

Full Paper

Simultaneous Detection of Dopamine and Uric Acid at Poly (Fast Sulfone Black F) Film Coated Graphite Pencil Electrode

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Abstract- The poly (fast sulfone black f) film was synthesized on the surface of graphite pencil electrode by cyclic voltammetric method. The synthesized polymer film coated electrode exhibit excellent electrocatalytic activity towards the detection of dopamine at 7.0 pH. The scan rate effect was found to be diffusion controlled electrode process. The concentration effect of dopamine was linear with current. The redox peak potentials of dopamine were depend on pH. This polymer film coated electrode was very good at simultaneous study of dopamine in presence of high concentrated uric acid. The separated peak potential of DA-UA was 150 mV by cyclic voltammetric technique.

Key words- Poly (Fast Sulfone Black F), Graphite Pencil Electrode, Dopamine, Uric acid, Cyclic Voltammetry, Simultaneous

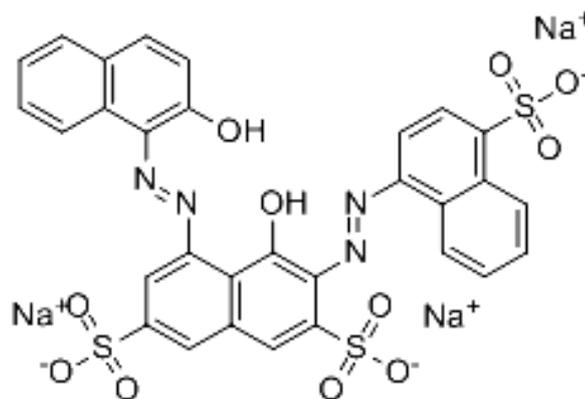
1. INTRODUCTION

Dopamine is an important neurotransmitter in the amygdala, a phylogenetically older structure of the brain, which is thought to play a critical role in limbic, cognitive and neuroendocrine functions [1,2]. Serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA-containing neurons [3-8]. Patient with this disease shows a low

level of DA. Therefore, determination of DA concentration has become important. Many methods were introduced to determine DA, such as spectroscopy, chromatography and electrochemistry [9-13]. Because of its electrochemical activity, DA can also be determined with electrochemical method [7,14]. Uric acid (UA) is the primary end product of purine metabolism in the human body [15]. In a healthy human being, the typical concentration of UA in urine is around 2 mM and in the blood is in between 120 μ M to 450 μ M ranges [16,17]. Extreme abnormalities of UA levels are symptomatic of several diseases, such as, cardiovascular disease [18], hyperuricaemia, uric acid stones [19], gout and Lesch-Nyhan syndrome [20]. Thus accurate determination of UA concentration is of great importance. Recently, electrochemical sensors have attracted much attention due to their advantages of simplicity, cheapness, fast analysis along with high sensitivity and selectivity [21]. The oxidation potential of DA and UA are very close such that, the bare electrode often suffers from fouling effects. The chemically modified electrodes have the ability to detect both DA and UA selectively .

The electropolymer film coated electrodes are playing an important role in sensor field. Ongera et al studied the simultaneous determination of dopamine in presence of ascorbic acid at electropolymer modified carbon paste electrode [3,4,22]. Gabriela Broncova et.al used poly (neutral red) modified electrode for determination of citrate in soft drinks [23]. M. Pandurangachar et.al prepared poly (patton's and reeder's) film coated carbon paste electrode for simultaneous detection of dopamine [7]. Sarah M. Kirwan studied the electrochemical properties of AA and H₂O₂ at Poly (o-phenylenediamine) film modified Platinum-iridium electrodes alloy wires [24].

In the present work, poly (fast sulfone black f) film coated graphite pencil electrode is used for the selective detection of DA in the presence of UA. Many electrochemical experiments have been done by electropolymerizing the fast sulfone black f (FSBF) indicator and discussing their voltammetric behavior by modifying at glassy carbon electrode [25-27]. The structure of FSBF was shown in scheme 1. The graphite pencil electrode (GPE) has been successfully applied to analyses of certain compounds in recent years [28-32]. The GPE is relatively new type of carbon electrode, it is less expensive, more convenient, and renewable compare to the commonly used CPE or GCE [32]. The electropolymerization film FSBF was coated on the surface of GPE by cyclic voltammetry (CV). The electrode had high concentration of negative-charged function group -SO₃⁻ and electron rich oxygen atom on its surface. The poly (FSBF) film coated GPE showed excellent electrocatalytical activity towards the selectivity and sensitivity of DA in the presence of UA in the range of pH 7.0 in acetate buffer solution. The peak to peak separation between DA and UA was 158 mV. This was large enough to identify the DA and UA individually.



Scheme 1. Structure of Fast sulfone black F

2. EXPERIMENTAL SECTION

2.1. Reagents

The pencil-lead rods were HB 0.5 mm in diameter and 6 cm length purchased from local bookstore. 25 mM FSBF stock solution was prepared in double distilled water. 10×10^{-4} M DA stock solution was prepared by dissolving in 0.1 M perchloric acid solution. 10×10^{-3} M stock solution of UA was prepared by dissolving in 0.1 M sodium hydroxide solution. Sodium acetate and acetic acid were used to prepare the 0.2 M acetate buffer solution. Chemicals mentioned above were all of analytical grade. The water used in the preparation of solutions was double distilled water.

2.2. Apparatus

The electrochemical experiments were carried out using a model-201 electroanalyser (EA-201 chemilink system). All the experiments were carried out in a conventional three electrochemical cell. The electrode system contained a working electrode was bare GPE and poly(FSBF) film modified GPE (0.5 mm in diameter), a platinum wire as counter electrode and saturated calomel electrode as reference electrode.

2.3. Preparation of poly (FSBF) modified GPE

The 1 mM FSBF was placed in the electrochemical cell with 0.05 M H_2SO_4 . The GPE was scanned by immersing 3 mm length in that solution (from -400 to 1400 mV) at 100 mV s^{-1} for 20 times. After this, the same GPE has enforced under sweeping from -400 to 1400 mV at 100 mV s^{-1} for multiple cycles (20 cycles) in the solution containing 1 mM FSBF with 0.01 M NaOH.

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization of FSBF on GPE

Fig. 1. showed the cyclic voltammogram for electropolymerisation of FSBF on the surface of GPE in the range from -400 to 1400 mV at the sweep rate of 100 mVs^{-1} at 20 multiple cycles. Before the electropolymerisation process the GPE was pretreated by scanning in the solution containing $1 \times 10^{-3} \text{ M}$ FSBF in $0.05 \text{ M H}_2\text{SO}_4$ for 20 times in the same potential range. After this the electrode is made to undergo multiple cycles in 0.01 M NaOH containing $1 \times 10^{-3} \text{ M}$ FSBF. During the process of multiple cycles the voltammogram has gradually descended with increase of cyclic time. This indicates that the poly (FSBF) film was formed and deposited on the surface of GPE [27-29].

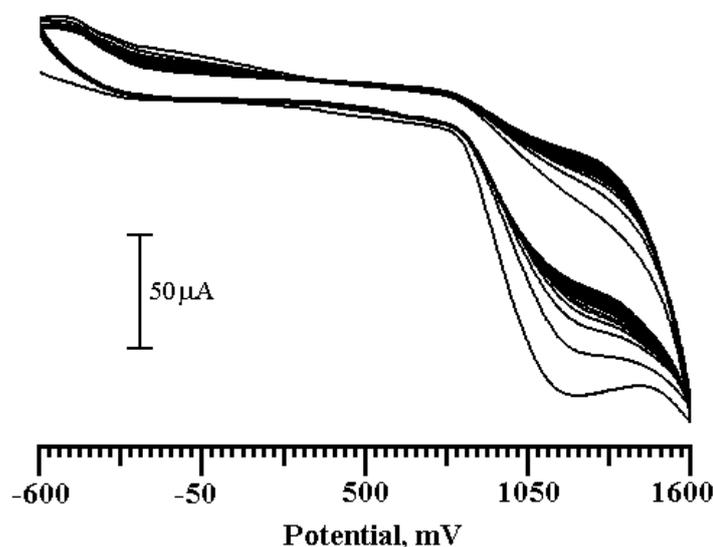


Fig. 1. Cyclic voltammogram of preparation of poly (FSBF) film coated GPE. 1 mM FSBF in 0.01 M NaOH at 20 cycles with sweep rate of 100 mVs^{-1}

3.2. Electrocatalytic response of DA at poly (FSBF) modified GPE

DA being an easily oxidizable catecholamine, showed quasi-reversible voltammogram with supporting electrolyte 0.2 M acetate buffer of $\text{pH } 7.0$ at 50 mVs^{-1} scan rate for bare GPE in the potential range of -400 to 800 mV Fig. 2. showed a pair of redox peak for bare GPE (dashed line), with E_{pa} 360 mV and E_{pc} 90 mV (vs. SCE). The separation of redox peaks (ΔE_{p}) was found to be 250 mV which was the characteristic of a quasireversible electrode process. However, at the poly (FSBF) modified GPE a pair of redox peaks are obtained with strong increased in both I_{pa} and I_{pc} (solid line). The poly (FSBF) modified GPE reduced the over potential which occurred for bare GPE. The E_{pa} and E_{pc} were located at 280 mV and 230 mV respectively. At poly (FSBF) modified GPE the E_{pa} was shifted negatively upto

80 mV and E_{pc} was positively upto 40 mV. The ΔE_p was found to be 50 mV. The shifting of redox peak potentials shows the excellent electrocatalytic activity of poly (FSBF) film coated GPE for detection of DA. Thus, the voltammogram obtained for DA at poly (FSBF) modified GPE was reversible with excellent enhancement of oxidation and reduction peak currents.

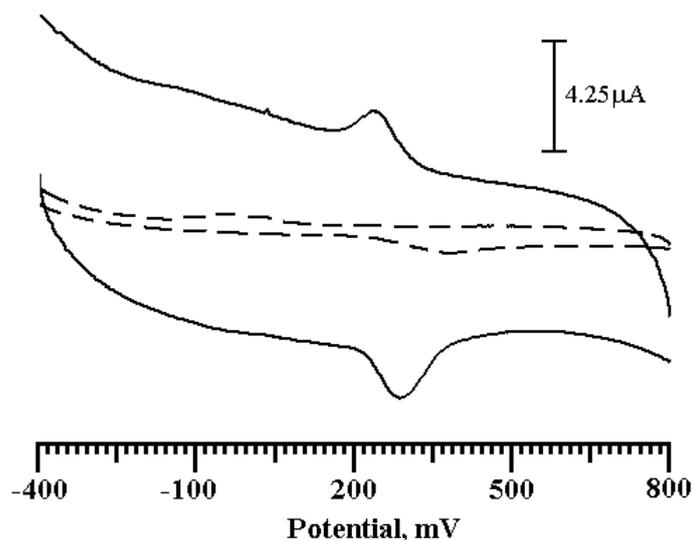


Fig. 2. Cyclic voltammogram of 0.1×10^{-3} M DA in 0.2 M acetate buffer solution of pH 7.0 at bare GPE (dashed line) and poly(FSBF) film coated GPE (solid line)

3.3. The effect of scan rate

The effect of scan rate on the anodic peak current of DA was studied at poly (FSBF) modified GPE by using CV technique (Fig. 3A). The scan rate was increased from 50 to 350 mVs^{-1} . The anodic peak current was increased with increase in scan rate. The graph of I_{pa} vs. square root of scan rate was plotted (Fig. 3B). The resulted graph showed excellent linearity with correlation co-efficient of 0.9997. This result showed that the electrode process was diffusion controlled.

3.4. Effect of pH

The electrochemical response of DA at poly (FSBF) film coated GPE is generally pH dependent. The voltammograms of DA were recorded at 0.2 M acetate buffer solutions of different pH by cyclic voltammetric method. Fig. 4A demonstrates the pH dependence of DA at poly (FSBF) film coated GPE at sweep rate of 50 mVs^{-1} . The both anodic and cathodic peak potentials were shifted to less positive side with increasing in the pH values. The anodic peak potential of DA shifted from 330 mV to 140 mV with respect the pH from 4 to 9. The potential diagram was constructed by plotting the graph of calculated E_0 vs. pH of the

solution (Fig. 4B). The graph has good linearity with a slope of 45 mV/pH this behaviour is nearly obeyed the Nernst Equation for two electron and two proton transfer reaction [33].

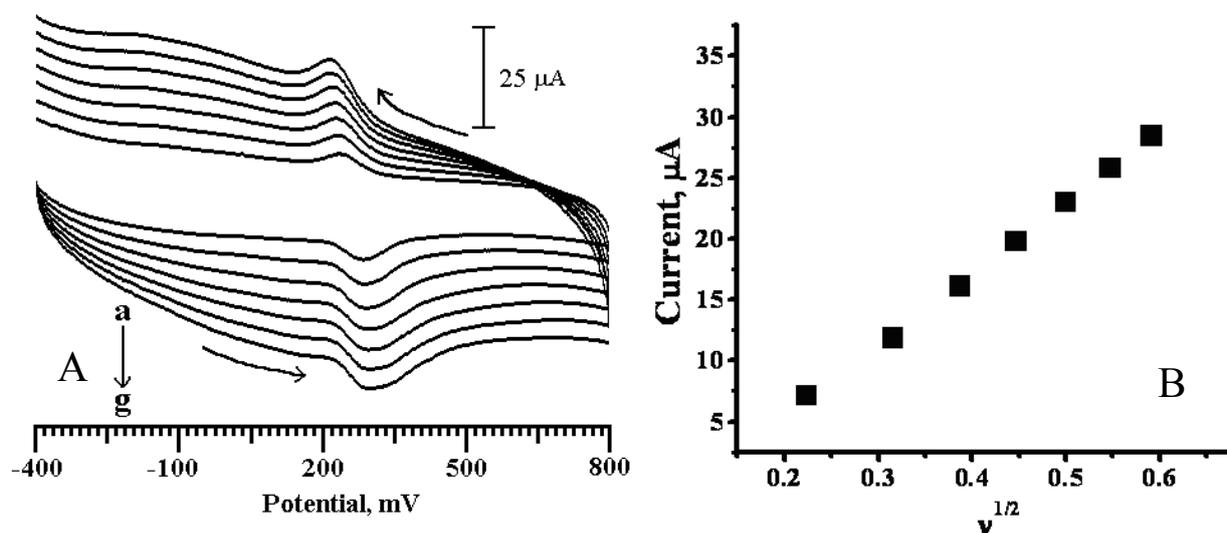


Fig. 3. A) Variation of scan rate for DA at poly (FSBF) film coated GPE (a-g; 50 to 350 mVs^{-1}). B) Graph of current vs. square root of scan rate

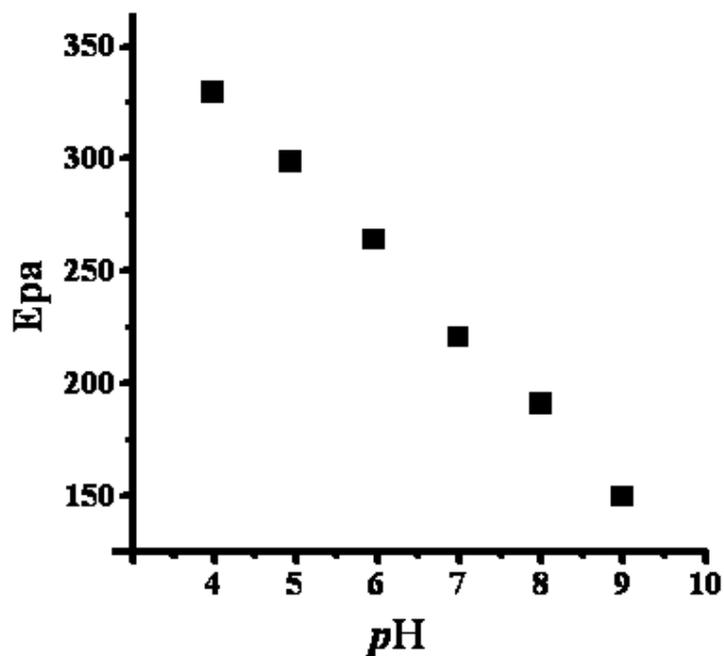


Fig. 4. Graph of E_p vs. pH

3.5. Effect of concentration of DA

The electrocatalytic oxidation of DA was carried out by varying its concentration at poly (FSBF) modified GPE. Fig. 5A showed that, by increasing the concentration of DA, the electrochemical anodic and cathodic peak current goes on increasing with shifting E_{pa} towards positive and E_{pc} towards negative direction. DA from 0.1×10^{-3} to 0.5×10^{-3} concentrations showed increase in redox peak currents. The graph of anodic peak current *vs.* concentration of DA was plotted (Fig. 5B). The anodic peak current was proportional to concentration of DA in the above range.

3.6. Simultaneous determination of DA and UA by cyclic voltammetry

UA is present along with DA in mammalian brain. The concentration of UA is much higher than that of DA. Since, the oxidation potential of UA is nearly same as that of DA result in an overlapped voltammetric response at bare CPE. However, the poly (FSBF) modified GPE has ability to separate the oxidation peak potentials of DA and UA. Fig. 6A showed the voltammograms were recorded for individual UA at both bare poly (FSBF) film modified GPE at sweep rate of 50 mVs^{-1} in the potential range from -400 mV to 800 mV. The voltammogram of UA has E_{pa} , which was found to be 450 mV in a pH 7.0 acetate buffer solution at bare GPE (dashed line). However the E_{pa} was shifted at 425 mV at poly (FSBF) modified GPE (solid line) with strong enhancement of I_{pa} . The plot of E_{pa} *vs.* pH was linear and slope was found to be -0.054 mV. The I_{pa} of uric acid was proportional to the y with correlation coefficient (r) 0.9995 (data was not shown).

The Fig. 6B showed the voltammogram for solution containing mixture of both 0.1×10^{-3} DA and 0.5×10^{-3} M UA in pH 7.0 acetate buffer solution at sweep rate of 50 mVs^{-1} from potential range -400 to 800 mV. The bare GPE (dashed line) showed only one broad anodic peak but not cathodic peak. The poly(FSBF) modified GPE has able to separate the oxidation peaks of DA and UA by showing two well separated anodic peaks and one cathodic peak (solid line). The electrocatalytical anodic peak of DA has showed at 280 mV and UA was found to be at 430 mV. The cathodic peak for dopamine was found to be 235 mV. The separation between DA-UA was found to be 150 mV.

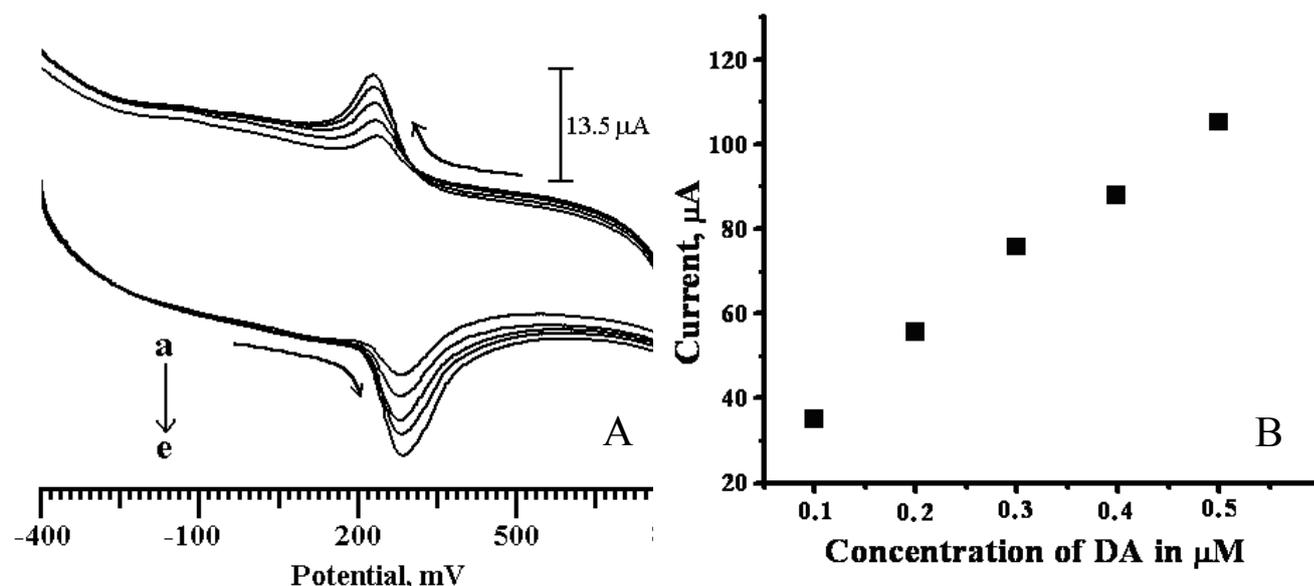


Fig. 5. A) Cyclic voltammogram of DA at different concentration (a–e; 0.1, 0.2, 0.3, 0.4, 0.5×10^{-3} M). B) Graph of current vs concentration of DA

3.7. Analytical Application

The modified electrode was applied to the determination of dopamine hydrochloride injection. The DA injection sample purchased from sterile specialities India Private Ltd with a specified content of DA of 40.0 mg/mL. The sample was used after suitable dilution. The results were shown in Table 1. The recovery and R.S.D. were acceptable, showing that the proposed methods could be efficiently used for the determination of DA in injections with recovery in the range 98.5 to 99.75%

Table 1. Detection of DA in injection samples (n = 5)

Sample	Content (mg/mL)	Found (mg/mL)	RSD (%)	Recovery (%)
1	4.0	39.4	2.2	98.5
2	4.0	3.97	2.4	99.25
3	4.0	3.99	2.0	99.75

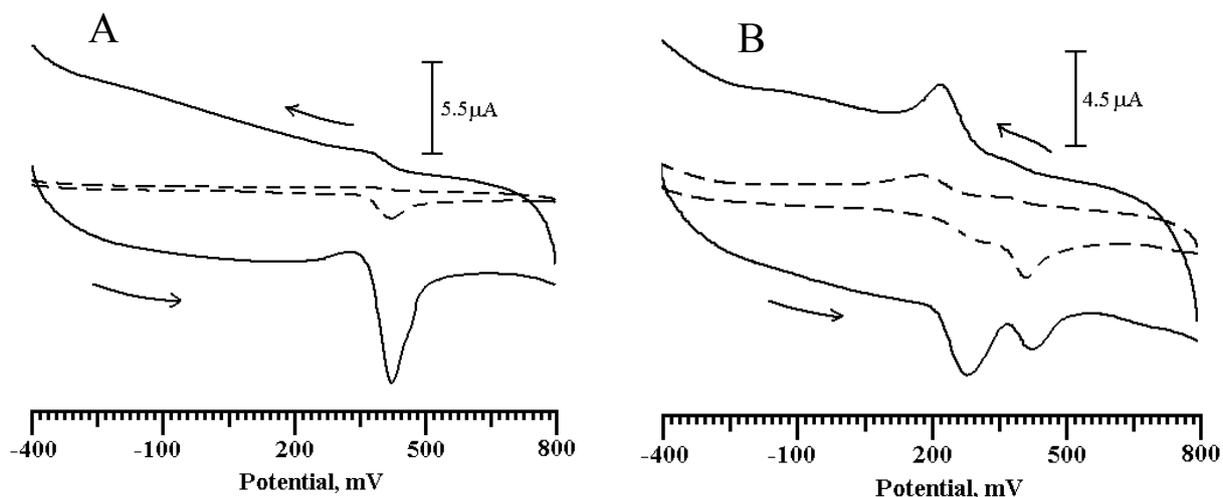


Fig. 6. A) Cyclic voltammogram of 0.5×10^{-3} M UA at bare GPE (dashed line) and at poly (FSBF) film coated GPE (solid line) in 0.2 M acetate buffer solution of pH 7.0. B) Simultaneous determination of 0.1×10^{-3} M DA and 0.5×10^{-3} M UA at bare GPE (dashed line) and at poly (FSBF) film coated GPE (solid line)

4. CONCLUSIONS

In this work, poly (FSBF) film coated GPE was used to investigate the electrochemical response of an interesting neurotransmitter DA. The poly (FSBF) film coated GPE enhanced both anodic and cathodic peak current strongly. The poly (FSBF) film coated GPE showed excellent selective and electrocatalytic activity towards the oxidation of DA in the presence of and UA. The poly (FSBF) film coated GPE has very low detection limit $0.05 \mu\text{M}$. Hence, poly (FSBF) modified GPE is acting as a good sensor for the detection of DA. We hope our modified electrode can be used for investigation of other neurotransmitters. The proposed methods can be applied to the detection of DA in injection.

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