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Delicate photoelectrochemical sensor for folic acid based on carbon nanohorns supported interwoven titanate nanotubes

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ABSTRACT

Herein, a signal-amplified photoelectrochemical sensing platform based on interwoven titanate nanotubes and carbon nanohorns conjugates was constructed for folic acid determination. Specifically, titanate nanotubes with reticulation structure were employed as optoelectronic element, which possessed fine photocatalytic activity and enhancement in facilitating fast and long-distance electron transport. Hierarchical-structured carbon nanohorns were introduced as the mainstay to provide as the electron-transport medium to capture and transmit electrons from excited titanate nanotubes to the sensing matrix owing to the prominent conductivity and large surface. Furthermore, the holes from valence band of stimulated titanate nanotubes could transfer to their surface and be consumed by folic acid, thus enhancing the photocurrent response. Hence, under the optimal conditions, a linear relationship between photocurrent increase and logarithm concentration of folic acid was obtained in the wide range from 1×10^{-10} to 5×10^{-5} M with a detection limit of $(2.5 \pm 0.005) \times 10^{-11}$ M. The well-designed transducer showed practical advantages, such as universality, simplicity and convenience, opening up a valuable application for other important molecules assessment.

1. Introduction

Photoelectrochemical (PEC) detection, as a newly emerging and rapidly developing analytical methodology, has received remarkable research scrutiny owing to its pronounced photocurrent response of the analyte and inexpensive photoelectric devices [1,2]. Such a detection system was based on the mechanism that photo-generated holes and electrons could transmit between semiconductor electrode and analyte under light irradiation. PEC detections have been utilized for numerous fields, such as DNA oligonucleotides, immune molecules, cells, enzyme inhibitors and small molecules assay [3]. Some undesired background signals could be reduced greatly owing to the efficient separation of the excitation source and fine detection signal, thus leading to ultra-high sensitivity [4]. Synchronously, the performance of PEC sensing is largely determined by the photoactive materials, for instance, quantum dots like cadmium sulfide (CdS) and cadmium selenide (CdSe) as well as traditional metal oxide like titania (TiO_2), cuprous oxide (Cu_2O), nihil album (ZnO) and hematite (Fe_2O_3) [5]. More especially, various TiO_2 materials, including TiO_2 nanoparticles, TiO_2 nanowire arrays, and TiO_2 nanotube arrays [6], have been widely investigated and reported as excellent photocatalysts in PEC sensing applications due to their unique structure and electronic properties. Moreover, the morphology and structure of photoelectric materials play a vital role to guarantee large surface area as well as fast transmission of charge carriers. Compared with TiO_2 NT arrays, the interwoven one-dimension (1D) titanate nanotubes (TNTs) with non-unitary linear arrays (shown in Scheme 1B(b)) possess more admirable photocatalytic activity, which was due to that the crisscrossing construction bares convenient transmission channels. Moreover, the 1D geometry facilitates long-distance and fast transport so that electrons from valence band could be segregated more promptly. Therefore, interwoven TNTs were functioned as light absorbing and charge carrier generating optoelectronic material in this platform.

Furthermore, to reinforce the electron transfer speed, various supported materials, such as metals [7], metal oxides [8] and metal-free carbon nanomaterials [9], have been applied for conductive supplement to promote the rapid photo-generated charge carriers segregation. The utilization of carbon materials is an acclaimed avenue to transfer the photo-illuminated electrons from photo-sensors to external circuit, such as grapheme and carbon nanotubes (CNTs) [10] and so on. Carbon nanohorns (CNHs) are one of the promising nanostructures which could be applied as the immobilization matrix to sensitize the photoelectric effect of photosensitive elements. Moreover, CNHs, as the metal-free carbon

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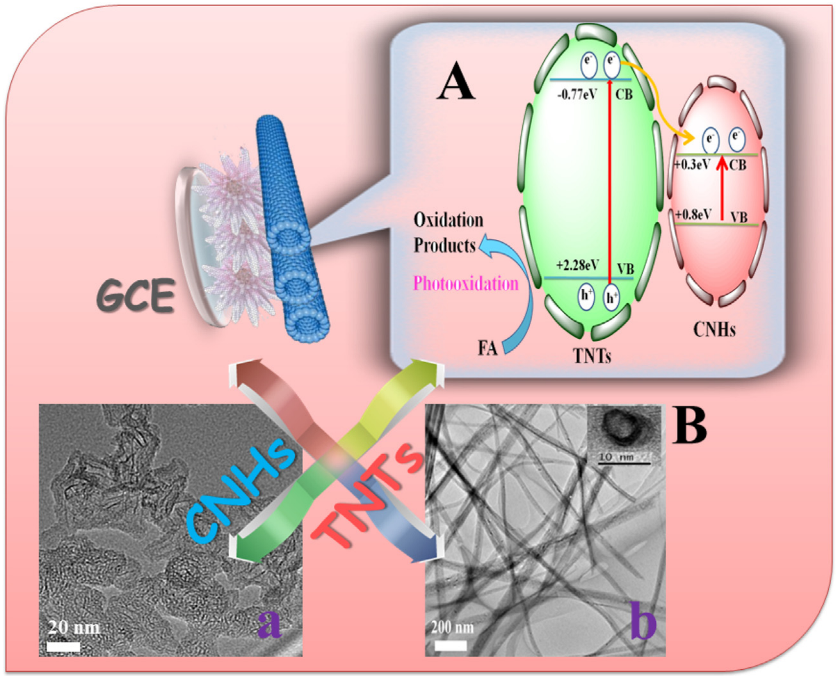

Scheme 1. (A) The mechanism illustration of the charge transfer on the TNTs/CNHs/GCE system under the light irradiation; (B) TEM images of CNHs (a), TNTs (b), and the inset is the amplified TNTs image of the open end.

nanomaterial with high purity, exhibit a high-surface-area hierarchical architecture and prominent conductivity [11,12], making it preferential for capturing electrons and suppresses electron–hole (e^-–h^+) pairs recombination because of their particular morphology. Thus, CNHs could be applied as supported matrix to improve the PEC performance of interwoven TNTs.

Dietary folic acid (FA), belongs to water-soluble B group vitamins, exists widely in most plant foods and animal, which is an admirable compound for normal human metabolic function that could prevent many diseases such as neural tube defects, heart attack, primarily anencephaly and spina bifida [13–15]. In light of this, it is of great significance to detect FA accurately to measure people whether taking appropriate quantity of FA or not on the ground that the way to obtain it is almost from daily diet or pharmaceutical tablets. Some analytical techniques have been reported for the determination of FA, such as spectrophotometry, fluorometric, chemiluminescence, high performance liquid chromatography, colorimetry and microbial methods [16–21]. These methods possess their own merits, however, at the same time exist certain shortcomings. Some of them need multistage pretreatment and the devices are expensive, additionally, the operation process is time-consuming and labor-intensive. Others have the limitations of narrow liner range and low detection limits. So far, there have been no reports for folic acid detection based on the PEC sensor.

Herein, a signal-amplified PEC sensing device with netlike TNTs and CNHs was first introduced for FA capacities assay. The concerned mechanism was proposed in Scheme 1A. Interwoven TNTs with excellent fast and long distance electron transport capability could restrain the recombination of the separated e^-–h^+ pairs so as to prompt the PEC performance. Meanwhile, the holes on the valence band of TNTs could be reacted by folic acid and then the photo-generated electrons could be more promptly arrived at the GCE substrate due to the fine conductivity of CNHs, posing a more apparent photocurrent generation. Based on this principle, a simply designed PEC sensor was established for FA determination and provided a general platform for other molecular substances evaluation in pharmaceutical and foodstuff industries.

2. Experimental

2.1. Materials and Reagents

Pharmaceutical folic acid tablets were purchased from Co., Ltd. (Beijing Silian, China) and utilized for preparation of the real samples, standard sample of the folic acid was acquired from the Aladdin Industrial Co., Ltd. (Shanghai, China). N,N-Dimethylformamide (DMF), and ethanol were obtained from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China) and used as received, potassium ferricyanide ($K_3Fe(CN)_6$), potassium chloride (KCl) were purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China), CNHs (5 mg mL^{-1}) were prepared with DMF for future use. Tetraethylammonium hydroxide (TEAOH) was obtained from Sigma and used without further purification. The phosphate buffer solution (PBS) was prepared by mixing a stock solution of 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4 to adjust the pH value. All reagents were of analytical reagent grade. TNTs were synthesized by a previously reported hydrothermal method [22]. The colloidal suspension of TNTs was prepared as follows: a suitable amount of TNT powder was dispersed in a 0.1 M HNO_3 solution under stirring and centrifugalization. The obtained deposit was further dispersed in 0.05 M TEAOH under stirring, resulting in a translucent suspension solution. The prepared suspension was diluted with ultrapure water and ultrasonicated for 5 min before using.

2.2. Apparatus

PEC measurements were performed with a homemade PEC system. Transmission electron microscopy (TEM, FEI F20 S-TWIN) and high-resolution TEM (HRTEM) analysis were performed on a JEOL-2100 transmission electron microscope. Open circuit potential–time (OCP), linear sweep voltammetry (LSV), cyclic voltammetry (CV) and amperometric *I*–*t* curves were performed on a CHI 430 electrochemical workstation (Shanghai Chenhua Instrument Co., China) with a conventional three-electrode system: Ag/AgCl electrode (sat. KCl), modified GCE (Φ = 3 mm) and a