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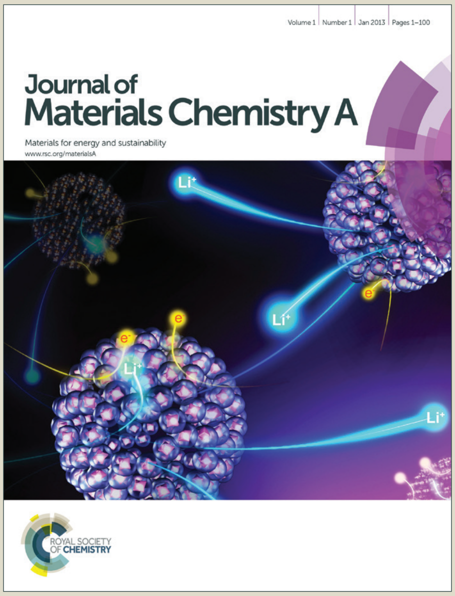

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Highly efficient Zinc Catalyst for Selective Electroreduction of Carbon Dioxide in Aqueous NaCl Solution

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A low-cost zinc catalyst, prepared by a facile electrochemical strategy, produces CO with up to 93% Faraday efficiency in aqueous NaCl solution. The catalytic activity of the Zn catalyst is demonstrated to be dependent on both the morphology of the catalyst and the catholyte anions.

Electrochemical reduction of carbon dioxide (CO_2) has been recognized to be an efficient way to convert CO_2 into reusable carbon fuel.[1] Currently, various efforts have been devoted to the development of efficient catalysts,[2, 3] and noble metals such as gold have been demonstrated to catalyze CO_2 reduction with high selectivity.[4, 5] However, from the aspect of scaled-up CO_2 reduction, a satisfactory catalyst should be inexpensive and efficient. Recently, some inexpensive catalysts such as Bismuth[6] and MoO_2[7] have been developed for the selective reduction of CO_2 to CO, which could be further used as feedstock to produce liquid fuels such as alcohols through convenient electrochemical reduction.[8] However, the volatile organic solvents used in these catalytic systems bring added cost and inconvenience to the subsequent separation of the product. CO_2 reduction in aqueous solution is preferable, whereas the development of suitable catalysts remains a challenge.

Among the metal catalysts, Zn is a promising material for its cost-effective advantages and potential activity toward the electro-reduction of CO_2 to CO. Despite these attractive properties, there has been scarce published work on the investigation of Zn electrodes in CO_2 electroreduction over the past decades.[9] The reason could be the low efficiency and selectivity of CO production on bulk Zn electrode in aqueous solution. Although Zn is capable of catalyzing CO_2 reduction in nonaqueous solution, its catalytic performance in aqueous solution is not satisfied.[9] More importantly, we found that Zn electrode would lose activity after continuous electrolysis in aqueous solution. Therefore, it is of great importance to develop new strategies to enhance the conversion efficiency of CO_2 on Zn catalysts.

Here, we demonstrate that nanoscale Zn is able to catalyze CO_2 reduction in a more efficient and selective manner than bulk Zn. More importantly, we discovered that the popular electrolyte sodium bicarbonate ($NaHCO_3$) is not optimum for CO_2 reduction here, and salt anions were found to greatly influence CO_2 conversion efficiency on Zn catalysts for the first time. With the combination of a nanoscale Zn electrode and NaCl electrolyte, significantly enhanced Faradaic efficiency is achieved for the conversion of CO_2 to CO in aqueous solution.

A schematic process is illustrated for the synthesis of a nanoscale Zn electrode (Scheme S1). Briefly, a piece of zinc foil was initially anodized to produce a film of ZnO, and it was then electrochemically reduced to metallic Zn for catalyzing CO_2 reduction. Figure 1a shows a SEM image of a Zn foil electrode after the anodization procedure. A dense layer of nanoplates ~ 1 μm in length and ~ 40 nm in thickness were formed on the electrode surface, and fine nanoparticles (30 ~ 50 nm) could be observed on the surface of the nanoplates. These nanoplates were actually a thick ZnO layer, as evidenced by the emerging XRD peaks at 31.8, 34.4 and 47.6° after anodization (Figure 1c).

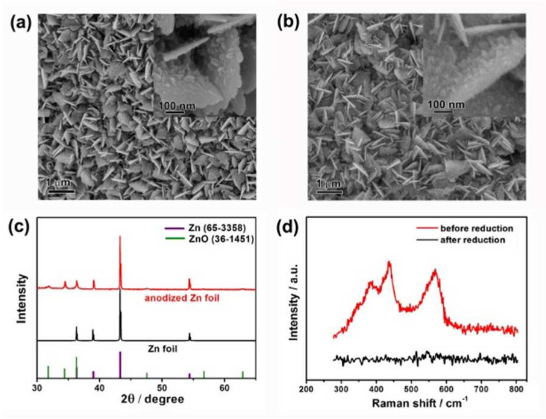

Figure 1. Characterization of Zn foil after anodization and electro-reduction. (a) SEM image of an anodized Zn electrode. (b) SEM image of a Zn electrode after anodization and electro-reduction. The inset figure is a high-magnification image. (c) XRD patterns of

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Electronic Supplementary Information (ESI) available: Experimental details and additional figures mentioned in the text. See DOI: 10.1039/x0xx00000x the Zn electrode before and after anodization. The peaks of standard Zn and ZnO samples are also presented. (d) Raman spectra of anodized Zn foil before (red) and after electro-reduction (black).

To determine the reduction potential of the ZnO, linear sweep voltammetry (LSV) was carried out in $NaHCO_3$ solution with anodized Zn as the working electrode. During the first LSV scan, there was a cathodic peak at -1.22 V, which was attributed to the reduction of ZnO to Zn (Figure S1). After electroreduction at constant potential of -1.3 V for 30 min, this cathodic peak disappeared, indicating that ZnO in contact with electrolyte was reduced to elementary Zn. In addition, the nanoplate morphology was not affected by the electroreduction and nanoparticles were still observed on the nanoplates (Figure 1b). The as-formed nanoscale Zn was hereafter referred to as "n-Zn". Moreover, we performed in situ Raman analysis on the anodized Zn electrode to check the change of surface structure during electroreduction (Figure 1d). The Raman peaks at 381, 435, and 565 cm^{-1} are assigned to the characteristic vibrational modes of ZnO,[10] which further confirms the presence of ZnO layer on the anodized Zn electrode. After electroreduction, these Raman peaks are essentially absent from the spectrum, indicating that the ZnO has been reduced to elemental Zn.

Electrocatalytic CO_2 reduction by Zn foil and n-Zn electrodes was evaluated by performing controlled potential electrolysis. As illustrated in Figure 2a, the maximum Faradaic efficiency for CO (FE_{CO}) was only 18% (at -1.6 V) on the Zn foil electrode in $NaHCO_3$ solution. At this potential, a considerable amount of H_2 was generated, and the Faradaic efficiency for H_2 was 75%. With n-Zn as the electrode, the resulting FE_{CO} in $NaHCO_3$ solution was improved a markedly and the maximum value (57%) was about three times that of Zn foil. In addition, hydrogen evolution was inhibited and the Faradaic efficiency for H_2 decreased to 39%. In addition to gaseous products, liquid products were measured by ion chromatograph and only a small amount of formate was produced with low Faradic efficiency (less than 5%) under all of the potentials on these two Zn electrodes. These results demonstrate that n-Zn catalyst exhibits improved selectivity toward the production of CO compared with bulk Zn electrode.

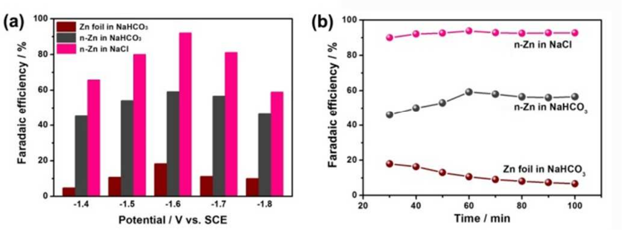

Figure 2. Comparison between Zn foil and n-Zn electrodes in CO_2 reduction. (a) FE_{CO} versus applied potential. (b) FE_{CO} versus electrolysis time at -1.6 V.

As a traditional electrolyte for CO_2 reduction, $NaHCO_3$ was found to serve as a proton donor, in which the proton was transferred from HCO_3^- to $CO_2^{\bullet -}$ intermediate.[5, 11] To test whether HCO_3^- ions participated in proton transfer during CO_2 reduction on n-Zn electrode here, we replaced the cathodic electrolyte of $NaHCO_3$ with NaCl without changing the anodic electrolyte. Interestingly, we unexpectedly found that the FE_{CO} was astonishingly enhanced to 93% at -1.6 V (Figure 2a). To the best of our knowledge, this is the highest FE_{CO} achieved by the use of a zinc catalyst in aqueous solution. Moreover, the FE_{CO} on the n-Zn electrode was stable during continuous electrolysis (Figure 2b), whereas the Zn foil electrode lost its activity in a short time. We ever tried longer electrolysis time (e.g. 10 h), and there was no obvious decay of FE_{CO} or the current density on the n-Zn electrode (Figure S2). The morphology of the n-Zn was also maintained well after electrolysis (Figure S3), indicating that the structure of n-Zn catalyst was stable under reduction condition.

The sharp contrast in FE_{CO} between $NaHCO_3$ and NaCl solutions indicates that the catholyte may affect the conversion efficiency of CO_2 on n-Zn electrode. Because the electrolytes in the anodic compartment were kept same, the only reason for the different FE_{CO} should originate from the catholyte anions. A series of experiments was thus carried out to clarify the roles of chloride ions in CO_2 reduction. We first employed bulk Zn foil as an electrode to study the sole effects of anions without the influence of catalyst size. Since the pH value of CO_2-saturated NaCl solution is 4.5, the other solutions (except $NaHCO_3$) were all adjusted to a pH of 4.5 before electrolysis. As illustrated in Figure 3a, similar enhancement of FE_{CO} (52%) was observed on the Zn foil electrode in NaCl solution, and the chloride ions exhibited the highest promotion effect among the halide ions. In comparison with the enhancement effects of other halide ions, FE_{CO} in NaF solution deceased sharply to 3.5%, and most of the gaseous product was hydrogen.

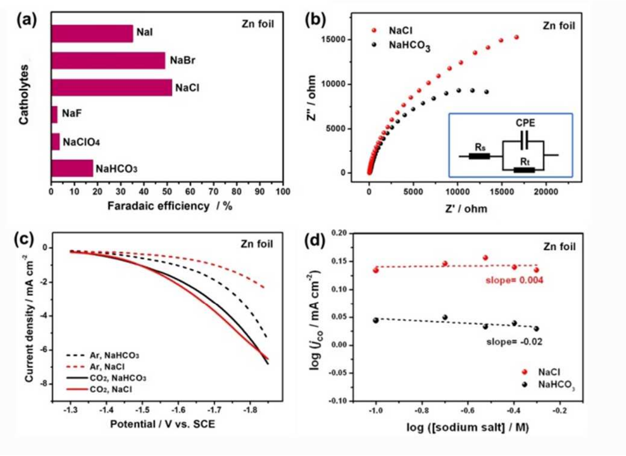

Figure 3. (a) FE_{CO} performed at -1.6 V in the presence of different catholytes. (b) Nyquist plots in Ar-saturated 0.5 M sodium salt solutions at -1.3 V. The frequency range is from 10^5 to 1 Hz. Inset is the equivalent circuit for the metal/solution surface (R_s: solution resistance, R_t: charge-transfer resistance, CPE: constant phase angel element).[12] (c) LSV curves recorded in $NaHCO_3$ (black line) or NaCl (red line) solution under different atmosphere. (d) Partial current density for CO (j_{CO}) versus concentration of sodium salt solution, where the total concentration of Na^+ was kept at 0.5 M by adding $NaClO_4$.

Considering that the CO_2 reduction takes place on the electrode surface, it is supposed that the anions may affect CO_2 conversion through surface adsorption. According to theoretic analysis,[13, 14] the adsorption strength of halide ions on metal electrode follows the sequence of $F^- < Cl^- < Br^- < I^-$. The highest FE_{CO} achieved in NaCl may be associated with the optimum adsorption strength of Cl^- ions on the Zn surface. We also tried another anion (ClO_4^-) with weak adsorption strength, and the resulting FE_{CO} (3.5%) was as low as that of NaF, further confirming that the adsorption behavior of anions affects the CO_2 reduction.

Electrochemical impedance was used to probe the adsorption of anions on the electrode (Figure 3b), and the double layer capacitance was calculated to be 10.5 $\mu F\cdot cm^{-2}$ in $NaHCO_3$ solution and 3.6 $\mu F\cdot cm^{-2}$ in NaCl. The obvious change of capacitance reflects the different adsorption behaviors of Cl^- and HCO_3^- ions. Further investigation through linear sweep voltammetry (LSV) revealed that hydrogen evolution current was greatly suppressed in the presence of chloride ions (Figure 3c), although the acidic environment of NaCl solution was more favorable for proton reduction than that of $NaHCO_3$ solution. The reason could be that the chloride ions blocked the adsorption and reduction of protons on the electrode surface.[15] A similar suppression effect of chloride ions on hydrogen evolution was also observed on the n-Zn electrode. By comparing the LSV curves in Ar-saturated sodium halide solutions (Figure 3c, Figure S4a, S4b and S4c), we can see that current densities from hydrogen evolution follow the sequence of $F^- > Cl^- > Br^- > I^-$. Although the presence of I^- ions inhibited the hydrogen evolution more efficiently than other ions, the resulting FE_{CO} is not the best. The reason could be that the strong adsorption strength of I^- ions may bring negative effect on the adsorption of CO_2, which leads to inferior CO_2 conversion efficiency compared with that of Cl^- ions.

The difference between current density from CO_2- and Ar-saturated solutions provides evidence for catalytic reduction of CO_2 at Zn electrode. Among these halide ions, the current density resulting from CO_2 reduction is the highest in NaCl solution (Figure S4d), indicating that the adsorption of Cl^- ions could be optimum for the CO_2 reduction and suppression of hydrogen evolution. In comparison, the hydrogen evolution in NaF or $NaClO_4$ solution is little affected due to the weak adsorption of anions, and most current is consumed in the proton reduction. As a result, the CO_2 reduction current is much lower (Figure S4d and Figure S5), which is in accordance with the low FE_{CO} obtained on Zn foil electrode.

To determine whether chloride ions participated in the CO_2 reduction, electrolyses were performed at NaCl concentrations ranging from 0.1 to 0.5 M, where the total concentration of Na^+ was kept at 0.5 M by adding $NaClO_4$. A plot of $\log(j_{CO})$ vs $\log[Cl^-]$ exhibits a slope of 0.04, indicating approximate zero-order dependence on the concentration of chloride ions in solution (Figure 3d). As for HCO_3^- ions, similar results were observed with a slope near to zero. These results reveal that chloride ions or HCO_3^- ions are not involved in the CO_2 reduction as reactants. Therefore, it is quite probable that the adsorbed chloride ions influence the heterogeneous CO_2 reduction on the electrode surface.

Besides the anions of electrolytes, the size of Zn catalysts has a significant effect on the CO_2 conversion efficiency. Here, commercial ZnO nanoparticles were coated onto a glass carbon electrode and utilized as precursors to fabricate Zn nanoparticles. The morphology of these ZnO samples is presented in Figure S6 and the particle sizes are in accordance with the parameters provided by the chemical supplier. Figure 4a shows the FE_{CO} achieved on various Zn catalysts under the constant potential of -1.6 V. A maximum FE_{CO} of 91% was observed on the Zn catalyst derived from reduction of ZnO nanoparticles (35 ~ 45 nm), which is close to that of particles observed on the n-Zn electrode (Figure 1b). It suggests that the excellent activity of n-Zn catalyst results from the optimum size of Zn nanoparticles, not the nanoplate structure. The same trend also existed at the potential range from -1.4 to -1.8 V. In addition, these nanoscale Zn catalysts all exhibited stable activity superior to that of bulk Zn electrode during continuous electrolysis (Figure S7). It was believed that the nanoscaled metal catalyst enabled the stable adsorption of intermediate, which led to efficient conversion of CO_2.[11,16] To investigate the effect of particle size on the adsorption of intermediate, the hydroxyl adsorption was examined as a representative for $CO_2^{\bullet -}$ intermediate.[11] A positive shift of onset potential for hydroxyl adsorption is observed with the increase of particle size (Figure S8), indicating that the smaller particles possess higher binding energy of hydroxyl. However, the smallest Zn nanoparticles (10 ~ 30 nm) did not exhibit the best activity toward CO_2 reduction. The reason could be that too strong affinity would hinder the following conversion of intermediate and release of product from the catalyst. The maximum FE_{CO} obtained on the Zn nanoparticles (35 ~ 45 nm) could be attributed to its optimum binding strength toward intermediates during CO_2 reduction.

To obtain insight into the mechanism of CO_2 reduction catalyzed by n-Zn, Tafel analysis was performed to explore the effect of catalyst size on the kinetics of CO_2 reduction (Figure 4b). The overpotential data are calculated in the same way reported in another article,[5] and the partial current density of CO is normalized to electroactive surface area (geometric area multiplied by roughness factor). The Tafel curve for the Zn foil electrode gives a linear relationship with a slope of 135 mV dec^{-1}, which is close to the 118 mV dec^{-1} expected for a rate-determining step (RDS) of initial reduction of CO_2 to $CO_2^{\bullet -}$ radical.[17, 18] In comparison, the slope for the n-Zn (76 mV dec^{-1}) electrode is much lower and close to 59 mV dec^{-1}, which suggests a mechanism involving a one-electron pre-equilibrium prior to a chemical RDS.[5, 11] This result indicates that the n-Zn electrode enables the formation of $CO_2^{\bullet -}$ intermediate and the overpotential of CO_2 reduction is reduced as a result.

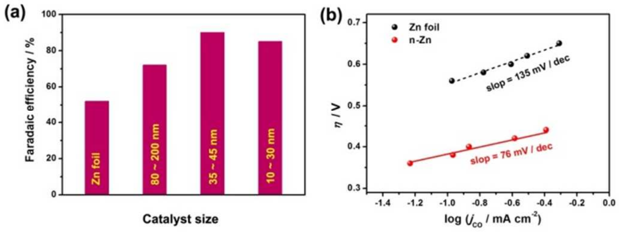

Figure 4. (a) Dependence of FE_{CO} on zinc catalyst size. (b) Tafel plots of overpotential against CO partial current density achieved on bulk Zn foil and n-Zn electrodes. All of the tests were performed in NaCl solution.

On the basis of above results, we propose a possible mechanism to explain how chloride promotes CO_2 reduction to CO on nanoscale Zn electrode as follows (Figure 5). With bulk Zn as electrode, the initial one-electron reduction of CO_2 to $CO_2^{\bullet-}$ radical is slow, whereas the competitive reaction of hydrogen evolution is relatively fast in $NaHCO_3$ solution even if it is somewhat inhibited by the adsorbed HCO_3^- ions (Figure 5a). As a result, less current is consumed in the conversion of CO_2 to CO, and the resulting Faradaic efficiency is low. When the electrolyte was replaced by NaCl solution, the proton reduction was greatly suppressed by the adsorbed chloride ions (Figure 5b). Meanwhile, the formation of $CO_2^{\bullet-}$ radical is accelerated on nanoscale Zn, and the conversion efficiency of CO_2 is greatly improved.

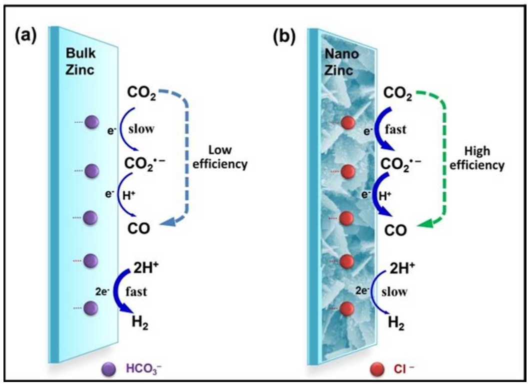

Figure 5. Schematic illustration of CO_2 reduction to CO on Zn electrodes in $NaHCO_3$ (a) and NaCl solution (b).

Considering that chloride ions are capable of promoting CO_2 conversion efficiency on nanoscaled Zn catalyst, is it true for other metals as well? To test this hypothesis, we chose silver (Ag) nanoparticles to investigate the effect of electrolytes on CO_2 reduction. As shown in Figure S9, the FE_{CO} obtained on Ag nanoparticles was 20% initially, and decreased to approximately 10% after continuous electrolysis in $NaHCO_3$ solution. In sharp contrast, a simple change of electrolyte to NaCl solution may increase the FE_{CO} to 70%, which is about 7 times higher than that obtained in $NaHCO_3$ solution. In addition, the FE_{CO} achieved in NaCl solution is stable during continuous electrolysis, further demonstrating the promotion effect of chloride ions for CO_2 reduction. Recently, an ionic liquid/H_2O solution was developed to accelerate reduction of CO_2 to CO on silver catalyst.[19, 20] It was believed that the cations of ionic liquid adsorbed on the electrode, and hydrogen evolution was inhibited as a result. However, for the Zn nanoparticle catalyst here, this strategy brought no obvious promotion effect (Figure S10), and the maximum FE_{CO} (44%) is much lower than that in NaCl solution. This suggests that the chloride salt could be optimum for accelerating CO_2 reduction catalyzed by a Zn electrode. Certainly, further work is required to elucidate the underlying CO_2 reduction mechanisms.

Conclusions

A significant result of this work is the observation that by the optimum combination of catalyst size and electrolyte anions, the activity of a Zn electrode could be dramatically enhanced toward the reduction of CO_2 to CO. In CO_2-saturated aqueous NaCl solution, a maximum FE_{CO} of 93% has been achieved on n-Zn electrode while the FE_{CO} is only 18% on bulk Zn electrode in $NaHCO_3$ solution. Moreover, this n-Zn catalyst is resistant to deactivation during long term electrolysis. The achieved high conversion efficiency is attributable to both the nano-size of the catalyst and the presence of chloride ions. We anticipate that the strategy adopted here may provide a promising way to improve the activity of inexpensive catalysts for CO_2 reduction.

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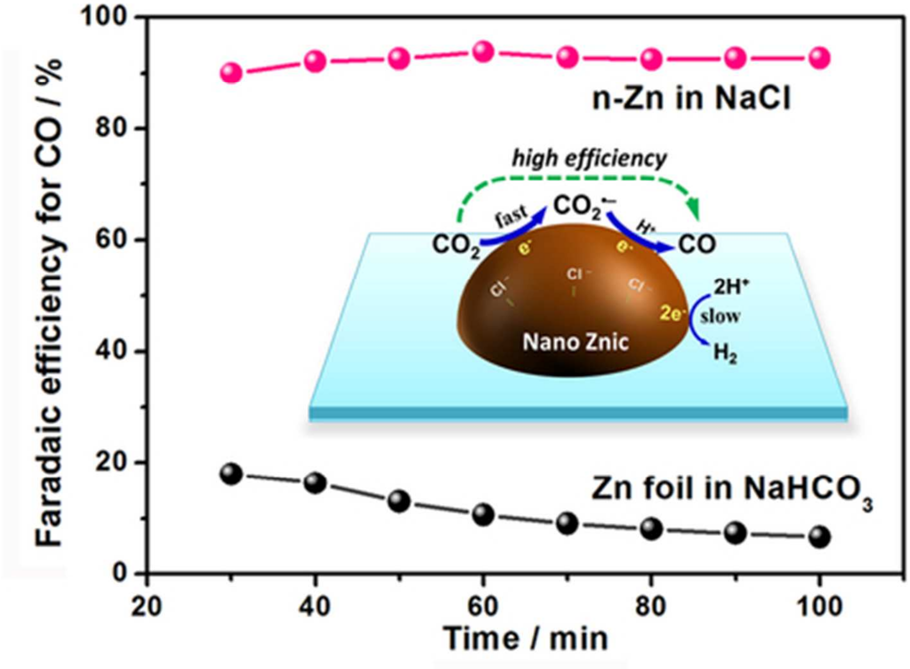

Graphical Abstract: A low-cost nanoscaled zinc catalyst, prepared by a facile electrochemical strategy, exhibits high ativity toward electrochemical reduction of CO_2 to CO with up to 93% Faraday efficiency in aqueous NaCl solution.
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