids, reduced sugars, organic acids, methanol, ethanol etc. commonly coexist with antioxidants in food system. In case the two-EPCS will achieve the requirement for antioxidant capacity detection of actual food samples, the anti-interference investigations should be carried out in premise. Experimentally, different interference species were added into the solution containing of 25 $\mu$mol L$^{-1}$ GA and the mixture were then introduced into the two-EPCS respectively for further detection. As shown in Fig. S4 (in Supporting information), 1000 times of L-histidine, methanol, ethanol, 500 times of L-proline, L-glycine, glucose, L-citric acid, L-malic acid and 200 times of L-threonine and fructose did not lead to distinct interference based on the two-EPCS. It is also investigated that, after keeping for 2 weeks in a desiccator under room temperature without light, such a photoelectrochemical sensor could still perform favorable stability (Fig. S5 in Supporting information) and remain at least 94.6% of the initial detection signals (Fig. S6 in Supporting information), which indicates that this photoelectrochemical platform can be reused with advisable reproducibility. These results further confirmed that the present two-EPCS should be considered as a practicable candidate for antioxidant capacity examination towards food quality evaluations.

Subsequently, practical antioxidant capacity assay of eleven brands of commercial drinking was performed on both of the traditional three-EPCS and the proposed two-EPCS as well as the F-C approach for controlled experiments (Table S1 in Supporting information). Upon data analysis, similar experimental signals and consistent response tendency have been obtained for these three methods. Samples of B1–B8 are the fruit type drinking, which show appreciable antioxidant capacity. There should be plenty of antioxidants in most of the natural fruits (Wang et al., 1996), especially blueberry (Howard et al., 2003) and grape (Jang et al., 1997). It is found that the blueberry juice (B5) and grape juice (B6) show extremely high antioxidant capacity (401.23 and 325.53 $\mu$mol L$^{-1}$, GA equivalent) among the fruit type beverages, which are well consistent with the literatures. Yet, the carbonated drinking (B9) presents lower antioxidant capacity which was found to be only 98.06 mg L$^{-1}$ (GA equivalent) due to the small antioxidant content. B10 and B11 which are marked by the manufacturer as tea drinking were observed to present the top antioxidant capacity (1352.70 and 819.77 mg L$^{-1}$, GA equivalent). These extraordinary antioxidant capacity should be ascribed to the plenty of polyphenols (Pulido et al., 2000) containing in the two drinkings. Overall, the results originated from different approaches are well agreed with each other (Table S1 in Supporting information), which can be well verified by the Paired-Samples t Test. Paired-Samples t Test performed with Origin 8.0 were then
applied to compare the results of the two-EPCS to that of the three-EPCS and F–C method. The values of \( t \) are \(-1.296 \) and \(-0.535 \) at the 95% confidence level, and the absolute value of which are less than the tabulated value of \( t \) (2.228) for \( (N-1)=10 \) degrees of freedom, which conforms that such a two-EPCS is as accurate and precise as the three-EPCS and F–C method.

The photoelectrochemical mechanism of two-EPCS is similar with that of the three-EPCS (Ma et al., 2014). When utg-C\(_3\)N\(_4\) is excited by visible light irradiation, electrons (e\(^-\)) and holes (h\(^+\)) generated, and an immediate electron transfer to the conduction band (CB) of TiO\(_2\) occurs. This is followed by the prompt arrival of the electron at the ITO substrate, leading to the generation of a photocurrent. Meanwhile, with the introduction of antioxidants (such as GA, EGCG, CA, and CT), the h\(^+\) of the utg-C\(_3\)N\(_4\) can be refilled by electrons from the antioxidants, and these occupied holes are then ready for the next excitation. This process could significantly enhance the photocurrent. Based on the above mechanism, the antioxidant capacity is detected in the two-EPCS setup.

3.4. Design of two-EPCS photoelectrochemical microfluidic chip

As discussed above, the two-EPCS should be considered as a feasible alternative for the three-EPCS, which is capable to be successfully applied as an efficient technique for antioxidant capacity assay in a certain range of potential. Since we have unloaded the burden of the reference electrode, it is much more convenient to design the microfluidic chip with two-EPCS. As shown in Fig. 5a and b, a microfluidic chip has been constructed for detection of antioxidant capacity through a simple lithography method. On such microfluidic chips, the antioxidant capacity of GA has been successfully assayed as the standard model and comparable detection concentration range and sensitivity were accomplished towards the two-EPCS (Fig. 5c). Furthermore, four of the above analyzed beverages (B2, B3, B4 and B5) were tested on such photoelectrochemical microfluidic chip. As is expected, all these four brands of drinkings show excellent signals on the microfluidic chip (Fig. 5d), whose results are well consistent with those of the two-EPCS and three-EPCS (B2: 136.07, B3: 232.43, B4: 110.36, B5: 408.52 mg L\(^{-1}\), GA equivalent). These outstanding performances of the photoelectrochemical microfluidic chip open a new field for the high-throughput analysis for antioxidant capacity in the future investigations.

3.5. Investigations of optoelectronic materials

In order to construct a general photoelectrochemical platform, several optoelectronic materials were synthesized and applied in this two-EPCS. As mentioned above, utg-C\(_3\)N\(_4\)/TiO\(_2\) composite is identified to be a suitable photocatalyst for the two-EPCS. Besides this, two kinds of other optoelectronic materials ZnO/utg-C\(_3\)N\(_4\) and CdS have also been synthesized and investigated as examples (Fig. S7 in Supporting information). The favorable photocurrent responses indicated that such a two-EPCS does not depend on the selected optoelectronic materials. It demonstrates advisable universality for considerable photoactive species, which makes itself a promising candidate of general photoelectrochemical platform constructions and practical applications.

4. Conclusions

In this work, a novel two-EPCS has been developed for detection of global antioxidant capacity without employment of the reference electrode. Particularly, the electrochemical modulation-free mode (detection at the potential of 0.0 V) greatly simplifies the analysis process, which will in result significantly facilitate the instrument integrations. Results evaluated from the standard antioxidant as well as the practical samples of commercial beverages on such a two-EPCS are well agreed with those of the traditional three-EPCS and F–C methods as comparison. Since the burden of the reference electrode has been unloaded, it is of great convenience to design a novel photoelectrochemical microfluidic chip based on the two-EPCS. During GA and commercial drinking analysis, comparable detection concentration range and sensitivity were then accomplished by applying the microfluidic chip technique. In addition, the two-EPCS is proved to be a universal platform which does not depend on selected optoelectronic materials

Fig. 5. The scheme (a) and the whole device (b) of microfluidic chip; The image of concentration vs photocurrent of GA (a) and four brands of drinking on the microfluidic chip.
but pervasive for general photocatalysts. In summary, the two-
EPCS should be considered as a feasible alternative to the three-
EPCS, which demonstrates promising prospects for miniaturiza-
tion design and development towards photoelectrochemical sen-
sing instrumentation in industrial and biomedical applications.

Acknowledgments

This work was supported by NSFC, China (21225524, 21475122,
21205112 and 21527806) and the Department of Science and
Techniques of Jilin Province (20150203002YY, 20150201001GX
and SYHZ0006) and Chinese Academy of Sciences (YZ201354,
YZ201355).

Appendix A. Supplementary information

Supplementary data associated with this article can be found in
the online version at http://dx.doi.org/10.1016/j.bios.2015.08.066.

References

9251–9258.
Jang, M.-S., Cai, E.-N., Udeani, G.-O., Slowing, K.-V., Thomas, C.-F., Beecher, C.-W.-W.,
Fong, H.-H.-S., Farnsworth, N.-R., Kinghorn, A.-D., Beecher, C.-W.-W.,
Chem. 83, 5783–5788.
146–154.
7771–7778.
Commun. 48, 5253–5255.
84, 917–923.
4974–4981.
Chem. 86, 3138–3145.