Alumina nanoparticles modified carbon paste electrode as a new voltammetric sensor for determination of dopamine

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Abstract

The present study examines a new dopamine sensor based on Alumina nanoparticles modified carbon paste electrode ($Al_2O_3NPsCPE$). Moreover, the present study focuses on the electrochemical act of the $Al_2O_3NPsCPE$ for the detection of dopamine by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). There is also a focus on the specification of the prepared modified electrode by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM), and there is a discussion on the influence of some experimental variables such as carbon paste composition, laboring solution pH, scan rate and possible interferences. The present study obtained a well-defined redox peak of dopamine (DA) on the Nano-Alumina/CPE at $E_{pa}=173mV$ and $E_{pc}=112mV$, respectively. The obtained response of the sensor was linear under the optimal conditions of the catalytic peak current, in the range of 8.0-330.0 µM, and the detection limit was 2.1 µM (S/N=3) for dopamine. The proposed sensor exhibited a high sensitivity, an excellent reproducibility, good selectivity, and it was successfully used in the determination of dopamine injection samples.

Keywords: Alumina nanoparticles; $Al_2O_3NPsCPE$; dopamine; cyclic voltammetry; differential pulse voltammetry.

Introduction

Dopamine (DA) is a typical important neurotransmitter in the catecholamine group and plays a significant role in renal, central nervous, hormonal, and cardiovascular systems [1-4]. Abnormal DA levels within the fluids of one's body might suggest that he or she is suffering from such diseases as Parkinsonism, Huntington, and Schizophrenia [5]. Many methods have been introduced for the determination of DA, for instance, chromatography [6-9], chemiluminescence [10], spectrophotometry [11,12], electrochemistry [13-19] and others. It was Zak et al. who first noticed that the presence of alumina particles dispersed on a glassy carbon surface could strongly adsorb substances such as catechols and that such particles can catalyze their oxidation [20]. Unique properties of the Al_2O_3 nanoparticles, such as their electrochemical activation, good adsorption, high reaction activation, large specific surface, porosity, and cheapness are features due to which Al_2O_3 nanoparticles have

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attracted much more attention in electrochemistry and electroanalysis [21-25]. Research on the carbon paste modified electrodes is relatively extensive, which is mostly due to the specific properties of carbon paste electrodes, for example, their wide potential windows, low-cost, and relatively low electrical resistance [26-30]. The modified carbon paste electrode DA determination, which had been previously reported, was on the basis of the voltammetry methods [31-41].

However, to our knowledge, a sensitive DA sensor has not been reported based on a nano-Al2O3 carbon paste electrode because high area surface for Al2O3 nanoparticles modified carbon paste electrode was obtained. Therefore, this sensor shows high reaction activation for the oxidation of dopamine. For the determination of DA, the present study reports the voltammetric behavior of Alumina nanoparticles modified carbon paste electrode. The modified carbon paste electrode was successfully examined in terms of its performance for the electrochemical determination of Dopamine in DA injection samples.

Experimental
Apparatus and reagents
Electrochemical studies were performed by means of Autolab PGSTAT12N potentiostat/galvanostat controlled by GPES 4.9 software (Eco Chemie, The Netherlands). A three-electrode system was used for all measurements: a bare or modified CPE as the working electrode, a Pt wire as the auxiliary electrode and an Ag/AgCl as the reference electrode. A Metrohm 780 pH/ion meter was also used for pH measurements. Scanning electron microscopy (SEM) images were taken with a scanning electron microscope

(FE-ESM, TESCAN, Czech), at an acceleration voltage of 15 kV. Graphite powder, dopamine (DA), and paraffin were purchased from Merck (Darmstadt, Germany). Alumina nanoparticles were purchased from (Germany, Evonik GmbH). All other chemicals used in the present study - were from Merck, and they were specifically used for analysis. Throughout the experiments, water doubly distilled was used. As a supporting electrolyte, 0.1 M phosphate buffer was prepared along with various pH values by mixing the stock solutions of 0.1 M H_3PO_4, NaH_2PO_4, Na_2HPO_4, and NaOH (Merck).

Electrode preparations
Manually, and using a mortar and pestle, graphite powder 70% w/w was mixed with Al_2O_3 nanoparticles15% w/w, and with paraffin oil 15% w/w in order to develop a consistent carbon paste. The modified carbon paste was then packed into an insulin syringe. A copper wire was inserted into the carbon paste, providing an electrical contact. When it was necessary to push an excess of paste out of the syringe, a new surface was obtained, which was then polished with weighing paper. Furthermore, unmodified CPE was prepared in the same way without adding Al_2O_3 nanoparticles to the mixture so as to compare and contrast different electrodes.

Results and discussion
Characterization of the electrode surface
A scanning electron microscope was utilized to describe the morphology of CPE and $Al_2O_3NPsCPE$. Figure 1 shows typical morphological views of the traditional CPE and the $Al_2O_3NPsCPE$ with the distinctions of the electrode surface being observed. In Figure 1A, it can be seen that the

surface of the CPE consists of isolated and irregular carbon flakes. Figure 1B shows the SEM of $Al_2O_3NPsCPE$. As it can be clearly seen, the presence of Al_2O_3 nanoparticles were shown on the surface of carbon paste. Figure 2 shows the impedance plots for (a) bare CPE and (b) Al_2O_3NPs/CPE surfaces in 5.0 mM $[Fe (CN)_6]^{3-/4-}$ (1:1) solution in 0.1M KCl. The values of the charge transfer resistance (Rct) were calculated for the bare CPE and Al_2O_3NPs/CPE as 5.20 and 1.56 $k\Omega$, respectively. It is, therefore, clear that the Al_2O_3NPs/CPE can increase the electron transfer, as compared with the bare CPE. The microscopic areas of the bare CPE and those of the Al_2O_3NPs/CPE were evaluated by cyclic voltammetry by 5mM $K_3Fe (CN)_6$ solution in 0.1 M KCl as a probe at different scan rates [42]. For a reversible process, the Randles- Sevcik equation is used:

$$I_{pa}=2.69\times10^5 n^{3/2} A\ C_o\ D_R^{1/2} v^{1/2}\ (1),$$

where I_{pa} refers to the anodic peak current, A is the surface area of the electrode, n is the electron transfer number, D_R is the diffusion coefficient, C_O is the concentration of $K_3Fe(CN)_6$, and v is the scan rate. For 5mM $K_3 Fe (CN)_6$ in the 0.1 M KCl electrolyte, n =1, $D_R=7.6 \times 10^{-6} cm^2 s^{-1}$, the surface area of electrodes could be computed by using the slope of I_{pa}-$v^{1/2}$ relation. The surfaces of CPE and Al_2O_3NPs/CPE were 0.0012, 0.003 cm^2, respectively. It was observed that the surface area of Al_2O_3NPs/CPE was 2.5 times greater than the bare electrode.
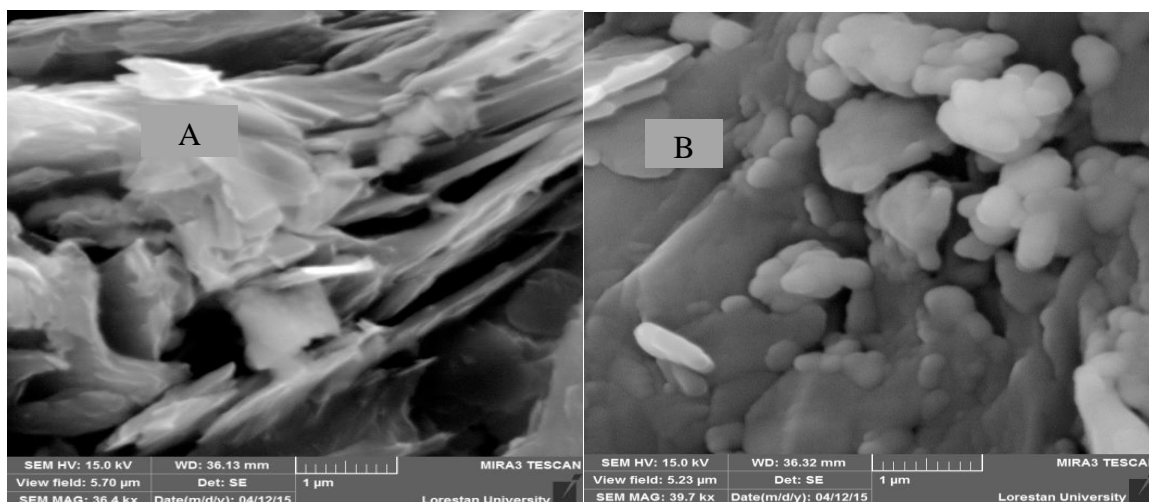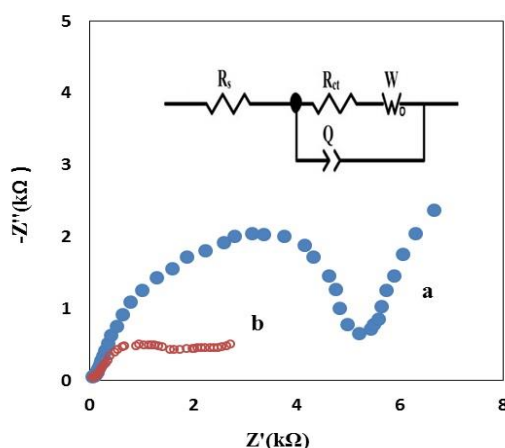

Figure1. SEM images of CPE (A), SEM images of $Al_2O_3NPsCPE$ (B)

Figure 2. EIS responses of (a) bare CPE and (b) Al₂O₃NPsCPE electrodes in the presence of 5.0 mM [Fe-(CN)6]$^{3-/4-}$(1:1) in 0.1 M KCl. The inset shows the corresponding equivalent circuit.

Influence of Alumina nanoparticles
In order to obtain the maximum current with the appropriate potential of the electrode in the present study, toward dopamine, the amount of Alumina nanoparticles was optimized. Figure 3 shows the oxidation peak currents of dopamine at different electrodes in terms of the percentage of Alumina nanoparticles. It is clear that the maximum current of oxidation was derived from the electrode containing 15% Alumina nanoparticles of the total amount of paste material.
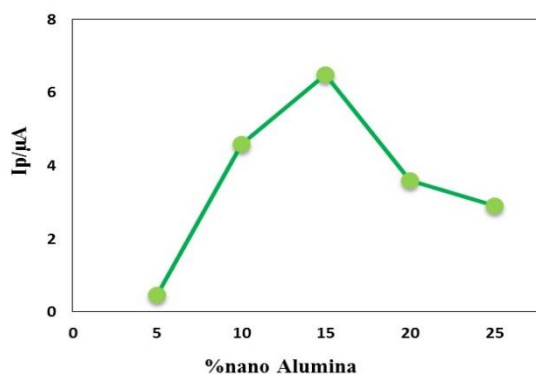

Figure 3. Effect of percentage of Alumina nanoparticles at Al₂O₃NPsCPE. Conditions: dopamine (1.0 mM), phosphate buffer solution, pH 8.0, scan rate of 0.1Vs^{-1}

Electro-oxidation of DA at the modified electrode and unmodified electrodes
Figure 4 exhibits the cyclic voltammograms acquired for the electrochemical response of 1.0 mM DA at the modified CPE (solid line) and bare CPE (dashed line) in 0.1 M phosphate buffer solution pH 8.0. At the bare CPE, the anodic and cathodic peaks appear at 203 mV and 93 mV (vs. Ag/AgCl), respectively. The value of separation in peak potential (ΔEp) is equal to 100mV, and the corresponding current ratio is I_{pa}/I_{pc}=7.69, which are the characteristics of a quasi-reversible electrode process. For the Al₂O₃NPsCPE, however, a pair of redox peak is obtained from a strong increase in both anodic-cathodic peak currents. The anodic peak potential was located at 173 mV, the cathodic peak

potential was located at 112 mV, and I_{pa}/I_{pc} was located at 4.62. Therefore, it was observed that the peak current at Alumina nanoparticles CPE is much higher than that at the bare one, which provides a high surface area of the Alumina nanoparticles, improves the electrode contacting area of DA, and increases its electrochemistry of the reaction product.
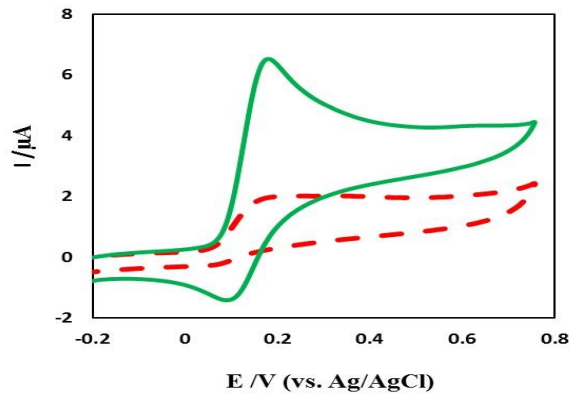

Figure 4. Cyclic voltammograms obtained for CPE (dashed line) and $Al_2O_3NPsCPE$ (solid line) in 0.1M phosphate buffer solution of pH 8.0 containing 1.0 mM DA. Scan rate 0.1 V s^{-1}

The electrochemical behavior of dopamine depends on the pH value of the aqueous solution. Therefore, the electrochemical behavior of DA was studied in the buffered solutions with different pH values (2≤pH≤12) at the surface of $Al_2O_3NPsCPE$ by means of the cyclic voltammetry. Figure 5A shows the effects of pH on the peak current. The maximum peak currents of DA occurred at pH 8.0. For this reason, it was selected as the optimal pH for the next experiments. The relationship existing between the anodic peak potential and pH value of the solution could be suitable for the regression equation of E_{pa} (V) = -0.0621 pH +0.7562, with the correlation coefficient being R^2 = 0.9924 (Figure 5B). A slope of 62mV per pH unit indicates the equal numbers of the electron transfer and the hydrogen ions partaking in the electrode reaction [43].
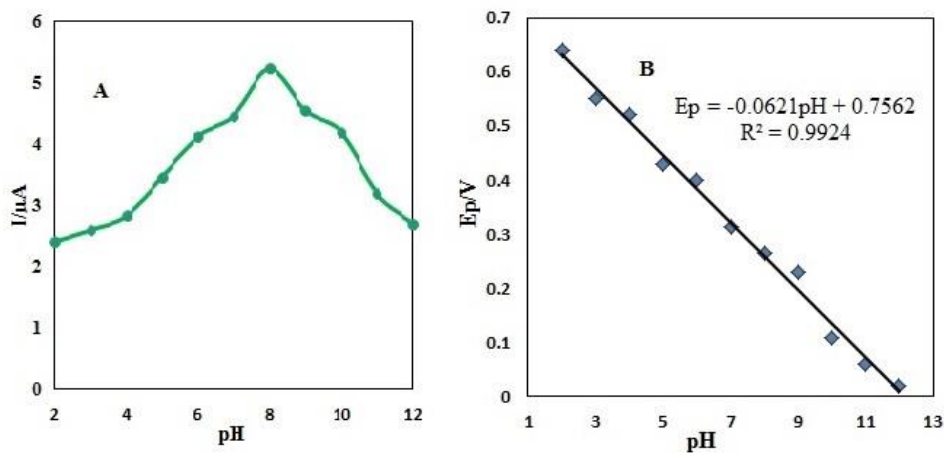

Figure 5. (A) Variation of the anodic peak current in the cyclic voltammograms of 1.0 mM DA. (B) Influence of the solution pH on the oxidation peak potential (E_{pa}) for 1.0 mM DA. Measurements carried out at the surface of $Al_2O_3NPsCPE$ in 0.1M buffered solution with

different pH values, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0, at scan rate of $0.05 Vs^{-1}$.

By means of the cyclic voltammetry, the effect of scan rates on the peak currents at the $Al_2O_3NPsCPE$ was examined in buffered phosphate solution (0·1 M, pH 8·0) in Figure 6A. The anodic and cathodic peak potentials of $Al_2O_3NPsCPE$ have an orientation towards positive and negative potentials, respectively. Therefore, the difference between the anodic peak potential and the cathodic peak potential ΔEp will increase as the scan rate increases. The plots of the anodic and cathodic peak currents were linearly proportional to the square root of the sweep rate $v^{1/2}$ with correlation coefficients of 0.9986 at every scan rate (Figure 6B). It can be seen that the nature of the redox process is diffusion-controlled.
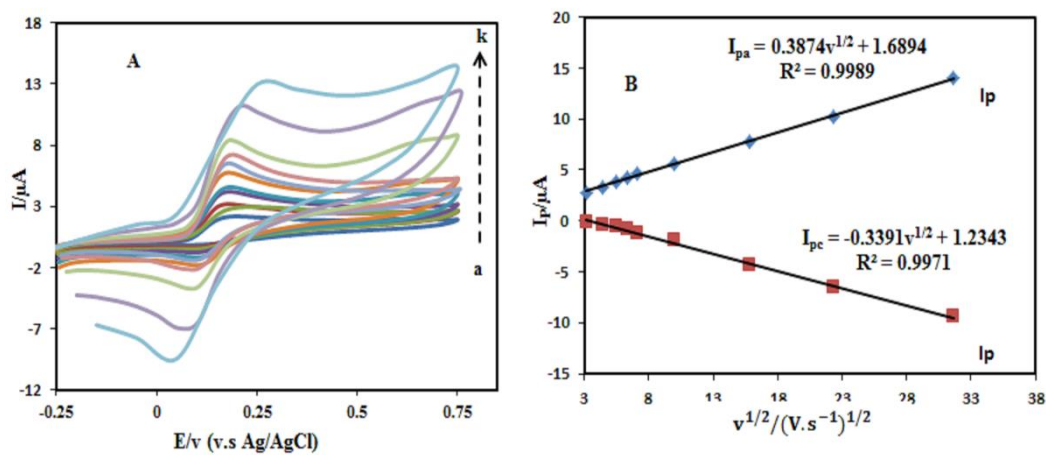

Figure 6. (A) Cyclic voltammograms of 1.0 mM DA on the $Al_2O_3NPsCPE$ with different scan rates (a–k: 10, 20, 30, 40, 50, 75, 100, 150, 250, 500, 1000 mV/s) in pH 8.0 PBS. (B) Redox peak current versus the square root of the scan rate

Determination of DA

The electrooxidation of DA was studied in 0.1M phosphate solution pH 8.0 at the surface of $Al_2O_3NPsCPE$ by means of the DPV technique. The results (Figure 7A) showed that DPVs of the DA oxidation were linearly dependent on the DA concentrations at the surface of the $Al_2O_3NPsCPE$ over the range of 8.0 to 330.0 µM (Figure 7B). The calibration curve was developed by measuring the peak current with optimized DPV parameters. An average of five continuous measurements was used for the development of the calibration curve in Figure 7B. The results showed that there was a linear relationship between the oxidation peak currents and the DA concentration in two different linear ranges of 8.0-100.0 µM (I_{pa} =0.0497C (µM) +0.7678) and 100.0-330.0 µM (I_{pa} =0.0224C (µM) +2.973) with correlation coefficients of R^2=0.9929 and 0.9993, respectively. The limit of detection for DA was found to be 2.1µM in the lower range region.
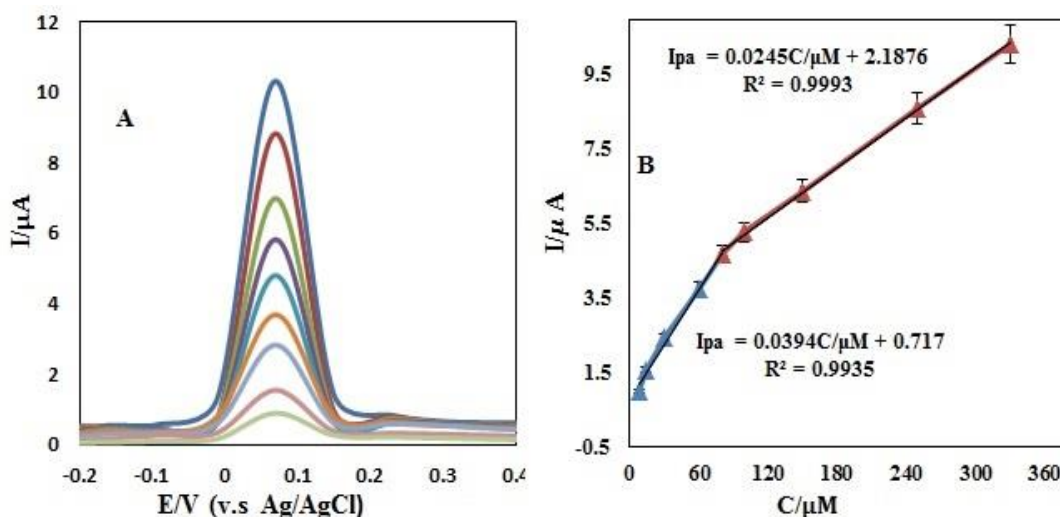
Figure 7. (A) Differential pulse voltammograms of Al_2O_3NPsCPE in 0.1M PBS (pH 8.0) containing different concentrations of DA, from inner to outer correspond to 8.0, 15.0, 30.0, 60.0, 80.0, 100.0, 150.0, 200.0, 280.0, and 330.0 μM of DA at scan rate of $0.05Vs^{-1}$. (B) Calibration plot observed for DA in two linear ranges of 8.0-100.0, and 100.0-330.0μM

Real sample analysis

In order to testify the performance of Al_2O_3NPsCPE, the biosensor was used to determine DA in a sample of dopamine hydrochloride injection (labeled 200mg per 5 mL Caspian Tamin pharmaceutical Co. Rasht-Iran). The sample was used after suitable dilution. As Table 1 shows, the standard addition method is suitable for a simple and rapid evaluation of DA. Table 1 shows the results. The recovery and RSD were acceptable, showing that the method proposed in the present study could be properly used for determining dopamine in injections with recovery in the range of 98.0% - 102.0%.

Table1. Determination of DA in commercially available dopamine hydrochloride injections (n=3) at Al_2O_3NPsCPE by DPV

Sample	Original content (μM)	Added (μM)	Found (μM)	RSD	Recovery%
1	40.0	15.0	53.9	1.58	98.0
2	40.0	30.0	71.4	1.46	102.0
3	40.0	50.0	89.55	1.42	99.5

Interference study

In order to evaluate the proposed electrode, the effects of different substances as the compounds potentially interfering with the determination of DA was investigated. The tolerable concentration ratios with respect to 50.0μM DA for interference at the 5% level were examined, and the results are shown in Table 2. These results confirmed that the Al_2O_3NPsCPE electrode had satisfactory selectivity toward the DA determination.

Table 2. Results of interference study for the determination of 50.0 µM dopamine in pH 8.0 at $Al_2O_3NPsCPE$

Species	Tolerance limits ($C_{species}/C_{dopamine}$)
Ca^{2+}, Na^+, Ba^{2+}, Mg^{2+}, K^+	1000
Fe^{3+}, Pb^{2+}, Fe^{2+}	5
SO_4^{2-}, CO_3^{2-}, I^-, Cl^-	1000
Ascorbic acid	10
Glucose, Maltose, Sucrose,	100

Reproducibility, repeatability, and stability

The long-term stability of the Al_2O_3NPs modified CPE was studied by examining its current response during storage under laboratory conditions. The electrochemical sensor showed no obvious reduction in the current response in the first week and sustained about 95% of its initial value after 1 month. Based on the six replicates of analysis, the relative standard deviations (RSD) for the DA determination were 2.63% for 200µM, and 3.95% for 10 µM, showing that this Al_2O_3NPs modified CPE has good reproducibility.

Conclusion

For the first time, the present study demonstrated the determination of DA using the Alumina nanoparticles modified CPE in 0.1 M phosphate buffer (pH 8.0) solution. Results indicate that DPV at an $Al_2O_3NPsCPE$ can be successfully used for the determination of DA with excellent sensitivity and selectivity. The proposed method was found to be precise and accurate with a good detection limit of 2.1 µM (S/N=3). The proposed electrode has a number of advantages including easy preparation, high stability, reasonable selectivity, fast response time, long-term stability, and applicability over a wide pH range. In addition, the electrode surface can be renewed with a simple polishing. The above mentioned advantages justify the construction of this modified electrode as a sensor for the dopamine determination. The real sample analyses reveal that the $Al_2O_3NPsCPE$ can be suitable for the selective determination of dopamine hydrochloride injection with satisfactory results.

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