

Rapid and specific sensing of gallic acid with a photoelectrochemical platform based on polyaniline/reduced graphene oxide/TiO₂

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Experimental Section

Chemical reagents

Titanium trichloride (TiCl₃), terephthalic acid (TA), Gallic acid (GA), aniline, Ammonium persulphate ((NH₄)₂S₂O₈) was obtained from Alfa. Ascorbic acid (AA), glutathione (GSH), L-cysteine (Cys), glucose, and F-C reagent (10%) were received from Sigma-Aldrich. Natural graphite powder (320 meshes) was bought from Shanghai chemical. Aniline was distilled before use. Other reagents were used as received without purification. The PBS buffer was made from sodium phosphate (NaH₂PO₄/ Na₂HPO₄, 81:19 (molar ratio)) and sodium chloride dissolved in deionized water at final concentrations of 10 mM (pH: 7.4). Four brands of red wine were obtained from local supermarket without pretreatment before detection.

Characterization

X-ray diffraction (XRD) patterns of the samples were carried out in the range of 15-80° (2θ) using a D/MAX 2500V/PC X-ray diffraction (Cu Kα radiation, λ = 0.15406 nm), operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) was recorded with an ESCALAB-MK II 250 photoelectron spectrometer with Al Kα X-ray radiation as the X-ray source for excitation. Transmission electron microscope (TEM) and high-resolution transmission electron microscope operating (HRTEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. The UV-visible diffused reflectance spectra (DRS) were performed on the dry-pressed disk samples using a Hitachi U-3900 spectrophotometer equipped with an integrating sphere assembly, using BaSO₄ as the reference sample. Fluorescence emission spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer with an excitation wavelength of 315 nm. All electrochemical experiments were performed with a CHI660A Electrochemical Workstation (CHI) and a conventional three-electrode system, comprising a glass carbon (GCE d=3 mm), ITO or modified ITO working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode (3 M KCl) as reference electrode. All potentials were reported versus Ag/AgCl reference electrode at room temperature. The PBS solution was applied as supporting electrolyte and bubbled with N₂ for 15 min before experiment. LED light (3 W, 420 nm) was used as source of photoelectrochemical sensor. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron 1255 B Frequency Response Analyzer (Solartron Inc. UK) in mixed solution of 1 mM [Fe(CN)₆]^{3-/4-} and 0.1 M KCl aqueous solution (amplitude 10 mV, 10⁻¹ to 10⁵ Hz). Mott-Schottky plot was obtained in 0.1 M PBS (pH: 7.4) with frequencies of 1000 Hz.

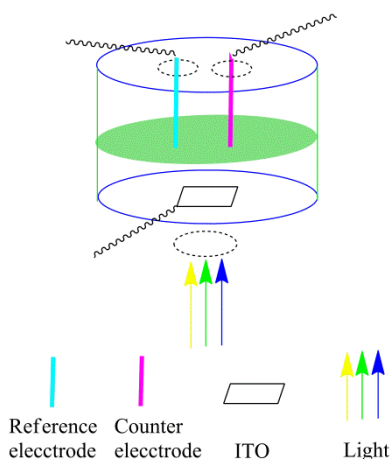
Preparation of PANI/rGO-TiO₂ and Modified ITO Electrodes

GO-TiO₂ nanoparticles were prepared by our previous method¹. 20 mg of GO-TiO₂ was dissolved in 20 ml ethanol solution (C₂H₅OH/H₂O, 2:1(v/v)) and redispersed by sonication for 0.5 h, and then the uniform solution was transferred in a Teflon-lined autoclave and heated at 120 °C for 12 h^{2,3}. The reaction solution was centrifugated and washed with ethanol and water three cycles, and finally dried at 70 °C in air for 24 h. The obtained production was denoted as rGO-TiO₂. The polyaniline was synthesized as following. 0.782 g of aniline monomer was diluted in 40 ml HCl(1 M) stirred for 30 min at -10 °C. The oxidant, (NH₄) S₂O₈ (0.478 g) was dissolved in 10 mL of aqueous HCl solution (1 M) and cooled to -10 °C. The polymerization was performed by rapid addition of the precooled oxidant solution, and the mixture was stirred for 24 h at -10 °C. An emerald flocculent precipitate was obtained and filtered and washed with a large amount of 0.1 mol/L HCl, ethanol. The product was dried at 45 °C for 24 h under vacuum. The PANI/rGO-TiO₂ was obtained through a simple method. 20 mg of was added to formic acid solutions (20 ml) PANI with the different mass ratios of rGO-TiO₂ to PANI (100:0.75, 100:1.5, 100:3, 100:6, 100:12). After continuously ultrasonicated for 3 h, the above suspension mixtures were filtered. Finally, the product was dried at 60°C under vacuum until the constant mass was reached.

After an ITO electrode had been cleaned with NaOH (1 mol L⁻¹) and H₂O₂ (30%), washed with acetone and twice-distilled water, and dried at room temperature, 20 μL of the PANI/rGO-TiO₂ suspension (1 mg mL⁻¹) was coated onto the ITO electrode and dried at room temperature to obtain an PANI/rGO-TiO₂-modified ITO electrode. A TiO₂ and rGO-TiO₂ modified ITO electrode was prepared similarly.

The process of assay on photoelectrochemical sensor

As shown in Scheme. S1, first, the sample was added into the photoelectrochemical cell. Then the light illuminated from the back of modified ITO. At last, the photoelectrochemical current was collected by computer. The red wines were added in the photoelectrochemical cell without any treatment. When the sample was assayed, the photoelectrochemical current was treated following the rule: $I = I_{\text{sample}} - I_{\text{blank}}$ (I_{sample} , the photoelectrochemical current, I_{blank} , the photoelectrochemical current without sample).



Scheme. S1 the scheme of the photoelectrochemical sensor.

F-C method was referenced by Ainsworth⁴. 100 μL of various tea diluted solution or GA solution 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 Na₂CO₃ (0.7 mol/L) was added to the above solution and the mixture was incubated at 20 °C for 2 hours. The reacted solution was detected by UV-visible spectrophotometer. The absorbance was recorded at 765nm.

Liquid chromatographic (HPLC, Waters, Acquity-H-class-Uplc) separation and detection were achieved on a Diamonsil C₁₈ column (250 mm × 4.6 mm, 5 μ m). The column and auto-sampler tray temperature were kept constant at 30 °C and 4 °C, respectively. The mobile phase consisted of methanol (A) and 0.1% acetic acid aqueous (B). The gradient program was as follows: 8 % A at 0-6 min, 8-20 % A at 6-7 min, 20-30 % A at 7-15 min, 30-80 % A at 15-27 min, 80-90 % A at 27-35 min, 8 % A at 35-40 min. The detector is ultraviolet-visible (280 nm). The injection volume was 10 μL.

Results and discussions

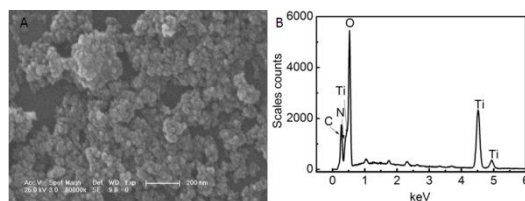


Fig. S1 SEM image of PANI/rGO-TiO₂ (A) and EDS image of PANI-rGO-TiO₂ (B).

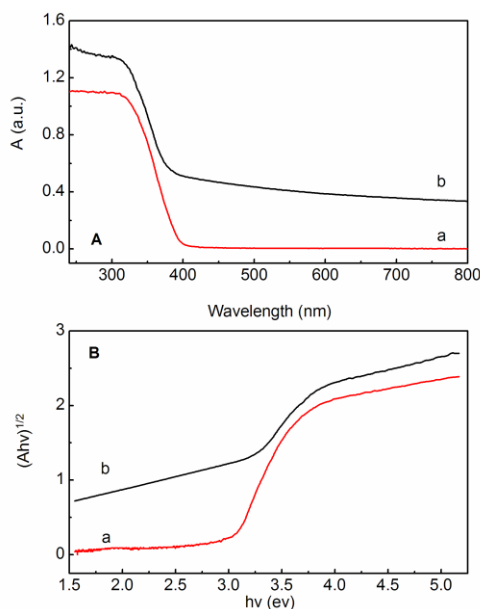


Fig. S2 (A) The UV-vis DRS of rGO-TiO₂ (a) and TiO₂ (b), (B) The plot of transformed Kubelka-Munk function versus the energy of light.

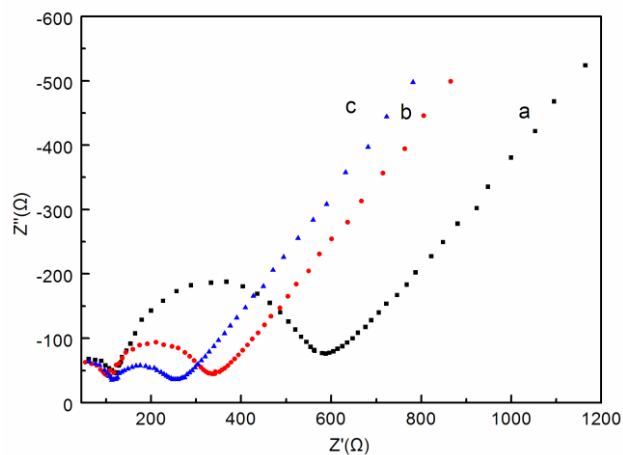


Fig. S3 EIS images of TiO₂ (a), rGO-TiO₂ (b) and PANI/rGO-TiO₂ (c) in mixed solution of 1 mM [Fe(CN)₆]^{3-/4-} and 0.1 KCl aqueous solution (amplitude 10 mV, 10⁻¹ to 10⁵ Hz).

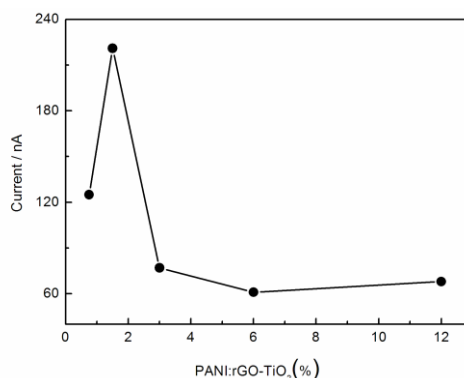


Fig. S4 Effects of mass ratio of PANI to rGO-TiO₂ on photocurrent response of PANI/rGO-TiO₂ modified ITO in 0.1 M pH 7.0 PBS containing 166.8 μM GA at 0V under 420 nm light excitation.

The increase of photocurrent should be attributed to the enhanced absorption of visible light originated from PANI. However, PANI film beyond the optimized thickness might lead to an electron transporting prevention from the LUMO of PANI to conduction band (CB) of TiO₂, and further decreasing the photocurrent response⁵. Therefore, the optimum of 1.5 % was favorable for the further study.

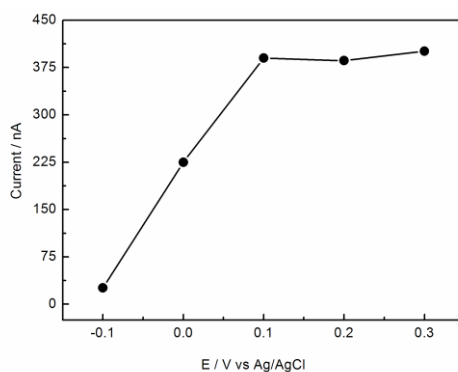


Fig. S5 Effects of applied potential on photocurrent response of PANI/rGO-TiO₂ modified ITO in 0.1 M PBS (pH: 7.4) containing 166.8 μM GA under 420nm light excitation.

As shown in Fig. S5, the photocurrent increment sharply increased as the applied potential increased from -0.1 V to 0.1 V and trended toward a maximum. The positive potential could drive electron from the CB of TiO₂ to ITO electrode, even when there was a relatively high concentration of electrons in the contact between ITO electrode and photocatalyst. The higher the applied potential, the lower the electron concentration at the contact and the larger was the gradient near it. Therefore, the photocurrent became much higher. However, when the applied potential was more than 0.1 V, the electron concentration in the contact was negligible and the photocurrent no longer depends on potential. Since the photocurrent at 0 V was 56.3 % of that at 0.3 V, it showed an acceptable sensitivity for the photoelectrochemical detection of GA. To maximum exclude the interference of other reductive species coexisting in the sample, 0 V was finally chosen for the photoelectrochemical sensor of GA.

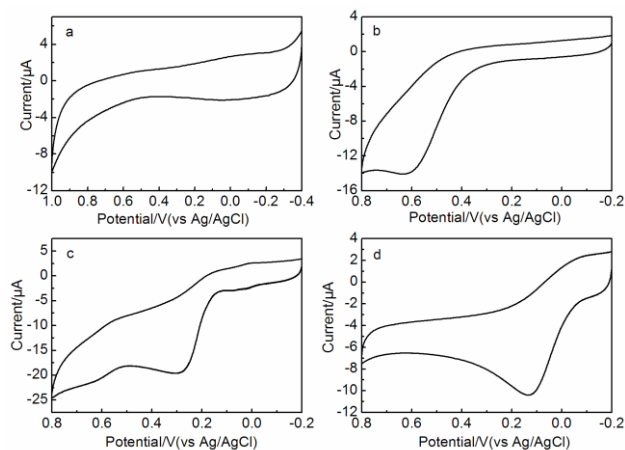


Fig. S6 The CVs 1.25 mM of GSH (a), CYs (b), GA (c) and AA (d) in 0.1 M PBS. The scan rate is 100 mV/s. Since no return cathodic peak of the four molecules, the oxidative potential was expressed by the potential halfway between $E_{p/2}$ and E_{pa} of the first peak⁶ in the present article. (E_{pa} , the potential of anodic peak; $E_{p/2}$, the half potential of anodic peak from the cathodic direction).

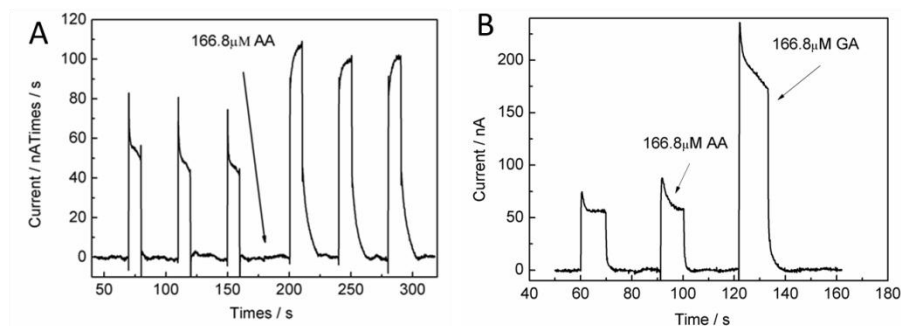


Fig.S7 The photoelectrochemical response of AA or GA on the rGO-TiO₂ (A) and PANI/rGO-TiO₂ (B) modified electrode.

(GA has the similar reductive potential with AA. Yet, GA can be selected to react with the hole of PANI, since it have an advantage of molecular structure (benzene ring and three hydroxyls). GA can easily adsorb on the PANI trough π - π interaction, which can assist the reaction between GA and the hole of PANI. As an electron-donating, Hydroxyl group makes the GA have low ionization energy, leading to low reductive potential⁷. Therefore, the PANI introduced in rGO-TiO₂ modified electrode can enhance the anti-inference of the present sensor.)

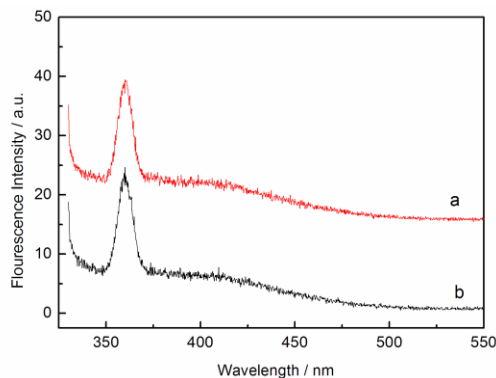


Fig. S8 Fluorescence emission of 0.5 mM terephthalic acid in PBS with light of 2 min (b) and without light (a).

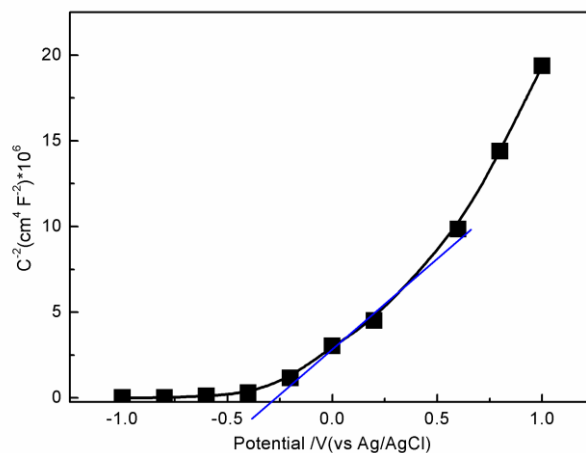


Fig. S9 Mott-Schottky plot of rGO-TiO₂ in 0.1 M PBS (pH: 7.4) with frequencies of 1000 HZ. The Mott-Schottky plot (-0.2 to 0.6V) can cross with X-axis, the intercept is the flatband potential (E_{FB}). And E_{FB} is the approximate value of LUMO.

Table S1. Detection of GA in red wine with two different methods.

Red wine	photoelectrochemical sensor	Folin-Ciocalteu method.	HPLC
Brand1	692.4±3.5	713.8±2.6	427.3 ±2.3
Brand2	1083.5 ±5.3	1244.3±3.2	769.4 ±4.5
Brand3	313.2 ±1.4	843.6 ±2.3	286.6 ±1.6
Brand4	166.7 ±1.1	663.5 ±1.8	143.9 ±0.7

All concentrations are in mg/L. Data are expressed mean of samples analyzed ± standard deviations (n=3).

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