Cu-Doped Carbon Nitride: Bio-Inspired Synthesis of H₂-Evolving Electrocatalysts using Carbon Nitride (g-C₃N₄) as a Host Material

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Abstract

Splitting water effectively to produce hydrogen (H_2) requires the development of non-noble-metal electrocatalysts that are able to make this reaction feasible and energy efficient. Herein, we present a novel “structure upgrading” synthetic approach for the design and synthesis of bio-inspired hydrogen-evolving electrocatalysts based on earth-abundant elements. Using g- C_3N_4 —an inexpensive inorganic polymer material—as a host material for copper ions, novel Cu-doped g- C_3N_4 materials with supramolecular structure, efficient electrocatalytic activity and modest overpotentials for hydrogen evolution reaction (HER) are synthesized. Compared with most single-molecule analogues of hydrogenases that work only in organic media, the supramolecular Cu-doped g- C_3N_4 materials can serve as heterogeneous electrocatalysts with greater stability and good catalytic activity for HER in aqueous media. The materials afford a current density as high as 10 mA cm^{-2} at an overpotential as low as 390 mV, and work well in acidic media for, at least, 43 hours.

Keywords. Carbon nitride, H_2 evolution, copper ions, electrocatalysis, water splitting.

Introduction

In the face of the unabated environmental impacts of fossil fuel sources, hydrogen (H_2) has long been considered as a promising energy carrier to meet these challenging problems. Unlike fossil fuels, which are widely used today but produce the primary greenhouse gas CO_2 upon combustion, hydrogen releases only water vapor as a byproduct during oxidation. Thus, hydrogen is widely regarded as one of the few possible renewable/“greener” energy sources of the future for a broad range of applications. However, in order for hydrogen to be a reliable alternative to fossil fuel sources, it must first be produced in a sustainable way. This requires, among other things, efficient hydrogen-evolving catalysts, preferably based on earth-abundant elements. In this regard, nature has already set good examples. For example, hydrogenases—a class of enzymes that many natural systems utilize to produce their energy—exhibit high catalytic efficiency in hydrogen production, and yet use only relatively inexpensive and highly abundant first-row transition metals, such as iron (Fe) and nickel (Ni), coordinated to carbon monoxide (CO) and cyanide (CN^-) ligands (Figure 1A) in their catalytically active sites [1-5].

Inspired by their unique structural features, coupled with their function, a considerable amount of research efforts has already been made to synthesize artificial analogues of these enzymes, which are capable of catalyzing the reduction of protons into dihydrogen ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) [6-15]. Such bio-inspired synthetic hydrogen evolving catalysts can be broadly classified in two categories. The first group consists of some elegant structural mimics of, and similar atomic composition and bonding patterns as, the active sites of hydrogenase enzymes (Figure 1B) [6-13]. The second category, on the other hand, includes some functional mimics of enzymes, which replicate the functional feature of hydrogenases but with different atomic compositions and bonding patterns from those present in the active sites of enzymes [14-29]. Most of these functional mimics (two examples are shown in Figures 1C and D) generally consist of isolated molecular units [28,29], which are made of a transition metal (*e.g.*, Co or Ni) coordinated with some organic ligands, such as bipyridines, (poly)-pyridines or nitrogen-rich macrocycles [14-29]. While this biomimetic approach to molecular type hydrogen

evolving catalysts provides a better understanding of the boundaries/relationships between the biological hydrogen evolving catalysts and their synthetic analogues, further structural upgrading from single molecules to supramolecular networks may provide additional advantages to these types of biomimetic catalysts serving in hydrogen evolution reaction (HER). Moreover, compared with single-molecular analogues of biological enzymes (or homogenous catalysts), most of which work only in organic media [16-27], the supramolecular mimics can be expected to serve as heterogeneous catalysts with improved stability in various media and/or offer greater number of active catalytic centers, and thereby endow better catalytic activity in HER.

In this paper, a “structure upgrading” synthetic strategy was explored to produce supramolecular hydrogen-evolving electrocatalysts by using the nanosized cavities of g-carbon nitride (g-C₃N₄) as the host material for the electrocatalytic active centers. Specifically, copper ions-doped g-C₃N₄ (Cu-C₃N₄, see Figure 1E) was synthesized, and the resulting material was successfully demonstrated to be electrocatalytically active for HER in aqueous solution. Please note that as the material is found to contain both Cu(I) and Cu(II) ions in different ratios (*vide infra*), it is denoted simply as Cu ions-doped g-C₃N₄. To the best of our knowledge, this is the first time a bio-inspired Cu ions-containing g-C₃N₄ material was successfully shown to electrocatalyze HER. Furthermore, the work demonstrates the successful application of a “structure upgrading” synthetic strategy to biomimetic electrocatalysts for HER by using inexpensive and earth-abundant materials, such as copper and g-C₃N₄, as precursors.

Experimental Section

Synthesis of copper ions-doped g-C₃N₄ (Cu-C₃N₄). The Cu-C₃N₄ electrocatalysts described here were synthesized through a one-step self-assembly procedure. Typically, dicyandiamide (12 mmol) was uniformly mixed with copper(II) chloride (1.2 mmol). The resulting mixture was then heated at 500 °C in a tube furnace for 5 h under N₂ atmosphere. After cooling to room temperature, the final solid product (Cu-doped g-C₃N₄) was collected without further purification. This material was found to

contain 0.31 mmol of Cu in it, and it was thus designated as 0.31Cu-C₃N₄. Similarly, another material was synthesized in the same way, but by decreasing the amount of copper(II) chloride to 0.85 mmol. This sample was found to have 0.12 mmol Cu, and it was, therefore, labeled as the 0.12Cu-C₃N₄. For comparison, pure g-C₃N₄ was also prepared by direct heating dicyandiamide in the absence of copper(II) chloride.

General Characterization. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and operating at 200 mA and 40 kV. The FT-IR spectra were acquired on a Brker IFS 66v/S FTIR spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromated X-ray source (Al KR $h\nu = 1486.6 \text{ eV}$). The energy scale of the spectrometer was calibrated using the peak positions of Au4f_{7/2}, Cu2p_{3/2} and Ag3d_{5/2}. The standard deviation for the binding energy (BE) values was 0.1 eV. The thermogravimetric (TG) analysis was performed in air on a NETZSCH STA 449C TG thermal analyzer from 25 to 800 °C at a heating rate of 10 °C/min. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by using a Micromeritics ASAP 2020M system. The solid-state ¹³C (100.64 MHz) NMR spectra were acquired on a Brker 400 MHz NMR spectrometer consisting of a 3.2 mm HXY Brker probe operating in HX mode at 298K. For ¹³C CP-MAS NMR experiments, 10.0 kHz spin rate, 3 s recycle delay, 2 ms contact time, $\pi/2$ pulse width of 5 μs (at 66 W) and at least 16 K scans using “Spinal 64” ¹H decoupling method were employed. The ¹³C chemical shift was referenced using adamantane as external standard. The spectra were processed in Brker Topspin (v 3.1) using conventional techniques and 50 Hz of line broadening window function was applied to all the spectra.

HER measurements. The electrocatalytic properties of the materials were studied with a three-electrode system using a PAR Versastat3 (Princeton Applied Research) potentiostat. A saturated calomel electrode (SCE) and a carbon rod were used as the reference electrode and as the counter electrode, respectively. To prepare the working electrode, 2 mg of catalyst and a solution containing 20 μL of 5 wt.% Nafion were dispersed in ethanol (180 μL) with sonication for at least 30 min to form a

homogeneous mixture. Then, 2 μL of this solution was drop-casted onto a 3 mm in diameter glassy carbon electrode (GCE), and it was left to dry in air, giving a catalyst loading of $\sim 0.28 \text{ mg/cm}^2$ on the GCE. By using this electrode, the electrochemical measurements of the samples with scan rate of 2 mV/s were measured in 0.5 M H_2SO_4 as a supporting electrolyte solution. The saturated calomel electrode (SCE) was calibrated with respect to reversible hydrogen electrode (RHE) using the equation: $E(\text{RHE}) = E(\text{SCE}) + 0.273 \text{ V}$.

Results and Discussion

We chose $\text{g-C}_3\text{N}_4$ as the host material for the synthesis of the electrocatalyst mainly for the following reasons: 1) $\text{g-C}_3\text{N}_4$ is composed of inexpensive, earth-abundant elements, 2) $\text{g-C}_3\text{N}_4$ can easily be prepared from commercially available and inexpensive starting materials, 3) $\text{g-C}_3\text{N}_4$ is chemically quite stable due to the strong covalent bonds involved in it [30-32], and 4) $\text{g-C}_3\text{N}_4$ contains nanosize cavities composed of three heptazine units (Figure 1E), which can function as macrocyclic ligands for inclusion of various catalytically active metallic ions or nanoparticles [33-35]. However, these appealing structural features of $\text{g-C}_3\text{N}_4$ need to be structurally/compositionally “up-graded” with electrocatalytic active groups to fully take advantage of them and utilize the material for electrocatalysis of HER.

To this end, we have carried out the synthesis of $\text{Cu-C}_3\text{N}_4$ catalysts. The synthetic method we employed to make the catalysts involved a one-step self-assembly procedure (see Experimental Section for details of the experimental procedures). This method was adopted from previously reported synthesis of $\text{Fe}^{3+}(\text{Zn}^{2+})$ -doped $\text{g-C}_3\text{N}_4$ hybrid materials by Wang et al. [33]. It is worth emphasizing here that despite the similarities in structures between the $\text{Cu-C}_3\text{N}_4$ reported here and the $\text{Fe}^{3+}(\text{Zn}^{2+})\text{-C}_3\text{N}_4$ reported in Ref. 33, as well as the similarities of the synthetic methods employed in both cases, it was only the Cu-doped $\text{g-C}_3\text{N}_4$ that we made showed electrocatalytic activity towards H_2 evolution reaction. In other words, our attempted tests of electrocatalysis of HER using the $\text{Fe}^{3+}(\text{Zn}^{2+})\text{-C}_3\text{N}_4$ materials that

we made as reported by Wang et al. [33] as well as many other types of metal ion containing C_3N_4 were all unsuccessful.

In a typical synthesis, copper(II) salt (*e.g.*, $CuCl_2$) was used as the source of copper, and dicyandiamide was used as an organic monomer for making the $g-C_3N_4$. When the mixture of copper(II) salt and dicyandiamide was thermally treated at elevated temperature (500 °C) under N_2 protection, the dicyandiamide became $g-C_3N_4$ while, at the same time, the copper ions were directly self-assembled *in situ* within the dicyandiamide-derived $g-C_3N_4$, forming the desired $Cu-C_3N_4$ materials. The relative amount of copper in the $Cu-C_3N_4$ material, which can be determined by thermogravimetric (TG) analysis (see below), was varied (or controlled) by changing the molar ratio of copper(II) salt and dicyandiamide. In this work, two $Cu-C_3N_4$ samples with different amount of copper, denoted hereafter as 0.12 $Cu-C_3N_4$ and 0.31 $Cu-C_3N_4$, because the molar ratios of $Cu/g-C_3N_4$ in them were 0.12:1.00 and 0.31:1.00, respectively, were synthesized. Pure $g-C_3N_4$ was also synthesized to serve as a reference material to compare the structures and properties of $Cu-C_3N_4$ materials with. The BET surface areas of $g-C_3N_4$ and Cu-doped carbon nitride are found to be 10 cm^2/g and 6 cm^2/g , respectively.

Figure 2A shows the X-ray diffraction (XRD) patterns of pure $g-C_3N_4$, 0.12 $Cu-C_3N_4$ and 0.31 $Cu-C_3N_4$. For pure $g-C_3N_4$, the strong peak at 27.4° for 2-theta, corresponding to a d-spacing value of 0.326 nm, was indexed as the stacking of (002) planes of graphitic $g-C_3N_4$, whereas the weak peak at 13.0° for 2-theta was attributed to the in-plane repeat units of heptazine in the $g-C_3N_4$ (Figure 1E). The XRD patterns of 0.12 $Cu-C_3N_4$ and 0.31 $Cu-C_3N_4$ were found to be similar to that of pure $g-C_3N_4$, except for a slight decrease in the intensity of the diffraction peaks, especially the one at 13.0° for 2-theta, in the latter. This result indicates that the three materials have similar structures, or conversely, the structural features of $g-C_3N_4$ remain unchanged upon doping with copper ions. Moreover, compared with the XRD pattern of $g-C_3N_4$, neither 0.12 $Cu-C_3N_4$ nor 0.31 $Cu-C_3N_4$ exhibited any new diffraction peak(s) associated with copper species (such as metallic copper, copper chlorides, copper carbides or copper nitrides). This result also suggests that the copper species in the two Cu-doped $g-C_3N_4$ samples are most likely present only as chemically immobilized and isolated species within the in-plane cavities of $g-$

C₃N₄ host by coordinating with the electron-donating N-based ligands, as observed in copper-based porphyrine systems [36-38]. These conclusions are also consistent with those reported by Wang et al. for Fe³⁺(Zn²⁺)-doped g-C₃N₄ [33]. The absence of copper-based nanoparticles is further supported by transmission electron microscopy images (TEM, Figure S1 in Supporting Information (SI)). From the TEM images, 0.31Cu-C₃N₄ maintains the flexible sheet-like morphology of g-C₃N₄, with no nanoparticles, possibly from Cu species, being observed on it.

In order to verify the local structure of g-C₃N₄ after doping with copper, ¹³C cross-polarization MAS solid-state NMR (¹³C CP-MAS) spectra were recorded for the g-C₃N₄ samples before and after Cu-doping (Figure 2B). It should be pointed out that ¹³C CP-MAS spectrum of a carbon-based solid-state material can provide some important qualitative information regarding the different types of carbon species present in the material [39-41]. The pure g-C₃N₄ sample showed two peaks, the first at 166.80 ppm (marked in orange) and the second at 159.04 ppm (marked in green). These chemical shifts correspond to different carbons of heptazine units, and are in accordance with the chemical shift values previously reported for different compounds containing heptazine units [39-41]. The peak at 166.80 ppm corresponds to the group of carbon atoms connected in a $\underline{\text{C}}\{(\text{N}1)_2\}\{(\text{N}3)_1\}$ fashion (C1's in Figure 2C), whereas the peak at 159.04 ppm is associated with the group of carbon atoms attached in a $\underline{\text{C}}\{(\text{N}1)_2\}\{(\text{N}2)_1\}$ mode (C2's in Figure 2C). The ¹³C CP-MAS NMR spectra of pure g-C₃N₄, and the two Cu-doped g-C₃N₄ samples (0.12Cu-C₃N₄ and 0.31Cu-C₃N₄) gave almost similar NMR peak shapes and intensities, indicating that the copper atom dopants did not alter the composition and bonding patterns of the basic building units (heptazine units) of g-C₃N₄. However, very small differences in chemical shifts were observed on the ¹³C solid-state spectra of g-C₃N₄ upon doping with copper. For example, the peak associated with C1's showed up at 166.80 ppm for pure g-C₃N₄, but the peak shifted to 166.23 ppm in 0.31Cu-C₃N₄. Similarly, the peak corresponding to C2's appeared at 159.04 ppm for pure g-C₃N₄, but moved to 158.86 ppm in case of 0.31Cu-C₃N₄. These peak shifts on the ¹³C CP-MAS NMR spectra can be expected to be only small, because the copper ions are not directly connected to the carbon atoms of g-C₃N₄ but rather to the nitrogen atoms. Nevertheless, this very small change in

chemical shift after doping of the g-C₃N₄ with a small amount of copper ions once again demonstrates that the ultimate copper species in the materials are likely to be chemically bound with the g-C₃N₄, rather than physically mixed with it.

Figure 2D shows the FTIR spectra of pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄. The spectra depict well-resolved and strong IR absorption bands, which are related to the typical molecular structure of g-C₃N₄ (Figure 1E). The intense, broad IR band ranging from 1232 to 1671 cm⁻¹ is assigned to the typical stretching vibration modes of heptazine units. The other intense IR band at 810 cm⁻¹ is attributable to the out-of-plane bending vibration of the same heptazine units. Although the three IR spectra appear very similar, small differences can be seen upon careful examination, especially when comparing the spectrum of Cu-doped g-C₃N₄ with respect to that of g-C₃N₄. This includes the appearance of a new weak absorption band at 2176 cm⁻¹ and the weakening of the absorption bands related to heptazine units in the copper-doped g-C₃N₄. The new, weak absorption band at 2176 cm⁻¹ was assigned to the stretching mode of carbon-nitrogen (C≡N) triple bond. The presence of C≡N bonds in the materials is not unexpected considering the fact that C≡N bonds sometimes form as defect sites within g-C₃N₄ materials [42-44]. Therefore, our result here further suggests that the doping of copper ions into the g-C₃N₄ promotes the formation of C≡N defect sites in the material. In addition, the weakening of the absorption bands related to heptazine units, especially in 0.31Cu-C₃N₄, demonstrates that copper ions must be chemical attached to the heptazine units (Figure 1E) through coordination bonds. Considering the fact that the incorporation of dopants in a host material almost always leads to some inherent changes in the local microstructure and the composition of the host material, the structural differences observed by FTIR in the Cu-doped g-C₃N₄ versus g-C₃N₄ materials are not unusual.

X-ray photoelectron spectroscopy (XPS) was performed to further obtain information about the composition of the materials. The XPS spectra for C1s of all the three samples (Figure S2A in SI) exhibit two similar peaks: the first at 284.8 and the second at 288.3 eV. The peak at 284.8 eV is due to adventitious elemental carbon. The peak at 288.3 eV, however, corresponds to C-(N)₃ carbon atoms

(both C1 and C2 type carbon species in Figure 2C) of g-C₃N₄. Unfortunately, it is difficult to distinguish between the C1 and C2 type carbon atoms based on XPS spectra (*cf.*, the two carbon species could be successfully identified in ¹³C CP-MAS spectra (Figure 2B)).

The XPS spectra of N1s of the three samples are shown in Figure S3B in SI. The N1s peak was deconvoluted into two components with two discernible binding energies: at 398.7 and 400.2 eV, which were ascribed to the nitrogen atoms of N-C₂ (N1's in Figure 2c) and N-C₃ (both N2's and N3's in Figure 2c) modes, respectively. The quantitative analysis of the XPS data revealed that the N1/(N2 + N3) atomic ratio was ~1.00:0.28 for all the three samples, which is very close to theoretical value of 1.00:0.33 (considering the contribution of different nitrogen atoms in unit cell of g-C₃N₄); this also confirms the successful synthesis of carbon nitride skeleton. The similarity in the XPS spectra of C1s and N1s (Figures S2A, B) of all the three materials and their similar values of N1/(N2 + N3) corroborate the conclusion made above that the bulk structure of g-C₃N₄ remains unchanged after copper doping.

Figure 3 shows the XPS spectra of Cu2p in 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄. The spectra exhibit the binding energies of Cu2p_{3/2} and Cu2p_{1/2} at 932.8 and 952.6 eV, respectively. The peak-fit for Cu2p_{3/2} peak revealed the presence of a major peak at 932.8 eV, with a shoulder at 934.6 eV. The major peak was assigned to Cu⁺ (3d¹⁰) species, whereas the shoulder and a shake-up satellite peak in the range of 940 - 950 eV were attributed to Cu²⁺ (3d⁹) species [36,45]. The quantitative analysis of the XPS data revealed that the Cu⁺/Cu²⁺ atomic ratios were 2.11:1.00 and 1.35:1.00 for 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄, respectively. The Cu⁺ ions were produced in the materials most likely due to the reduction of Cu²⁺ by NH₃ gas generated *in situ* when the dicyandiamide underwent polymerization during the formation of the Cu-doped g-C₃N₄ materials. This is not unusual given the fact that Cu²⁺ ions have a tendency to reduce to Cu⁺ ions in reaction systems possessing some nitrogen-containing ligands [46,47].

The XPS analysis also allowed us to determine the Cl/Cu molar ratios in the samples, which were found to be 0.12 and 0.13 for 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄, respectively. These values are obviously much lower than the Cl/Cu atomic ratio (2:1) in the CuCl₂ precursor used. This result is consistent with

the very low Cl/Fe molar ratio reported for Fe³⁺-doped g-C₃N₄, which was synthesized by using FeCl₃ as the source of iron [33]. This result confirms further that Cu ions (both Cu⁺² and Cu⁺) in Cu-doped g-C₃N₄ are mainly coordinated with the g-C₃N₄ host *via* coordination bond with the N-atoms of g-C₃N₄, rather than with Cl⁻ ions. In other words, the charges in the copper ions must be counter-balanced mainly by the electron-donating N-based ligands of g-C₃N₄, and not by Cl⁻ ions.

The thermogravimetric (TG) analysis for the pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄ was carried out in air from 25 to 800 °C, and the TG curves are shown in Figure 4. The pure C₃N₄ was observed to be very stable up to 537 °C in air, and it then lost all of its weight from ~537-720 °C. By contrast, the thermal decomposition temperatures of 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄ began at significantly lower temperatures of 413 and 365 °C, respectively. The decreased thermal stability of g-C₃N₄ as a result of its doping with a small amount of copper further unequivocally demonstrates that copper ions must be chemically incorporated into the g-C₃N₄ crystal structure, rather than physically mixed with g-C₃N₄. This also indicates that although copper doping does not change the core chemical skeleton of g-C₃N₄ much (as revealed by XRD, NMR, IR and XPS characterizations above), it appears to have a strong influence on the nature of chemical bonds in g-C₃N₄, and thus its thermal stability. It is worth mentioning herein that the highest theoretical amount of Cu in g-C₃N₄ is about 0.5 mol Cu per mol of g-C₃N₄ (where all cavities in g-C₃N₄ are occupied by Cu ions), but it is difficult to synthesize the Cu-doped g-C₃N₄ with a higher Cu amount (above 0.31) by the current experimental method, possibly because additional Cu doping compromises the stability of g-C₃N₄. From the amount of inorganic residue (CuO) left after the thermal decomposition of 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄, the empirical compositions of the two copper-doped g-C₃N₄ materials were deduced to be 0.12Cu·C₃N₄ and 0.31Cu·C₃N₄, respectively.

As mentioned above, the properties of some single-molecular functional mimics of hydrogenases as homogenous electrocatalysts for HER have already been explored [16-27]. However, most of these single-molecular type HER catalysts work only in organic media and in the presence of organic acids as the proton source [16-27]. Furthermore, many of these single-molecular type electrocatalysts are

difficult to synthesize due to the requirement of special ligands, some of which are unstable and/or can be synthesized only in a non-aqueous media [16-27]. Despite there have recently been some advances in the development of electrocatalysts in aqueous media [14,15], the stability of many electrocatalysts made in aqueous media still remains an area of concern in HER. One of the goals of our synthetic strategy presented herein is, therefore, to demonstrate the synthesis of stable, heterogeneous catalyst for HER *via* an approach of “structure upgrading” of single molecules into supramolecular networks. To achieve this, we specifically employed carbon nitride, which has significant water- and acid-stability. After doping its structure with copper (and other transition metals), we investigated the properties and potential catalytic activities of the resulting metal-doped g-C₃N₄ materials for electrochemical HER. It is worth mentioning here again that among the materials we have synthesized only Cu-doped g-C₃N₄ showed catalytic activity for HER; thus, only the results on Cu-doped g-C₃N₄ will be discussed in detail here. Before the electrochemical catalytic tests, the water- and acid-stability of the metal-doped materials was assessed. In a typical experiment, the as-obtained 0.31Cu-C₃N₄ was dispersed in dilute sulfuric acid (0.5 M), and the resulting mixture was then stirred at room temperature. After 10 h, the crystal structure of the sample remained intact as confirmed from its XRD pattern, and no copper ions were detected in the solutions, indicating 31Cu-C₃N₄'s water- and acid-stability.

The electrocatalytic activity of Cu-C₃N₄ materials toward in HER was measured by depositing the materials on glassy carbon electrode (GCE) and by using a typical three-electrode system in 0.5 M H₂SO₄ solution (see details in Experimental section). For comparison, the activity of a blank GCE and a GCE containing pure g-C₃N₄ was also measured. As shown in Figure 5A, pure C₃N₄ electrode exhibited a similar polarization curve (*i*-*V* plot) as the blank GCE. Moreover, even though the applied potential was increased to -0.8 V, only a very small current was observed for the GCE containing pure g-C₃N₄. These results indicate that pure C₃N₄ is not active for the electrocatalytic HER. In sharp contrast, the GCE containing Cu-C₃N₄ showed a significantly decreased onset overpotential for HER (Figure 5A), whose cathodic current rose rapidly under more negative applied potential. The superiority of Cu-doped carbon nitride for electrocatalysis of HER as compared with carbon nitride was further supported by the

fact that the former had a much lower Faradaic impedance than the latter (Figure S3 in SI), and correspondingly the electron transfer rate in HER was much faster in the presence of Cu-doped carbon nitride than carbon nitride. Additionally, the onset overpotential of Cu-C₃N₄ electrodes for HER appeared to be dependent on the amount of copper in the Cu-doped g-C₃N₄ samples. For instance, the onset overpotentials of 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄ were about 0.5 and 0.26 V, respectively (for comparison, the thermodynamically-based reduction potential for H₂ evolution from HER is zero). 0.31Cu-C₃N₄ afforded a current density of 10 mA cm⁻² (*i.e.*, the current density expected for a 12.3% efficient solar water-splitting device) at relatively low overpotential of 390 mV. The overpotential values for Cu-C₃N₄ for HER are modest in comparison with various types of homogeneous and heterogeneous electrocatalysts reported for HER [14-29,48-51]. For instance, HER overpotential values ranging from ~0.1 to ~0.9 V were reported for homogenous electrocatalysts in various reaction systems [14-29]. On the other hand, HER overpotential values between ~0.1 and ~0.4 V, with the values being strongly dependent on the preparation/modification methods of MoS₂, were reported for MoS₂ catalyst—one of the best heterogeneous noble-metal-free electrocatalysts reported for HER so far [48-51].

Apart from Cu ions, a series of other 3d transition metals (TMs), including Fe³⁺, Zn²⁺, Mn²⁺, Co²⁺ and Ni²⁺, were used as dopants in g-C₃N₄ to produce various other TM-doped C₃N₄ and, most importantly, to investigate the electrocatalytic properties of these various TM-doped g-C₃N₄ for HER. However, interestingly except Cu-C₃N₄, all the other TM-doped g-C₃N₄ composite materials, including those reported in Ref. 33, were found to be electrocatalytically inactive for HER (Figure S4 in SI).

The above results clearly showed the superiority of Cu-doped carbon nitride towards HER as compared with carbon nitride. Our results also indicate that the Cu species in Cu-doped carbon nitride is responsible for the material's catalytic activity toward HER, with the carbon nitride in the material rendering only structural support and/or cooperative effects. Nevertheless, further investigation may still be required to determine how the Cu species of Cu-doped carbon nitride are involved in the catalytic cycle, and to determine how the complicated interplay between Cu and carbon nitride affects the

catalytic efficiency of the material. In addition, we believe that the catalytic activity of the Cu-doped carbon nitride material might be further improved by constructing it in ultrathin nanosheets, creating porous structure in it, and coupling it with conductive substrates (*e.g.*, with graphene and carbon nanotube), etc.

The stability of Cu-doped g-C₃N₄ (0.31Cu-C₃N₄) in HER was examined by continuously monitoring its cathodic current (of ~10 mA cm⁻²) at applied potential of -0.39 V for several hours (Figure 5B). After 43 hours, no loss of electrocatalytic activity was observed, clearly indicating that the material has good electrochemical stability under acidic HER conditions. Moreover, the experiment revealed that the total charge passed during the course of 43-hour electrolysis far exceeds the mol of the Cu-C₃N₄ sample used in the reaction, suggesting that the observed electrochemical signal is originated from a catalytic process rather than from a simple chemical reaction.

Figure 6 shows the Tafel plots for pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄. Because the linear portions of the Tafel plots were fit to the Tafel equation ($\eta = a + b \log j$, where η is the overpotential, j is the current density and b is the Tafel slope) [48,52], the corresponding Tafel slopes were calculated to be ~164, ~112 and ~76 mV/decade for pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄, respectively. This clearly reveals that copper doping decreases the Tafel slope of C₃N₄. The lower Tafel slope obtained from 0.31Cu-C₃N₄ suggests that this material is a more effective catalyst for HER than 0.12Cu-C₃N₄. It is known that the Tafel slope gives insights into the intrinsic electrochemical catalytic property of an electrocatalyst and how the rate-limiting step is during the catalyst's activity during HER. For heterogeneous electrocatalysts in HER, the initial step is generally considered to be the formation of adsorbed hydrogen atoms (H_{ads}) on the catalyst's surface (Volmer step, $H^+ + e^- \rightarrow H_{ads}$), followed by the release of molecular hydrogen *via* either one or both of the following processes: Tafel step, $2H_{ads} \rightarrow H_2$ or/and Heyrovsky step, $H^+ + e^- + H_{ads} \rightarrow H_2$ [46-51]. The Tafel slope value in our case, coupled with the ones reported for other HER electrocatalysts recently [53-55], suggest that the HER on 0.31Cu-C₃N₄ are dictated mainly by the Volmer and Tafel steps.

Conclusions

In summary, we presented a “structure upgrading” approach for bio-inspired design and synthesis of hydrogen-evolving electrocatalysts based on earth-abundant elements. By using g-C₃N₄—an inexpensive yet mechanically/physically robust inorganic polymeric material—as a host material for copper ions, Cu-doped g-C₃N₄ materials possessing supramolecular structure were synthesized. The resulting materials were demonstrated to serve as novel g-C₃N₄-based catalysts for electrolytic HER with modest overpotential. Further research to understand the catalytic mechanism in the materials, particularly as to why only the Cu-doped g-C₃N₄ materials, but not other types of metal-doped g-C₃N₄, exhibit electrocatalytic activity as well as how to further improve their electrocatalytic activity *via* additional structural modification is currently underway. The synthetic strategy reported here is expected to open up new biomimetic synthetic routes to advanced electrocatalytic materials with superamolecular structures and possessing earth-abundant and inexpensive elements such as C, N, and Cu, and efficient electrocatalytic activity for a HER, a reaction that is currently among the most important reactions in electrocatalysis but that still needs effective electrocatalysts to perform.

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Figure 1. (A) The active site of an [FeFe]-hydrogenase. (B) A typical structural mimic of an active site in hydrogenase. (C, D) Representative functional mimics of hydrogenase; (E) An idealized copper ions-containing g-C₃N₄ sheet.

Figure 2. (A) XRD patterns of pure C₃N₄, 0.12Cu-C₃N₄, and 0.31Cu-C₃N₄; (B) solid-state ¹³C CP-MAS spectra of pure C₃N₄, 0.12Cu-C₃N₄, and 0.31Cu-C₃N₄; (C) the basic structural unit of g-C₃N₄; and (D) FTIR spectra of pure g-C₃N₄, 0.12Cu-C₃N₄, and 0.31Cu-C₃N₄.

Figure 3. Cu2p XPS spectra of 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄. The Cu2p_{3/2} peaks are deconvoluted into two peaks at 932.8 and 934.6 eV, respectively.

Figure 4. TG curves measured in air for pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄.

Figure 5. (A) Polarization curves obtained with pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄ and (B) current density vs. time (*I*-*t*) curve of HER over 0.31Cu-C₃N₄ at an overpotential of 390 mV over 43 h-long electrocatalytic reaction.

Figure 6. The Tafel plots obtained with pure g-C₃N₄, 0.12Cu-C₃N₄ and 0.31Cu-C₃N₄.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table of Contents Graphic and Synopsis

We present a novel “structure upgrading” synthetic approach for the design and synthesis of bio-inspired hydrogen-evolving electrocatalysts based on Cu-doped g-C₃N₄.

Graphical abstract