Electrochemical determination of hydrogen peroxide at a glassy carbon electrode modified with palladium nanoparticles

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Abstract: Herein the modifications of a glassy carbon electrode (GCE) with palladium nanoparticles and a palladium film are reported. The response to hydrogen peroxide on the modified electrode was examined using cyclic voltammetry and amperometry (at –0.2 V *vs.* Ag/AgCl reference electrode in the phosphate buffer solution, pH 7.4). The palladium film and palladium nanoparticle-modified GCE showed a linear response to hydrogen peroxide in the concentration range 10 μM to 14 mM and 1 μM to 14 mM with detection limit of 6.79 and 0.33 μM, respectively.

Keywords: palladium; nanoparticles; hydrogen peroxide; glassy carbon electrode.

INTRODUCTION

Nanotechnology has recently become one of the most exciting forefront fields in analytical chemistry.[1–3] A wide variety of nanomaterials, especially nanoparticles (NPs) with different properties, have found broad application in many kinds of analytical methods.[1–3] Accordingly, electrode development has concentrated more on surface modification of electrodes with nanotubes or nanoparticles.[2,3] Nanoelectrochemistry plays a significant role in the fabrication of various nanomaterials and devices for detecting molecules at very low concentrations.

Electrochemical deposition approaches are often reported as the methods of choice for simple and low cost nanostructuring and nanopatterning of electrode surfaces.[4] The fabrication of metal NPs modified electrodes by electrochemical techniques is advantageous because it is a single-step process involving reduction of the metal salt at an applied potential, which is a convenient, fast and low-cost method.[5–7]

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The introduction of NPs with catalytic properties into electrochemical sensors and biosensors can decrease overpotentials[8] of many analytically important electrochemical reactions, and even realize the reversibility[8] of some redox reactions that are irreversible at common unmodified electrodes. For instance, a sensitive NO microsensor was developed through the modification of a platinum microelectrode with gold NPs in which the gold NPs catalyzed the electrochemical oxidation of NO with an overpotential decrease of about 250 mV.[9]

Palladium is a well-known catalyst for many reactions, such as the electrocatalytic oxidation of hydrazine[10] and formaldehyde,[11,12] hydrogenation of unsaturated hydrocarbons,[13–15] for the reduction of oxygen,[16] the oxidation of alcohols,[17,18] the oxidation of hydrogen to hydrogen peroxide,[19] and is routinely used in the automobile industry in catalytic converters to reduce the amounts of nitrogen oxides, carbon monoxide, unburned hydrocarbons.[20]

Hydrogen peroxide has wide applications in environmental, pharmaceutical, clinical, and industrial research. It is also a by-product of reactions catalyzed by a large number of oxidase enzymes. Therefore, the detection of hydrogen peroxide is important in biomedical and environmental applications.[21]

Glassy carbon electrode (GCE) is a useful electrode material because of its high electrical conductivity, impermeability to gases, high chemical resistance, reasonable mechanical and dimensional stability and widest potential range of all carbonaceous electrodes.[22] Many attempts have been made to improve the electrochemical properties of glassy carbon electrodes by chemical modifications, such as the addition of a variety of molecular catalysts and mediators to the electrode surface by adsorption, covalent bonding of electroactive catalysts, and entrapment of metals within an affixed polymer film and vapour or electro-deposition of metals directly onto the electrode.[22] It is also known that a GCE is a convenient material for surface modification with metals, *e.g.*, mercury[23] and bismuth.[24]

EXPERIMENTAL

Chemicals

Palladium dichloride ($PdCl_2$, 99.9 %, Aldrich), sodium perchlorate ($NaClO_4$, 98 %, Sigma), potassium hydroxide (KOH, BDH), citric acid (99.5 %, Wardel Chemicals), HCl (37 %, Riedel de Haen), NaCl (99.8 %, Riedel de Haen), potassium hexacyanoferrate (97 %, Labmark Chemicals), potassium hydrogen phosphate (K_2HPO_4, 98 % (Finkem), potassium dihydrogen phosphate (KH_2PO_4), potassium iodide (KI, 99 %, Riedel de Haen), sulphuric acid (98 %, Riedel de Haen) and sodium thiosulphate ($Na_2S_2O_3$, Riedel de Haen) were used as received without any treatment.

Instrumentation

The cyclic voltammetry and amperometric experiments were realized using a BASi Epsilon EC-Version 1.40.67 voltammetric analyzer (Bio-analytical Systems, USA), controlled with basic Epsilon software. A conventional three-electrode setup was used with a

glassy carbon electrode (3 mm diameter, BASi, MF 2012) as the working electrode and a platinum wire counter electrode (BASi, MW 1032). An Ag/AgCl electrode (BASi, MF 2079) served as the reference electrode. All potentials are reported with respect to this reference electrode. A magnetic stirrer (BASi C3 Cell stand at 500 rms) was used for stirring.

Methods

Solution preparation. A 7.5 mM $PdCl_2$ deposition bath was prepared by dissolving, 6.65 mg of $PdCl_2$ in 50 mL, pH 2, citrate buffer and left overnight in the dark, after which period a clear solution was obtained. Finally, the pH of the solution was adjusted to 3 by the addition of dilute KOH.

Hydrogen peroxide was standardized by iodimetric titration.[25] A stock standard solution containing H_2O_2 was prepared freshly each day. Working standard solutions of lower concentrations were prepared immediately before use. Double distilled water was used to prepare all aqueous electrolyte solutions throughout the analysis.

Electrode preparation. Glassy carbon rods (Bioanalytical Systems, BASi, USA) with a diameter of 3 mm were used. The electrode surface was polished with 0.3 μm alumina slurry (BASi). After polishing, the electrodes were carefully rinsed with double distilled water and electrochemically conditioned by potential scanning from –1.1 to 1.4 V in 0.1 M $NaClO_4$ for at least five complete scans at 50 mV s^{-1}, during which the high background current due to glassy carbon oxidation diminished and a reproducible cyclic voltammograms was obtained.[26] The background current of the bare electrode was measured by cyclic voltammetry within the potential window of 0 to 0.7 V. Electrodes with a high background current above a selected reference were excluded. The electrodes were used immediately following the cleaning and conditioning steps.

Fabrication of Pd film and Pd nanoparticles-modified GCE. Palladium film and nano-modified electrodes were prepared by potentiostatic deposition of Pd on the cleaned GCEs from the Pd deposition bath. To fabricate Pd film-modified electrode, palladium was electrochemically deposited in the solution of $PdCl_2$ by stepping the potential from the rest potential of 1.10 V for 1 s to the deposition potential of 0 V for 30 s. In the case of the Pd nano-modified GCE, the same potentials were used except the deposition potential was applied from 1 to 5 s.[27] The modified GCEs were rinsed with double distilled water and immediately used for electrochemical determination of hydrogen peroxide.

Real sample preparation and analysis. For real sample analysis, hair colouring cream (Crust Hair Dye Lotion, Thai-meko Co., Ltd.; Bangkok, Thailand) which contains H_2O_2 solution was used. The concentration of H_2O_2 in the hair colouring cream was determined by titration.[25] Amperometric determination of H_2O_2 at the modified GCEs was realized by the standard addition method. Thus, 1 mL of sample solution was diluted to 100 fold and 0.5 mL of this solution was spiked into 10 mL of the buffer and successive ejection of 1, 2, 3, 4 and 5 mL of 10^{-5} M H_2O_2 standard solution was added to the spiked buffer.

Chronoamperometric measurements. Amperometric experiments were performed in a stirred system under the optimized experimental conditions for the working electrodes and the addition of freshly prepared H_2O_2 standard solution to the PBS buffer. Current-time data were recorded after steady state current had been achieved.

RESULTS AND DISCUSSION

Voltammetric analysis of Pd in the deposition path using GCEs was performed to obtain the appropriate reduction potentials for Pd. The voltammogram

recorded was in good agreement with the experimental results reported by Soreta, *et al.*[26] A deposition potential of 0 V was selected. In the same manner, palladium film and palladium NP electrodeposition procedure was based on the work of Soreta *et al.*[26,27] It was reported[27] that for 1 s deposition time, the estimated Pd NPs diameter was within the range of 48±25 nm, and for 3 s deposition, it was 85±58 nm. Hence, short deposition times caused nucleation of Pd NPs. On extension of the deposition time, the nuclei centres became bigger and bigger, nearby nuclei centres merged and finally a Pd film was formed.[26]

Optimization of the parameters for H_2O_2 detection

The cyclic voltammograms of H_2O_2 at the bare, Pd NPs-modified and Pd film-modified electrodes over a wide range of potentials are depicted in Fig. 1. It is evident that the voltammograms of Pd NPs and Pd film modified electrodes differed substantially from that of the bare electrode. There was no obvious peak corresponding to the reduction and oxidation of hydrogen peroxide (0–25 mM) in phosphate buffer at the bare GCE within the studied potential window. This is in line with experimental results reported by Compton *et al.*[28], where no reduction or oxidation peak for hydrogen peroxide was seen at a bare glassy carbon electrode.
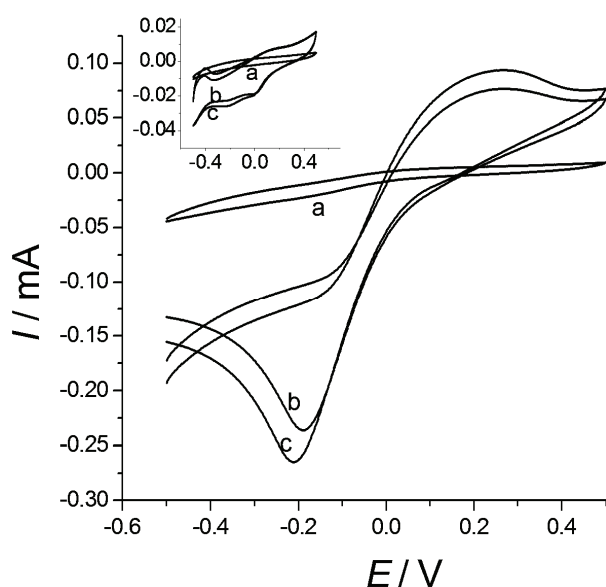

Fig. 1. Cyclic voltammograms of 0.01 M H_2O_2 in pH 7.4 PBS (0.1 mol L⁻¹) at a) bare glassy carbon electrode, b) Pd film-modified glassy carbon electrode and c) Pd NPs-modified glassy carbon electrode. Inset: the corresponding voltammograms in blank phosphate buffer. All the voltammograms were recorded at a scan rate of 50 mV s⁻¹.

From the voltammograms, the reduction potential of –0.2 V was selected for chronoamperometric studies as at this potential reduction of H_2O_2 occurred at a higher magnitude and the selected potential was safe to avoid unwanted side reactions at the working electrode, such as reduction of hydrogen ions.

The pH of the electrolyte was also an important parameter that could influence the response of the electrode in the electroanalysis of H_2O_2. The effect of the pH of the supporting electrolyte on the electrode response was studied in the range 5.8–7.6. Study on effect of pH below 5.8 was purposefully excluded by anticipating that palladium may adsorb hydrogen on its surface at higher concentrations of hydrogen ions and may interfere with the analyte of interest. With increasing buffer pH within the studied range, the voltammetric response for the reduction of H_2O_2 at the modified electrodes increased until pH 7.4. Further increase in pH of the buffer led to a decrease in the response, possibly due to instability of palladium under these conditions where it can form stable hydroxo complexes.[26] Therefore, pH 7.4 was taken as the optimal pH for the electroanalysis of H_2O_2 in PBS, which is in close agreement with previous reports.[28] In addition to the working potential and pH, the deposition time for both the NPs and film were optimized. For the deposition of Pd NP the optimization starts from 1 s and it was found that the CV response of the modified GCE increased up to 5 s deposition of particles (Fig. 2), after which a further increase in the deposition time led to a decline in the response. Therefore, Pd NPs were deposited on the GCE for 5 s and electrodes prepared under this condition are referred to as Pd NPs modified GCE.
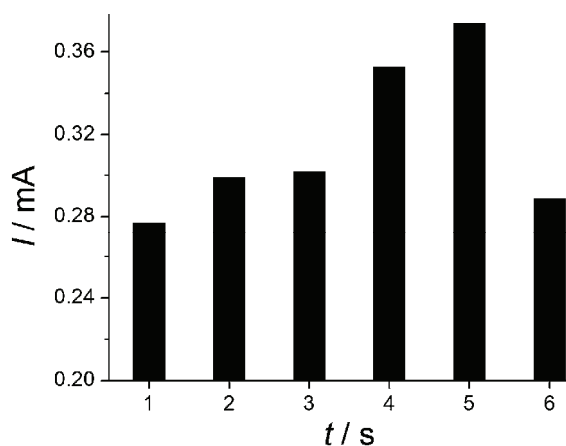

Fig. 2. Effect of Pd NPs deposition time on the electrode voltammetric response for 0.01 M H_2O_2 (cyclic voltammetry run at a scan rate of 50 mV s^{-1} in PBS (0.1 M, pH 7.4)).

For the deposition of a palladium film, the optimization for the deposition time started from 10 s and the CV response of the modified GCE towards the analyte continued to increase until a time of 30 s (Fig. 3). Further increase of the deposition time led to a decrease in the response. The electrode prepared by deposition of Pd for 30 s on GCE is referred to as Pd film-modified GCE.

The electrochemical parameters were optimized to obtain maximum sensitivity for the modified electrode towards H_2O_2 and values for the optimized parameters are summarized in Table I.
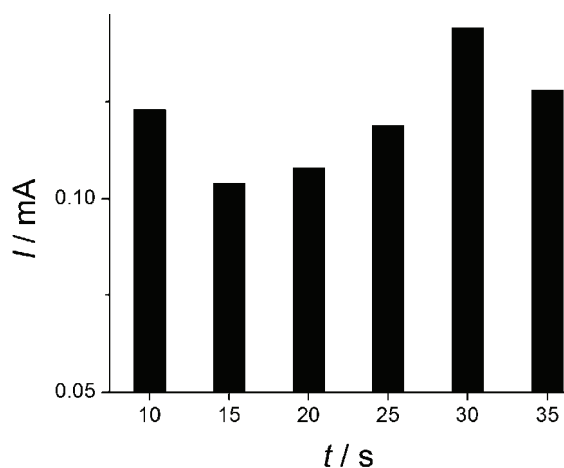
Fig. 3. Effect of Pd film deposition time on the electrode voltammetric response of 0.01 M H_2O_2 (cyclic voltammetry run at a scan rate of 50 mV s^{-1} in PBS (0.1 M, pH 7.4)).

TABLE I. The optimized experimental parameters and their values

Parameter	Value
Working potential	–0.2 V
Working pH	7.4
Pd NP deposition time	5 s
Pd Film deposition time	30 s

Determination of H_2O_2 amperometrically

Since amperometry under stirred condition is much more sensitive than cyclic voltammetry, this method is usually employed for the determination of lower concentrations of analytes.[29] In this work, amperometric measurements were performed for the determination of H_2O_2 at the modified electrodes and their analytical performance was compared with respect to that of a bare GCE. The current-time responses of the Pd NPs and Pd film-modified GCE with successive injection of hydrogen peroxide at an applied potential of –0.20 V are displayed in Fig. 4.

The amperometric response of both the Pd NPs and Pd film modified GCE for successive additions of H_2O_2 increased stepwise with each additions of hydrogen peroxide. In addition, the GCE modified with Pd NPs exhibited better amperometric response to H_2O_2 than the Pd film modified GCE. This signal enhancement was believed to be attributable to the unique reactivity and electrocatalytic activity of the Pd NPs as compared to those of the Pd film. The size effect (higher surface area to volume ratio) of the NPs is the main reason for the observed high reactivity of H_2O_2 at the Pd NPs modified GCE than at the Pd film-modified GCE.

The calibration plots in Fig. 4 are the amperometric responses of the Pd NPs modified GCE and the Pd film at –0.20 V (*vs*. Ag/AgCl) in 0.1 M PBS (pH 7.4)

with varying concentration of hydrogen peroxide, ranging from 1 µM to 13 mM for the former and 10 µM to 13 mM for the latter.

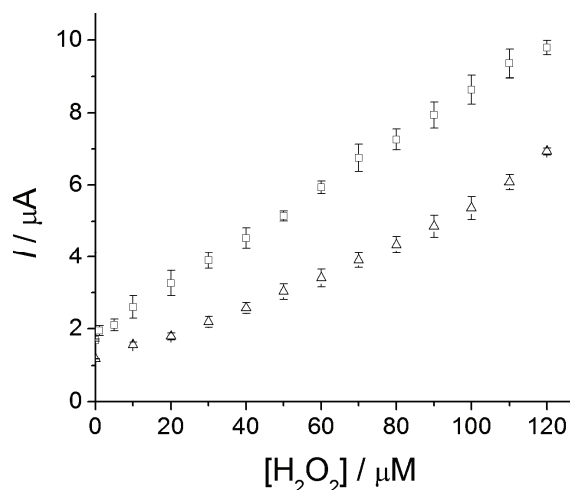Fig. 4. Calibration curves for the determination of H_2O_2 with amperometric measurements using: ( ) Pd NP-modified GCE; (Δ) Pd film-modified GCE for the determination of hydrogen peroxide.

As depicted in Fig. 4, there is an obvious linear relationship between the current and the concentration of hydrogen peroxide in the studied concentration ranges. The sensitivity for determination of hydrogen peroxide as determined from the slope of the calibration curves for the three electrodes is in the order of Pd NPs > Pd film >> bare GCE. The values clearly demonstrate substantial improvements of the sensitivity of the measurements as a result of GCE surface modification with Pd NPs and Pd film.

The detection limits for the modified electrodes were found to be 0.33 and 6.79 µM for the Pd NPs and Pd film modified GCE, respectively. The detection limit was calculated as the concentration equivalent to three times the standard deviation for five blanks and fitted to the calibration curve. Comparisons of the detection limit of the developed sensor with those previously reported works were also made and the values are summarized in Table II. Therefore, the hydrogen peroxide sensor reported herein could be a good candidate for H_2O_2 analysis.

Inter-electrode reproducibility and stability

The inter-electrode reproducibility was investigated both for Pd NPs and Pd film modified GCEs by preparing three electrodes under the same deposition conditions. Triplicate determination of 0.1 mM H_2O_2 with each electrode was used to estimate the reproducibility. The reproducibility expressed in relative standard deviation was found to be 3.52 % for the Pd NPs modified GCE. In the same manner, a relative standard deviation of 4.31 % was obtained for the Pd film-modified GCE. The results showed good reproducibility of the electrode modification.

TABLE II. Comparison of the developed sensor with previously reported modified electrodes for the determination of H_2O_2

Electrode	Detection limit, μM	Ref.
Gold nanoelectrode ensembles (NEE)	4	31
Pd NPs/onion-like mesoporous carbon vesicle (MCV)	0.079	21
Multi walled carbon nanotubes (MWCNTs)–Pd NPs on a modified GCE	0.3	30
Immobilization of horseradish peroxidase in chitosan matrix cross-linked with glyoxal	8	32
Pd NPs-modified GCE	0.33	This work

The modified electrode showed low stability. The current response of the Pd NPs-modified GCE declined for the determination made on the same electrode on consecutive days. The current response had decreased by about 29 % on the second day of the experiment. On the 4th, 6th, 8th and 10th day of the experiment, the current response had decreased by 49, 55, 62 and 71 %, respectively. This could be due to the high surface reactivity of Pd NPs. It is recommended that a fresh surface be prepared prior to each experiment.

Interference study

The ability of the electrochemical sensors developed to withstand potential interferents was studied by chronoamperometric measurements. The effect of common interfering electroactive substances, such as uric acid (UA), ascorbic acid (AA) and glucose were assessed. The amperometric response of the Pd NPs modified GCE for the subsequent injection of 5.0 mM glucose, 0.15 mM AA, 0.5 mM UA and 1.0 mM H_2O_2 at –0.2 V are depicted in Fig. 5. These concentrations were selected because the level of endogenous AA, glucose, and UA is, respectively, about 0.125 mM, 4.4–6.6 mM and 0.33 mM in the blood sample.[30]
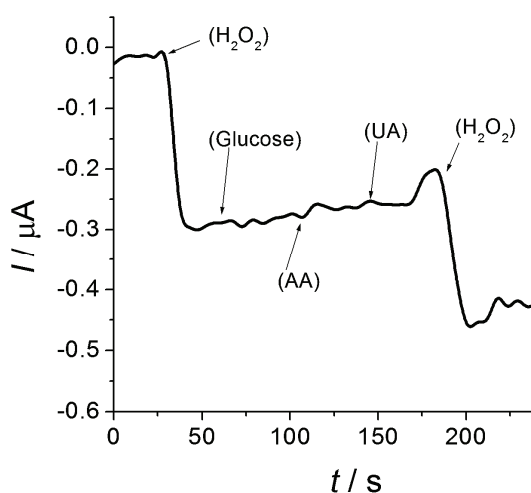

Fig 5. Amperometric response of the Pd NPs-modified GCE upon addition of 1.0 mM H_2O_2, 0.15 mM ascorbic acid, 5.0 mM glucose, 0.5 mM uric acid and 1.0 mM H_2O_2. Applied potential: –0.2 V.

The current response of AA, glucose and UA were much smaller than those of H_2O_2. The influence of the species tested on the H_2O_2 response was negligible, indicating high selectivity of the palladium modified electrodes for H_2O_2.

Real sample analysis

In order to demonstrate the applicability of the modified electrode for real sample analysis, hair colouring cream containing H_2O_2 solution was analysed. The bulk concentration of H_2O_2 in the hair colouring cream was first determined by titration. The concentration of H_2O_2 obtained was 1.49±0.012 M. Thus, the 1.49 M solution was diluted 100 fold and spiked into the buffer and the successive ejection of 0.01 mM H_2O_2 standard solution into the spiked buffer. Finally the concentration was determined by the standard addition method using the bare and modified GCEs. The results are given in Table III.

TABLE III. Concentration of H_2O_2 detected in a real sample

Working electrode	Concentration of H_2O_2 detected
Bare GCE	Not detected
GCE modified with Pd NPs	0.015±0.0015 mM
GCE modified with Pd film	0.018±0.0047 mM

Pd modified GCEs were able to detect lower concentrations of H_2O_2 in the hair colouring cream. The amounts of hydrogen peroxide detected by the modified electrodes were in good agreement with the actual value determined by the standard method. The relative error for Pd NPs and film modified GCE were 0.67 and 21 %, respectively. The Pd NPs modified GCE was found to be more accurate than the Pd film modified GCE under the studied conditions.

CONCLUSIONS

In this work, the amperometric determination of H_2O_2 using Pd NPs and Pd film modified GCE was studied. The electrodes were modified by electrochemical deposition of palladium from Pd deposition bath at different deposition times. The developed sensor exhibited higher sensitivity for H_2O_2 than unmodified GCEs. The catalytic properties of Pd NPs and Pd film gave enhanced electrochemical responses for hydrogen peroxide. The improved analytical performance makes Pd NPs and film modified GCE promising amperometric sensor for hydrogen peroxide. Remarkable electrocatalytic activity and significantly lower detection limits were achieved with these modified electrodes that could be favourably compared to unmodified and other enzyme modified electrodes reported in the literature. Furthermore, the demonstrated modification procedure is less expensive and more convenient than previously reported sensors. The analytical performances of the modified electrodes indicate that they could be used as sensitive amperometric detectors for the determination of lower concentrations of

hydrogen peroxide as compared to the bare GCE. In this study, determination of H_2O_2 in more a complex matrix, such as blood samples, was not investigated. Further study need to be performed on the employment of these electrodes for the electroanalysis of H_2O_2 in biological samples.

И З В О Д

ЕЛЕКТРОХЕМИЈСКО ОДРЕЂИВАЊЕ ВОДОНИК-ПЕРОКСИДА НА ЕЛЕКТРОДИ ОД СТАКЛАСТОГ УГЉЕНИКА МОДИФИКОВАНОЈ НАНОЧЕСТИЦАМА ПАЛАДИЈУМА

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У раду је приказана модификација стакластог угљеника наночестицама паладијума и филмом паладијума. Активност модификованих електрода у присуству водоник-пероксида је испитивана цикличном волтаметријом и амперометријом (на −0,2 V према Ag/AgCl референтној електроди у фосфатном пуферу, pH 7,4). Електроде модификоване филмом паладијума и наночестицама паладијума показале су линеарну зависност струје редукције водоник-пероксида у опсегу концентрација 10 µM–14 mM и 1 µM–14 mM уз границу детекције од 6,79 и 0,33 µM, редом.

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