



# Facile synthesis of flexible gold film electrodes for highly selective photoelectrochemical sensing of ascorbic acid



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## ABSTRACT

A simple electroless method for fabricating inexpensive and flexible gold film electrodes was reported. The method was established by the spontaneous adsorption of gold nanoparticle (GNP) seeds on polyethylene terephthalate (PET) film substrates and the self-catalytic growth of the adsorbed GNP seeds into conductive gold layers. The resulting gold–PET composite film electrode (GPETFE) not only possessed better flexibility and conductivity as compared with the widely used indium tin oxide (ITO) substrates, but also exhibited apparently higher conversion efficiency for photoelectrochemical (PEC) sensing. As a result, the modification of GPETFE by a hybrid photovoltaic material that comprised carboxylated multiwalled carbon nanotubes, Congo red and fullerene (MWNTCOOH–CR–C<sub>60</sub>) created a disposable and highly selective thin-film PEC sensor of ascorbic acid (AA), i.e., the PEC response of 1.0 mM AA was hardly influenced by interferents like 100 folds of dopamine (DA) and hydroquinone (H<sub>2</sub>Q). The produced PEC sensor also showed a sensitive PEC response toward AA with wide calibration ranges from 2.5 μM to 2.5 mM and a low detection limit of 0.5 μM ( $S/N = 3$ ), which was successfully applied to the detection of AA in real samples like fruits, vegetables and beverages.

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## 1. Introduction

As a newly developed analytical method, photoelectrochemical (PEC) sensing techniques have received considerable interest because of their high signal-to-noise ratio and excellent sensitivity [1–3]. The analytical performance of PEC sensors is usually affected by substrate electrodes and modified photovoltaic materials. At the early stage, metal oxides are the most extensively studied photovoltaic materials for PEC sensing. And, benefiting from the advancement of material sciences, some new photovoltaic materials or nanostructures with higher conversion efficiency are also employed, such as *p–n* heterojunction materials [4–6], carbon materials [7,8] and nanowires [9,10].

Unfortunately, contrary to the well-developed photovoltaic materials, only few works focus on the development of suitable substrate electrodes. To date, the most widely used substrate electrodes for PEC sensing are transparent and conductive indium tin oxide (ITO) [11–13] or fluorine-doped tin oxide (FTO) electrodes [14–16]. Besides, to adapt to specific applications or environments, non-transparent electrodes like glass carbon electrodes (GCE) [17,18], circular carbon electrodes [19] and screen-printed paper electrodes [20] are also

employed recently. Although these electrodes have good conductivity and PEC performance, their rigidity and poor processability bring great trouble to practical applications. Therefore, it is of great significance to develop new electrode platforms for PEC sensing that have the advantages of easy construction, good processability, high conversion efficiency and low cost.

Ascorbic acid (AA, also known as vitamin c) is a ubiquitous water-soluble micronutrient that plays a crucial role in many biological processes. AA exists in many fresh fruits, vegetables and fruit juices, and is widely used as sour agents and fortifying agents in food industry [21]. Considering the importance and wide existence of AA, the determination of AA in food samples is meaningful. Electrochemical techniques are increasingly popular analytical methods for their high sensitivity, high integration and low cost. In the past decades, many electrochemical sensors have been constructed for the detection of AA [22–24]. However, the oxidation potentials of AA, dopamine (DA), hydroquinone (H<sub>2</sub>Q) and some other phenols are close to each other, making it difficult to selectively detect AA in the presence of high concentrations of these phenols [25,26]. In the field of PEC conversion or sensing, AA is often used as an electron donor to scavenge photogenerated holes [27,28] and consequently influences photocurrents. Due to the strong oxidation capacity of the commonly used metal-based photovoltaic materials, the PEC response of AA is often influenced by phenols like DA and H<sub>2</sub>Q. Therefore, only few works report the selective detection of AA by PEC sensors [29,30].

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In this work, a simple electroless method for the scalable fabrication of disposable and flexible gold–PET films electrodes (GPETFE) for PEC sensing was reported. GPETFE was proved to possess high conductivity, excellent flexibility, good size controllability and also an apparently higher PEC conversion efficiency as compared with ITO. Very interestingly, GPETFE modified with an all-carbon photovoltaic material, i.e., the carboxylated multiwalled carbon nanotube–Congo red–fullerene nanohybrid (MWNTCOOH–CR–C<sub>60</sub>) [8], showed a very sensitive and selective PEC response toward AA, reflected by the hardly influenced photocurrent of 1.0 mM AA in the presence of 100 folds of potential interferences like DA and H<sub>2</sub>Q. This unique property, together with the excellent processability of GPETFE, established a simple but effective PEC approach to the selective detection of AA in various food samples.

## 2. Experimental

### 2.1. Chemicals

Ascorbic acid, L-cysteine, chloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O), hydroxylammonium chloride (NH<sub>2</sub>OH·HCl), trisodium citrate dehydrate (cit), sodium borohydride (NaBH<sub>4</sub>), disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O), sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O), potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>), potassium ferrocyanide (K<sub>4</sub>Fe(CN)<sub>6</sub>), potassium chloride (KCl), hydrochloric acid (HCl), acetic acid (CH<sub>3</sub>COOH), sodium acetate (CH<sub>3</sub>COONa), potassium iodide (KI), copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O), soluble starch, hydroquinone, dopamine, citric acid, tartaric acid, oxalic acid, malic acid, glucose, sucrose and Congo red (CR) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Multiwalled carbon nanotubes (MWNTs, diameter 10–20 nm, length > 50 μm) were purchased from Times Nano, Chengdu, China. Fullerene (C<sub>60</sub>) was the product of J&K Scientific Ltd., China. Projection PET films were obtained from Dongting screen factory (Wuxi, China). Nitrogen (N<sub>2</sub>, purity > 99.9%) was purchased from WISCO Oxygen, Wuhan, China. Buffer solutions including the phosphate (PBS), acetate (ABS) and HCl–KCl buffers were adjusted to suitable pH values with 1.0 M HCl or NaOH by a pH meter (PB-10, Sartorius). All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared using ultrapure deionized water (>18 MΩ cm) produced on Heal Force, Nison Instrument Ltd., Shanghai, China.

### 2.2. Apparatus

All the electrochemical measurements were performed on a CHI 830 analyzer (CH Instruments, Shanghai, China). Scanning electron microscopic (SEM) images were obtained on a Sirion 200 microscope (FEI, Holland). X-ray powder diffraction (XRD) measurements were carried out on XRD-2000X (Shimadzu, Japan). Sheet resistance was measured by a four-probe method using ST-21H, Probes Tech, Guangzhou, China. The electrode system contained a GPETFE working electrode, a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE). All the photocurrent responses were collected at open circuit potentials.

### 2.3. Fabrication of MWNTCOOH–CR–C<sub>60</sub> modified GPETFE

Procedures for fabricating GPETFE are similar to those of previously reported gold filtering membranes [31]. Briefly, a piece of PET film (1.3 cm × 7.0 cm) was washed in 10 mL mixed solvents of water and ethanol (water:ethanol = 5:1, v/v) for 5 min by sonication, rinsed with water and dried at 60 °C in vacuum. Then, the cleaned PET film was immersed in GNP seed solutions [32] for 14 h at 4 °C under darkness, and finally rinsed with copious water to remove unbounded GNPs. The seeded growth treatment was achieved by placing the PET film with adsorbed GNP seeds in the growth solution (i.e., a 8 mL

aqueous solution containing 120 μL of 1.0 wt% HAuCl<sub>4</sub> and 60 μL of 0.2 M NH<sub>2</sub>OH·HCl [32] for 20 min with gentle shaking. A gold–PET composite film was formed after certain cycles of growth process (typical seven cycles), thoroughly rinsed with water and dried at 60 °C in vacuum. The resulting gold–PET composite film was carefully cut into desired shape/size and conducted by copper wire with the aid of conductive silver glue for preparing GPETFE. The sensing area of the electrode was controlled to be a circle of 2 mm in diameter by a punched tape (Fig. 1). The PEC sensor of AA was fabricated by casting 2.0 μL of 1.0 mg/mL MWNTCOOH–CR–C<sub>60</sub> on the sensing area of GPETFE and dried under an infrared lamp. The synthesis method and detailed characterizations of MWNTCOOH–CR–C<sub>60</sub> can be found in our previous reference [8].

### 2.4. Photoelectrochemical sensing of AA

For the PEC sensing of AA at the MWNTCOOH–CR–C<sub>60</sub> modified GPETFE (MWNTCOOH–CR–C<sub>60</sub>/GPETFE), the working electrode was placing in a 10 mL acetate buffer (0.1 M, pH 4.7) containing various concentrations of AA. For the control experiments free of oxygen, the test solution was firstly degassed with N<sub>2</sub> for 30 min and then a N<sub>2</sub> atmosphere was kept over the solution during electrochemical measurements. During the PEC sensing process, a 50 mW green laser light of 525 nm was used as the light source [8].

### 2.5. Preparation and analysis of real samples

For the extraction of AA from juices and vegetables, 100 g of cleaned samples (orange or radish) and 10 mL of acetate buffer (0.1 M, pH 4.7) was added into a mortar. Then, the mixed sample was carefully ground into slurry and filtered with a filter paper. The obtained filtrate was collected in a volumetric flask and diluted with the acetate buffer to 100 mL for detection. In the case of commercial orange juice or lemon drink, the liquid sample was directly diluted with the acetate buffer before use.

## 3. Results and discussion

### 3.1. Characterizations of GPETFE

Fig. 2 shows the SEM images and XRD spectra of PET films at different stages of the seeded growth process. The naked PET film has a planar surface with plenty of irregular nanopores (Fig. 2A). Through a simple seeded growth treatment, a continuous and compact gold layer comprising GNP particles of about 100 nm is formed (Fig. 2B), producing a gold–PET composite film with good conductivity and high surface

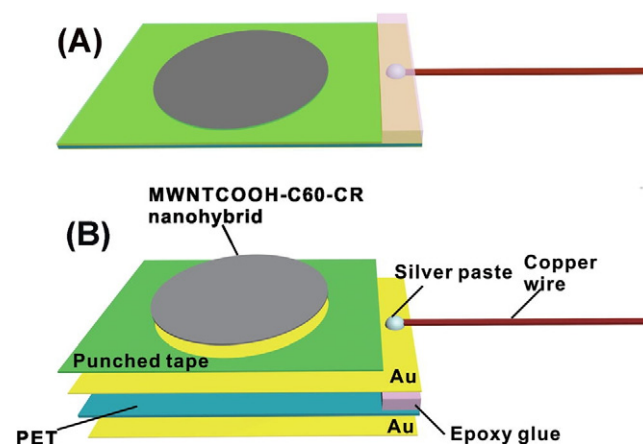


Fig. 1. Schematic representation of the integrated (A) and separated (B) structure of GPETFE modified by the MWNTCOOH–CR–C<sub>60</sub> nanohybrid.

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