

Functionalized TiO₂ Nanotubes as Three-Dimensional Support for Loading Au@Pd Nanoparticles: Facile Preparation and Enhanced Materials for Electrochemical Sensor

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A new composite nanostructure made of unique TiO₂-based nanotubes (TiO₂NTs) and coating 3-Aminopropyltrimethoxysilane (APTMS) anchor Au@Pd nanoparticles (Au@Pd NPs) has been demonstrated. APTMS covalent bonding of its functional silane groups onto the surface of hydrophilic TiO₂NTs crystals, meanwhile APTMS acted as a linker, which provided metal-ligand bonding and hydrogen bonding interaction with Au@Pd NPs, resulting in the formation of Au@Pd NPs/f-TiO₂NTs hybrid nanostructures. The resulting Au@Pd NPs/f-TiO₂NTs hybrid nanostructures were characterized by SEM, TEM and Nitrogen adsorption-desorption isotherms and the results suggest the existence of the uniform distribution of Au@Pd NPs on the TiO₂NTs surface with the help of APTMS. Moreover, the hybrid nanostructures were used as a promising catalyst in nonenzymatic electrochemical sensor because of its satisfactory or even enhanced electrocatalytic properties from both Au@Pd NPs and TiO₂NTs. The electrochemical results indicate that as-prepared Au@Pd NPs/f-TiO₂NTs hybrid nanostructures modified glassy carbon electrode (GCE) exhibits high electrocatalytic activity toward H₂O₂ at low potential, the detection limit for H₂O₂ were found to be 2×10⁻⁸ M (S/N=3).

Keywords: TiO₂ nanotubes, APTMS, Au@Pd NPs/f-TiO₂NTs hybrid nanostructures, Nonenzymatic electrochemical sensor, H₂O₂

1. INTRODUCTION

Ordered amine-functionalized nanomaterials have received considerable attention in recent years due to their numerous potential applications in adsorption, catalysis, separations and

biomolecules immobilization [1, 2]. Intensive ongoing research effort is devoted to the development of various aminosilanes and experimental functionalizing procedures, the goal being to grow homogeneous amine-functionalized nanomaterials, in order to further enable its widespread applications. The amino centers of aminopropylalkoxysilanes are generally used in various applications as coupling agents to immobilize different kinds of transition metal and noble metal nanoparticles on the surface of solid substrates (e.g., Si [3,4], SiO₂ and TiO₂ [5]). Researchers pointed out that these functionalized hybrid materials combined with the properties of various functional nanomaterials to achieve excellent catalytic activity and stability, which will play an important role in wider range of applications [6,7]. Base on these advantages, it is worthy to develop such multifunctional hybrid nanostructures attaching certain metal nanoparticles onto TiO₂ nanotubes.

There are some reports about the design and preparation of amine-functionalized hybrid nanostructures, especially the design of multifunctional noble metal nanoparticles (MNPs) supported on 1D nanomaterials, which have found many promising applications especially in electrochemical sensor [8,9], Li-ion batteries [10] and catalysis [11] for their unique properties. As an important family of amine-functionalized hybrid nanomaterials, functionalized TiO₂ hybrid nanostructures have been considered as a good photocatalyst or electrocatalyst candidate, because of the important optical and electronic properties, facile and environment friendly synthesis, non-toxicity and tunable size, it is useful for catalyst support, sensors, and so on [12,13]. More significantly, TiO₂ nanotubes (TiO₂NTs) with high length-to-diameter ratio, pore volume and large specific surface area that can significantly increase the number of reaction sites and can remarkably enhance the absorption of nanomaterials such as Au [14], Au-Pd [15] and AgCu [12]. More interestingly, synthesis of TiO₂NTs coaxial nanocables has attracted more attention due to TiO₂NTs as a good supporting substrate can effectively prevent MNPs from aggregation and enhance their stability, which has been proved as an effective way to combine the unique electronic and mechanical properties of the supports, with the size- and shape-dependent physicochemical properties of MNPs [16]. Recent studies have also shown that entrapping MNPs in an active matrix (TiO₂) improves the electrocatalytic activity and stability to a great extent due to the TiO₂NTs's promising structural attributes including tubular inner pores and metal oxide properties [17]. Furthermore, MNPs present on the surface of TiO₂NTs can induce additional electronic states in the band gap of TiO₂ thereby inhibiting the possibility of the recombination of the electron-hole pairs, resulting in the quicker charge transfer abilities and catalytic activity [18]. As a result, considerable efforts have been directed toward covalently or noncovalently attaching certain MNPs onto TiO₂NTs and constructing the corresponding multifunctional hybrid nanostructures [7].

With regard to MNPs were immobilized on TiO₂NTs, multimetallic nanoparticles structures are attractive materials, which exhibit better catalytic properties than their monometallic counterparts because of their composition-dependent optical, catalytic, electronic and magnetic properties [19]. It also has been reported that multimetallic nanoparticles modified electrodes have exhibited higher electrocatalytic activities for the detection of some small molecules such as methanol [20] and glucose [21] than single nanoparticles. Among the various bimetallic nanoparticles, the synergistic effects of the addition of Pd to Au in enhancing the overall catalytic activity, selectivity and stability of the catalyst [22,23]. More interestingly, unusual shape Au@Pd bimetallic nanostructures can use as an outstanding catalyst effectively increase the active sites and electrochemically active surface area, and

efficiently accelerate the electron transfer between catalyst and target molecules leading to an extraordinary electrochemical result [24, 25]. Inspired by above considerations, searching a simple and relatively inexpensive method for preparing amino-functionalized MNPs/TiO₂NTs hybrid nanostructures are of great importance in nanotechnology.

There are some reports about the design and preparation of TiO₂NTs functionalized by MNPs, which typically involve impregnation or sol-gel-based processes [26], sol technique [27], sonochemistry and light illumination [28]. Despite these successes in preparing MNPs/TiO₂ hybrid nanostructures, most of the sequential methods involve complicated procedures or rigorous conditions. In the present study, we developed a facile functionalization of TiO₂NTs (f-TiO₂NTs) by 3-aminopropyltrimethoxysilane (APTMS), aimed at the preparation of chemically modified nanotube surface capable of binding Au@Pd NPs, forming Au@Pd NPs/f-TiO₂NTs coaxial hybrid nanostructures. APTMS are widely used coupling agents for solid-based materials because of their bifunctional nature, which lies in the fact that there are many possible ways for it to interact with surface silanol/silanolate groups, via hydrogen bonds, electrostatic attractions and siloxane bonds [29]. Nucleophilicity of -NH₂ groups in aminosilanes is taken advantage of in promoting adhesion in glass-resin composites, i.e., glassy carbon electrode (GCE). Herein, APTMS react with the hydroxyl groups for self-assembling amine functionality on the surface of TiO₂NTs, forming surface-functionalized TiO₂NTs, which is negatively charged in alkaline conditions and offers a versatile solid support for oppositely charged Au@Pd nanostructures. In this modified process, constructing Au@Pd NPs/f-TiO₂NTs hybrid nanostructures using homogeneous TiO₂NTs as a spacer has obvious advantages.

Hydrogen peroxide (H₂O₂) plays a significant role in the chemical, food, environmental and pharmaceutical industries as an oxidizing, bleaching and sterilizing agent [30]. However, at high concentrations, H₂O₂ causes irritation to the eyes and skin, and affects human health [31]. Therefore, the determination of H₂O₂ is not only related to the increased awareness of the environmental hazards but the need for safer procedures [32]. Electrochemical sensing of H₂O₂ is one of the most promising approaches to monitor H₂O₂. To date, the application of Au@Pd NPs/f-TiO₂NTs coaxial hybrid nanoclusters as high-performance electrocatalysts for constructing a H₂O₂ electrochemical sensor has rarely been explored. Thus the modified electrodes based on Au@Pd NPs/f-TiO₂NTs hybrid nanostructures were detected to H₂O₂ in 0.1 M phosphate buffer solution (pH 7.4) in this literature. Moreover, the structure-activity correlations for the prepared hybrid nanocatalysts were systematically investigated by various characterizations.

2. EXPERIMENTAL

2.1. Reagents

TiO₂ powder (P25, 70% anatase and 30% rutile) was purchased from Degussa, and their primary particle diameters were in the range of 30-50 nm. K₂PdCl₄ and HAuCl₄·4H₂O were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 3-Aminopropyltrimethoxysilane (APTMS) and NaBH₄ were obtained from J&K Chemical Co. Ltd. H₂O₂ was the product of Guangzhou Chemical Reagent Company (Guangzhou, China), and a fresh solution of H₂O₂ was

prepared daily. The working solutions were prepared by diluting the stock solution with phosphate buffer solution (PBS) and water. A 0.1 M PBS consisting of KH_2PO_4 and Na_2HPO_4 was employed as the supporting electrolyte. All other chemicals used were of analytical reagent grade. Ultra-pure water was obtained with a Milli-Q plus water purification system (Millipore Co. Ltd., USA) (18 M Ω).

2.2. Characterization techniques

All the electrochemical measurements including cyclic voltammetry (CV) and chronoamperometric experiments were performed using CHI 660B electrochemical workstation (CH Instrument Company, Shanghai, China). A counter electrode (a Pt wire), reference electrode (an Ag/AgCl electrode) and a working electrode (a modified glassy carbon electrode (GCE)) formed a three-electrode compartment cell, and all experiments were carried out at room temperature. Electrocatalytic H_2O_2 reduction measurements were carried out in a 0.1 M PBS solution containing 0.5 mM H_2O_2 . Surface morphologies of the samples across the entire substrate were characterized by field-emission scanning electron microscopy (FE-SEM, Nova Nano SEM 230, FEI, USA). The UV-vis spectra (Perkin-Elmer Lambda 900 USA), High-resolution transmission electron microscope (HRTEM) image was obtained using Tecnai G2 F20 S-TWIN, 200 kV (FEI Company, USA). ξ -potential value measurement was performed on Zeta Sizer3000 Laser Particle Size and Zeta Potential Tester (Malvern Corporation, UK) with the Au@Pd NPs in aqueous solution. Nitrogen adsorption-desorption isotherms were obtained using Autosorb-1 (Quantachrome Instruments, USA), and specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using adsorption isotherms.

2.3. Preparation of Au@Pd NPs/f-TiO₂NTs hybrid nanostructures

Au@Pd NPs were prepared according to seed-mediated growth method, with Au nanoparticles as seeds and without any surfactant, where tens of small Pd nanoparticles (~3 nm) aggregated on gold seeds (~20 nm). These nanoparticles with positive charges were performed on zeta (ξ) potential analyzer, and the ξ -potential is determined to be +51.8 mV [25].

Surface hydroxyl groups seem to be necessary for the formation of the alkoxy silane molecules on the TiO₂NTs surfaces, thus TiO₂NTs was prepared by hydrothermal method [33]. Most importantly, the post-thermal treatment of TiO₂NTs avoid the elimination of surface OH group and to stabilize tube morphology [34], ensuring the methoxy groups of APTMS react with the native hydroxyl groups adorning the TiO₂NTs surface [35], forming f-TiO₂NTs, which is negatively charged in alkaline conditions (the ξ -potential was determined to be -17.6 mV (Fig.1), as a result of the hydrolyzation of APTMS and offers versatile solid supports for Au@Pd nanostructures. In brief, 0.05 g TiO₂NTs and 20 mL ethanol were placed in a beaker equipped with magnetic stirring bars. In the second step, 200 μL of APTMS was added to the above solution, followed by the addition of 2 mL of water and 2 mL of ammonia. In the third step, the resulting solution was stirred for more than 12 h and then centrifuged to remove the excess APTMS and further washed with ethanol and water for three times, respectively. Finally, the collected white precipitation was dissolved into 10 mL of water. It is crucial to preparation

of hybrid nanostructures with large-area high-quality while maintaining superior electrocatalytic activity and stability. Here, Au@Pd NPs/f-TiO₂NTs hybrid nanostructures were synthesized by adding excess Au@Pd NPs (5 mL) to 0.5 mL of f-TiO₂NTs, and then sonicated for 30 min. During the sonication process, f-TiO₂NTs with more anchors can facilitate uniform dispersion of Au@Pd NPs. Finally, the hybrid nanostructures were centrifuged and washed 2-3 times with distilled water, and the purified Au@Pd NPs/f-TiO₂NTs nanostructures were dispersed in 2 mL of water, which formed a gray, stable and homogeneous suspension that could stay stable for at least 1 month [36].

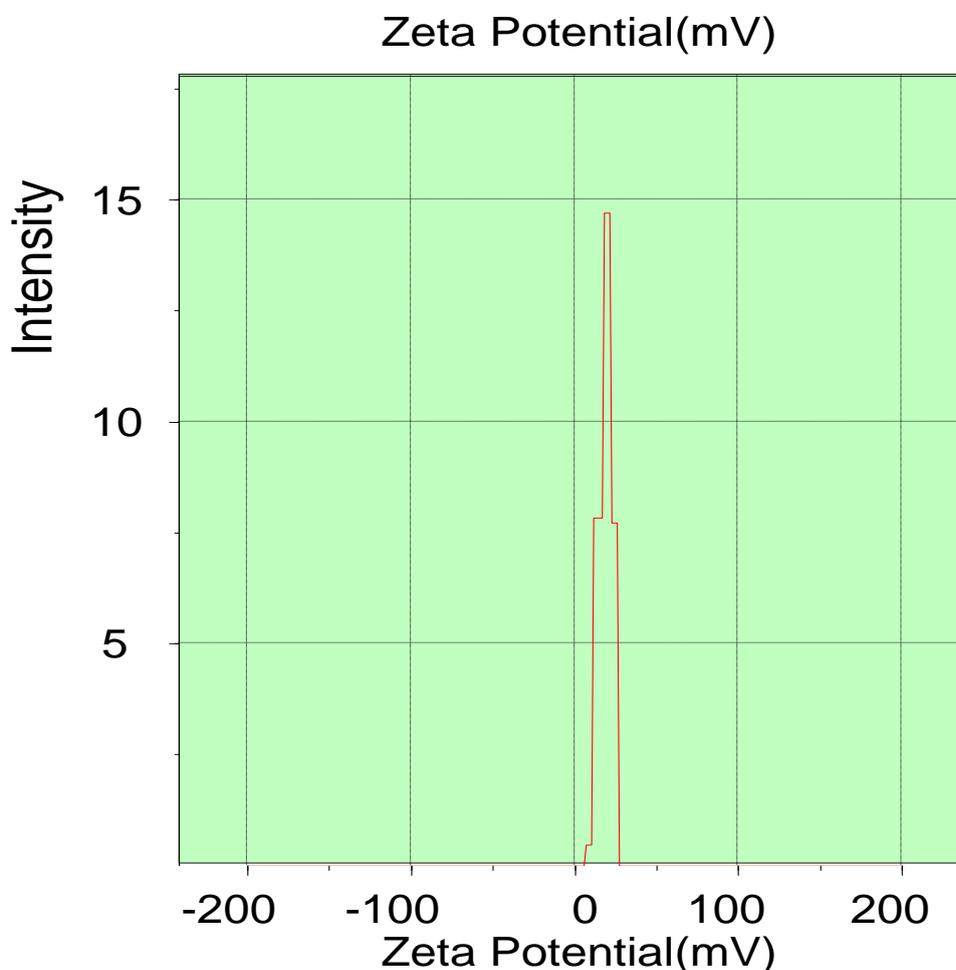


Figure 1. The ξ -potential of f-TiO₂ NTs in the neutral media solution.

2.4. Preparation of the electrochemical sensor

Prior to preparation of electrochemical sensor, the clean GCE was polished to mirror smooth with alumina (under 0.3 and 0.05 μm diameter) slurries, and subsequently washed by water and ultrasonicated in distilled water and ethanol bath. Finally, the electrode was dried under pure N₂. The modified electrode was loaded with Au@Pd NPs/f-TiO₂NTs hybrid nanostructures (10 μL) and dried under an infrared lamp. Thus a uniform film coated electrode (Au@Pd NPs/f-TiO₂NTs/GCE) was obtained. The other modified electrodes as were fabricated through similar method.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Characterization

Obviously, APTMS played a crucial role in the formation of Au@Pd NPs/f-TiO₂NTs hybrid nanocomposites, the accessibility of the amine functional groups in TiO₂NTs and offers a versatile solid support for Au@Pd nanostructures was investigated by UV-vis spectra in Fig.2. UV-vis spectrum of f-TiO₂NTs shows one absorption band around ~290 nm, which exhibited a blue shift compared with not functionalized TiO₂NTs (Fig.2(a)), indicating the methoxy groups of APTMS reacted with the native hydroxyl groups adorning the TiO₂NTs surface. It can be observed that a very pronounced gold characteristic peak at 510 nm is obtained while f-TiO₂NTs support for Au nanoparticles (Fig.2(b)). Nevertheless, while tens of small Pd nanoparticles were aggregated on gold seeds, the intensity of the surface plasmon resonance peak of gold fades away (Fig.2(c)). Unlike the absorption characteristics of Au nanoparticles, Pd nanoparticles show a rather broad and strong absorption in the 200-800 nm region, which gradually increases toward the blue [37].

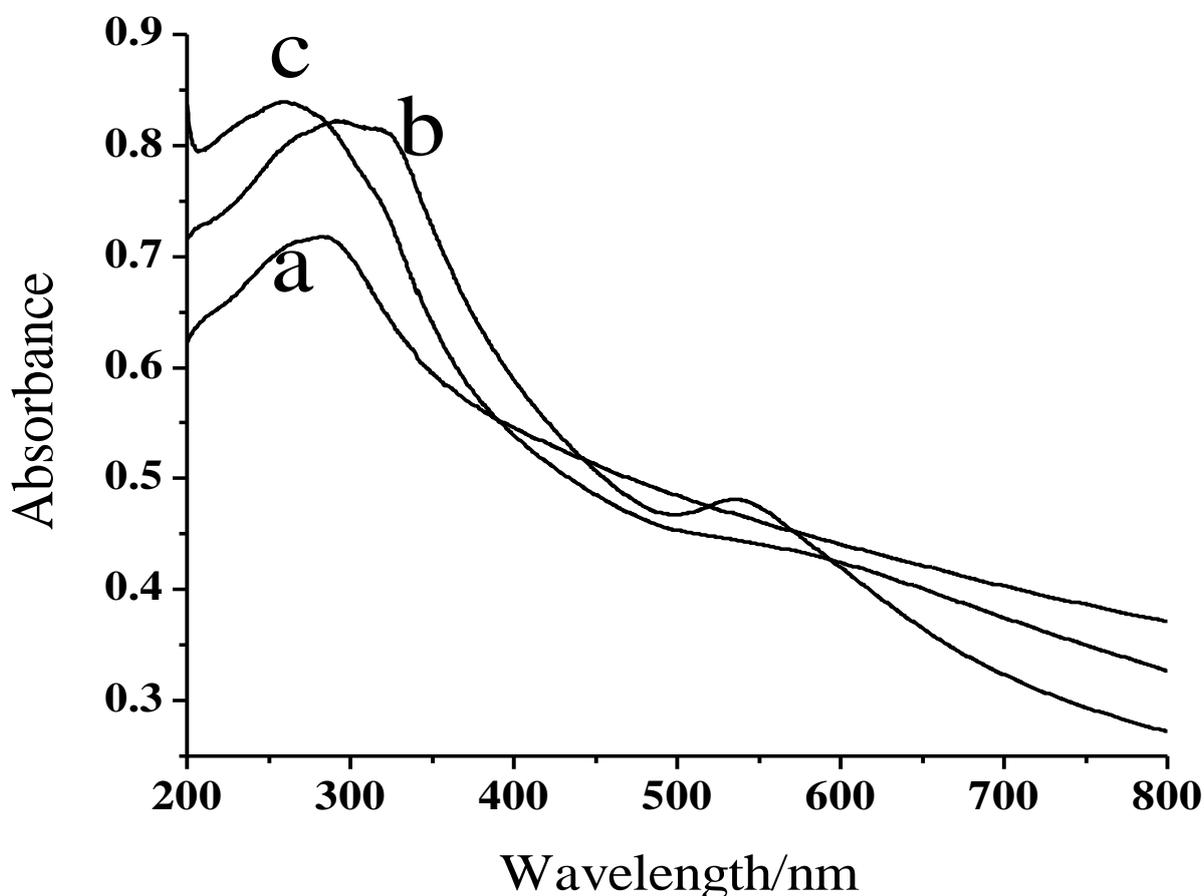


Figure 2. UV-vis spectrum of f-TiO₂NTs (a), f-TiO₂NTs-Au (b) and Au@Pd NPs/f-TiO₂NTs hybrid nanostructures (c).

SEM images of TiO₂NTs (Fig. 3) demonstrated that TiO₂NTs have a length range of 2~3 μm with a diameter of 30~50 nm and become crystalline upon annealing, and that the TiO₂NTs were

loosely tangled together. The large number of cavities which appeared on the surface of the TiO₂NTs confirmed their porous characteristic, consistent with the results of BET analysis shown below.

The HRTEM technique was applied to observe the deep nanostructure inside TiO₂NTs. Fig. 4 a, b shows typical HRTEM images of the as-made TiO₂NTs at different magnifications. In Fig. 4a, a great number of 1D open-ended TiO₂NTs possessed long tubular structure with a wall thickness of about 2-3 nm and uniform inner diameters of about 25 nm could be observed. Due to the incomplete growth of the nanotubes, a small number of shorter TiO₂NTs was obtained. Interesting, the TiO₂NTs were open-ended, which can be observed more clearly in Fig. 4b, the formation mechanism is trititanate (Ti₃O₇)₂-sheets may grow within the intermediate phase, caused by the reaction between NaOH and TiO₂ nanoparticles [38]. The nanosheets grow with an increasing tendency of curling, leading to the formation of nanotubes with open-ended. The as-obtained TiO₂NTs arrays possess a larger surface area and one-dimensional channel, which can provide a higher number of accessible surface sites and a more rapid electron transportation resulting in superior electrochemical performance to H₂O₂ reduction.

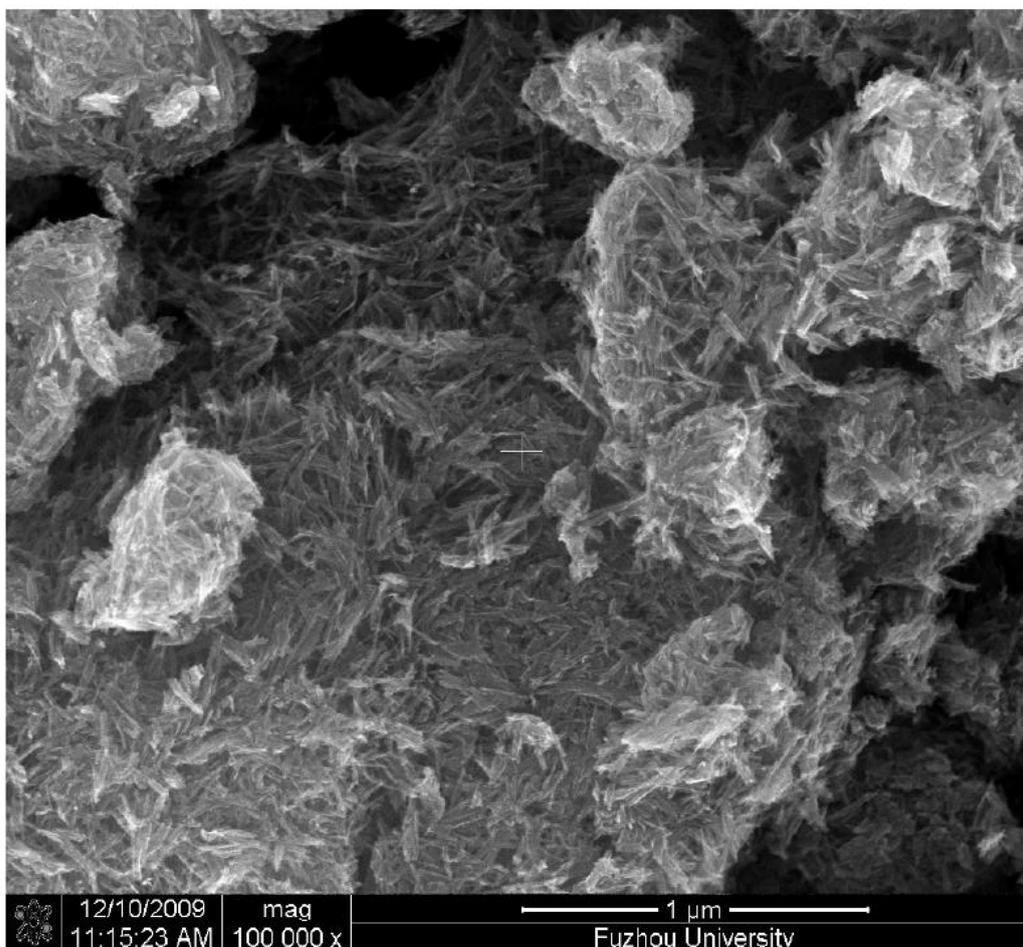


Figure 3. SEM images of TiO₂ nanotubes were prepared by hydrothermal method.

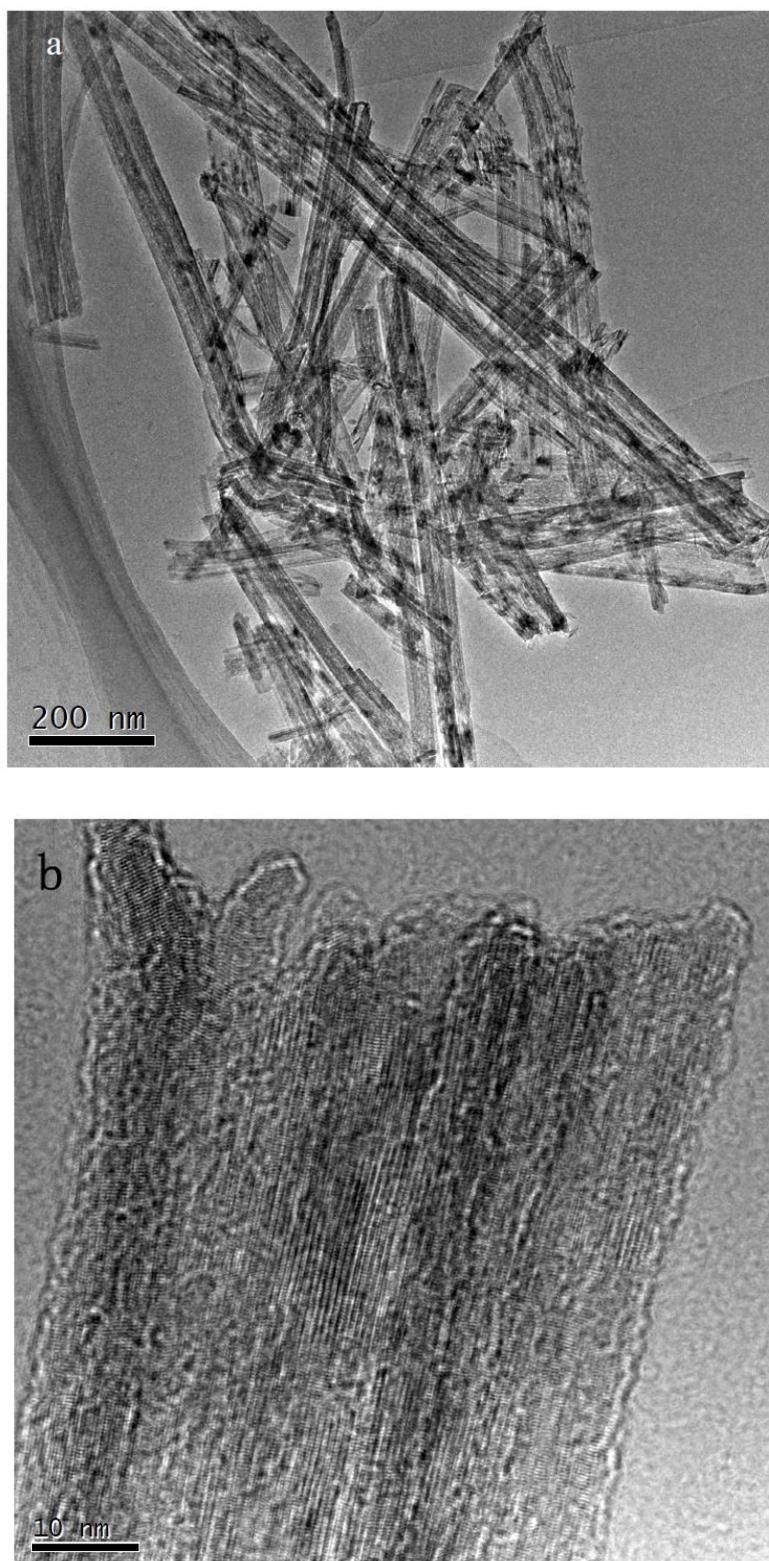
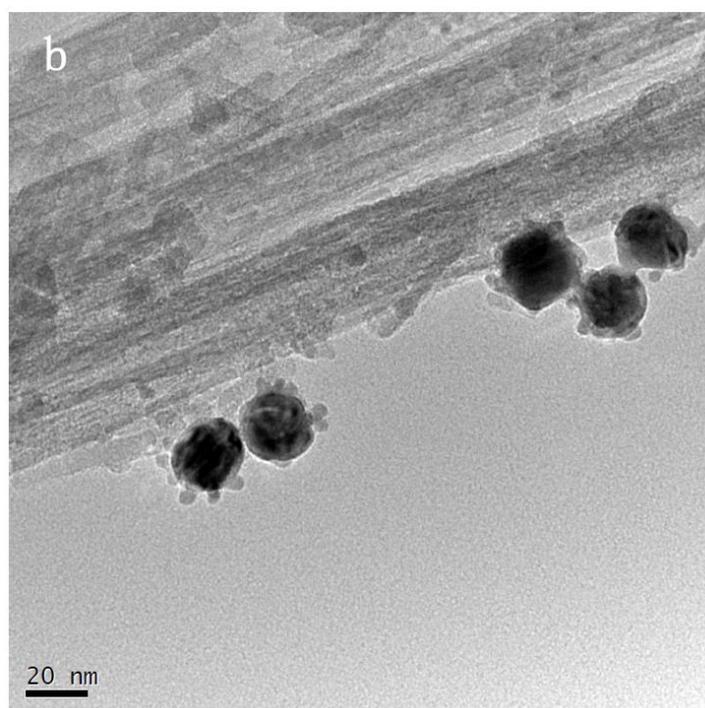
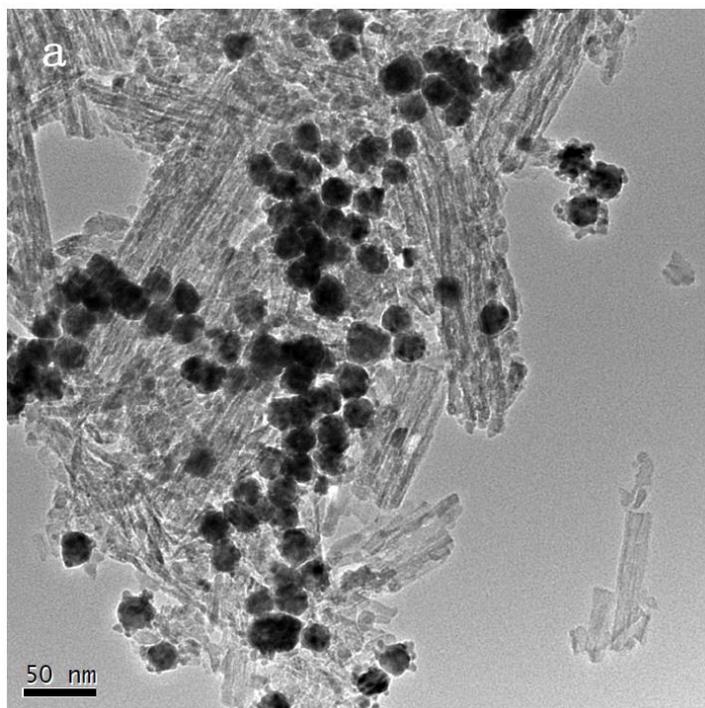


Figure 4. HRTEM image of TiO₂ nanotubes (a), open-ended TiO₂ nanotubes (b).

It is interesting to note that after functionalization with a -NH₂ group, f-TiO₂NTs coaxial nanotubes could easily adsorb Au@Pd NPs. Fig. 5 shows the typical as-prepared structures composed of tubular amine-functionalized TiO₂NTs and Au@Pd NPs, indicating that the Au@Pd NPs with sizes

of about ~25 nm had been completely anchor on f-TiO₂NTs. Moreover, compared with TiO₂NTs (Fig. 4), the f-TiO₂NTs have a rougher surface due to APTMS. A high-magnification image (Fig. 5b) shows that very homogeneous APTMS layers are coated on the surface of the TiO₂NTs, and Au@Pd NPs anchor on TiO₂NTs through -NH₂ groups of APTMS.

A contrast difference in Au@Pd NPs with a darker center surrounded by a lighter edge is observed, confirming their core/shell structure.



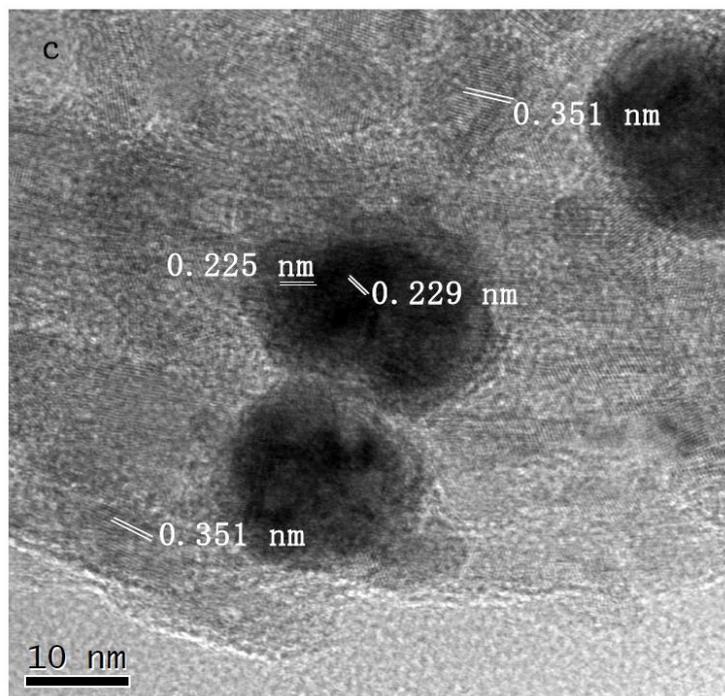


Figure 5. (a) TEM images of the Au@Pd NPs/f-TiO₂NTs hybrid nanostructures. (b) An augmentation of Au@Pd NPs/f-TiO₂NTs hybrid nanostructures. (c) HRTEM image displaying the lattice fringes of the Au@Pd NPs/f-TiO₂NTs hybrid nanostructures.

An Au@Pd crystal phase appeared and showed good crystallinity in Fig. 5c, the inner core (Au) and external flower layer (Pd) have values of lattice spacing of 0.235 and 0.225 nm in Au@Pd NPs, corresponding to the mean value of the (111) planes of face-centered cubic (fcc) Au and Pd, respectively. The lattice spacing of 0.351 nm is assigned to (101) plane of anatase TiO₂NTs. Because of the -NH₂ groups of APTMS anchor Au@Pd NPs with hydrogen bonds and metal-ligand coordination bonds, and the methoxy groups are available for the covalent linkage with abundant -OH groups from the surfaces of the TiO₂NTs, there coaxial hybrid nanostructures can shorten the electronic transmission distance from the analyte to the surface of the modified electrode, thus enhancing significantly electrocatalytic active of the hybrid nanocatalysts.

TiO₂ nanoparticles (P25), TiO₂NTs and Au@Pd NPs/f-TiO₂NTs hybrid nanostructures were characterized by N₂ adsorption-desorption at -195 °C, as shown in Fig. 6. The N₂ adsorption-desorption isotherm of TiO₂NTs and Au@Pd NPs/f-TiO₂NTs hybrid nanostructures presented a type IV isotherm according to the IUPAC classification, displaying the porous characteristics of nanotubes. An adsorption-desorption hysteresis loop was observed at $P/P_0 \approx 0.58$, indicating capillary condensation inside the mesoporous TiO₂NTs, which was in agreement with the TEM results. Due to excellent biocompatibility, ion-changeable ability, special geometry (porous structure) and high ratio of surface to volume, TiO₂NTs can be used as an excellent carrier for quantitative loading of Au@Pd NPs to amplify the electrical catalytic signal, which leads to highly sensitive nonenzymatic sensor. After Au@Pd NPs were anchored to the surface of f-TiO₂NTs, the BET surface area reduced from 184.9 to 160.6 m²/g, which is due to the f-TiO₂NTs appear some aggregation after functionalization with APTMS. Correspondingly, the BET surface area of the raw material (P25) is only 53 m²/g,

indicating that TiO₂NTs with high surface area and adsorption ability, providing favorable condition to support Au@Pd NPs.

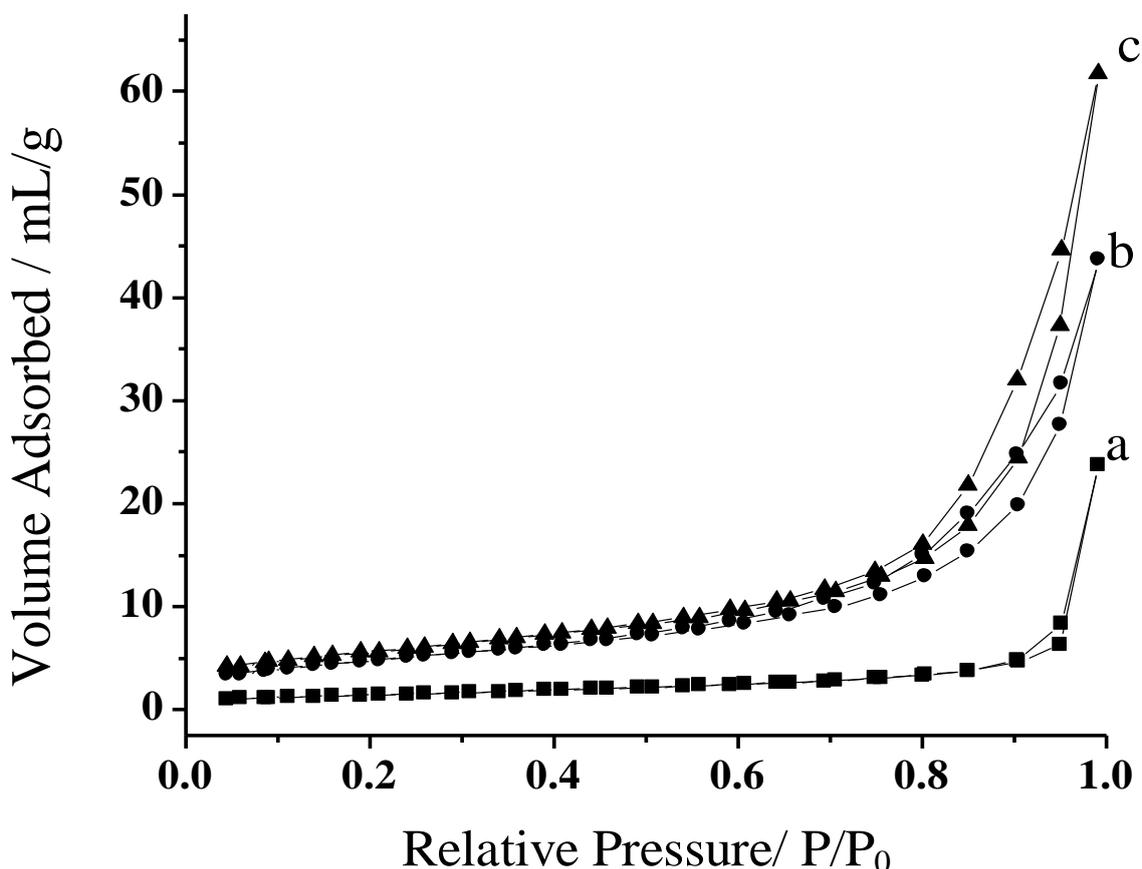


Figure 6. Isotherm of nitrogen adsorption-desorption at $-195\text{ }^{\circ}\text{C}$ on the surface of TiO₂ nanoparticles (P25) (a), TiO₂NTs (b) and Au@Pd NPs/f-TiO₂NTs hybrid nanostructures (c).

3.2. Detection of Hydrogen Peroxide

The reliable, accurate and rapid determination of H₂O₂ is practical important, and the present Au@Pd NPs/f-TiO₂NTs/GCE provides a good opportunity to build a highly sensitive H₂O₂ electrochemical sensor. Fig. 7 shows the CVs of bare GCE (line a) and GCEs modified by f-TiO₂NTs (line b) and Au@Pd NPs/f-TiO₂NTs nanocomposites (lines c) in presence of 0.5 mM H₂O₂ in 0.1 M PBS (pH 7.0). It was observed that the Au@Pd NPs/f-TiO₂NTs/GCE exhibits strong reduction current starting at around 0.25 V, and an obvious peak current (115 μA) occurs at 0.0 V while no reduction peaks of H₂O₂ were observed at the bare GCE and f-TiO₂NTs/GCE (line b), indicating that the Au@Pd NPs/f-TiO₂NTs nanocomposites modified electrode showed well electrocatalytic activity toward H₂O₂ reduction. In inset of Fig. 7, CVs measured using the Au@Pd NPs/f-TiO₂NTs/GCE in the absence (d) and presence (c) of 0.5 mM H₂O₂. These results indicate that Au@Pd NPs can effectively choose and catalyze H₂O₂ reduction on the electrode surface.

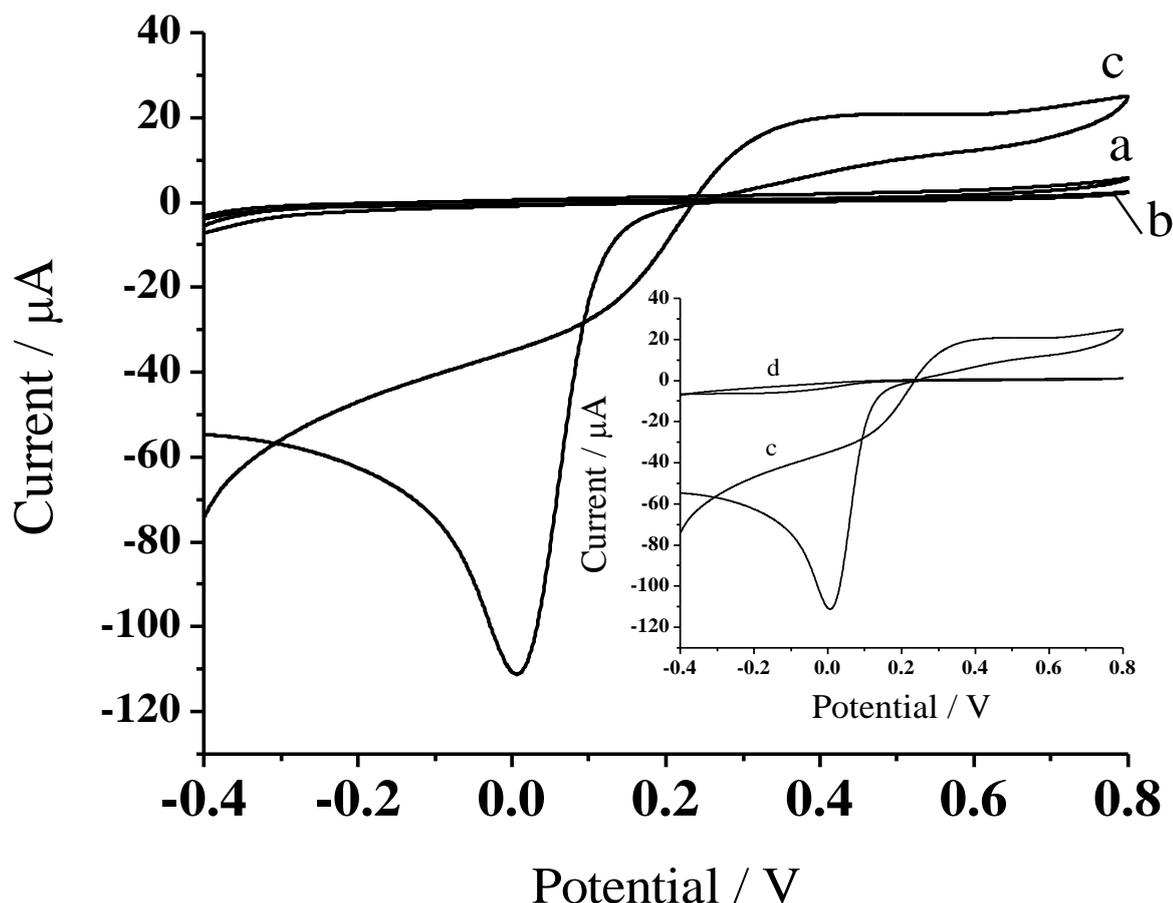


Figure 7. CVs obtained for the bare GCE (a) f-TiO₂NTs/GCE (b) and Au@Pd NPs/f-TiO₂NTs/GCE (c), immersed in 0.1 M 20 mL PBS (pH 7.4) containing 0.5 mM H₂O₂ at the scan rate of 50 mV s⁻¹. The inset is CVs of the Au@Pd NPs/f-TiO₂NTs/GCE in the absence (d) and presence (c) of 0.5 mM H₂O₂, the scan rate at 50 mV s⁻¹.

To investigate the reaction kinetics and the fast electron-transfer properties of the Au@Pd NPs/f-TiO₂NTs hybrid nanocatalysts, the effect of scan rate on the reduction of H₂O₂ at the Au@Pd NPs/f-TiO₂NTs/GCE is shown in Fig. 8. As shown in Fig. 8, when the scan rates increase from 20 to 160 mV/s, the cathodic peak currents increase and the regression equation is $I_p = -33.675 - 5.646 \times v^{1/2}$ with $R^2 = 0.998$. The peak currents increase linearly with the square root of the scan rate in the range of 20-160 mV/s, indicating that it was a diffusion controlled process.

To reveal the electrocatalytic activity of Au@Pd NPs/f-TiO₂NTs nanocomposites toward the reduction of H₂O₂, the amperometric behavior of H₂O₂ was investigated at Au@Pd NPs/f-TiO₂NTs/GCE. Fig. 9 shows the *i-t* curve recorded at the Au@Pd NPs/f-TiO₂NTs/GCE polarized at 0.0 V in 0.1 M stirring N₂-saturated PBS (pH 7.4), where a H₂O₂ stock solution was added. The low potential 0.0 V was chosen according to the results from Fig. 7, thus the risks of the electroactive interferences could be avoided. Upon addition of H₂O₂, the sensor responded rapidly to the substrate and achieved the steady-state current, indicating a fast amperometric response to the reduction of H₂O₂. The sensor had a linear relationship with the concentration of H₂O₂ from 1×10⁻⁷ to 5×10⁻⁴ M with a correlation coefficient of 0.996, and the detection limit was found to be 2×10⁻⁸ M (S/N=3). The

sensing performance between our present work and others regarding the performance of H₂O₂ assays is presented in Table 1. With a wider linear response range, a relatively lower limit of detection and applied potential for H₂O₂, as-prepared Au@Pd NPs/f-TiO₂NTs hybrid nanostructures can even be compared advantageously with respect to most others nonenzymatic H₂O₂ sensors [30,39-43].

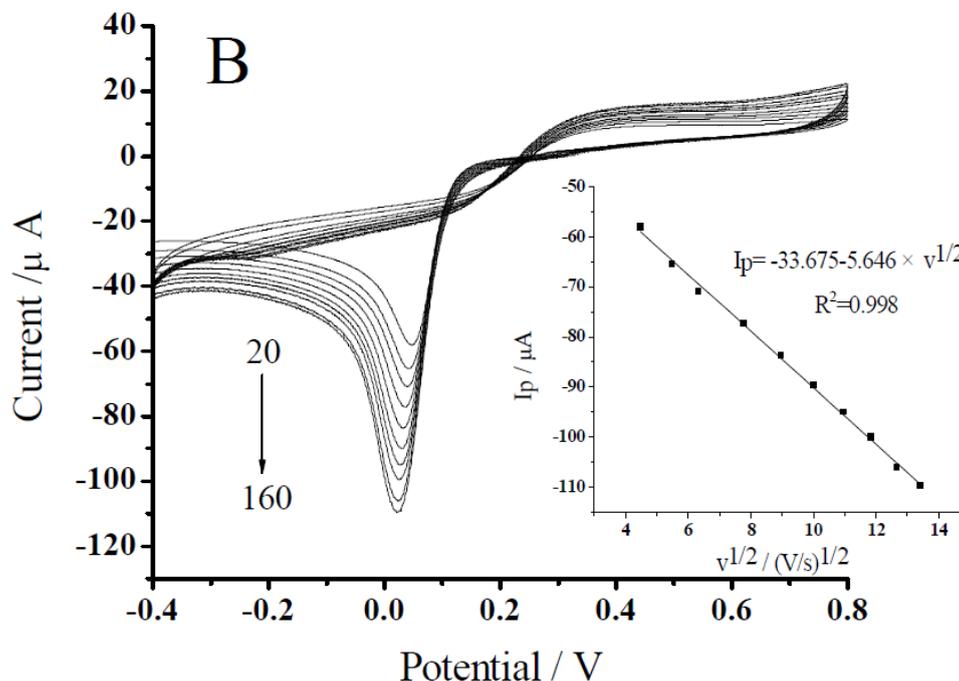


Figure 8. CVs of H₂O₂ reduction at the Au@Pd NPs/f-TiO₂NTs/GCE in 0.1 M 20 mL PBS (pH 7.4) containing 0.5 mM H₂O₂ at different scan rates (from top to bottom: 20, 30, 40, 60, 80, 100, 120, 140 and 160 mV/s). The inset is the relationship between the reduction peak current (I_p) and the scan rate (V/s).

Table 1. A comparison of this work with literature works regarding the performance of the H₂O₂ assays.

Electrode material	Detection limit (µM)	Linear range	Sensitivity (µA mM ⁻¹ cm ⁻²)	Applied potential (V)	Refs.
PtW/MoS ₂ /GCE	0.005	1.00 µM–0.20 mM	171.00	–0.25	[30]
AgNP–TiO ₂ NWs/GCE	1.70	0.10 mM–60.00 mM	—	–0.30	[39]
PB–TiO ₂ composite film/GCE	1.50	—	1726.8	–0.05	[40]
Au–Pd/MoS ₂ /GCE	0.16	0.80 µM–10.00 mM	184.90	—	[41]
AuPd /C/GCE	8.40	—	195.30	0.25	[42]
Pt-IL-pGR/GCE	0.42	10.00µM–4.00 mM	942.15	0.074	[43]

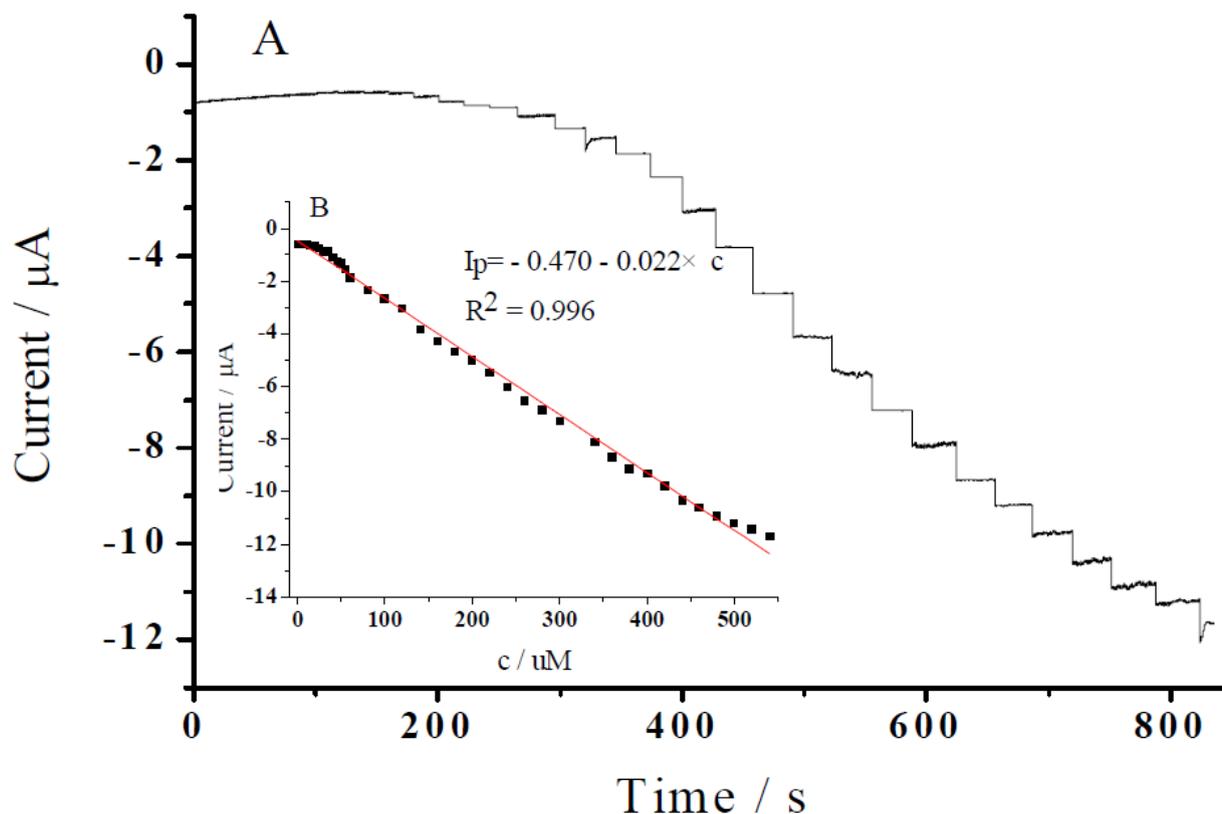


Figure 9. (A) Amperometric current response of the Au@Pd NPs/f-TiO₂NTs/GCE on successive injection of H₂O₂ into stirring N₂-saturated PBS (pH 7.4) at an applied potential of 0.0 V. (B) Calibration curve for H₂O₂ concentration from 1×10⁻⁷ to 5×10⁻⁴ M.

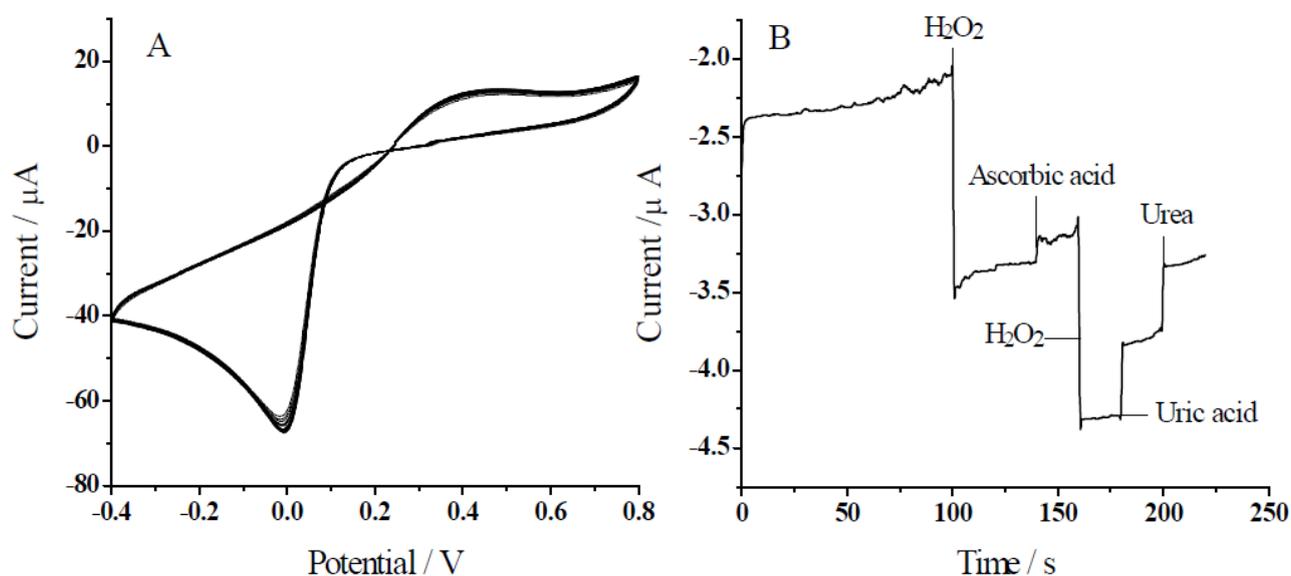


Figure 10. (A) CVs of H₂O₂ reduction at the Au@Pd NPs/f-TiO₂NTs/GCE in 0.1 M 20 mL PBS (pH 7.4) containing 0.5 mM H₂O₂ for 20 consecutive cycles. (B) Amperometric responses of Au@Pd NPs/f-TiO₂NTs/GCE upon subsequent additions of 0.05 mM H₂O₂, 0.5 mM AA, 0.05 mM H₂O₂, 0.5 mM UA and 0.5 mM Urea at 0.0 V.

To testify the reproducibility and stability of as-prepared Au@Pd NPs/f-TiO₂NTs/GCE sensor, five Au@Pd NPs/f-TiO₂NTs/GCEs were investigated in 0.5 mM H₂O₂ at a scan rate of 50 mV/s. The relative standard deviation (R.S.D.) was 3.6%, confirming that the preparation method was highly reproducible. Stability of the modified electrode was tested by scanning the electrode continuously in 0.5 mM H₂O₂, and it was found that there was no apparent decrease in the current response for 20 consecutive cycles (Fig. 10A), which indicates that the fabricated Au@Pd NPs/f-TiO₂NTs/GCE sensor had excellent stability. The selectivity of the f-TiO₂NTs-Au@Pd/GCE for the detection of H₂O₂ was also evaluated. Fig. 10B shows the current responses of 0.05 mM H₂O₂, 0.5 mM AA, 0.05 mM H₂O₂, 0.5 mM UA and 0.5 mM Urea on the Au@Pd NPs/f-TiO₂NTs/GCE at 0.0 V. As seen, the current responses of AA, UA and Urea observed were much smaller than those of H₂O₂, indicating that the Au@Pd NPs/f-TiO₂NTs/GCE has excellent selectivity for the detection of H₂O₂.

In order to evaluate the applicability of the proposed electrode, human blood serum sample was selected as real sample and detected with the optimal experimental procedure. In a typical procedure, the human serum was diluted 100 times with 0.10 M pH 7.4 PBS to fit the linear range of the proposed method and also reduce the matrix effect. In addition, to ascertain the correctness of the results, amperometric response was recorded after each addition of the standard H₂O₂ solution at 0.0 V, the recovery was 95.96-106.21%. These results indicate that the prepared sensor is suitable for H₂O₂ determination in real samples with a sufficient precision.

4. CONCLUSIONS

In summary, a novel hybrid nanostructure with enhanced electrocatalytic performances was prepared by simple surface-modified method. Hybrid nanostructure was fabricated with assistance of APTMS, which acted as a linker. It was found that the as-prepared f-TiO₂NTs is negatively charged in alkaline conditions as a result of the hydrolyzation of APTMS and offer versatile solid supports for Au@Pd NPs with opposite charge. The formation mechanism of such a composite nanostructure has been proposed, i.e., the -NH₂ groups of APTMS anchor to Au@Pd NPs with hydrogen bonds and metal-ligand coordination bonds, and the methoxy groups are available for the covalent linkage with abundant -OH groups from the surfaces of TiO₂NTs. It is found that the fabricated non-enzymatic electrochemical sensor exhibited high electrocatalytic activity toward H₂O₂ at low potential. The detection limit for H₂O₂ is 2×10^{-8} M, which was lower than certain enzyme-based biosensors. Most importantly, this electrochemical sensor has high sensitivity for H₂O₂, and applied successfully to selective determination of H₂O₂ in real sample with satisfactory recovery range.

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