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# Three-Dimensional Nanoporous Iron Nitride Film as an Efficient Electrocatalyst for Water Oxidation

Fang Yu,<sup>†,‡</sup> Haiqing Zhou,<sup>†,‡</sup> Zhuan Zhu,<sup>§</sup><sup>®</sup> Jingying Sun,<sup>†</sup> Ran He,<sup>†</sup> Jiming Bao,<sup>§</sup><sup>®</sup> Shuo Chen,<sup>\*,†</sup> and Zhifeng Ren<sup>\*,†</sup><sup>®</sup>

<sup>†</sup>Department of Physics and TcSUH, University of Houston, Houston, Texas 77204, United States

<sup>§</sup>Department of Electrical and Computer Engineering, University of Houston, Houston, Texas 77204, United States

**Supporting Information** 

**ABSTRACT:** Exploring efficient and durable catalysts from earth-abundant and cost-effective materials is highly desirable for the sluggish anodic oxygen evolution reaction (OER), which plays a key role in water splitting, fuel cells, and rechargeable metal—air batteries. First-row transition-metal (Ni, Co, and Fe)-based compounds are promising candidates as OER catalysts to substitute the benchmark of noble-metalbased catalysts, such as  $IrO_2$  and  $RuO_2$ . Although Fe is the cheapest and one of the most abundant transition-metal elements, there are seldom papers reported on Fe-only



compounds with outstanding catalytic OER activities. Here we propose an interesting strategy by growing iron nitride  $(Fe_3N/Fe_4N)$  based nanoporous film on three-dimensional (3D) highly conductive graphene/Ni foam, which is demonstrated to be a robust and durable self-supported 3D electrode for the OER featuring a very low overpotential of 238 mV to achieve a current density of 10 mA/cm<sup>2</sup>, a small Tafel slope of 44.5 mV/dec, good stability, and 96.7% Faradaic yield. The high OER efficiency is by far one of the best for single-metal (Fe, Co, and Ni)-based catalysts, and even better than that of the benchmark  $IrO_2$ , which is attributed to the fast electron transfer, high surface area, and abundant active sites of the catalyst. This development introduces another member to the family of cost-effective and efficient OER catalysts.

KEYWORDS: iron nitride, oxygen evolution reaction, three-dimensional, nanoporous, water splitting

# INTRODUCTION

The oxygen evolution reaction (OER), which is the process of generating molecular oxygen through electrocatalytic water oxidation, plays an important role in many energy conversion and storage technologies, including water splitting for hydrogen production, regenerative fuel cells, and metal-air batteries.<sup>1</sup> However, the OER is a sluggish process with slow kinetics, since it involves multiproton-coupled electron transfer steps.<sup>4,5</sup> Especially for water splitting, which is considered to be a promising route for hydrogen fuel generation from abundant water, the OER is considered as a major bottleneck, since it is kinetically slow and requires a high overpotential to reach a substantial current density in water electrolysis. This reaction can be improved once some efficient catalysts are utilized. Thus, extensive attention has been paid to seeking efficient OER catalysts from earth-abundant and cost-effective elements,<sup>6-8</sup> to replace the rather scarce and expensive RuO<sub>2</sub> and IrO<sub>2</sub> catalysts.<sup>2</sup>

First-row transition-metal-based compounds have attracted great attention as OER catalysts, including oxides,<sup>10,11</sup> hydroxide,<sup>12,13</sup> oxyhydroxide,<sup>14</sup> sulfides,<sup>3,15</sup> selenides,<sup>8</sup> and phosphides.<sup>16,17</sup> Considerable efforts have been devoted to fabricating catalysts from nickel (Ni)- or cobalt (Co)-based compounds, while much less attention has been paid to pure or

mainly iron (Fe)-based compounds, even though Fe is the most abundant transition metal in the earth's crust. At present, several Fe-based catalysts have been investigated, but their catalytic performance is still inefficient probably due to the low electrical conductivity of the material itself (FeS<sub>x</sub>, FeO<sub>x</sub>, etc.),<sup>18,19</sup> which results in the formation of Schottky barriers at both catalyst-electrolyte and catalyst-support electrode interfaces, thus limiting the improvement of the OER efficiency. It is appealing to find an efficient catalyst with high electrical conductivity to ensure fast electron transfer from the catalyst surface to the support electrode. In this regard, first-row transition-metal (Fe, Co, and Ni) nitrides are promising alternatives, owing to their almost metallic properties with good electrical conductivity.<sup>20-22</sup> Particularly, it is well-known that three-dimensional (3D) porous architectures could significantly enhance the catalytic activity and reaction kinetics because of high catalyst loading and large contact area between the catalyst and electrolytes. Therefore, considering the low cost, natural abundance, and environmental benignity of iron, it would be

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attractive if we could prepare an efficient and durable 3D porous OER catalyst mainly from metallic iron nitride.

In this work, we report a new catalyst mainly based on an Fe compound that is constructed by growing nanoporous  $Fe_3N/Fe_4N$  ( $Fe_xN$ ) film on a 3D electrically conductive interconnected graphene network, which is confirmed to be an efficient and durable 3D self-supported electrode for efficient OER activity. This hybrid catalyst exhibits outstanding catalytic performance with a very low overpotential (238 mV) to achieve a 10 mA/cm<sup>2</sup> geometric current density and small Tafel slope of 44.5 mV/dec, which is by far the best iron-based catalyst, even better than the benchmark  $IrO_2$ . The superior catalytic performance of the nanoporous  $Fe_xN$  film/graphene hybrid can be attributed to its good electrical conductivity, abundant active sites, and high surface area of the hybrid.

#### RESULTS AND DISCUSSION

An effective way to enhance the OER efficiency is to make the catalysts in three dimensions with nanoporous or macroporous structures. Here we selected Ni foam as the scaffold for preparing 3D catalysts due to its low price, high electrical conductivity, rich macroporosity, and commercial availability (Figure S1 in the Supporting Information).<sup>23–25</sup> However, the problem of the foam is the possible difficulty in tailoring its properties and structures, such as pore structures. In our experiment, we first coated the Ni foam with highly electrically conductive graphene networks, as confirmed by SEM and a Raman spectrum (Figure S2 in the Supporting Information). Then the samples were decorated with the  $Fe(NO_3)_3$  precursor in dimethylformamide (DMF) solvent and slowly dried in a sealed sample box. After that, the samples were annealed under an Ar atmosphere at 400 °C for 30 min and thermally nitrided by NH<sub>3</sub>/Ar gas at 400 °C for 1 h. According to the typical SEM images (Figure 1a-c), it is obvious that the iron nitride film is uniformly formed on the surface of graphene/Ni foam after thermal nitridation. More interestingly, it is clearly shown that the iron nitride film is in the form of nanoporous structures, rather than a uniform dense film. This is probably due to the low volatility of DMF solvent at room temperature, which results in uniform distribution of the Fe(NO<sub>3</sub>)<sub>3</sub> precursor on



Figure 1. (a-c) Typical SEM images showing the nanoporous structures of as-prepared iron nitride catalyst on 3D macroporous graphene/Ni foam. (d) Typical HRTEM image showing the crystal structures of the as-prepared catalyst.

graphene and gradual decomposition with an increase in the heating temperature. In contrast, once we change the solvent from DMF to ethanol solution, the as-prepared iron nitride catalyst tends to aggregate on the graphene surface, and no such nanoporous structure can be observed, probably due to the low boiling point and volatile feature of the ethanol solvent (Figure S3 in the Supporting Information). Our method is much simpler in comparison to the normal procedures for making porous materials, such as electrochemical anodization,<sup>10</sup> template synthesis,<sup>26</sup> etc. This additional porosity in the iron nitride film plays a positive role in the catalytic process, as it can engineer the number of active sites in the catalyst.<sup>27</sup> In addition, high-resolution transmission electron microscopy (HRTEM) was utilized to analyze the crystal structures of the as-prepared iron nitride catalysts (Figure 1d). According to the HRTEM image shown in Figure 1d, there are distinct lattice fringes with spacing distances of 0.19, 0.21, and 0.24 nm, which are identical with the (002) lattice plane of  $Fe_4N^{28}$  and (111) and (120) lattice planes of Fe<sub>3</sub>N crystals, respectively. Moreover, we can find many nanocrystals with sizes of several nanometers, as shown in the TEM image, indicating that there are abundant active sites in the catalyst, which play an important role in high catalytic performance. These observations indicate that the asprepared iron nitride catalyst is nanoporous and highly crystalline.

The structural information of the as-obtained samples was further examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Figure 2a shows the XRD pattern of the as-prepared samples. For comparison, the standard XRD peaks of metallic Ni (ICSD-76667), Ni<sub>3</sub>N (ICSD-76402), and Fe<sub>3</sub>N (ICSD-20398) are also included here. Obviously, XRD patterns of the as-prepared samples exhibit a prominent peak at  $26^{\circ}$  corresponding to the (002) face of graphene<sup>29</sup> and three strong peaks at 44.4, 51.7, and 76.1° originating from the (111), (002), and (022) faces of metallic Ni foam, respectively, and the rest of the peaks are due to the faces of Fe<sub>3</sub>N, Fe<sub>4</sub>N,  $^{28}$  and Ni<sub>3</sub>N crystals. Meanwhile, XPS was employed to confirm the surface chemistry and composition of the iron precursor, in which the Fe, C, and N elements are obviously detected (Figure 2b-d and Figure S4 in the Supporting Information). It is seen from the XPS spectra that there is an obvious peak located at 397 eV for the N element,<sup>30</sup> and the Fe  $2p^{3/2}$  peak position at 707.5 eV is characteristic of unoxidized Fe in iron nitride, further confirming the formation of iron nitride by NH<sub>3</sub> nitridation.<sup>20,22</sup> According to XPS elemental analysis, the atomic ratio between Fe and N elements is above 3 (Table S1 in the Supporting Information), which is consistent with that of the mixed Fe<sub>3</sub>N/Fe<sub>4</sub>N compound identified by XRD and HRTEM. Thus, XRD and XPS analyses confirm the successful conversion of the iron precursor into iron nitride via NH<sub>3</sub> nitridation at 400 °C.

An efficient oxygen evolution catalyst should have high current density at very low overpotentials, small Tafel slope, and good durability. To identify whether nanoporous  $Fe_xN$  film is a promising electrocatalyst for the OER with high catalytic activity, electrochemical measurements were carried out via a standard three-electrode system in O<sub>2</sub>-saturated 1 M KOH solution. This self-standing hybrid foam was directly used as the working electrode with a catalyst loading of 4 mg/cm<sup>2</sup>. As shown in Figure 3a, the as-prepared nanoporous  $Fe_xN$  catalyst has a much lower onset potential and higher current density than the support (NH<sub>3</sub>-treated graphene/Ni foam) and iron



Figure 2. XRD and XPS analysis of the as-prepared  $Fe_xN$  catalysts: (a) typical XRD patterns; (b) C 1s, (c) Fe 2p, and (d) N 1s XPS spectra of the  $Fe_xN$  catalyst.



Figure 3. Electrochemical performance of as-prepared nanoporous  $Fe_xN$  film for oxygen evolution in comparison with the support and iron oxide: (a) polarization curves and (b) Tafel plots recorded on different catalysts; (c) long-term cycling tests of the  $Fe_xN$  catalyst; (d) time dependence of anodic current density during electrolysis at a current density of 80 mA/cm<sup>2</sup> for the  $Fe_xN$  catalyst.

oxide (Figure S5 in the Supporting Information), suggesting that nanoporous iron nitride film is the best OER catalyst studied here. To assess the catalytic performance, an overpotential at a current density of 10 mA/cm<sup>2</sup> was obtained as a common criterion for every catalyst. Our nanoporous electrode requires a very small overpotential (238 mV) to achieve a geometric current density of 10 mA/cm<sup>2</sup>, which is much smaller than that of the support (389 mV) and iron oxide catalyst (339 mV), demonstrating that the conversion of iron

oxide to nanoporous  $Fe_xN$  film can significantly boost the catalytic performance. This overpotential (238 mV) is also much lower than that for most of the reported Ni- or Co-based compounds (Table S2 in the Supporting Information) such as sulfides,<sup>31</sup> oxides,<sup>10,11</sup> phosphides,<sup>17,31</sup> and nitrides,<sup>30,32,33</sup> and furthermore, it is better than that for the IrO<sub>2</sub> benchmark for OER (Figure S6 in the Supporting Information),<sup>17</sup> suggesting that our as-prepared nanoporous iron nitride catalyst is a good OER catalyst.



**Figure 4.** Characterization of the different electrodes for OER by EIS and a simple CV method. (a) EIS spectrum of nanoporous  $Fe_xN$  catalyst (red curve) in comparison with iron oxide (black curve) and the graphene/Ni foam support (blue curve). (b) CV curves of as-prepared iron oxide catalyst at different scanning rates ranging from 10 to 100 mV/s with an interval point of 10 mV/s. (c) CV curves of  $Fe_xN$  catalyst at different scanning rates ranging from 10 to 100 mV/s with an interval point of 10 mV/s. (c) CV curves of  $Fe_xN$  catalyst at different scanning rates ranging from 10 to 100 mV/s with an interval point of 10 mV/s. (d) Plot showing the extraction of the  $C_{dl}$  values from different electrodes: iron oxide (black) and nanoporous  $Fe_xN$  (red). (e) Detection of  $O_2$  gas from the  $Fe_xN$  electrode by a gas chromatography instrument. (f) Experimental and theoretical  $O_2$  amounts by an  $Fe_xN$  electrode at a fixed oxidative current of 20 mA.

To gain further insight into the superior performance of the nanoporous Fe<sub>x</sub>N film, we have further analyzed the Tafel slopes of different catalysts (Figure 3b). Evidently, this Fe<sub>x</sub>N catalyst has a very small Tafel slope of 44.5 mV/dec, which is much smaller than those of the support (91.7 mV/dec) and iron oxide catalyst (79.6 mV/dec). This is appealing, since a small Tafel slope is very beneficial to a fast increase in the reaction rate with an increase in potential. Another critical criterion to assess the electrocatalysts is the long-term electrochemical durability. We have investigated the stability of the as-prepared Fe<sub>x</sub>N catalysts by long-term cycling for 1000 cycles (Figure 3c) and a chronoamperoetry test for over 17 h (Figure 3d). Obviously, after the 1000 cycle test, the polarization curve recorded on the nanoporous Fe<sub>x</sub>N catalyst is basically identical with the initial curve, indicating that no degradation has taken place. Particularly, the anodic current density for the Fe<sub>x</sub>N catalyst remains stable and exhibits no obvious degradation for oxygen electrolysis at a current density of 80 mA/cm<sup>2</sup> for over 17 h (Figure 3d), meaning that this catalyst can stably perform over a long time in an electrochemical process. The low overpotential (238 mV) to achieve a current density of 10 mA/cm<sup>2</sup>, small Tafel slope (44.5 mV/

dec), and good durability corroborate that the  $Fe_xN$  film is an outstanding OER catalyst.

To elucidate the physical origins of the high catalytic performance in the Fe<sub>x</sub>N catalyst, electrochemical impedance spectroscopy (EIS) was utilized to examine the electrode kinetics under the OER operating conditions (Figure 4a). On the basis of the Nyquist plots, it is clearly revealed that the charge-transfer resistance for the Fe<sub>x</sub>N electrode is largely reduced in comparison with that of iron oxide or the graphene/ Ni foam support, which is in good agreement with the lowest Tafel slope in Figure 3b, suggesting that nanoporous Fe<sub>x</sub>N film has the fastest charge transfer process among these three catalysts. This is probably related to the good electrical contact between the catalyst and its support originating from the intrinsically metallic feature of iron nitride and good conductivity of graphene/Ni foam, resulting in rapid electron transfer from the electrode to the catalyst surface. Active surface area is another important factor for the catalysts in the OER, which is directly associated with the number of active sites. The electrochemically active surface area can be evaluated by measuring the electrochemically effective double-layer capacitance  $(C_{dl})$  through a simple cyclic voltammetry (CV) method.<sup>23,25,34</sup> As shown in Figure 4b-d and Figure S7 in the Supporting Information, we can obtain the  $C_{dl}$  values for different catalysts, which are half the values of the linear slopes in the plots, showing the relationship between the positive and negative current density differences  $(\Delta j = j_a - j_c)$  and the CV scan rates at a given potential (1.074 V vs RHE). Obviously, the nanoporous Fe<sub>x</sub>N electrode exhibits a C<sub>dl</sub> value of 13.92 mF/  $cm^2$ , which is nearly twice that of the iron oxide (7.89 mF/  $cm^2$ ), meaning that more active sites are introduced in the iron nitride catalyst. The higher active surface area of the nanoporous Fe<sub>x</sub>N catalyst can be attributed to the nanopores and nanocrystals in Fe<sub>x</sub>N film, which accordingly results in the improved catalytic performance. Furthermore, to unveil the possible mechanisms, high-resolution XPS spectra were collected to check the composition change after 1000 cycles for the OER test (Figure S8 in the Supporting Information). It was noticed that the characteristic Fe  $2p^{3/2}$  peak at 707.5 eV and the N 1s peak at 397 eV for the Fe, N cannot be detected and that the O 1s peak exhibits an obvious increase in the peak intensity, confirming that Fe atoms have been partially oxidized, and an iron oxide shell is formed on the surface of Fe<sub>x</sub>N catalysts. This means that the inner Fe, N cores serve as highly conductive layers to provide reliable electron transfer to the surface active sites and can efficiently overcome the poor electrical conductivity of iron oxide. This is why the chargetransfer resistance of iron nitride derived catalysts is much smaller than that of iron oxide extracted from the EIS spectra (Figure 4a). All of this information allows the conclustion that the real catalytic active sites for the OER probably originate from the oxidized iron species at the catalyst surface, which is in good agreement with recent results on the Co4N catalyst for the OER.<sup>33</sup> Finally, the gaseous products from the OER by this Fe, N electrode were determined using gas chromatography (Supporting Information). Oxygen is found to be the only product with a high Faradaic efficiency, calculated to be close to 96.7% (Figure 4e,f). The 3.3% difference may be related to the existing side reactions of the partial oxidation of iron nitride at the surface.

In general, in comparison to the majority of OER catalysts, the as-prepared nanoporous Fe<sub>x</sub>N catalyst has the following advantages. First, iron nitride itself and the 3D graphene network on Ni foam both have good electrical conductivity, ensuring good electrical contact and fast electron transfer from the electrode to the catalyst surface. Thus, it is not necessary to require an additional overpotential to overcome the possible barrier formation at the interface. Second, 3D porous architectures are highly desirable for catalyst fabrication, since they exhibit a high surface area for catalyst loading and high contact area for the electrolyte to access the catalyst surface. Our as-prepared Fe<sub>x</sub>N catalyst is composed of many nanosized particles and shows many additional nanopores. Together with the macroporous structures in Ni foam, the Fe<sub>x</sub>N catalyst exhibits a high active surface area with an abundance of active sites exposed to the electrolyte. Accordingly, the reaction kinetics during the OER process can be greatly enhanced because of the sufficient pathways for electron transfer from the electrode to the catalyst surface and easy diffusion of the electrolyte into the active sites. Therefore, these advantages make the nanoporous Fe<sub>x</sub>N catalyst a promising and efficient OER catalyst with outstanding catalytic activity.

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In conclusion, we have introduced a simple strategy to fabricate nanoporous Fe-based Fe<sub>x</sub>N film on 3D graphene/Ni foam as an efficient OER catalyst. This 3D hybrid catalyst has an outstanding catalytic OER performance featured by high current density at a low overpotential, small Tafel slope, and long-term stability; these are better than those of most of the Ni- or Co-based catalysts and the  $IrO_2$  benchmark. The excellent catalytic activity of this Fe<sub>x</sub>N catalyst is mainly attributed to the fast charge transfer between the metallic Fe<sub>x</sub>N catalyst and its support, increased active catalytic sites from the nanoporous structures of the Fe<sub>x</sub>N catalyst, and great contact area with the electrolyte from the macroporous structures of graphene/Ni foam. This work demonstrates that Fe-based compounds have the potential to be used as efficient catalysts for catalytic oxygen evolution.

#### EXPERIMENTAL SECTION

**Synthesis of Graphene on Ni Foam (NF).** Graphene was synthesized directly on NF via chemical vapor deposition. First, the NF was thermally annealed at 950 °C under a flow of 400 standard cubic centimeters (sccm) of  $H_2$  for 10 min under atmospheric pressure. Subsequently, 400 sccm Ar and 10 sccm carbon source of  $C_2H_4$  were introduced into the chamber for 10 min. Then  $C_2H_4$  was turned off and the samples were quickly removed to the room-temperature zone of the quartz tube. Finally, the samples were cooled to room temperature under the protection of  $H_2$  and Ar.

**Synthesis of Iron Nitride (Fe<sub>x</sub>N) Film on Graphene/NF.** Graphene/NF was immersed into an  $Fe(NO_3)_3$  dispersion (0.755 g of  $Fe(NO_3)_3$ , 0.1 g of PVP, and 5 mL of dimethylformamide (DMF)) for several seconds. After slow drying, the samples were placed in a quartz tube furnace. Before the furnace was heated, a flow of 600 sccm Ar gas (99.999%, ultrahigh purity) was introduced into the chamber to purge the system for 30 min. Then the furnace was programmed to 400 °C with a heating rate of 20 °C/min and kept at this temperature for 30 min, followed by introduction of 100 sccm NH<sub>3</sub> gas for thermal nitridation at 400 °C for 1 h. After the growth, the furnace was automatically turned off, and the samples were naturally cooled with the protection of an Ar flow.

Synthesis of Iron Oxide Film on Graphene/NF. For comparison, the only difference in the growth of iron oxide from that of iron nitride is that the  $NH_3$  gas was not supplied. The support (graphene/NF) decorated with  $Fe(NO_3)_3$  dispersion was annealed under the same conditions as those of iron nitride.

**Preparation of IrO<sub>2</sub> Catalyst on Graphene/NF.** To prepare the IrO<sub>2</sub> working electrode, 40 mg of IrO<sub>2</sub> and 60  $\mu$ L of 5 wt % Nafion (117 solution, Aldrich) were dispersed in 540  $\mu$ L of ethanol and 400  $\mu$ L of distilled water, and the mixture was ultrasonicated for 30 min. Then, the dispersion was coated onto a graphene/NF support (catalyst loading ~4 mg cm<sup>-2</sup>), which was dried in air overnight.

**Electrochemical Measurements.** The electrocatalytic performance of the catalysts was studied in a three-electrode setup (Gamry, Reference 600) at room temperature using 1 M KOH as the electrolyte. A Pt wire and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. The as-prepared samples were used directly as the working electrodes. Linear sweep voltammetry with a scan rate of 2 mV/

s and a step size of 2 mV was conducted in O2-saturated 1 M KOH solution. For the cycling test, the catalyst was measured for 1000 CV cycles in the potential range from 1.024 to 1.624 V vs the reversible hydrogen electrode (RHE) at a scan rate of 50 mV/s. Chronoamperometry was measured under a constant potential. Electrochemical impedance spectroscopy was carried out when the working electrode was biased at a constant potential while the frequency was swept from 100 kHz to 0.1 Hz with a 10 mV ac dither. The impedance data were fit to a simplified Randles circuit to extract the series and charge transfer resistances. During the test, the system was continuously purged with high-purity O2. All of the potentials were calibrated to the RHE by adding a value of 0.925 V ( $E_{\rm RHE}$  $= E_{Hg/HgO} + (0.0591 \times pH) + 0.098)$ . The OER equilibrium potential  $(E^0)$  is 1.23  $\hat{V}$  vs RHE. The overpotential is the potential difference between  $E_{\rm RHE}$  and  $E^0$ .

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03132.

Experimental methods and characterization data (PDF)

#### AUTHOR INFORMATION

#### Corresponding Authors

\*E-mail for S.C.: schen34@uh.edu. \*E-mail for Z.R.: zren@uh.edu.

# ORCID <sup>®</sup>

Zhuan Zhu: 0000-0003-4377-9053 Jiming Bao: 0000-0002-6819-0117 Zhifeng Ren: 0000-0001-8233-3332

#### **Author Contributions**

<sup>‡</sup>These authors contributed equally to this work.

#### Notes

The authors declare no competing financial interest.

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