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Direct Simultaneous Electrochemical Determination of Hydroquinone and Catechol at a Poly(glutamic acid) Modified Glassy Carbon Electrode

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A simply and high selectively electrochemical method for simultaneous determination of hydroquinone (HQ) and catechol (CC) has been developed at a glassy carbon electrode modified with electropolymerized films of glutamic acid (*p*-Glu). This *p*-Glu modified electrode is used to simultaneous electrochemical determination of HQ and CC and shows an excellent electrocatalytical effect on the oxidation of HQ and CC by cyclic voltammetry (CV) in 0.1 M acetate buffer solution (pH 4.5). In differential pulse voltammetric (DPV) measurements, the *p*-Glu modified electrode could separate the oxidation peak potentials of HQ and CC present in binary mixtures by about 102 mV though the bare electrode gave a single broad response. A successful elimination of the fouling effect by the oxidized product of HQ on the response of CC has been achieved at the *p*-Pen modified electrode. The determination limit of HQ in the presence of 0.1 M CC was 1.0×10^{-6} M and the determination limit of CC in the presence of 0.1 M HQ was 8.0×10^{-7} M. The proposed method has been applied to simultaneous determination of HQ and CC in a water sample with simplicity and high selectivity.

Keywords: Chemically modified electrode; Glutamic acid; Hydroquinone; Catechol; Electrochemical determination

1. INTRODUCTION

The determination of phenolic compounds is of interest in many fields, such as environmental control.[1] Hydroquinone (HQ) and catechol (CC) are two isomers of dihydroxybenzenes. Dihydroxybenzenes are important environmental pollutants because they are toxic to humans and difficult to degrade. Furthermore, because HQ and CC have similar structures and properties, they

usually coexist in products. Therefore, it is very important to develop simple and rapid analytical methods for dihydroxybenzene isomers [2]. The established methods for the determination of HQ and CC are commonly performed after pretreatment and separation [3]. This sample pretreatment and separation, as well as the significant operating complexity, the long times required and the large volumes of reagents consumed by established techniques, make it important to develop a new method capable of simultaneous determination without the need for prior separation of these compounds.

HQ and CC have a basic quinone structures that might be electrochemically oxidized at a platinum or carbon electrodes [4]. The oxidation process to quinone has been widely studied from electrochemical point of view[5-6]. But so many difficulties are existed to simultaneously determine HQ and CC. The major difficulty is that the voltammetric peaks corresponding to oxidation/reduction of two phenol isomers are, in many cases, highly overlapped. Moreover, the competition of the phenolic isomers by electrode surface makes the relationship between the voltammetric response and the isomers concentrations, in the mixtures, non-linear [1].

Recently, an enormous amount of research has been devoted to the development of new chemically modified electrodes (CMEs) for monitoring HQ or CC [7-16]. The simultaneous determination of HQ and CC at a glassy carbon electrode modified with multiwall carbon nanotubes has been proposed with potential wave separations of 102 mV between the oxidation peaks of HQ and CC [4]. Up to the present, few literatures for the simultaneous determination of HQ and CC using polymer-modified electrodes (PMEs) have been reported. Polymer-modified electrodes prepared by electropolymerization have received extensive interest in the determination of analytes because of their selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the films [17-19]. Polymer-modified electrodes are promising approach to determination of isomers and it has been used to simultaneously determine isomer such as dopamine and serotonin [20]. To our best knowledge, the simultaneous determination of HQ and CC at poly(glutamic acid) modified electrode has not been reported.

In an effort to develop a voltammetric method for the simultaneously selective and sensitive determination HQ and CC, the present work employed a glassy carbon electrode which was modified with poly(glutamic acid). The poly(glutamic acid) modified electrode could be used as a new sensor for simultaneously selective and sensitive determination of HQ and CC in binary mixtures by successful elimination of the fouling effect by the oxidized product of HQ on the response of CC. The proposed method has been applied to simultaneous determination of HQ and CC in a water sample with simplicity and high selectivity.

2. EXPERIMENTS

2.1. Reagents

L-Glutamic acid was purchased from Shanghai Chemical Factory (China) and it was used as received. Hydroquinone and catechol were obtained from Beijing Chemical Factory (China). All other chemicals were of analytical grade and were used without further purification. A 0.1 M acetate buffer solution (ABS) was used to control the pH. All solutions were prepared with deionized water treated in

a Millipore water purification system (Millipore Corp.). All experiments were carried out at room temperature.

2.2. Apparatus

Voltammetric measurements were performed with a CHI 440 electrochemical analyzer (CH Instruments, Chenhua Co. Shanghai, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a platinum wire counter electrode and a bare or modified glassy carbon disk working electrode (GCE). The pH values were measured with a PB-10 pH meter (Satorius). Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N_2 and kept under a N_2 blanket.

2.3. Preparation of poly(glutamic acid) modified glassy carbon electrode

Prior to electrochemical modification, the bare GCE with a diameter of 3 mm was polished with diamond pastes and alumina slurry down to 0.05 μm on a polishing cloth (Buehler, Lake Bluff, IL). Then it was rinsed with water and sonicated in 1 +1 HNO_3, acetone and water for 10 min, respectively. After being cleaned, the electrode was then placed in 0.01 M glutamic acid solution (pH 7.0 phosphate buffer solution) which was previously deaerated with high purity nitrogen for 10 min. The electrode was treated with cyclic scanning between -1.5 and 2.5 V at a scan rate of 100 mV s^{-1}, four times. A uniform adherent blue polymer was found on the GCE surface. After modification, the modified electrode was electroactivated by cyclic voltammetry from -0.2 to 0.8 V at 100 mV s^{-1} in pH 4.5 ABS. Then the electrode was ready for use after the final washing with water. Hereafter the modified electrode will be referred as the *p*-Glu modified electrode.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of HQ and CC at the p-Glu modified electrode

Fig. 1 shows cyclic voltammograms of HQ (A) and CC (B) at a scan rate of 100 mV s^{-1} in 0.1 M ABS (pH 4.5) at bare GCE (a) and *p*-Glu modified electrode (c), respectively. From Fig. 1A curve a, it can be seen, that at the bare electrode, the oxidation and reduction of HQ result in broad waves with the corresponding peak potentials of 272 mV and 91 mV. So it shows irreversible behavior with ΔE_p, the difference between the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}), 181 mV. However, at the *p*-Glu modified electrode, the reversibility of HQ is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 233 mV and the reduction peak positively shifts to 164 mV with ΔE_p = 69 mV. The peak current is 9.50-fold larger than the corresponding one at the bare GCE. These suggest that the *p*-Glu can act as a promoter to enhance the electrochemical reaction. *p*-Glu, itself, is electroinactive in the potential rage from -0.2 to 0.6 V (Fig. 1A curve b). Due to the high porosity of the *p*-Glu, the real surface area of the modified electrode is far greater than that of bare GCE. So the peak current increases evidently together with the background voltametric response at the *p*-Glu coated GCE stronger than that at the bare surface.

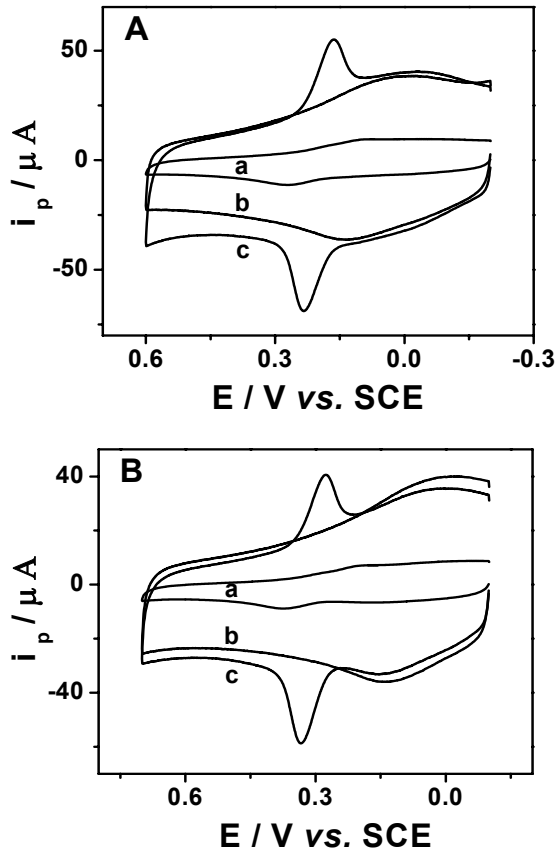

Figure 1. CVs at bare GCE (a) and *p*-Glu modified electrode (b, c) in presence of 0.1 mM analyte (a, c) and in the absence of analyte (b) in 0.1 M ABS (pH 4.5) at the scan rate of 100 mV s^{-1}. (A) HQ; (B) CC.

The CVs of CC at *p*-Glu modified electrode is also compared with that at bare GCE at a scan rate of 100 mV s^{-1} in 0.1 M ABS (pH 4.5) (Fig. 1B). At the bare electrode, the oxidation and reduction of CC result in broad waves with the corresponding peak potentials of 374 mV and 191 mV. And ΔE_p of CC at bare GCE was 183 mV. However, at the *p*-Glu modified electrode, the reversibility of CC is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 334 mV and the reduction peak positively shifts to 277 mV with ΔE_p = 57 mV. The peak current is 11.17-fold larger than the corresponding one at the bare GCE. These results indicated that *p*-Glu can accelerate the rate of electron transfer of CC in pH 4.5 ABS, and may be called a promoter.

Fig. 2 shows the CVs (Fig. 2A) and DPVs (Fig. 2B) obtained for HQ and CC coexisting at bare GCE (curve a) and *p*-Glu modified electrode (curve b). As shown in Fig. 2, the bare electrode cannot separate the voltammetric signals of HQ and CC. Only one broad voltammetric signal was observed for both analytes. The fouling of the electrode surface by the oxidation products results in a single voltammetric peak for HQ and CC. Therefore it is impossible to use the bare electrode for the voltammetric determination of CC in the presence of HQ.

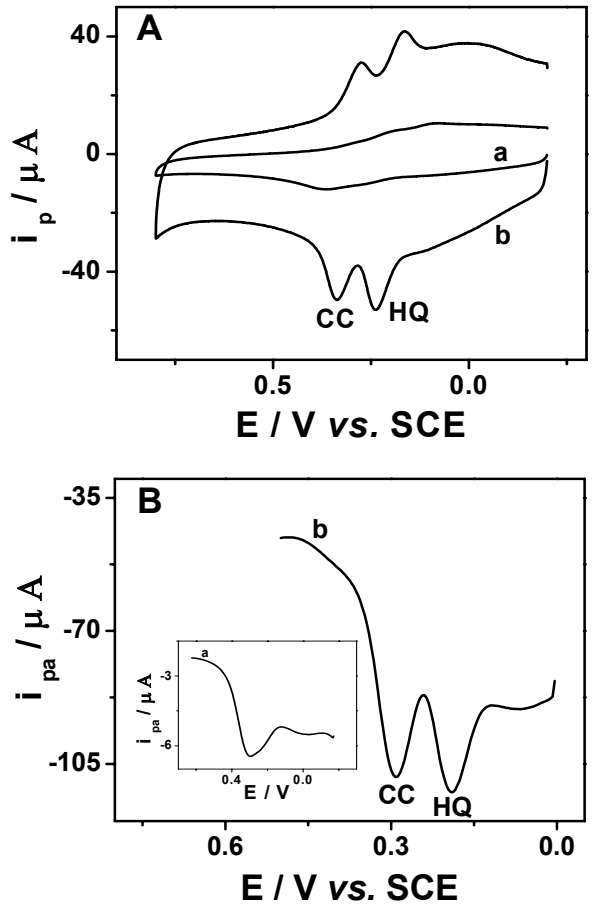

Figure 2. CVs (A) and DPVs (B) for the binary mixtures of 0.1 mM HQ and 0.1 mM CC at bare (a) and *p*-Glu modified electrode (b) in 0.1 M ABS (pH 4.5). (A) Scan rate, 100 mV s^{-1}; (B) scan rate: 4 mV s^{-1}; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms.

Moreover, the *p*-Glu modified electrode resolved the mixed voltammetric signals into two well-defined voltammetric peaks. The *p*-Glu modified electrode shows good selectivity and excellent sensitivity in the simultaneous determination of HQ and CC. The peaks observed at 292 and 190 mV in DPV recording is corresponding to the oxidations of CC and HQ, respectively (Fig. 2B). In theory, the density of the electron cloud is lower from HQ to CC, therefore their electroactivity is decreasing and the oxidation of the HQ is easier than that of CC, which shows that the potentials of their oxidation peaks increase. The experimental results accord with this theory [2]. As the oxidation potential of HQ is shifted to the less positive side, the anodic current of CC has no contribution from HQ, because HQ is readily oxidized well before the oxidation potential of CC reached. Thus elimination of the fouling of the electrode surface by the oxidation products could be achieved and the precise determination of CC in the presence of HQ is possible at the *p*-Glu modified electrode. The voltammetric signals of HQ and CC remained unchanged in the subsequent sweeps, indicating that the *p*-Glu modified electrode does not undergo surface fouling. Furthermore, the separation between the DPV oxidative peaks of HQ

and CC is large (ca. 102 mV) and thus the simultaneous determination of HQ and CC or the selective determination of CC in the presence of HQ is feasible at the *p*-Glu modified electrode.

3.2. Effect of scan rate on the peak current in binary mixtures of HQ and CC

Fig. 3 shows the cyclic voltammograms for the binary mixtures of 0.1 mM HQ and 0.1 mM CC in 0.1 M ABS (pH 4.5) at the *p*-Glu modified electrode at different scan rates. The oxidation peak potentials of the two compounds were observed to shift positively with the increase in scan rate. In addition, the oxidation peak current for the oxidation of HQ exhibited a linear relation to the square root of the scan rate, $v^{1/2}$, in the range from 20 to 300 mV s^{-1}, with the linear regression equation i_{pa} / μA= 0.1504 + 1.5192 $v^{1/2}$ / (mV s^{-1}) $^{1/2}$ (correlation coefficient, r=0.9951), suggesting that the oxidation of HQ at the *p*-Glu modified electrode is a diffusion-controlled process. Simultaneously, the oxidation peak current for the oxidation of CC also exhibited a linear relation to the square root of the scan rate, $v^{1/2}$, in the range from 20 to 450 mV s^{-1}, with the linear regression equation i_{pa} / μA= -10.7376 + 2.9277 $v^{1/2}$ / (mV s^{-1}) $^{1/2}$ (correlation coefficient, r=0.9952), suggesting that the oxidation of CC at the *p*-Glu modified electrode is a diffusion-controlled process.

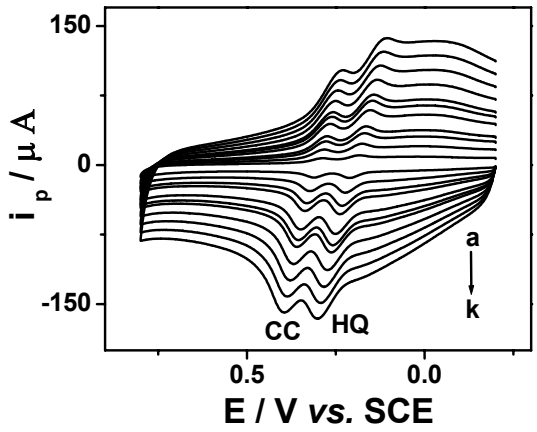

Figure 3. CVs for the binary mixtures of 0.1 mM HQ and 0.1 mM CC in 0.1 M ABS (pH 4.5) at the *p*-Glu modified electrode at different scan rates: (a) 20 mV s^{-1}; (b) 50 mV s^{-1}; (c) 80 mV s^{-1}; (d) 100 mV s^{-1}; (e) 150 mV s^{-1}; (f) 200 mV s^{-1}; (g) 250 mV s^{-1}; (h) 300 mV s^{-1}; (i) 350 mV s^{-1}; (j) 400 mV s^{-1}; (k) 450 mV s^{-1}.

3.3. Effect of pH on the oxidation HQ and CC in binary mixtures

The effect of the pH value of ABS on the responses of binary mixtures of HQ and CC was investigated by CV. The responses of HQ and CC were well-behaved in ABS, as the solution pH increases, the anodic peak potentials shift to the negative and the potentials of E_{pa} *vs.* pH in phosphate buffer solution have a good linear relation in the range of pH 3.05 - 6.57. The linear regression equations E_{pa} / V = 0.4532 – 0.0511 pH (correlation coefficient, r = 0.9960) for HQ and E_{pa} / V = 0.5584 – 0.0520 pH (correlation coefficient, r = 0.9957) for CC were obtained, which showed that the uptake of electrons is accompanied by an equal number of protons for both HQ and CC. For the

mixtures containing of HQ and CC, 0.1 M ABS was used to control the pH of mixture and the pH 4.5 was chosen, at this pH the oxidations of the two compounds have high electrochemical response.

3.4. Simultaneous determination HQ and CC

The above results indicate that the *p*-Glu modified electrode showed an excellent electrocatalytical effect on the oxidation of HQ and CC. In DPV measurements, the oxidation potential of HQ at the *p*-Glu modified electrode was found to be more negative by ca. 102 mV than that of CC. Therefore, this fact encouraged us to apply the *p*-Glu modified electrode to the simultaneous determination of HQ and CC.

The next attempt was taken to determine HQ and CC simultaneously by using the *p*-Glu modified electrode with DPV. Fig. 4 represents the DPV recordings at different concentrations of HQ where the concentration of CC was kept constant. The oxidative peak current for HQ was increased linearly with the increase in HQ concentration in the range of 5.0×10^{-6} -8.0×10^{-5} M. The linear regression equation was i_{pa} / μA = 2.4394 + 0.3009 C / μM (correlation coefficient, r = 0.9971) and the detection limit was 1.0×10^{-6} M in the presence of 0.1 mM CC. Furthermore, while HQ peak current increased with the increase in HQ concentration, the peak current of CC kept almost constant. Thus, it is confirmed that the responses of HQ and CC at the *p*-Cys modified electrode are independent.

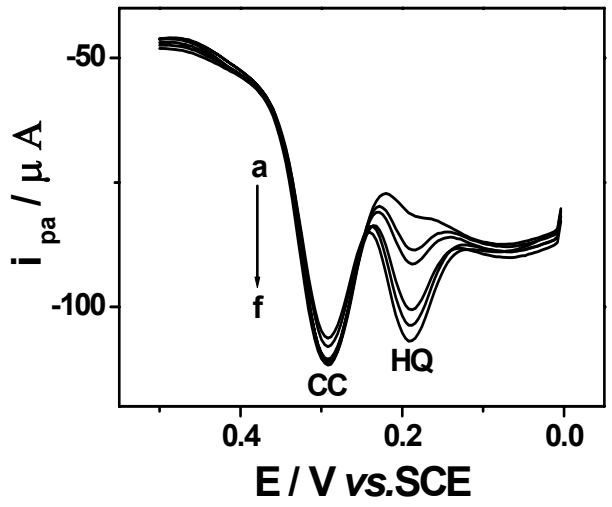

Figure 4. DPVs for the binary mixtures of HQ and CC at *p*-Glu modified electrode in 0.1 M ABS (pH 4.5), [CC] was kept constant and [HQ] was changed (i.e., [CC] = 0.1 mM, [HQ]: (a) 5, (b) 15, (c) 20, (d) 40, (e) 60, (f) 80 μM).

Fig. 5 represents the DPV recordings at different concentrations of CC where the concentration of HQ was kept constant. Here also the oxidative peak current for CC was increased linearly with the increase in CC concentration in the range of 1.0×10^{-6} -8.0×10^{-5} M. The linear regression equation was i_{pa} / μA = 1.1430 + 0.3490 C / μM (correlation coefficient, r = 0.9980) and the detection limit was

8.0×10^{-7} M in the presence of 0.1 mM HQ. Furthermore, while CC peak current increased with the increase in CC concentration, the peak current of HQ kept almost constant. This suggests that the fouling effect by the oxidized product of HQ on the response of CC cannot occur at the *p*-Glu modified electrode. Thus, the simultaneously selective and sensitive determination of HQ and CC was achieved at the *p*-Glu modified electrode.

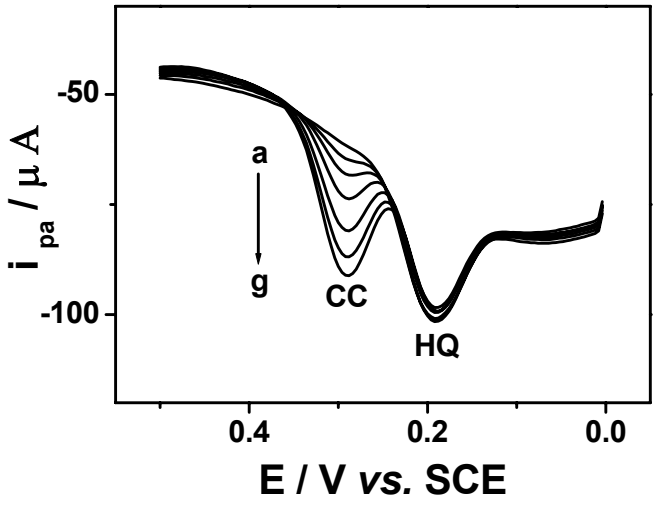

Figure 5. DPVs for the binary mixtures of HQ and CC at *p*-Glu modified electrode in 0.1 M ABS (pH 4.5), [HQ] was kept constant and [CC] was changed (i.e., [HQ] = 0.1 mM, [CC]: (a) 1, (b) 5, (c) 10, (d) 20, (e) 40, (f) 60, (g) 80 μM).

To ascertain further the reproducibility of the results, three different GCE was modified with *p*-Glu and their responses towards the oxidation of HQ and CC were tested. The separation between the voltammetric signals of HQ and CC and the sensitivities remained the same at all three modified electrode, confirming that the results are reproducible.

Table 1 Simultaneous determination results for HQ in local tap water containing CC

Sample No.	Tap water containing CC (μM)	HQ added (μM)	HQ found [a] (μM)	Recovery (%)
1	20.0	30.0	29.5	98.3
2	20.0	40.0	39.1	97.8
3	20.0	50.0	50.8	101.6

[a] Average of five determinations

Table 2 Simultaneous determination results for CC in local tap water containing HQ

Sample No.	Tap water containing HQ (μM)	CC added (μM)	CC found [a] (μM)	Recovery (%)
1	20.0	20.0	20.6	103.0
2	20.0	30.0	30.5	101.7
3	20.0	40.0	39.4	98.5

[a] Average of five determinations

3.5. Analytical applications

In order to assess the possible applications of the proposed method in direct simultaneous determination of HQ and CC, synthetic sample consisting of HQ and CC in local tap water were tested. The determination of HQ and CC in the samples was carried out using DPV at the *p*-Glu modified electrode in 0.10 M ABS (pH 4.5). The results are listed in Table 1 and Table 2. When known amount of HQ were added to the water control samples containing CC, quantitative recoveries of 97.8% - 101.6% were obtained. When known amounts of CC were added to the water control samples containing HQ, quantitative recoveries of 98.5% - 103.0% were obtained. A feasibility of the *p*-Glu modified electrode in the direct simultaneous determination of HQ and CC is evident.

4. CONCLUSIONS

The present study demonstrates an excellent approach for the development of a novel voltammetric sensor of hydroquinone and catechol based on poly(glutamic acid) coating. Fast electron transfer, high selectivity and excellent sensitivity for the oxidation of hydroquinone and catechol are achieved at the poly(glutamic acid) modified electrode. The present modified electrode showed excellent sensitivity, selectivity and antifouling properties and can separated oxidation peaks towards hydroquinone and catechol, which are indistinguishable at the bare electrode. As the voltammetric signals of hydroquinone and catechol are well separated at the poly(glutamic acid) modified electrode, the sensitive determination catechol in the presence of hydroquinone or the simultaneous determination of hydroquinone and catechol can be achieved. Chemically modified electrode modified with poly(glutamic acid) is a promising approach to determination of isomers.

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