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PAPER

Simultaneous electrochemical determination of dopamine and paracetamol based on thin pyrolytic carbon films

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This paper describes the determination of dopamine and paracetamol using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The selective, stable and reproducible simultaneous measurement of the two compounds is achieved using thin pyrolytic carbon (PyC) films as working electrodes. These are created *via* a reliable, non-catalytic chemical vapour deposition (CVD) process, and the electron transfer characteristics of the films are optimised using a simple oxygen plasma treatment. This new class of carbon electrode can detect dopamine in the range 18 to 270 μM, with a 2.3 μM limit of detection (LoD), while simultaneously sensing paracetamol in the range 15 to 225 μM (LoD 1.4 μM). A 225 mV separation between the two competing signals is realised. The accuracy of the sensor is demonstrated using human serum and commercially available pharmaceutical products. This is the first report of the application of PyC to this problem, and the performance is shown to be competitive with the leading carbon electrodes available today, particularly edge-plane pyrolytic graphite (EPPG). This work will serve as an important benchmark in the development of inexpensive, disposable, high-performance nano-structured electrodes for sensors, fuel cells and energy conversion.

Introduction

Paracetamol (acetaminophen or *N*-acetyl-*p*-aminophenol) is among the most extensively used drugs in the world, being suitable for the treatment of moderate pains and the reduction of fevers.[1] It is metabolised predominantly in the liver, where it generates toxic metabolites. Overdoses result in an accumulation of the latter, and can be fatal. Hence there is a demand for fast, simple and accurate paracetamol sensors, and techniques such as titrametry,[2] spectrophotometry,[3] chemiluminescence[4] and liquid chromatography[5] have been explored for this purpose. Dopamine (3,4-dihydroxyphenylmethylamine) is an important neurotransmitter of the catecholamine group which exists in the mammalian central nervous system. Its metabolites leave the body through urine, therefore urine tests are commonly used to determine catecholamine levels. Paracetamol is known to interfere with these measurements,[6] so the development of new materials which can resolve the two competing signals is desirable. The speed and selectivity of electroanalytical techniques have, in recent years, been utilised for this purpose,[7–10]and these approaches appear to be viable alternatives to the somewhat arduous techniques mentioned above.

Carbon materials are widely used in electroanalysis due to their wide potential window and considerable electro-catalytic activity.[11] The latter depends very much on microstructure and surface chemistry, and the various allotropes have very different electrochemical properties. The electrochemistry of 'traditional' sp^2-hybridised materials such as glassy carbon and highly ordered pyrolytic graphite has been thoroughly probed. The last decade has seen an extraordinary amount of research into the electrochemical properties of carbon nanotubes,[12–14] and graphene-based electrodes[15–19] have emerged in recent years. While the electrochemical properties of nanotube (NT) electrodes are impressive, nanotube devices suffer from relatively inefficient processing and contacting. Similar vagaries afflict graphene, where the best-performing materials are still produced by mechanical exfoliation. Despite the many unanswered questions regarding the manufacturability of NT and graphene electrodes, little attention has been given to thin films of pyrolytic carbon (PyC) for electroanalytical applications. PyC is a form of nano-crystalline graphite made by the non-catalytic chemical vapour deposition (CVD) of hydrocarbon precursors. These conductive, thermally stable thin films are composed of small (1–2 nm) graphitic crystallites. This material has been known for decades[20] and its growth mechanism has been described by Dong and Hüttinger.[21] In the past it has been used in lithium batteries,[22] vertical interconnect structures[23] and integrated as an electrode material in dynamic random access memory cell capacitors.[24]

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Hadi *et al.* have reported electrodes based on PyC grown on graphite rods.[25–27]

Recently, we described the electrochemical properties of PyC films created using non-catalytic CVD on Si/SiO_2 wafers.[28] The growth conditions permit deposition on a variety of substrates, and the infiltration of porous materials and fibres is also possible. After deposition, the electron transfer characteristics of the films are optimised using a simple oxygen plasma treatment. The latter also reduces the thickness of the films to around 150 nm. In this paper, the application of this material to the simultaneous determination of dopamine and paracetamol is reported. Using human serum and commercially available pharmaceutical products, the performance is shown to be competitive with expensive edge-plane pyrolytic graphite electrodes, which have previously been described as the 'best-case scenario' in carbon electrochemistry.[19,29,30] This work illustrates the great potential of pyrolytic carbon with regard to the pursuit of new high-performance electrode materials which can be easily and cheaply manufactured and contacted. It is noteworthy that the deposition of PyC, unlike nanotubes and graphene, occurs directly on insulating substrates and therefore the material does not need to be lifted off and transferred, taking with it catalyst residues which obscure its electro-catalytic properties. Having said this, recent work by the Banks group[31–33] involving commercially available graphene grown on nickel, indicates that CVD-grown graphene can be electrochemically characterised on the growth substrate. Furthermore, the growth of pyrolytic carbon is entirely reliable and reproducible, and can be scaled up without difficulty.

Experimental

Dopamine hydrochloride, acetaminophen, ascorbic acid and uric acid were purchased from Sigma-Aldrich. Dopamine injection solution and paracetamol tablets were purchased from a local pharmacy. Drug-free human blood, obtained from a healthy volunteer, was centrifuged at 3500 rpm for 40 min at room temperature. Acetonitrile (3 cm^3) was added to the serum (5 cm^3) to remove serum protein. After 30 s of vortex, the mixture was centrifuged for 15 min at 10 000 rpm to remove the serum protein residues. The supernatant was removed carefully and diluted with buffer for analysis. All solutions were prepared with water (resistivity 18.2 MΩ cm). The 50 mM, pH 7 phosphate buffer solution was prepared by dissolving monosodium dihydrogen phosphate trihydrate ($NaH_2PO_4 \cdot 2H_2O$) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) (Merck) in water in the appropriate ratio.

The formation and plasma treatment of the PyC films have been described previously.[28] In short, the films were treated in a custom-built chamber with a 1000 W downstream microwave oxygen plasma, generated using a R^3T source at room temperature. SEM analysis was carried out using a Zeiss Ultra Plus FESEM. Cross-sectional images were obtained using a 45° tilt. An accelerating voltage of 2 kV was used with an in-lens detection system. HRTEM studies were performed on cross-sections of PyC on SiO_2 prepared in a Zeiss Auriga focussed ion beam (FIB) with a Cobra ion column. A reactive gas injection system was used for reactive ion etching and deposition of a platinum capping layer. Images of these cross-sections were taken at 300 kV using a FEI Titan 80-300 (S)TEM equipped with a S-TWIN objective lens and a high brightness (X-FEG) Schottky field emission gun with monochromator. XPS analysis in our recent work[35] indicates that the as-grown films contain trace amounts of nitrogen and fluorine.

An Autolab PGSTAT30 potentiostat was used to perform electrochemical measurements, along with a three-electrode configuration. IJ Cambria supplied Ag/AgCl reference electrodes (CHI111) and platinum wire counter electrodes (CHI115). Pyrolytic carbon films were used as working electrodes. These were incorporated into the electrochemical cell by placing the substrates in an electrode designed in-house. The design is described in our previous work.[28,34] Contact with the films was made using a Pt wire, and a nitrile 'O' ring defined PyC disc electrodes of radius 1.5 mm. All current densities were calculated with respect to this area. Control experiments were carried out using basal-plane pyrolytic graphite (BPPG, product number 002252) and edge-plane pyrolytic graphite (EPPG, 002253) working electrodes (both of radius 1.5 mm) obtained from ALS Ltd (Japan). Since only anodic potential windows were used, solutions were not purged with inert gas. All measurements were performed at room temperature. Differential pulse voltammetry was carried out using a pulse modulation of +50 mV, a duration of 50 ms and a period of 0.5 s.

Results and discussion

The morphology of the PyC films on Si/SiO_2 substrates was investigated using electron microscopy. Fig. 1(a) and (b) show low- and high-magnification SEM images of the interface between PyC and the substrate. It can be seen that there is uniform coverage over a large area. An image of the cross-sectional interface between PyC and SiO_2, obtained using

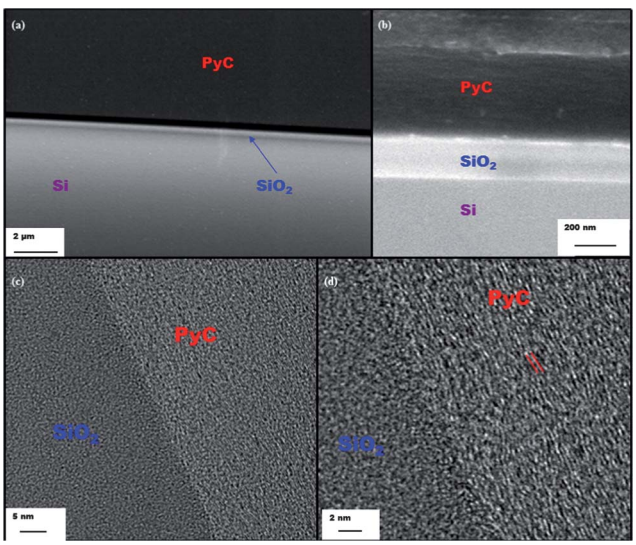

Fig. 1 (a) Low-magnification SEM image (45° tilt) showing the interface between as-grown PyC and substrate. (b) High-magnification SEM image showing the same interface. (c) Low-magnification HRTEM image showing the interface between PyC and the SiO_2 substrate. (d) High-magnification HRTEM image showing the same interface. Nano-crystalline PyC domains are evident (red lines).

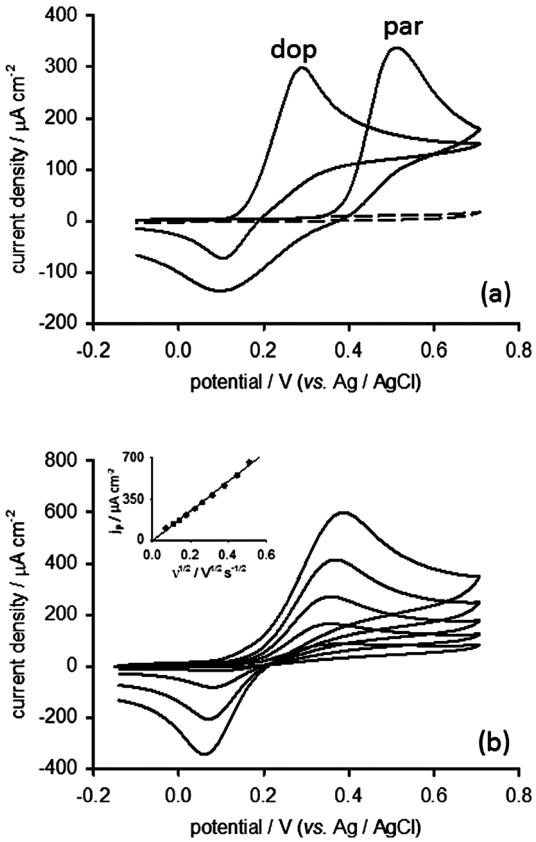

Fig. 2 (a) Cyclic voltammograms recorded at plasma-treated PyC electrodes in (separately) 1 mM dopamine and paracetamol in 0.1 M phosphate buffer (pH 7) at a sweep rate of 100 mV s^{-1}. Also shown is the background electrolyte response (dashed). (b) Voltammograms recorded in 1 mM dopamine at scan rates of 12, 32, 70, 145 and 260 mV s^{-1}. The inset shows the resulting plot of anodic peak current density against the square root of the scan rate.

HRTEM, is shown in Fig. 1(c), suggesting a laminar-like deposition. The higher-magnification image in Fig. 1(d) permits the discernment of crystallites roughly 2 nm in size.

Preliminary electrochemical studies involved the use of cyclic voltammetry to examine the oxidation of dopamine and

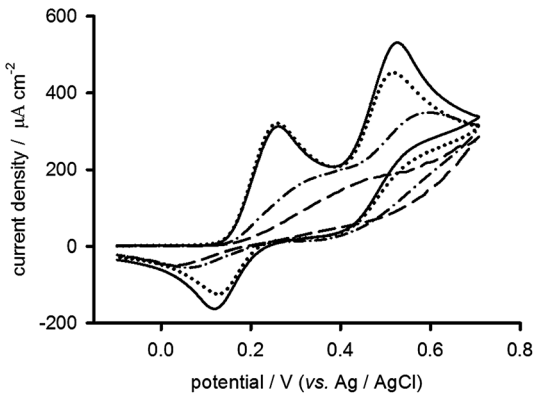

Fig. 3 Cyclic voltammograms recorded at as-grown (dashed) PyC, plasma-treated (solid) PyC, BPPG (dashed-dotted) and EPPG (dotted) electrodes in 1 mM dopamine and paracetamol in 0.1 M phosphate buffer (pH 7) at a sweep rate of 50 mV s^{-1}.

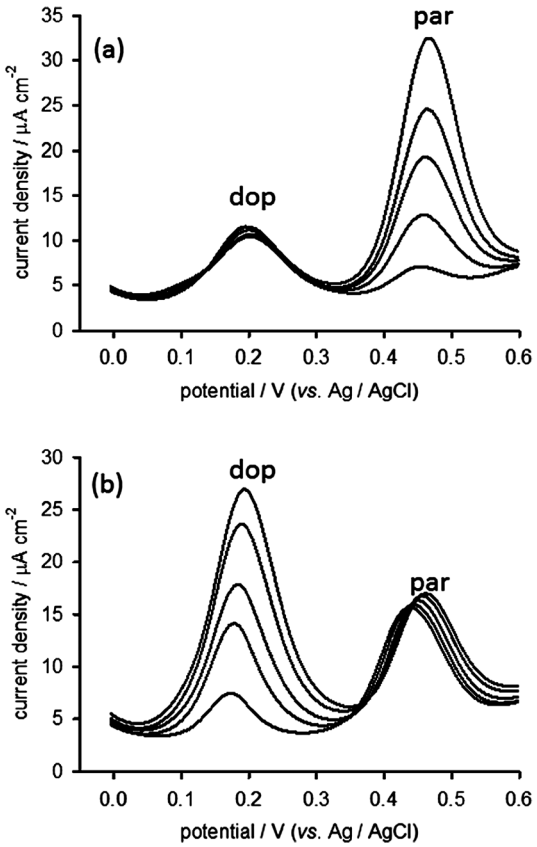

Fig. 4 (a) Differential pulse voltammograms recorded at plasma-treated PyC electrodes in 30 μM dopamine and (from bottom to top) 20, 40, 60, 80 and 100 μM paracetamol. (b) Same in 50 μM paracetamol and 20, 40, 60, 80 and 100 μM dopamine.

paracetamol in separate phosphate buffer solutions. It can be seen from Fig. 2(a) that the oxidation peaks are well-separated (225 mV) at plasma-treated PyC, and that the background current at these electrodes is low. The impressive separation is attributed to the outstanding electron transfer properties of this

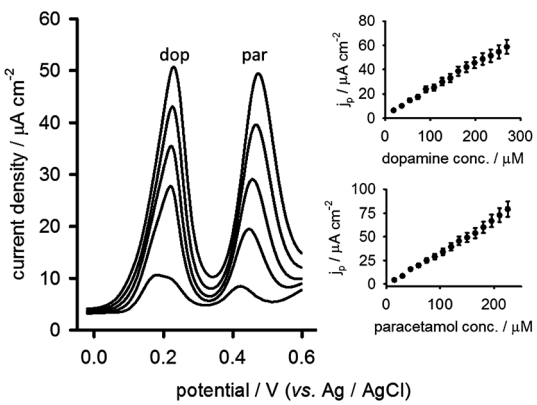

Fig. 5 Differential pulse voltammograms recorded at a plasma-treated PyC electrode in increasing concentrations of dopamine and paracetamol (40, 115, 150, 185 and 225 μM). The insets show the resulting plots of peak current density against concentration for each compound, and the error bars represent the standard deviation found using five duplicate electrodes.

Table 1 Reported literature values for dopamine and paracetamol useful ranges and detection limits. CCE = carbon-ceramic electrode; Gr = graphite; PDDA = poly (diallyldimethylammonium chloride); PSS = poly styrene sulphonate; PF = polyfuran; SDSLDH = layered double hydroxide sodium modified with dodecyl sulphate; AuNP = gold nanoparticles

System	Dop range/μM	Dop LoD/μM	Par range/μM	Par LoD/μM	Reference
PyC	18–270	2.3	15–225	1.4	This work
CCE/CNT	0.4–150	0.22	0.2–100	0.12	37
Gr/PDDA/PSS/CNT	Not given	Not given	25–400	0.5	38
GC/CNT	3–200	0.8	3–300	0.6	10
Pt/PF/Pd	0.5–100	0.048	0.5–100	0.076	39
GC/SDSLDH/AuNP	0.5–300	Not given	0.5–400	0.13	40

material, caused by its high density of edge-plane sites and defects,[28] which have high local densities of states near the Fermi energy due to dangling bonds and/or terminating functional groups generated during plasma treatment. Fig. 2(b) shows that the anodic peak current density for dopamine is proportional to the square root of the sweep rate over the range 5 to 260 mV s^{-1} (correlation coefficient 0.996, $N = 10$). This behaviour is characteristic of diffusion-controlled electrochemical reactions, and similar results were obtained for paracetamol (not shown).

The next set of experiments involved the simultaneous detection of dopamine and paracetamol in solution using cyclic voltammetry. Fig. 3 shows that the two signals do not interfere with each other when plasma-treated PyC electrodes are used, and the separation between the peaks is the same as when the two processes are examined separately. Included in the figure is a comparison with the as-grown material, in order to illustrate the importance of oxygen plasma treatment to the electron transfer properties of the electrode. In the absence of plasma etching, the signals are indistinguishable from each other. This effect can be understood using experiments involving commercially available EPPG and BPPG electrodes, as also shown in the figure. The behaviour of these is analogous to that of treated and untreated PyC, confirming that the creation of additional edge-plane sites and defects by plasma treatment is responsible for the dramatic enhancement in electron transfer properties, permitting the simultaneous determination of the two compounds. Note that we do not see the functionalisation of the films with oxygenated groups as contributing to this effect. Differential pulse voltammetry was used to demonstrate simultaneous measurement, and Fig. 4 shows the results obtained when the concentration of one compound was held constant and that of the other was increased by increments. The signal increases in proportion with concentration, without significantly affecting the response to the spectator species. It can be seen in Fig. 4(b) that the oxidation peak potential of paracetamol increases slightly as more dopamine is added. This is probably due to the adsorption of the latter and/or its oxidation products, but it will be shown now that this shift is of no analytical consequence.

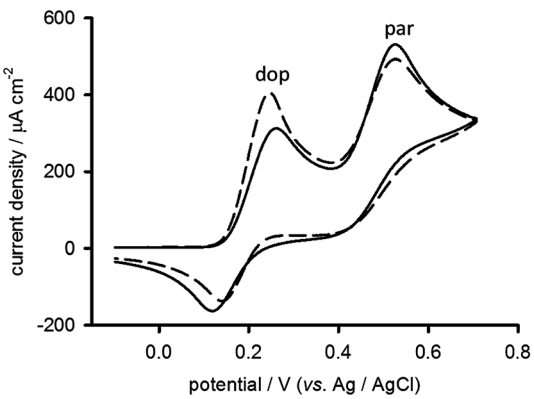

Fig. 6 Cyclic voltammograms recorded at a plasma-treated PyC electrode in 1 mM dopamine and paracetamol in 0.1 M phosphate buffer (pH 7) before (solid) and after (dashed) the introduction of 10 mM ascorbic acid and uric acid. The sweep rate was 50 mV s^{-1}.

The response of the signals to simultaneous increases in the concentrations of dopamine and paracetamol was studied. Fig. 5 shows how the anodic peak current density (j_p) increases for both compounds with successive additions, along with the resulting calibration plots. As in Fig. 4(b), a slight positive shift in paracetamol's oxidation peak potential is observed as the dopamine concentration increases. For dopamine, the calibration plot was linear (correlation coefficient 0.995, $N = 15$) over the range 18 to 270 μM. The limit of detection (LoD) was found to be 2.3 μM, based on a standard deviation of 0.154 μA cm^{-2} (ten blank measurements) and a sensitivity of 0.20 μA μM^{-1} cm^{-2}. A more detailed description of this approach to LoD calculation can be found in our previous work.[36] The minimum reliably measurable dopamine concentration (based on a signal-to-noise ratio of 3) was found to be 12 μM. For paracetamol, the linear range was 15 to 225 μM, the detection limit was 1.4 μM, the sensitivity was 0.33 μA μM^{-1} cm^{-2} and the minimum reliably measurable concentration was 9 μM. Table 1 shows that these values are competitive with those reported for carbon nanotube-modified electrodes and also with more laborious systems previously reported for this application, such as polyfuran-coated platinum coated with palladium nano-clusters and glassy carbon coated with gold nanoparticles and an organophilic layered double hydroxide. It can be seen that PyC electrodes represent a viable alternative to these systems, offering greater simplicity and ease of preparation.

In biological samples, ascorbic acid and uric acid often interfere with the desired signal. Voltammetry was therefore carried out in the presence of these species (10 mM each), and Fig. 6 shows that there was no significant evidence of interference in the voltammogram. The ability of the plasma-treated PyC electrodes to avoid these problems is attributed to oxygenated functionalities created on the carbon surface during plasma treatment. At neutral pH, these have a negative charge, and this repels the two acids, which themselves carry a negative charge at this pH value. In order to test the stability of the PyC electrodes, they were kept in pH 7 PBS for twenty days, after which the voltammetric

Table 2 Determination of dopamine and paracetamol in pharmaceutical samples. Listed values are an average of those found using five duplicate PyC electrodes

Sample		Content/μM	Detected/μM	Recovery/%	RSD/%
Dopamine	1	53	54.7	103	2.8
injection solution	2	106	105.1	99.2	2.7
Paracetamol	1	50	48.1	96.2	3.0
tablets	2	100	96.5	96.5	1.7

Table 3 Determination of dopamine and paracetamol additions to human serum samples. Measured values are an average of those found using five duplicate PyC electrodes

	Added/μM		Detected/μM		Recovery/%		RSD/%	
Sample	Dop	Par	Dop	Par	Dop	Par	Dop	Par
1	20	20	20.1	20.3	101	102	3.8	2.7
2	100	100	97.8	104.3	97.8	104	4.2	4.0

response was compared with that recorded for the freshly prepared material. Again, no appreciable difference was observed. Ten successive measurements of 1 mM dopamine and paracetamol showed RSDs of 2.5 and 3.5%, respectively. Three PyC electrodes, prepared using separate runs in the furnace, showed RSDs of 4.2 and 4.0% for 1 mM dopamine and paracetamol.

In order to demonstrate the analytical utility of PyC electrodes, they were used to determine dopamine and paracetamol in real pharmaceutical products (dopamine injection solution and paracetamol tablets) *via* the method of standard additions. Based on the content stated by the manufacturers, the dopamine solution was diluted with PBS and the paracetamol tablets were dissolved in PBS to give solutions with concentrations near the lower end of the linear ranges reported above. Pulse voltammetry signals were recorded for these solutions, and also after five successive 20 μM spikes with the relevant compound. The data was then extrapolated to give a value for the original concentration. Table 2 shows that in all cases, recoveries and RSDs (based on five duplicate electrodes) were satisfactory, showing that this material can be used for the determination of dopamine and paracetamol in real samples. Table 3 shows that PyC electrodes perform to an acceptable standard in the determination of dopamine and paracetamol additions to human serum samples. It should be pointed out that similarly impressive results were found using EPPG electrodes, but the findings shown here indicate that PyC should be considered as a cheaper and disposable alternative, since hundreds of these electrodes can be produced per day using a single furnace.

Conclusions

For the first time, the simultaneous detection of dopamine and paracetamol using pyrolytic carbon electrodes has been demonstrated. The nano-crystalline graphitic surface exhibits excellent electron transfer properties and low background current, permitting sufficient resolution of the two competing signals. This ability was shown to be due to the high density of edge-plane sites and defects on the plasma-treated surface. The sensor is selective, stable and reproducible, with a low detection limit, high sensitivity and broad linear range. Its accuracy has been verified using human serum and commercially available pharmaceutical products. The electroanalytical properties of PyC were found to be competitive with the best carbon electrodes on the market, and these findings constitute a significant step in the development of a new class of inexpensive, disposable, high-performance nanostructured electrodes for sensors, fuel cells and energy conversion.

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