Breaking Pt Nanoparticles to Single-Atomic Pt-N₄ sites for Enhanced Solar to Hydrogen Conversion

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Abstract

Effective transfer and utilization of the photogenerated electrons have been regarded as the key factor for achieving high efficiency H₂ generation through a photocatalytic water splitting. In addition to the activity of co-catalyst, the interface between the co-catalyst and semiconductor is of particular importance. Herein, guided by density-functional theory (DFT) calculations, single atom (SA) Pt doped carbon nitride (CN) is successfully synthesized for use as co-catalyst of semiconducting CuS. The newly designed catalyst system (Pt1-CN@CuS) exhibits an enhanced photocatalytic performance for water splitting with a H₂ generation rate of 25.4 μmol/h and an apparent quantum yield (AQY) of 50.3% under the illumination of LED-530. Moreover, the solar-to-hydrogen (STH) conversion efficiency is calculated to be 0.5% under AM 1.5 illumination. This work provides fundamental insights into the interface migration and reaction of the photogenerated carriers.

Introduction

Hydrogen (H₂) generation via a water splitting using a powder semiconductor photocatalysis is expected to play a critical role in hydrogen economy. Therefore,

achieving high solar-to-H₂ (STH) conversion efficiency has been the subject of intense exploration [1-3]. When a semiconductor is activated by the incident photons, the electron-hole pairs are generated with a certain lifetime and migrated to the surface for the specific reduction and oxidation reactions. These steps, however, suffer from the slow kinetics; and the use of co-catalysts has become an effective strategy to accelerate the reactions [4-8]. Platinum (Pt) based materials have been proven to be the most efficient catalysts for H₂ evolution and employed widely as the electron consumption co-catalyst. However, the high-cost and scarcity of Pt hinder the large-scale and long-term application. More importantly, the inner Pt atoms of the nanoparticles is generally not participated in the surface reactions, and thus resulting in significant atomic waste [9-13]. Therefore, lowering the Pt load, while achieving remarkable H₂ generation, is a promising strategy.

Since recently, single-atom-Pt (SA-Pt) catalysts have attracted significant attention for use in many catalytic reactions such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), nitrogen reduction reaction (NRR) and CO₂ reduction reaction (CO₂RR) [14-17] owing to the efficient participation of Pt atoms in the catalytic process. For the SA-Pt based samples, the support is crucial as it not only stabilizes the loaded Pt atoms but also assists the reactions. Carbon-based materials have been widely used as the support, especially carbon nitride (CN) [18-26]. Many strategies have been reported to obtain the SA-Pt doping into CN, including solution chemical adsorption [27-28] and high-temperature calcination methods [29-30]. However, for the photocatalytic systems, the loading of SA-Pt doped co-catalysts onto the surface of one semiconductor with excellent activity is still challenging with no success reported to date. It has been realized that the fast extraction and transfer of photogenerated electrons in semiconductor system are the key influencing factors for high efficiency solar-to-H₂ conversion [26-30]. Furthermore, the interface between semiconductor and co-catalyst is one of the main factors that determine the final performance [31-35]. Therefore, developing stable single atom doped co-catalyst that has excellent interfacial contact with the semiconductor is of great interest.

Herein, theory-guided synthesis of a SA-Pt doped CN co-catalyst for efficient photocatalytic H₂ production is presented. We used density-functional theory (DFT) calculations to reveal that the Pt nanoparticles can be changed into SA-Pt doping into CN at high-temperature treatment. The composite of SA-Pt doped CN (Pt1-CN) and

CuS (Pt1-CN@CuS) is then experimentally synthesized using a high-temperature calcination method. Owing to its excellent photocatalytic activity, Pt1-CN supports CuS to efficiently split water with an apparent quantum yield (AQY) of 56.29% under LED-530 illumination. This work paves the way for designing highly efficient SA-based catalysts for photocatalytic H₂ production, while providing fundamental understanding on the interfacial steps of water splitting.

Results and discussion

Figure 1. (a) Molecular dynamic trajectories of system temperature and the number of SAs at high temperature (1100 K) to simulate the dynamic formation of SA-Pt on CN materials. Top is the snapshots of MD trajectories at 20 ns, 30 ns and 40 ns, where the trapped SA-Pt states were highlighted by red circles. (b) Binding energy comparison of SA-Pt by tuning the surrounded C:N ratios and (c) their corresponding adsorption free energies of hydrogen. Inset is the optimal catalytic site with the optimized hydrogen adsorption configuration.

Molecular dynamic (MD) simulations and first-principles calculations were united to investigate the formation and stability of SA-Pt doped CN at high temperature and

also their corresponding HER catalytic activities, which is expected to provide a targeted guideline for the experiments.

As shown in **Figure 1a**, at the initial state (0 ns), two Pt₃₈ nanocubes were covered on the 3.4 nm × 3.9 nm rectangle graphene nanosheet, in which the nitrogen-doped carbon matrix was randomly pre-etched by vacancies to simplify the surface of CN materials. Then 40 ns MD under the reactive force field (ReaxFF) was implemented to reveal the dynamic formation of SA-Pt at a temperature of around 1100 K. It is found that the system temperature tends to become steady state after 1 ns MD, and such a high temperature is able to drive Pt nanocubes to disperse into small clusters or even single atoms and diffuse at the CN surface disorderedly from the snapshot of MD trajectories at 20 ns, 30 ns and 40 ns. Accordingly, we analyzed the number of SAs for every MD trajectory and about 20% of Pt nanocubes are prone to escape from its aggregated counterpart and form single-atom state, which is possible to be trapped by diverse defects of CN surface during their random thermal vibration processes. This also clearly illustrated the SA formation mechanism in which high temperature plays a vital factor to provide enough driving force for the escape of metal atoms. Once trapped in the defects, single Pt atom would be stabilized by forming covalent Pt-C and ionic Pt-N bonds.

We quantitatively evaluated the binding energies of Pt atoms with six coordination environments by tuning the C:N ratios at the edge of vacancies. **Figure 1b** indicated that the binding energies of Pt in these vacancies are obviously larger than the cohesive energy of bulk Pt. Also, the Pt-C bonds are stronger than the Pt-N bonds, which is effective to stabilize the single atom state. Therefore, high-temperature and vacancies of CN materials are of great importance to the formation and stabilization of SA-Pt for the experimental synthesis.

Furthermore, we pre-screened the adsorption free energy of hydrogen on these potential SA-Pt sites to evaluate the HER activity of Pt-CN based on the computational hydrogen electrode theory. As can be seen in **Figure 1c**, a variety of coordination environments, including C:N ratios, can modulate the electronic properties of SA and thus influence the catalytic performance. By selecting the catalytic site with an adsorption energy closer to zero, we found that Pt-C bonds not only stabilize the SA-Pt, but also enhance the hydrogen adsorption as compared to the

SA-Pt bonded with four nitrogen (Pt-0C4N). The Pt-4C0N motif (-0.27 eV) was the optimal site to balance the first proton adsorption and the following hydrogen desorption, which is a potential site for enhancing the HER activity and deserves for further experimental synthesis and confirmation.

Figure 2. (a) Schematic illustration of the preparation of Pt1-CN@CuS. (b) XRD pattern and (c)-(d) TEM image and (e) HRTEM image of the selected area in 2d of Pt1-CN@CuS sample. (f) Spherical aberration correction HAADF-STEM image of (f) Pt1-CN@CuS and (g) the part of Pt1-CN in Pt1-CN@CuS sample; and (h) the corresponding FT-EXAFS results.

Copper oxide (CuO) nanosheet (**Figure S1**) and thiourea (CS(NH₂)₂) were employed as the precursors for the synthesis of CN@CuS. After calcination at 400 °C in Ar atmosphere, the mixture of CuO and CS(NH₂)₂ was transformed into the target product of CN@CuS with the standard hexagonal copper sulfide (PDF: 79-2321), as shown in **Figure S2a**. The nanosheet morphology was not changed (**Figure S2b**), and the sample showed the element species of Cu, S, C and N based on transmission electron microscopy (TEM) elemental mapping (**Figure S2c**). For the synthesis of

monatomic-Pt doped CN, the CN@CuS was loaded with 1 wt% Pt using a photo-deposited process to obtain the Pt/CN@CuS, which was further annealed at 800 °C in Ar (**Figure 2a**). Then the Pt1-CN@CuS sample with a hexagonal CuS was confirmed by the x-ray diffraction (XRD) pattern (**Figure 2b**). As shown in **Figure 2c**, TEM image does not reveal obvious agglomeration after high-temperature calcination, suggesting that this strategy does not affect the core material of CuS. After magnifying the TEM image, the core-shell structure of Pt1-CN@CuS can be clearly observed in **Figure 2d**. That is, the amorphous CN (actually, nitrogen doped carbon) enfolds the crystallized CuS. In **Figure 2e**, the high-resolution TEM (HRTEM) images provides the lattice spacing value of 0.326 nm, which can be assigned to the lattice planes of (100) and (010), suggesting that the orientation of CuS follows the [001] projection [36].

Figure 2f illustrates the spherical aberration correction high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the Pt1-CN@CuS sample, showing the two parts of amorphous CN and crystallized CuS. The edge section was further analyzed and has white dots embedded onto the amorphous carbon support by single-atom status (**Figure 2g**). The X-ray absorption near-edge structure spectra (XANES) of Pt L₃-edge in **Figure S3** reveals that the white-line intensity of Pt1-CN@CuS sample is higher than the bare Pt, suggesting that the monatomic Pt is in an oxidation state [23-24]. The Fourier transformations (FT) of k^3 -weighted for the extended X-ray fine structure (EXAFS) was further carried out (see **Figure 2h**). Clearly, the reference Pt exhibits a main peak at ca. 2.5 Å, which can be attributed to the metallic bond of Pt-Pt. Meanwhile, the Pt1-CN@CuS sample showed the peak at ca. 1.93 Å which can be assigned to Pt-N bonds. Therefore no Pt-Pt bond was detected, confirming that the Pt atoms exist in the single atom form which is consistent with the above HAADF-STEM results and DFT simulation (**Figure 1c**). According to the DFT calculation (**Figure 1a**), the doped Pt single atoms are anchored to the N atoms in the CN support, as shown in **Figure 1h**. The element distribution of the Pt1-CN@CuS sample was further carried out (see **Figure S4**). It should be pointed out that the Pt elements were uniformly distributed on the CN framework.

The thermal induced single-atom doping process was carried out at different calcination times such as 0, 15 and 60 min. As shown in HAADF-STEM image in **Figure S5**, the CN@CuS sample with a loading of 1 wt% Pt nanoparticles (Pt-

CN@CuS-800-0) was obtained using a photo-deposition method. Without 800 °C treatment, the size of the Pt nanoparticles can be detected to be ca. 7 nm (**Figure S5a**) and the element mapping confirms the Pt particle state (**Figure S5b-e**). When the sample was treated 15 min at 800 °C (Pt-CN@CuS-800-15), there were some Pt single atoms appearing around the Pt particles (**Figure S6a**), confirming that the thermal-treatment induces the Pt element migration. **Figure S6b-e** show the elemental mapping of Cu, S and Pt and further suggests the dissociation of the Pt particles. Indeed, for the sample prepared by annealing at 800 °C for 60 min (Pt-CN@CuS-800-60), no Pt particles can be detected (**Figure S7a**), and the element mapping shows uniformly distributed Pt (**Figure S7b-e**), further suggesting that the energy supply via heating induced the change of Pt nanoparticles to single Pt atom in N doped carbon. **Figure S8** exhibits the corresponding energy dispersive spectrometer (EDS) spectra, and Table S1 summarizes the element molar ratios of Cu, S and Pt. Clearly, for the three samples (Pt-CN@CuS-800-0, Pt-CN@CuS-800-15 and Pt-CN@CuS-800-60), the molar ratios do not change significantly, suggesting that there is no elemental loss during the high-temperature calcination. The higher temperature treatment of 900 and 1000 °C were further used and the products showed the loss in Cu element due to the production of Cu₂S and Cu_{7.4}S₂ (**Figure S9**).

The formation mechanism of the Pt1-CN@CuS was further studied. The starting sample (CN-CuS) obtained by the calcination at 400 °C (**Figure S2**) was used for two main purposes. One was used for loading Pt nanoparticles via a photo-deposition method while the other was employed as the reference sample. As shown in the Fourier transform infrared (FTIR) spectrum (**Figure S10a**), the peaks at 1200-1700 cm⁻¹ can be assigned to the typical g-C₃N₄ signals [37-39]. There is no visible Cu-S absorption band at ca. 1100 cm⁻¹. For the high resolution X-ray photoelectron spectroscopy (XPS) C 1s, two peaks positioned at 284.6 and 288.0 eV can be detected. The peak at 288.0 eV can be assigned to the sp²-hybridized carbon in g-C₃N₄ skeleton, while the peak at 284.6 eV is typically associated with the sp² C–N in graphitic carbon nitride (**Figure S10b**) [37-39]. There are three peaks centered at 398.6, 400.0 and 404.4 eV in the XPS N 1s spectra (**Figure S10c**), which can be attributable to the sp² N, bridging nitrogen atoms N–(C)₃ and charging effects in the g-C₃N₄ structure [39-40], respectively.

The CN-CuS sample was treated with calcination at temperatures of 500, 700 and 800 °C to obtain the reference samples of CN@CuS-500, CN@CuS-700 and CN@CuS-800. As shown in the XRD patterns in **Figure S11**, all three samples did not change the phase of typical hexagonal CuS, demonstrating their high thermal stability. **Figure S12a** depicts the XPS Cu 2p spectra with two main peaks centered at *ca.* 931.4 and 951.2 eV for all three samples, which are attributable to the Cu 2p_{3/2} and 2p_{1/2} of Cu²⁺ [41-42]. **Figure S12b** shows the XPS S 2p spectra with one main peak, which can be deconvoluted into two peaks loaded at *ca.* 161.4 and 162.7 eV attributable to the 2p_{3/2} and 2p_{1/2} of S²⁻, respectively [41-42]. The XPS C1s spectra in **Figure S12c** shows that three fitted peaks at *ca.* 284.6, 285.4 and 286.2 eV are formed, suggesting that the samples contain the C=O, C=N and C=C groups, respectively [43].

According to the XPS N 1s result in **Figure S13a**, the CN@CuS-700 and CN@CuS-800 exhibit the obvious difference from the CN@CuS-500, which shows the similar g-C₃N₄ skeleton, suggesting that the high-temperature calcination induced the structural change of the CN. Typically, there are three peaks centered at 398.2, 400.3 and 401.3 eV, which can be attributable to the pyridinic-N (Pyri-N), pyrrolic-N (Pyrr-N) and graphitic-N (Grap-N), respectively, [44-46] for the CN@CuS-700 and CN@CuS-800, suggesting that the nitrogen-doped carbon is successfully formed after the high-temperature treatment. The percentage of the three types of N in the CN structure was further studied. Clearly, the Pyrr-N and Grap-N are increased with increasing the calcination temperature, while the Pyri-N has the main contribution in the N doped carbon structure (**Figure S13b**). **Figure S14** displays the TEM images of CN@CuS-500, CN@CuS-700 and CN@CuS-800 samples with a clear structure of CN packed CuS.

The structure transformation from CN-CuS loaded Pt nanoparticles (Pt-CN-CuS) to Pt1-CN@CuS was further explored by thermal treatment. Similar to the process described earlier, the Pt-CN-CuS was also calcined at 500, 700 and 800 temperatures to synthesize Pt-CN@CuS-500, Pt-CN@CuS-700 and Pt-CN@CuS-800 (Pt1-CN@CuS) samples. The XRD patterns show that all three samples exhibit typical CuS peaks (**Figure S15** and **Figure 2b**), and no Pt phase signals can be detected. However, STEM images reveal visible Pt nanoparticles for the Pt-CN@CuS-500 and Pt-CN@CuS-700 (**Figure S16a-b**). It should be noted that the Pt nanoparticles were restored well after the treatment at 500 °C; and for the sample obtained at 700 °C, there

are some dissociation of the Pt nanoparticles (**Figure S16c**), suggesting that the loaded Pt has started to change at that temperature.

Figure S17a-b show the high-resolution XPS Cu 2p and S 2p spectra of the three samples, confirming that the Cu and S ions are positive and negative bivalent, respectively. Almost no shift in the binding energy values of the XPS Cu 2p or S 2p was detected, suggesting that the calcination process has no influence on CuS. However, for the Pt 4f XPS result in **Figure S18**, the Pt-CN@CuS-700 and Pt-CN@CuS-800 exhibit the obvious different curves as compared to the Pt-CN@CuS-500 sample. For the Pt-CN@CuS-500, there are two main peaks loaded at 70.9 and 74.3 eV attributable to $4f_{7/2}$ and $4f_{5/2}$ of Pt^0 [47-48], respectively. Meanwhile, there are two relatively weak peaks loaded at 72.2 and 75.5 eV, which can be assigned to $4f_{7/2}$ and $4f_{5/2}$ of Pt^{2+} , respectively, as reported in the literatures [48-49]. For the Pt-CN@CuS-700 and Pt-CN@CuS-800, only two main peaks located at ca. 72.3 and 75.6 eV attributable to the signals of Pt^{2+} can be detected. Moreover, there are some high binding energy shift from Pt-CN@CuS-500 to Pt-CN@CuS-800, suggesting that on one hand the Pt^0 is oxidized to Pt^{2+} during the calcination in Ar, on other hand the Pt^{2+} ions are bonded by other ions by the calcination at 700 °C to 800 °C. **Table S2** provides the detailed binding energy values for the three samples.

Figure 3. Schematic illustration of structural transformation of carbon nitride loaded with Pt nanoparticles to single-atom Pt doped CN.

The XPS C1s spectra of the three samples show the similar curves with the reference samples of CN@CuS as shown in **Figure S19a**. However, for the XPS N1s spectra (**Figure S19b**), all the samples exhibit the similar peaks with CN@CuS-700 and CN@CuS-800. That is, the structural transformation of Pt-CN@CuS-500 sample

is completed from g-C₃N₄ to N doped carbon, suggesting that the loading of Pt will accelerate the above process. Typically, the percentage of Pyri-N becomes low from Pt-CN@CuS-500 to Pt-CN@CuS-800, meanwhile, the parts of Pyrr-N and Grap-N increase slightly (**Figure S19c**). The structural transformation from Pt nanoparticles loaded carbon nitride to single-atom Pt doped CN can be described as shown in **Figure 3**. Upon calcination, carbon nitride started the process of C=N bond breaking and then formed the carbon coupling. Meanwhile, the Pt loaded surface will boost above steps (**Figure S13a**, **Figure S19b**) with its dissociation. With the treatment of persistent overheating, the single-atom Pt doping with the nitride doped graphene were formed, and the parts of Pt⁰ were all oxidized into Pt²⁺ (**Figure S18**) with parts of carbon reduction.

Figure 4. (a) H₂ evolution rates of the reference CN@CuS (CN@CuS-800), Pt@CN@CuS (Pt@CN@CuS-800, obtained from the in situ photo-deposition method) and Pt1-CN@CuS under visible-light illumination ($\lambda > 420$, 150 W) and AM 1.5 (100 W). (b) H₂ generation performance of Pt1-CN@CuS under different LED lamps illumination. (c) The relationship between AQY plots obtained from LED-450, 530, 550 and 610, and UV-Vis absorption spectrum for the Pt1-CN@CuS. (d) The stability measurement of the Pt1-CN@CuS. (e) The corresponding FT-EXAFS results before

and after the stability test of Pt1-CN@CuS. (f) XPS N 1s spectra before and after the stability test of Pt1-CN@CuS.

The optical properties of the Pt1-CN@CuS were also studied as shown in **Figure S20**. Specifically, both samples (Pt1-CN@CuS and CN@CuS) show the similar absorption band edge with a threshold value of *ca.* 600 nm, which can be converted to a bandgap of 2.07 eV (**Figure S20a**). Moreover, Pt1-CN@CuS sample exhibits the obvious tail absorption at the wavelength range of 600-900 nm, suggesting that the single-atom Pt doping in CN can increase the photon absorption. The room temperature photoluminescence (PL) spectra shows the lower intensity of the Pt1-CN@CuS sample than the reference sample (CN@CuS) under the excitation wavelength of 400 nm (**Figure S20b**), suggesting that the monatomic Pt in CN can suppress the recombination of photogenerated carriers.

The photocatalytic water splitting performances of Pt1-CN@CuS and CN@CuS were then studied. The effect of sample usage on the photocatalytic performance was first tested for the Pt1-CN@CuS, and the optimal condition of 50 mg was obtained under the visible-light ($\lambda > 420$ nm, 150 W, **Figure S21a**) and AM 1.5 (100 mW/cm², **Figure S21b**). In detail, this sample showed the hydrogen evolution rates of 508.8 $\mu\text{mol/h}$ and 362.5 $\mu\text{mol/h}$ under the above two illumination conditions (**Figure 4a**), respectively. Meanwhile, the reference sample (CN-CuS) showed the rates of only 22.0 and 26.9 $\mu\text{mol/h}$ under the same measurement conditions, and when it loads with Pt nanoparticles (Pt@CN@CuS) via an in-situ photo-deposition method, the photocatalytic H₂ generation rates enhanced to be 68 and 72.2 $\mu\text{mol/h}$ (**Figure S22**), which were still lower than the Pt1-CN@CuS, confirming that the single-atom Pt doping boosts the photocatalytic water splitting to H₂ generation. The photocatalytic activity of CN@CuS and Pt-CN@CuS samples were studied under the two illumination conditions of visible light and AM 1.5. As given in **Figure S23** and **Figure S24**, the samples containing Pt show better performances than the reference samples (CN@CuS), suggesting that adding Pt enhances the utilization of photogenerated electrons. Moreover, the single-atom Pt doping (Pt-CN@CuS-800 sample) exhibits the best activity, further confirming that the monatomic Pt doping promotes the co-catalyst performance for H₂ generation.

The photocatalytic H₂ generation performances under different LED-lamps (450, 530, 550 and 610) were then investigated for the Pt1-CN@CuS sample. A continuous increase in the H₂ evolution can be detected under four conditions (**Figure S25**) with the LED-530 showing the best performance. The H₂ generation rates have been summarized in **Figure 4b** to be 13.9, 25.4, 11.8 and 10.2 $\mu\text{mol/h}$ under the corresponding LED-lamps illumination (450, 530, 550 and 610), respectively. The corresponding apparent quantum yield (AQY) values were also calculated to be 30.8%, 50.3%, 22.2% and 19.2%. Moreover, the AQY plot was consistent with the optical absorption (**Figure 4c**), confirming that the co-catalyst of CN with single-atom Pt doping can commendably absorb and utilize the incident photons.

The stability of Pt1-CN@CuS sample was tested by taking the use of four cycles of H₂ generation under AM 1.5 illumination. No obvious decrease in the activity was observed as shown in **Figure 4d**. In order to obtain the direct evidence about the chemical stability, XPS and XAFS measurements were further conducted. As shown in FT-EXAFS curves (**Figure 4e**), the Pt signal displayed the same peak location before and after the stability measurement, confirming that the single-atom doped Pt still stably exists in the CN. Moreover, the XPS C 1s, Cu 2p and S 2p spectra did not show the significant change (**Figure S26**), i.e. binding energy and normalized intensity, as well as the XPS N 1s result in **Figure 4f**, confirming that the chemical valances of the three elements kept the same after the four cycles tests.

The Pt1-CN@CuS sample possesses excellent extraction and utilization capabilities of photogenerated electrons, and thus the holes will be expected to provide the extended lifetime. The photocatalytic water oxidation activity was further carried out and the results are shown in **Figure S27**. Under two illumination conditions of visible-light ($\lambda > 420\text{ nm}$, 150 W) and AM 1.5 (100 mW/cm²), the apparent O₂ evolution of Pt1-CN@CuS sample increased with increasing the reaction time (**Figure S27a**). The O₂ generation rates during 2h reaction were measured to be 17.6 and 11.7 $\mu\text{mol/h}$ for the illumination of $\lambda > 420$ and AM 1.5, respectively (**Figure S27b**). The photocatalytic O₂ generation of Pt1-CN@CuS under LED-530 illumination was also carried out (**Figure S27c**), and the O₂ generation was continuously increasing with the increase of reaction time, confirming its response under LED-530 condition. The overall water splitting performance was further

studied. As shown in **Figure S28**, the Pt1-CN@CuS exhibits the H₂ and O₂ gases signal with the approximate ratio of 2:1 under the AM 1.5 illumination. The corresponding solar-to-hydrogen (STH) conversion efficiency was calculated to be 0.5%.

Figure 5. Electrochemical results of Pt1-CN@CuS sample. (a) Polarization curve, (b) the corresponding Tafel plots, and (c) the R_{ct} values of the sample measured in 0.5 M Na₂SO₄ electrolyte.

The underlying reasons for the excellent photocatalytic performance of Pt1-CN@CuS sample were studied based on electrochemical measurements in 0.5 M Na₂SO₄ solution. As shown in **Figure 5a** and **Figure S29a**, Pt1-CN@CuS exhibits a good electrocatalytic H₂ generation in comparison to the reference CN@CuS, Pt-CN@CuS-500 and Pt-CN@CuS-700, and the lowest overpotential was even comparable to the commercial 20 wt% Pt/C. The overpotential values were measured to be 92 and 284 mV for Pt1-CN@CuS and CN@CuS (CN@CuS-800), respectively (**Table S3**). Moreover, the corresponding Tafel slopes were calculated to be 64 and 93 mV/dec (**Figure 5b**), and other references were measured to be in the range of 70~110 mV/dec (**Figure S29b**). It is well established that smaller the Tafel slope, faster the charge transfer process [50-51]. Because the surface reaction of photocatalytic water splitting is related to the electrocatalytic steps, the single-atom Pt doping is confirmed to be beneficial to the co-catalyst effect in CN. The carrier migration process involves the interface impedance, which is the other important factor that influences the catalytic efficiency. The electrochemical impedance spectroscopy (EIS) was carried out and the spectra are plotted in **Figure S30a**. Clearly, the semicircle plots were reduced from the sample of CN@CuS-500 to Pt-CN@CuS-

800 (Pt1-CN@CuS), suggesting that the resistance reduced after adding Pt and the single-atom doping further resulted in a low resistance. **Figure S30b** shows the fitting circuit, in which the R_{CT} and R_{sol} are the charge transfer and solution resistances, respectively and the C_{DL} is the interface capacitance [50-51]. As summarized in **Table S3**, the fitted R_{sol} values for all the studied samples are close, suggesting that the solution makes no difference for the H_2 evolution. However, there is an obvious decrease in the R_{CT} value between the CN@CuS-500 and Pt-CN@CuS-800. For the CN@CuS (CN@CuS-800) and Pt1-CN@CuS samples, the R_{CT} values were fitted to be 130.7 and 40.8 ohm/cm^2 (**Figure 5c**), respectively, further confirming that the monatomic Pt doping significantly decreases the interface resistance of CN and thus boost the carrier migration across the catalyst-solution interface.

Conclusions

Herein, by following the DFT calculation, we demonstrate the process of the structural evolution of carbon nitride loaded with the Pt nanoparticles to the single-atom Pt doped CN, which shows an outstanding performance for photocatalytic water splitting when acting as a co-catalyst for CuS semiconductor. Our newly designed Pt1-CN@CuS exhibits the visible-light photocatalytic H_2 generation of 13.9, 25.4, 11.8 and 10.2 $\mu\text{mol}/\text{h}$ under the illumination of LED-lamps (450, 530, 550 and 610), and the corresponding AQY values of 30.8%, 50.3%, 22.2% and 19.2%, respectively. Moreover, the overall water splitting is also carried out with the STH conversion efficiency of 0.5% under AM 1.5 illumination. Experimental results reveal that the single-atom Pt doping in CN can lower the H_2 evolution overpotential, and thus boost the reaction kinetics and reduce the interface resistance of carrier migration greatly. This work not only introduces an efficient way for the synthesis of single-atom doping, but also provides fundamental insight into the photocatalytic interface processes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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