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## Multilayer films of cationic surfactants incorporating polyoxometalate on electrodes

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**Abstract** A new kind of multilayer of didodecyldimethylammonium bromide (DDAB) and 1:12 phosphomolybdic anions ( $\text{PMo}_{12}$ ) was achieved on the surface of a wax-impregnated graphite (WIG) electrode by ion exchange and electrostatic interaction. The characterization and electrochemical behavior of the multilayer films of DDAB/ $\text{PMo}_{12}$  is described in detail. The chemically modified electrode was shown to exhibit an excellent electrocatalytic activity toward the reduction of  $\text{BrO}_3^-$  anion in 0.5 M  $\text{H}_2\text{SO}_4$  and possesses several attractive features, such as simple preparation, fast response, good stability, etc.

**Keywords** Multilayer films · Phosphomolybdic acid · Didodecyldimethylammonium bromide · Chemically modified electrode · Electrocatalysis

### Introduction

Polyoxometalates (POMs) are inorganic metal-oxygen cluster compounds that are unique in their topological and electronic versatility. POMs with well-defined primary structures are currently attracting much attention as building units of novel inorganic materials that are useful in catalysis, solid state devices, photo- and electrochromic displays, biochemistry, and medicine [1, 2, 3]. In recent years, POMs have received increasing interest in the field of chemically modified electrodes, owing to their excellent chemical stability, reversible redox activities, and special electrocatalytic properties. Attaching POMs onto electrodes not only simplifies their electrochemical study but also facilitates their applications. In general, there are three main strategies for attaching these species to an

electrode surface: electrochemical deposition [4, 5], adsorption [6, 7, 8, 9] and immobilization as a dopant in conductive polymeric matrices [10, 11, 12, 13]. Recently, a new kind of immobilization method for POMs has been reported, namely a layer-by-layer method based on electrostatic interaction between oppositely charged species has been used to build up a variety of well-defined multilayer assemblies of POMs with a precisely controlled thickness and layer sequence [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. The controlled incorporation of metal nanosized particles into a well-defined solid matrix is of widespread interest in materials science. POMs are an attractive class of nanoparticles because of their particularly interesting nanosized structure [26, 27] and their potential applications.

Developing electrode coatings designed for specific tasks has been a major research goal of recent years. Rusling and co-workers reported the incorporation of anionic metal phthalocyanines into cast films of didodecyldimethylammonium bromide (DDAB), and used these stable multilayer films to catalyze reductive dechlorination [28, 29, 30, 31, 32]. Insoluble surfactants used for cast films typically have two or three hydrocarbon chains of 12 or more carbon atoms. Films of water-insoluble surfactants can be prepared by casting their solution onto a solid support and evaporating the organic solvent. Casting films of insoluble surfactants onto electrodes seems a particularly easy method to make multilayer coatings. Stable, ordered surfactant films have a wide range of potential applications.

In the present study, we report on the preparation of multilayer films of cationic surfactants incorporating polyoxometalates on electrodes and the electrochemical behavior and electrocatalysis of the modified electrodes. The cationic surfactant DDAB and keggin-type 1:12 phosphomolybdic anions ( $\text{PMo}_{12}$ ) have been selected as examples. The modified electrodes exhibit remarkable electrocatalytic effects on the reduction of  $\text{BrO}_3^-$  and have very good stability.

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## Experimental

### Reagents

Reagent grade 1:12 phosphomolybdic acid [ $\text{H}_3(\text{PMo}_{12}\text{O}_{40}) \cdot x\text{H}_2\text{O}$ ] (denoted as  $\text{PMo}_{12}$ ) was purchased from the Beijing Chemical Reagent Company. Didodecyltrimethylammonium bromide (DDAB) was from Aldrich. All other chemicals were of analytical reagent grade and were used as received. All solutions were prepared with double distilled water.

### Instrumentation

Electrochemical experiments were performed with a CHI660A electrochemical workstation (USA). All experiments were done using a three-electrode cell configuration with a modified or unmodified wax-impregnated graphite (WIG) electrode as the working electrode, a saturated calomel reference electrode (SCE) and a platinum wire as the auxiliary electrode. All potentials were measured and reported versus the SCE (saturated KCl). The XRD pattern in the low-angle region was measured on a graphite monochromator, with the diffraction vector perpendicular to the plane of the film using Cu K $\alpha$  irradiation ( $\lambda = 1.5418 \text{ \AA}$ ; angular resolution  $0.02^\circ$ ) by a Rigaku D/max rA X-ray diffractometer.

### Fabrication of multilayer films of DDAB incorporating $\text{PMo}_{12}$ on WIG electrodes

Surfactant coatings were cast onto WIG electrodes as described [32]. DDAB films were prepared by pipetting  $10 \mu\text{L}$  of  $0.1 \text{ M}$  DDAB/chloroform onto the freshly abraded tip of a WIG electrode. Chloroform was evaporated overnight in air. DDAB electrodes loaded with  $\text{PMo}_{12}$  were prepared by soaking DDAB-WIG electrodes in  $1 \text{ mM}$   $\text{PMo}_{12} + 0.1 \text{ M}$   $\text{H}_2\text{SO}_4$  solution for 30 min, then washing with  $0.1 \text{ M}$   $\text{H}_2\text{SO}_4$  solution and drying in air.

Fabrication of the multilayer films on a graphite monochromator is similar to that of above system by substituting the WIG electrode with a graphite monochromator.

## Results and discussion

### Preparation and characterization of multilayer films of DDAB/ $\text{PMo}_{12}$

Films of the water-insoluble surfactant DDAB can be prepared by casting its solutions onto the tip of a WIG electrode and evaporating the organic solvent. Evaporation of the solvent leaves self-assembled multi-bilayer films, similar to stacks of biomembranes [33]. In the films, polar headgroups which contain positive charges link with each other, while nonpolar tails which usually contain long hydrocarbon chains also link with each other. So stable films can be cast from surfactants that are insoluble in water and do not form micelles. The anionic redox catalyst  $\text{PMo}_{12}$  can be introduced into liquid crystalline DDAB films on the surface of the electrodes by ion exchange and electrostatic interaction from aqueous solutions. An ideal model of multilayer films of DDAB/ $\text{PMo}_{12}$  on a WIG electrode is shown schematically in Fig. 1. The periodicity of the multi-bilayer structure in the film was investigated by XRD measurements. The composite film has more distinct

(001), (002), and (003) Bragg peaks at  $3.32^\circ$ ,  $6.62^\circ$ , and  $9.90^\circ$ , respectively, corresponding to  $d$  values of 26.61, 13.31, and  $8.87 \text{ \AA}$  (Fig. 2). These Bragg peaks indicate that the composite film forms a well-organized multi-bilayer structure with an interlayer spacing of  $26.61 \text{ \AA}$ .

### Electrochemical behavior of the multilayer films of DDAB/ $\text{PMo}_{12}$ on WIG electrodes

$\text{PMo}_{12}$  anions that have the keggin structure are unstable in neutral and basic aqueous solution and undergo a series of hydrolysis processes. Therefore electrochemical studies of the multilayer films of DDAB/ $\text{PMo}_{12}$  on WIG

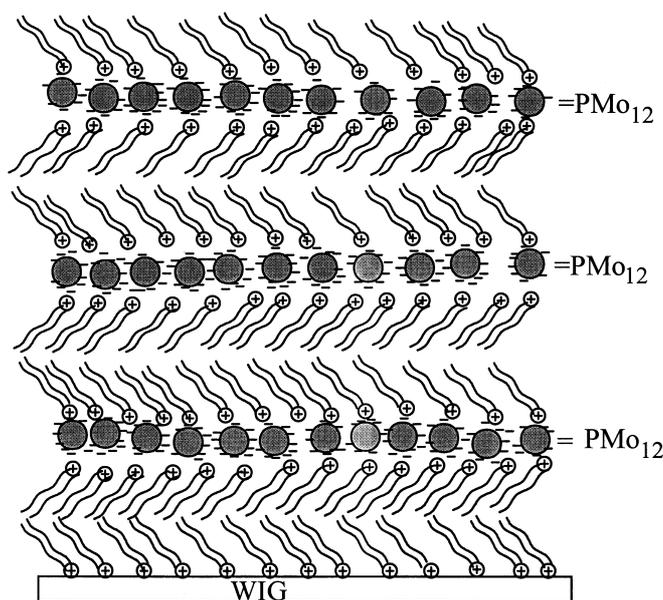


Fig. 1. Ideal model of the multilayer films of DDAB/ $\text{PMo}_{12}$  on a WIG electrode. Open circles containing a + symbol are cationic headgroups; curved lines are hydrocarbon tails

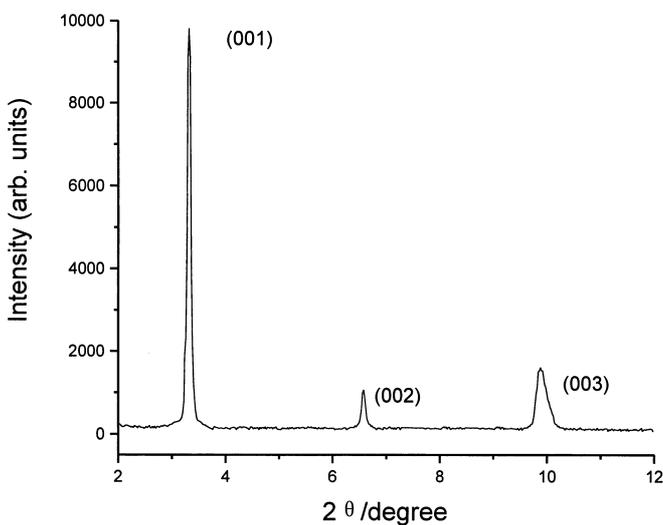


Fig. 2. XRD pattern of the multilayer films of DDAB/ $\text{PMo}_{12}$  in the low-angle region

electrodes were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Figure 3 shows the cyclic voltammograms in an aqueous solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> of a bare WIG electrode and a WIG electrode modified with DDAB/PMO<sub>12</sub>. From Fig. 3 it can be seen that in the potential range +0.6 to -0.2 V vs. SCE there is no redox peak at the bare WIG electrode (Fig. 3a), while at the DDAB/PMO<sub>12</sub> modified WIG electrode, three reversible redox peaks appear (Fig. 3b). The mean peak potentials,  $E_{1/2} = (E_{pa} + E_{pc})/2$ , are +0.295 (I), +0.180 (II), and -0.045 V (III), respectively. The peak potential separations are 50 (I), 60 (II), and 60 mV (III), respectively. Redox peaks I-I', I-II', and I-III' correspond to reduction and oxidation through two-, four-, and six-electron processes, respectively [34]. These experimental results show that PMO<sub>12</sub> anions can be fabricated on the surface of a WIG electrode by DDAB, based on ion exchange and electrostatic interaction. In addition, on comparing Fig. 3a and Fig. 3b it can be seen that the background current at the WIG electrode with multilayer films of DDAB/PMO<sub>12</sub> was larger than that at bare WIG electrode. This is because the double-layer capacitance of the latter is less than that of the former.

Figure 4A shows cyclic voltammograms of the multilayer films of DDAB/PMO<sub>12</sub> on WIG electrodes at different scan rates in a potential range from +0.60 to -0.20 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The peak currents of three redox couples increased linearly with the scan rate between 30 and 450 mV s<sup>-1</sup> (Fig. 4B), as expected for a surface process. Moreover, the cathodic peak currents were almost the same as the corresponding anodic peak currents and the peak potentials did not change with increasing scan rate.

In general, the reduction of heteropolyanions is accompanied by protonation; therefore, the pH of the solution has a great effect on the electrochemical behavior of heteropolyanions. Figure 5 shows the effect of pH on the electrochemical behavior of the multilayer films of DDAB/PMO<sub>12</sub> on WIG electrodes. PMO<sub>12</sub> anions are

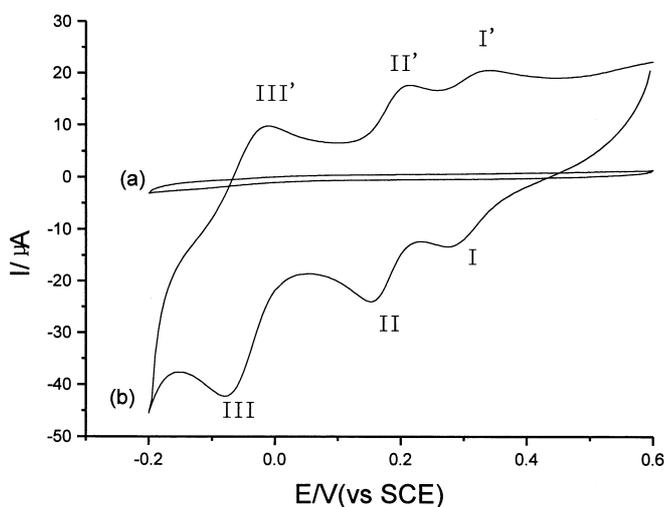


Fig. 3. Cyclic voltammograms of 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a bare WIG electrode (a) and at a WIG electrode modified with PMO<sub>12</sub> anions (b). Scan rate 50 mV s<sup>-1</sup>

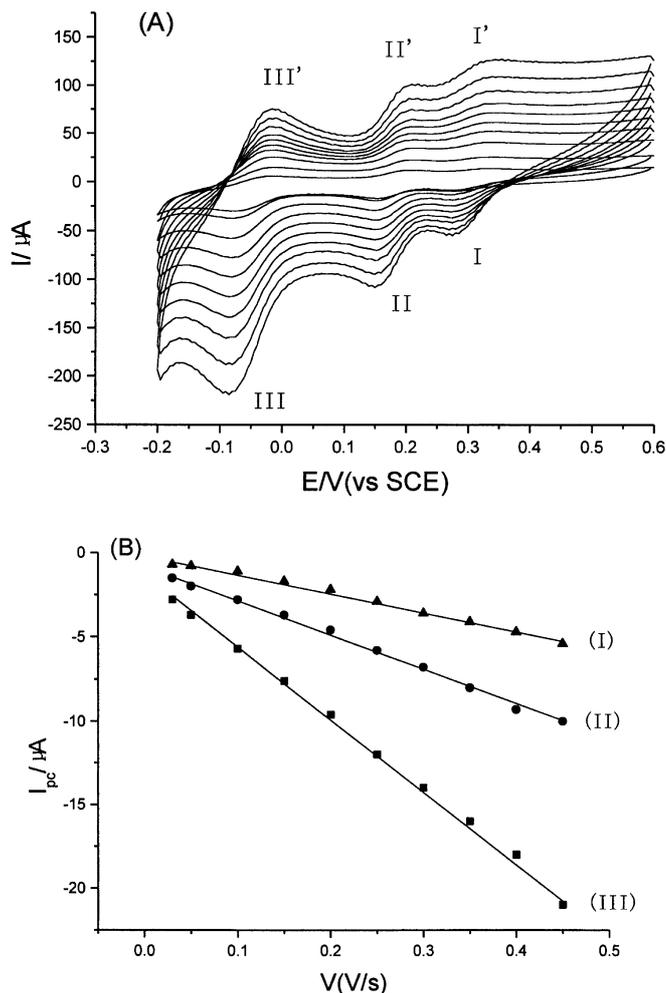


Fig. 4. A Cyclic voltammograms of the multilayer films of DDAB/PMO<sub>12</sub> on a WIG electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at different scan rates (from inner to outer curve: 30, 50, 100, 150, 200, 250, 300, 350, 400, and 450 mV s<sup>-1</sup>). B Relationship between peak current  $I_{pc}$  and scan rate

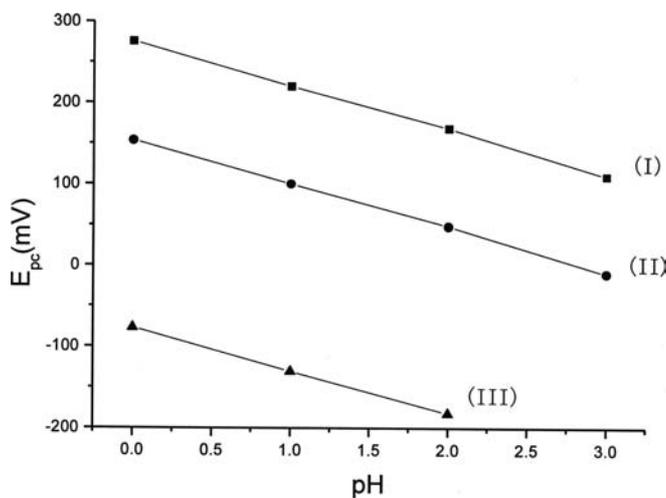
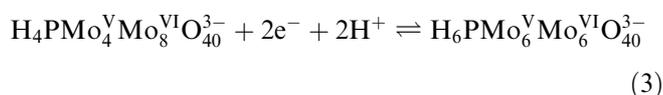
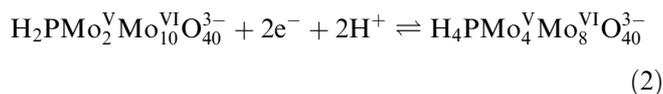
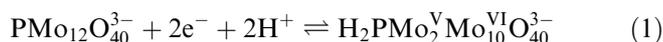


Fig. 5. Relationship between  $E_{pc}$  and pH for the modified electrode

stable in aqueous media at a pH of less than 4.0. Beyond this pH range,  $\text{PMo}_{12}$  anions become unstable owing to hydrolytic decomposition. From Fig. 5 it can be seen that within the pH range of stable anions, the mean peak potentials for all three redox couples are dependent on the pH. In the range  $1.0 < \text{pH} < 4.0$ , only two redox couples appear in the potential range  $+0.60$  to  $-0.20$  V. With the increase of the solution pH, the peak potentials shift negatively, and a linear relationship is observed between the peak potential and the solution pH value, which is clearly seen in Fig. 5. From Fig. 5, the values of  $dE_{\text{pc}}(\text{I})/d\text{pH}$ ,  $dE_{\text{pc}}(\text{II})/d\text{pH}$ , and  $dE_{\text{pc}}(\text{III})/d\text{pH}$  are calculated as  $-55$ ,  $-52$ , and  $-55$  mV, respectively. All these values are close to the theoretical value of  $-60$  mV/pH units for a  $2e^-, 2\text{H}^+$  process, confirming that, in the multilayer films of DDAB/ $\text{PMo}_{12}$ , the two-electron exchange is accompanied by two protonation reactions.

According to the above results, the three redox processes of the multilayer films of DDAB/ $\text{PMo}_{12}$  on a WIG electrode can be described as follows:



The stability of the multilayer films of DDAB/ $\text{PMo}_{12}$  on the electrode was investigated. The multilayer film electrode showed a high stability. In the potential range from  $+0.60$  to  $-0.20$  V vs. SCE and in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution, after about 30 scanning cycles the current response remained almost unchanged. When the electrode was stored in the atmosphere or in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution, the current response remained almost unchanged for one month. In experiments we found that the stability of the multilayer film electrode depended on the acidity of the electrolyte solution and the applied potential. On increasing the solution pH, the peak potential moved in a negative direction (see Fig. 5). When the pH of the solution was more than 4, the wave shapes became ill-defined and the stability of the multilayer film electrode decreased. When the applied potential was lower than  $-0.2$  V vs. SCE, the multilayer film surface of the WIG electrode was destroyed.

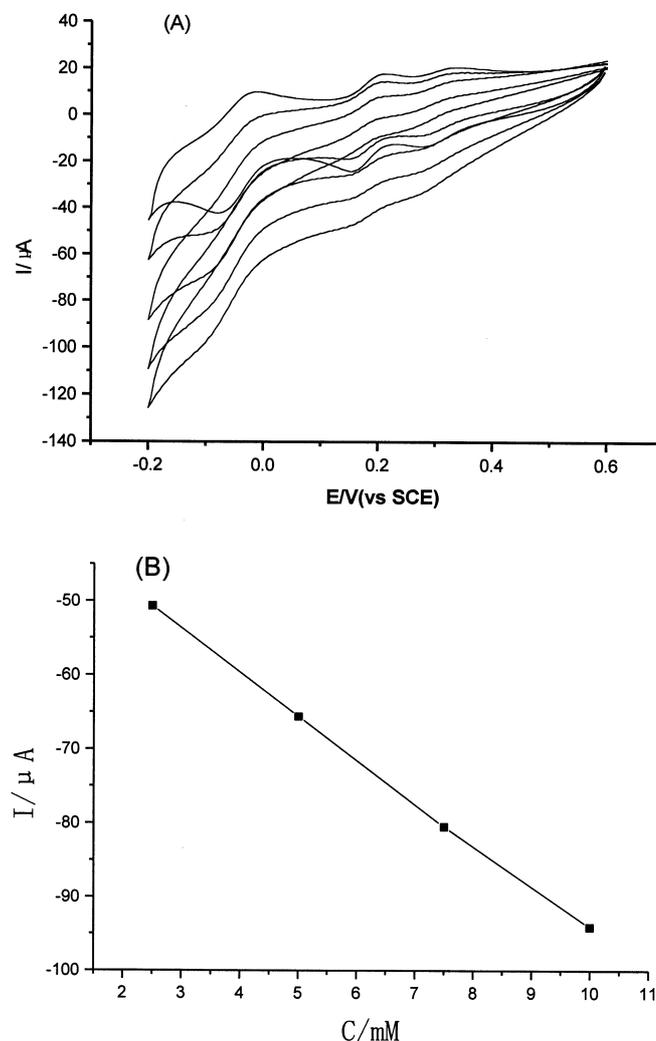
Catalytic reduction of the  $\text{BrO}_3^-$  anion at the multilayer films of DDAB/ $\text{PMo}_{12}$  on WIG electrodes

Unoura et al. [35] and Dong and Jin [11] have studied the catalytic effect of  $\text{PMo}_{12}$  anions on the reduction of  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  in homogeneous aqueous solution and at a  $\text{PMo}_{12}$ /PPy film electrode, respectively. Here, we

investigated the electrocatalytic reduction of  $\text{BrO}_3^-$  by the multilayer films of DDAB/ $\text{PMo}_{12}$  on WIG electrodes. Figure 6A shows cyclic voltammograms of the multilayer films of DDAB/ $\text{PMo}_{12}$  on the electrodes in  $0.5$  M  $\text{H}_2\text{SO}_4$  solutions containing  $\text{BrO}_3^-$  anion at various concentrations. From Fig. 6A it can be seen that the reduction currents rise while the oxidation currents decrease and disappear. The catalytic wave appeared mainly on the third reduction wave (peak III) of the  $\text{PMo}_{12}$  anions, corresponding to six-electron to four-electron reduction of  $\text{PMo}_{12}$  anions. The catalytic currents were proportional to the  $\text{BrO}_3^-$  concentration in the range  $2.5 \times 10^{-3}$  M to  $1.0 \times 10^{-2}$  M, as shown in Fig. 6B.

## Conclusions

It has been demonstrated that multilayer films of DDAB/ $\text{PMo}_{12}$  can be fabricated on the surface of a



**Fig. 6.** **A** Cyclic voltammograms of the multilayer films of DDAB/ $\text{PMo}_{12}$  on a WIG electrode in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution containing  $\text{BrO}_3^-$  anion concentrations of (from top to bottom)  $0.00$ ,  $2.5 \times 10^{-3}$ ,  $5.0 \times 10^{-3}$ ,  $7.5 \times 10^{-3}$ , and  $1.0 \times 10^{-2}$  M. Scan rate  $50$  mV  $\text{s}^{-1}$ . **B** Catalytic current  $I$  vs.  $\text{BrO}_3^-$  anion concentration  $C$

WIG electrode, based on ion exchange and electrostatic interaction. The chemically modified electrode can catalyze electroreduction of the  $\text{BrO}_3^-$  anion and has many advantages, such as simple fabrication, fast response, good stability, and independence of basic electrode size and topology.

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