


 Cite this: *RSC Adv.*, 2021, **11**, 36166

# Ultrafast synthesis of near-zero-cost S-doped Ni(OH)<sub>2</sub> on C<sub>3</sub>N<sub>5</sub> under ambient conditions with enhanced photocatalytic activity†

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Planting highly efficient and low-cost Ni-based noble-metal-free active sites on semiconductors is of great significance in the field of photocatalysis. Herein, taking wide visible-light-responsive 2D C<sub>3</sub>N<sub>5</sub> as a model semiconductor, an impressive near-zero-cost 2D S-doped nickel hydroxide (S–Ni(OH)<sub>2</sub>) is grown on C<sub>3</sub>N<sub>5</sub> ultrafast within 30 min under ambient conditions by facile reaction between extremely low-cost Ni(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S in aqueous solution. The fabricated 2D S–Ni(OH)<sub>2</sub>–C<sub>3</sub>N<sub>5</sub> hybrid exhibits enhanced photocatalytic performance for both H<sub>2</sub> production from water and NO removal for air purification. The H<sub>2</sub> production rate on S–Ni(OH)<sub>2</sub>–C<sub>3</sub>N<sub>5</sub> is ~7 times higher than that of Ni(OH)<sub>2</sub>–C<sub>3</sub>N<sub>5</sub> and even slightly higher than that of Pt–C<sub>3</sub>N<sub>5</sub>, demonstrating its potential as a candidate for noble metal catalysts like Pt. In particular, an apparent quantum yield (AQY) value of 30.9% at 420 nm for H<sub>2</sub> production is reached on 1.0 wt% S–Ni(OH)<sub>2</sub>–C<sub>3</sub>N<sub>5</sub> due to quick internal charge transfer efficiency. In addition, ~42% of NO can be purified in a continuous flow reaction system. This work affords a cost-efficient strategy to steer the photocatalytic property of Ni-based catalysts.

Received 29th September 2021

Accepted 22nd October 2021

DOI: 10.1039/d1ra07275g

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## Introduction

In the past decades, the ever-increasing energy crisis and environmental pollution have drawn wide concern considering the sustainable development of human society and public health.<sup>1–3</sup> Among the various clean technologies, the environmentally friendly semiconductor-based photocatalytic oxidation and reduction is deemed as the most potential one.<sup>4–7</sup> In this field, photocatalytic solar H<sub>2</sub> production and NO removal lie in the core attributed to the huge energy consumption and the high risk respiratory diseases. Up to now, different semiconductors including metal oxides/sulfides (TiO<sub>2</sub>, CdS, ZnIn<sub>2</sub>S<sub>4</sub>, *etc.*),<sup>8–12</sup> metal-free materials (carbon nitride, COFs, conjugated polymers, *etc.*)<sup>13–17</sup> and heterojunctions are all widely investigated to solve these issues.<sup>12,18–20</sup> Of these strategies, constructing a heterojunction between different materials to combine the superiority of each one can significantly improve the whole photocatalytic efficiency. For example, K. Domen *et al.* selectively photodeposited Rh/Cr<sub>2</sub>O<sub>3</sub> and CoOOH on different facets of the SrTiO<sub>3</sub>:Al photocatalyst as cocatalysts for hydrogen and oxygen evolution respectively and an external quantum efficiency up to 96% at 350–360 nm was obtained.<sup>21</sup>

Recently, carbon nitride has drawn enormous attention due to its low-cost, high stability and suitable band position for water splitting;<sup>22–25</sup> however, the band-gap of conventional carbon nitride (~2.7 eV for C<sub>3</sub>N<sub>4</sub>) is still too wide to obtain ideal photocatalytic activity. To alter the photocatalytic efficiency of carbon nitride, structural and band position regulation by doping (S, O, P, N- or C-rich modification) and fabricating heterojunctions (TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>, CdS/C<sub>3</sub>N<sub>4</sub>, CNN/BDCNN, *etc.*) with type II or Z/S-scheme mechanisms are widely adopted.<sup>15,26–31</sup> Recently, N-rich carbon nitride (*i.e.* C<sub>3</sub>N<sub>5</sub>) was reported;<sup>31–36</sup> it possessed a narrower band-gap and higher catalytic activity than common C<sub>3</sub>N<sub>4</sub>, which represents a new direction for exploring carbon nitride based materials. For example, our previous work found that photocatalytic H<sub>2</sub> production activity over Pt–C<sub>3</sub>N<sub>5</sub> was ~2.2 times higher than that of Pt–C<sub>3</sub>N<sub>4</sub>.<sup>36</sup> Nickel based materials exhibit excellent catalytic reduction and oxidation activities in the field of both photocatalysis and electrocatalysis,<sup>37–43</sup> and thus can be used as co-catalysts on C<sub>3</sub>N<sub>5</sub>. Moreover, it has been reported that S doping can significantly improve the electrocatalytic performance of Ni/Fe (oxy)hydroxide materials;<sup>44</sup> thus doping of S in nickel-based co-catalysts may further improve their performance. However, these Ni-based species were commonly synthesized by hydrothermal or heat-treatment at high temperature, which was time and cost exhaustive. Therefore, construction of highly effective Ni-based catalysts in short time with low cost and energy consumption is of great importance for potential industrialization of photocatalytic technology.

Herein, taking 2D C<sub>3</sub>N<sub>5</sub> as a model semiconductor, 2D S-doped Ni(OH)<sub>2</sub> (denoted as S–Ni(OH)<sub>2</sub>) was facilely planted on its surface by a one-step precipitation method between Ni(NO<sub>3</sub>)<sub>2</sub> and

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra07275g

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$\text{Na}_2\text{S}$  in water (co-existence of  $\text{S}^{2-}$  and  $\text{OH}^-$ ) under stirring within 30 minutes at room temperature, as revealed in Scheme 1. The hybrid photocatalyst ( $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$ ) was evaluated by photocatalytic activity for  $\text{H}_2$  production and NO oxidation removal. Experimental results depicted that  $\text{S-Ni(OH)}_2$  can promote the photogenerated  $e^-/ h^+$  separation of  $\text{C}_3\text{N}_5$  after light excitation and favor the generation of active oxygen species (ROS) participating in the subsequent photocatalytic procedure. In particular, the visible-light-induced photocatalytic  $\text{H}_2$  production rate over  $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$  is even higher than that of  $\text{Pt-C}_3\text{N}_5$ , while the cost of  $\text{S-Ni(OH)}_2$  (taking the  $\text{H}_2$  production test as an example: in 45 mg 1.0 wt%  $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$ ) is calculated to be just  $\sim 0.0032$  ¥ or  $\sim 0.00049$  \$ based on the price of  $\text{Ni(NO}_3)_2$  and  $\text{Na}_2\text{S}$ . The present work provides new insights into the design of low-cost and noble-metal-free catalysts for energy and environmental applications.

## Experimental section

### Material preparation

All chemicals used were purchased from Aladdin and used without purification.  $\text{C}_3\text{N}_5$  was prepared by heating 3-amino-1,2,4-triazole at  $500^\circ\text{C}$  in air according to our previous work.<sup>36</sup> Generally,  $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$  was synthesized by mixing a certain amount of  $\text{C}_3\text{N}_5$ ,  $\text{Ni(NO}_3)_2$  and  $\text{Na}_2\text{S}$  in water and stirring for 30 min. And then, the precipitate was washed with distilled water and absolute ethanol several times and dried in a vacuum at  $80^\circ\text{C}$  for 12 h. The loading amount of  $\text{S-Ni(OH)}_2$  on  $\text{C}_3\text{N}_5$  was calculated based on the initial input nickel mass fraction in the hybrid, and a series of  $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$  hybrids with  $\text{S-Ni(OH)}_2$  loading amount varying between 0.5 and 3.0 wt% were prepared by changing the amount of  $\text{Ni(NO}_3)_2$  and  $\text{Na}_2\text{S}$  accordingly. Pristine  $\text{S-Ni(OH)}_2$  was also prepared by the same method in the absence of  $\text{C}_3\text{N}_5$ . By the way,  $\text{Ni(OH)}_2\text{-C}_3\text{N}_5$  was prepared by the same method using  $\text{NaOH}$  instead of  $\text{Na}_2\text{S}$ .

### Catalyst characterization

XRD patterns were recorded on a powder X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (D8 Advance Bruker Inc., Germany). TEM and HRTEM images were acquired on an FEI TALOS F200. SEM and EDS mapping images were acquired on a Gemini Sigma 300. The Brunauer–Emmett–Teller (BET) specific surface area was evaluated using nitrogen adsorption–desorption apparatus (ASAP 2040,

Micrometrics Inc., USA) with all samples degassed at  $120^\circ\text{C}$  for 12 h prior to measurements. Valence state of each element in the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectroscope. A Shimadzu UV-3100 recording spectrophotometer and fluorescence spectrometer (F-4600, Hitachi Inc., Japan) were used to record UV-vis diffuse reflectance (DRS) and PL spectra measurements respectively. Time-resolved fluorescence spectra (TRFS) were obtained on an Edinburgh FLS 1000. Electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA200 EPR spectrometer. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a radical spin-trapping reagent for  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$ . 2,2,6,6-Tetramethylpiperidine (TEMP) was used as the trapping agent for  $^1\text{O}_2$ .<sup>3</sup> The photocurrent and electrochemical impedance measurements were recorded on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three electrode configuration. Pt foil and  $\text{Ag/AgCl}$  (saturated KCl) were used as the counter electrode and reference electrode respectively. The working electrode was made by spreading a catalyst/Nafion slurry on FTO glass and 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as the electrolyte.

### Photocatalytic activity tests and photoelectrochemical measurements

The photocatalytic  $\text{H}_2$  production rate and AQY measurements were carried out on a top-irradiated reaction vessel containing the catalyst and sacrificial reagent (TEOA) connected to a closed gas system with a 300 W Xe-lamp (PLS SXE300, Beijing Perfectlight Inc., China) equipped with a cutoff filter ( $\lambda > 420$  nm) or band-pass filters ( $\lambda = 420, 500$  nm, etc.); the photocatalytic  $\text{H}_2$  production system is shown in Fig. S1.† The  $\text{H}_2$  production rate was detected using a GC (SP7820, TCD detector, 5 Å molecular sieve columns, and Ar carrier), and AQY values were calculated according to our previous work:<sup>17</sup>

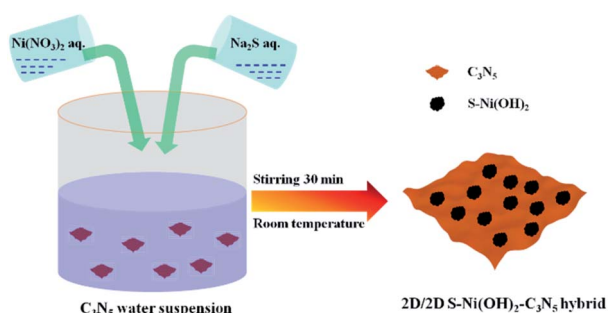
$$\text{AQY} = \frac{2 \times (\text{number of evolved } \text{H}_2 \text{ molecules})}{\text{number of incident photons}} \quad (1)$$

For photocatalytic NO removal, a continuous flow reactor under ambient conditions was adopted according to our previous work.<sup>7</sup> The volume of the rectangular reactor was 4.5 L (30 cm  $\times$  15 cm  $\times$  10 cm). 25 mg catalyst was dispersed into the mixture of ethanol and water and then transferred into a culture dish with a diameter of 12 cm, and then the dish was placed in the reactor after the solvent was dried at  $45^\circ\text{C}$ . A 30 W visible LED (General Electric) was used as a light source. The gas (containing NO and air) flow rate through the reactor was controlled at  $1000 \text{ mL min}^{-1}$  using a mass flow controller with an initial NO concentration of  $\sim 600$  ppb. The NO and  $\text{NO}_2$  concentrations were recorded on a  $\text{NO}_x$  analyzer model T200 (Teledyne API). The generation of  $\text{NO}_3^-$  was detected by ion chromatography on a Thermo DIONEX ICS-900.

## Results and discussion

### Crystal phase and micro morphology analyses

The pristine  $\text{S-Ni(OH)}_2$  prepared from the ultrafast reaction between  $\text{Ni}^{2+}$  and  $\text{Na}_2\text{S}$  in water under ambient conditions



Scheme 1 Illustration of ultrafast preparation of the  $\text{S-Ni(OH)}_2\text{-C}_3\text{N}_5$  hybrid.



within 30 min is firstly detected by XRD, as depicted in Fig. S2,† which demonstrates the formation of S-Ni(OH)<sub>2</sub> with low diffraction peaks corresponding to the PDF card of 73-1520 for Ni(OH)<sub>2</sub>, indicating the low crystallinity of the present S-Ni(OH)<sub>2</sub> material. Herein, the confirmation of S doping will be illustrated in the following section. It should be noted that pristine Ni(OH)<sub>2</sub> without S doping is prepared by reaction between Ni<sup>2+</sup> and NaOH for comparison, and the diffraction peaks of this Ni(OH)<sub>2</sub> are also in agreement with the same PDF card (Fig. S2†), indicating that the comparison is reasonable. For the XRD patterns of C<sub>3</sub>N<sub>5</sub> and S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid (Fig. 1a), only two distinct peaks corresponding to (100) and (002) planes of C<sub>3</sub>N<sub>5</sub>,<sup>32,35,36,45</sup> are observed even with a high loading amount of S-Ni(OH)<sub>2</sub> up to 3.0 wt%, which should relate to the low crystallinity of present S-Ni(OH)<sub>2</sub>. In addition, no obvious shift happens in the main peaks of C<sub>3</sub>N<sub>5</sub> after the loading of S-Ni(OH)<sub>2</sub>, revealing that the procedure for hybrid preparation does not destroy the basic structure of C<sub>3</sub>N<sub>5</sub>.

The element component of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is analyzed by elemental analysis and ICP-MS (Table S1†). From the elemental analysis result, the C/N ratio of the catalysts was determined to be 3 : 4.7, which is much lower than that of C<sub>3</sub>N<sub>4</sub> and very close to that of C<sub>3</sub>N<sub>5</sub>, and the result is in good agreement with previous literature.<sup>35</sup> As revealed in Fig. 1b, S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is composed of C, N, Ni, O and S elements, demonstrating the existence of S-doping in Ni(OH)<sub>2</sub> during the reaction between Ni<sup>2+</sup> and Na<sub>2</sub>S preliminarily. In addition, the result depicts the successful combination of S-Ni(OH)<sub>2</sub> and C<sub>3</sub>N<sub>5</sub>. The high resolution spectra of C 1s (Fig. S3a†) and N 1s (Fig. S3b†) in S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> are similar to that of pristine C<sub>3</sub>N<sub>5</sub> shown in our previous work,<sup>36</sup> and no obvious peak shifts are found, revealing that the structure of C<sub>3</sub>N<sub>5</sub> is well kept during the loading of S-Ni(OH)<sub>2</sub>. The existence of Ni ions is confirmed by the high resolution spectrum of Ni 2p, in which two distinct spin-orbit peaks at ~855.8 (Ni 2p<sub>3/2</sub>) and ~873.5 eV (Ni 2p<sub>1/2</sub>) along with two satellite peaks (identified as "Sat.") are clearly observed (Fig. 1c).<sup>40,42</sup> The O 1s spectra mainly consist of

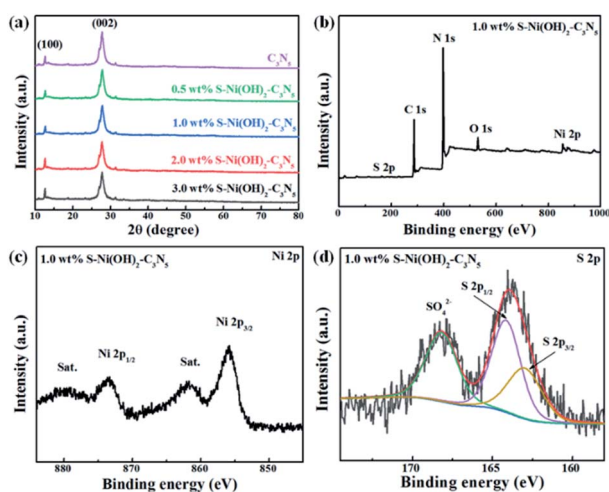


Fig. 1 (a) XRD patterns of C<sub>3</sub>N<sub>5</sub> and S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> with different loading amounts of S-Ni(OH)<sub>2</sub>. (b) XPS survey, (c) Ni 2p and (d) S 2p spectra of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> respectively.

a peak at 531.79 eV, (see Fig. S3c†) which can be assigned to the O<sup>2-</sup> species in Ni(OH)<sub>2</sub>.<sup>46</sup> Most importantly, two peaks are observed in the high resolution spectrum of S 2p, in which the peak centered at ~164 eV represents the metal-sulfur bond and S<sup>2-</sup>, while the other peak in the high binding energy region can be considered as residual SO<sub>4</sub><sup>2-</sup> adsorbed on the material (Fig. 1d).<sup>40,42,47</sup> That is, the existence of the Ni-S bond can support the formation of S-doping in Ni(OH)<sub>2</sub>.

To further confirm the successful fabrication of the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid, TEM and SEM images are acquired and shown in Fig. 2. It has been reported in our previous work that the micro morphology of pristine C<sub>3</sub>N<sub>5</sub> is nanosheet.<sup>36</sup> Fig. 2a and b display the TEM and HRTEM images of S-Ni(OH)<sub>2</sub>. As shown in Fig. 2a, S-Ni(OH)<sub>2</sub> also exhibits a micro morphology of nanosheets and a clear lattice fringe of 0.23 nm corresponding to the (011) plane of S-Ni(OH)<sub>2</sub> is observed (Fig. 2b). In particular, no lattice fringe representing nickel sulfide is found, demonstrating the existence state of S-doping in S-Ni(OH)<sub>2</sub>. Fig. 2c displays the TEM image of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>, in which 2d nanosheets containing S-Ni(OH)<sub>2</sub> and C<sub>3</sub>N<sub>5</sub> are observed. In addition, S-Ni(OH)<sub>2</sub> and C<sub>3</sub>N<sub>5</sub> come into tight contact with each other and it is difficult to distinguish each material due to their similar micro morphology. The high resolution region (Fig. 2d) of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> can be clearly divided into an amorphous region corresponding to C<sub>3</sub>N<sub>5</sub> and a crystalline region for S-Ni(OH)<sub>2</sub> with a clear lattice fringe of 0.23 nm corresponding to the (011) plane of S-Ni(OH)<sub>2</sub>. By the way, the two different regions in Fig. 2d come into tight contact with each other, which will be favorable for the internal transfer of photogenerated carriers.

Fig. 2e depicts the SEM and element mapping images of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>. As revealed, the hybrid is basically composed of nanosheets containing S-Ni(OH)<sub>2</sub> and C<sub>3</sub>N<sub>5</sub>, which is in good agreement with the above results of TEM. The element mapping images convey that the hybrid contains C, N, Ni, O and S, and all of the elements disperse uniformly in the observed region. Moreover, the existence of S-doping in S-Ni(OH)<sub>2</sub> is confirmed from the mapping of S in the material. Based on the above-mentioned XRD, XPS, TEM and SEM analyses, the product of reaction between Ni<sup>2+</sup> and Na<sub>2</sub>S is named S-Ni(OH)<sub>2</sub> considering that no any information corresponding to nickel sulfide is detected

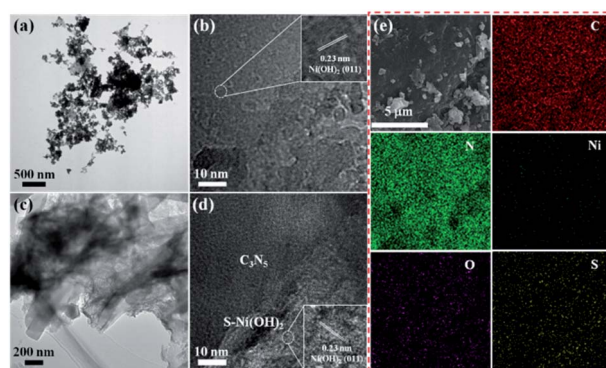


Fig. 2 TEM and HRTEM of S-Ni(OH)<sub>2</sub> (a and b) and 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> (c and d). SEM and EDS mapping of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> (e).





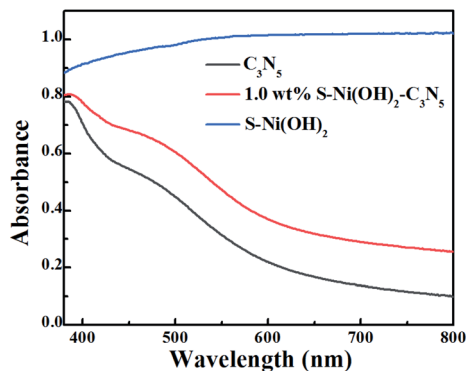


Fig. 3 DRS spectra of S-Ni(OH)<sub>2</sub>, C<sub>3</sub>N<sub>5</sub> and 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>.

while the Ni-S bond exists in the hybrid, and the hybrid of 2D S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is successfully constructed.

### DRS and e<sup>-</sup>/h<sup>+</sup> separation analyses

In the field of photocatalysis, the light responsive region plays a significant role in the performance of catalysts. The visible light absorption properties of S-Ni(OH)<sub>2</sub>, C<sub>3</sub>N<sub>5</sub> and S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> are compared in Fig. 3. In brief, C<sub>3</sub>N<sub>5</sub> possesses a narrow band-gap of ~2.25 eV according to our previous work,<sup>36</sup> and can absorb the visible light region of 400–600 nm with high intensity, while pristine S-Ni(OH)<sub>2</sub> exhibits a strong absorption across the spectral range of 200–2400 nm (Fig. S6<sup>†</sup>). For the hybrid material, 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> exhibits a similar visible light absorption region to C<sub>3</sub>N<sub>5</sub>, but the absorption intensity is slightly increased by the hybridization of black S-Ni(OH)<sub>2</sub>. In a word, this wide and strong visible light absorption property of the hybrid is favorable for achieving high photocatalytic performance.

Light absorption is the first step for a photocatalytic procedure, and the subsequent photogenerated e<sup>-</sup>/h<sup>+</sup> separation is of great importance to the whole performance. Monitoring of the PL behavior of photocatalysts can find out some information on

e<sup>-</sup>/h<sup>+</sup> separation after light excitation.<sup>26,48,49</sup> As revealed in the steady-state PL spectrum in Fig. 4a, C<sub>3</sub>N<sub>5</sub> exhibits strong PL intensity, demonstrating its high photogenerated e<sup>-</sup>/h<sup>+</sup> recombination rate after light excitation. However, the emission intensity of C<sub>3</sub>N<sub>5</sub> can be efficiently quenched by S-Ni(OH)<sub>2</sub>. The lower PL intensity of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> than C<sub>3</sub>N<sub>5</sub> demonstrates that the recombination of e<sup>-</sup>/h<sup>+</sup> pairs on C<sub>3</sub>N<sub>5</sub> after excitation is restrained, which should be caused by the electron transfer from C<sub>3</sub>N<sub>5</sub> to S-Ni(OH)<sub>2</sub> since Ni-based species such as nickel sulfide and Ni(OH)<sub>2</sub> are often used as co-catalysts for photocatalytic H<sub>2</sub> production.<sup>43,50–52</sup> Mott-Schottky analysis was further conducted on S-Ni(OH)<sub>2</sub> to verify whether the CB position of S-Ni(OH)<sub>2</sub> is sufficient to capture the photo-generated electrons from C<sub>3</sub>N<sub>5</sub> (Fig. S7<sup>†</sup>). The CB position of S-Ni(OH)<sub>2</sub> was determined to be -0.58 V vs. NHE, which is less negative than that of C<sub>3</sub>N<sub>5</sub> (-0.98 V vs. NHE).<sup>36</sup> So, under irradiation, the photogenerated electrons of C<sub>3</sub>N<sub>5</sub> could migrate to S-Ni(OH)<sub>2</sub> and be captured. The time-resolved fluorescence spectra (TRFS) of C<sub>3</sub>N<sub>5</sub> and 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> are compared in Fig. 4b to further illustrate this viewpoint. As depicted, the PL intensity of C<sub>3</sub>N<sub>5</sub> decays quickly after excitation, indicating its low fluorescence lifetime which is not favorable for photogenerated e<sup>-</sup>/h<sup>+</sup> separation. However, the decay tendency of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> exhibits a clear slowdown under the same conditions, demonstrating that the fluorescence lifetime is prolonged, which should be related to the internal electron transfer from C<sub>3</sub>N<sub>5</sub> to S-Ni(OH)<sub>2</sub>.<sup>48,53</sup> For comparison, the fluorescence lifetime of C<sub>3</sub>N<sub>5</sub> and 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is calculated to be ~8.50 and 14.02 ns respectively via a biexponential fitting. The enhanced e<sup>-</sup>/h<sup>+</sup> separation efficiency of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> compared to pristine C<sub>3</sub>N<sub>5</sub> is further confirmed by photocurrent-time and EIS behaviors. As revealed in Fig. 4c, sharp photocurrent is generated under light irradiation and then decreases suddenly when light is turned off, demonstrating that the current is light-switched and produced by the photogenerated e<sup>-</sup>/h<sup>+</sup> separation after the semiconductor is excited.<sup>20,54,55</sup> In comparison, 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> exhibits a much higher photocurrent value than pristine C<sub>3</sub>N<sub>5</sub>, indicating that the separation of photogenerated e<sup>-</sup>/h<sup>+</sup> on C<sub>3</sub>N<sub>5</sub> is facilitated by loading of the S-Ni(OH)<sub>2</sub> co-catalyst. In addition, a smaller arc radius is recorded on the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> electrode, revealing the smaller resistance for charge transfer which is favorable for e<sup>-</sup>/h<sup>+</sup> separation.<sup>53,56</sup> All these results convey that the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid possesses quick internal charge transfer efficiency, which will facilitate the subsequent photocatalytic performance.

### Photocatalytic H<sub>2</sub> production performance

In consideration of the wide visible light absorption region and quick photogenerated e<sup>-</sup>/h<sup>+</sup> separation efficiency of the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid, its photocatalytic performance for H<sub>2</sub> production from water with TEOA as a sacrificial reagent under visible light irradiation ( $\lambda > 420$  nm) is evaluated firstly. A blank experiment shows that almost no H<sub>2</sub> production is observed on pristine C<sub>3</sub>N<sub>5</sub> due to the lack of a co-catalyst. And pristine S-Ni(OH)<sub>2</sub> also cannot produce H<sub>2</sub> under these conditions.

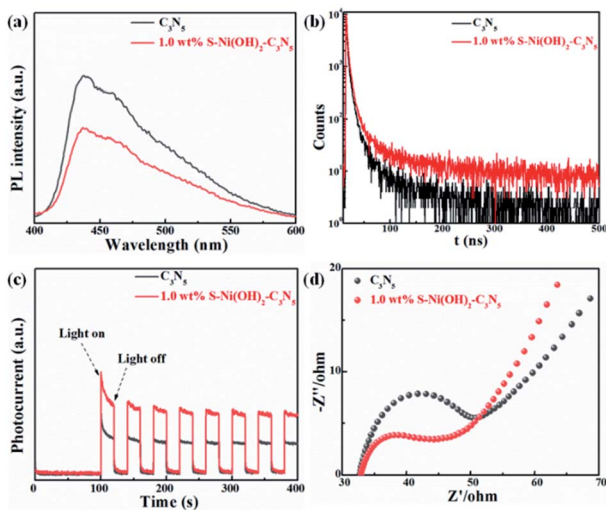


Fig. 4 Comparison of steady-state PL (a), time-resolved PL (b), photocurrent-time (c) and EIS (d) curves of C<sub>3</sub>N<sub>5</sub> and 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>.



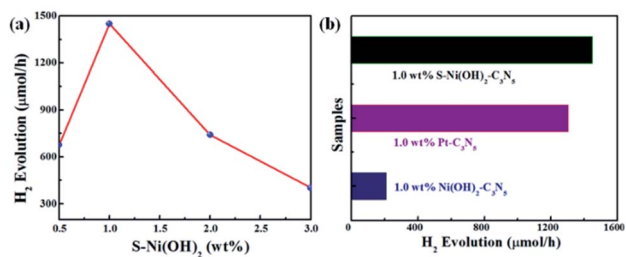


Fig. 5 (a) Influence of S-Ni(OH)<sub>2</sub> loading amount on the H<sub>2</sub> production activity of the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid. (b) Comparison of H<sub>2</sub> production activity over 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>, 1.0 wt% Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> and 1.0 wt% Pt-C<sub>3</sub>N<sub>5</sub> catalysts. Conditions: 45 mg catalyst, 10 vol% TEOA/water aqueous,  $\lambda > 420$  nm.

However, as displayed in Fig. 5a, the H<sub>2</sub> production rate is dramatically enhanced even with a low loading amount of 0.5 wt% S-Ni(OH)<sub>2</sub> on C<sub>3</sub>N<sub>5</sub>. Generally, a volcano-type relationship between the loading amount of a cocatalyst and the whole photocatalytic activity will be obtained,<sup>57</sup> suggesting that the fraction of S-Ni(OH)<sub>2</sub> in the hybrid must be screened to explore the highest H<sub>2</sub> production rate. As shown in Fig. 5b, the maximum H<sub>2</sub> production rate is 1450  $\mu\text{mol h}^{-1}$  on the catalyst of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>. Notably, excessive loading of S-Ni(OH)<sub>2</sub> will influence the visible light absorption of C<sub>3</sub>N<sub>5</sub>, and then the whole photoactivity is decreased. In addition, the initial concentration of Na<sub>2</sub>S in the procedure of catalyst preparation will influence the concentration of OH<sup>-</sup> and S<sup>2-</sup>, which participate in the formation of S-Ni(OH)<sub>2</sub>. The influence of initial mol ratio between Ni<sup>2+</sup> and Na<sub>2</sub>S (Ni/S) in the preparation procedure on the photoactivity is shown in Fig. S4,<sup>†</sup> and the selected condition for S-Ni(OH)<sub>2</sub> preparation is Ni/S = 1/3.

To explore the influence of S doping on the photocatalytic H<sub>2</sub> production performance, the comparison of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> and 1.0 wt% Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is shown in Fig. 5b. Unexpectedly, 1.0 wt% Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> exhibits much lower H<sub>2</sub> production activity (209  $\mu\text{mol h}^{-1}$ ), which is only one seventh of the value over the 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid. That is to say, a novel method is explored to prepare a highly efficient Ni(OH)<sub>2</sub>-based co-catalyst by simply changing the initial reactant from NaOH to Na<sub>2</sub>S that reacts with Ni<sup>2+</sup> under ambient conditions ultra-fast. The photocatalytic performance is also evaluated using Pt nanoparticles as a reference since Pt is generally considered as the most efficient co-catalyst for photocatalytic H<sub>2</sub> production.<sup>15,23</sup> As depicted in Fig. 5b, the H<sub>2</sub> production rate on 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is slightly higher than that of 1.0 wt% Pt-C<sub>3</sub>N<sub>5</sub>, demonstrating that the present S-Ni(OH)<sub>2</sub> is a highly efficient co-catalyst for H<sub>2</sub> production and is promising in consideration of the facile preparation procedure and low cost of Ni-based materials compared with noble metals like Pt.

The AQY values of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> under a series of monochromatic light irradiation are shown in Fig. 6a, in which the AQY values decrease gradually with the increase of light wavelength and the highest AQY value (30.9%) is obtained at 420 nm. The change tendency of AQY is in agreement with the DRS spectrum of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>, demonstrating that the

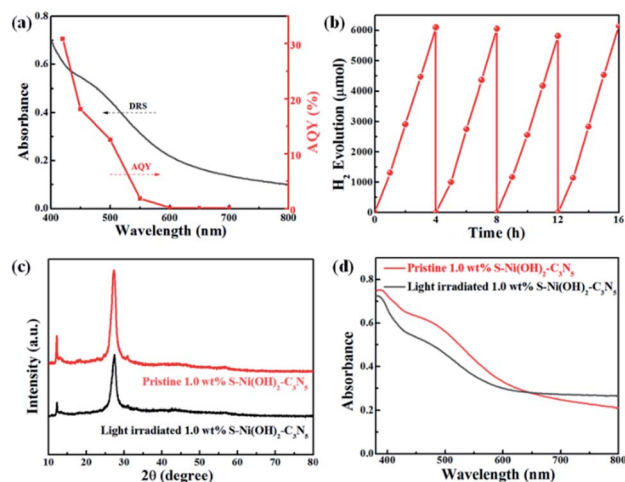


Fig. 6 (a) Changing tendency of AQY values of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> with monochromatic light irradiation. (b) Cycle performance of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> for H<sub>2</sub> production under visible light irradiation. Comparison of XRD (c) and DRS (d) spectra of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> before and after photocatalytic performance.

photocatalytic performance of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is determined by its light absorption behavior. Long-term stability of a photocatalyst is an important norm in the field of H<sub>2</sub> production. Fig. 6b reveals the cycling performance of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> and no obvious attenuation of H<sub>2</sub> production rate happens after 16 h and 4 runs of photocatalytic test, demonstrating the excellent photocatalytic stability of the present S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid. To further evaluate the stability of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> in photocatalysis, the samples are collected after long-term light irradiation and monitored by XRD and DRS. As depicted in Fig. 6c and d, no obvious change happens in the XRD peaks of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> experiencing the photocatalytic test, indicating that the basic structure of the hybrid is maintained. Meanwhile, the collected sample exhibits a similar visible light absorption region compared with fresh S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>, demonstrating the stability of the hybrid again.

### Photocatalytic NO oxidation performance

Except for H<sub>2</sub> production, the photocatalytic performance of S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is also tested for NO oxidation to demonstrate the potential of the catalyst in purification of atmospheric pollution. A control experiment shows that pristine S-Ni(OH)<sub>2</sub> has no activity for NO removal. As revealed in Fig. 7a, the oxidation of NO can reach equilibrium in 25 min in the present continuous flow reaction system. Briefly, NO removal efficiencies on C<sub>3</sub>N<sub>5</sub> and S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> with 0.5, 1.0, 2.0, and 3.0 wt% S-Ni(OH)<sub>2</sub> fraction after 25 min of light irradiation are 35.0, 37.0, 42.0, 35.0 and 35.0% respectively and the most efficient catalyst is 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid, indicating that the photocatalytic performance of C<sub>3</sub>N<sub>5</sub> is enhanced by loading of S-Ni(OH)<sub>2</sub>. And the above-mentioned quick internal charge transfer from C<sub>3</sub>N<sub>5</sub> to S-Ni(OH)<sub>2</sub> under light excitation should play a significant role in this process. Fig. 7b evaluates the durability and stability of the 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid



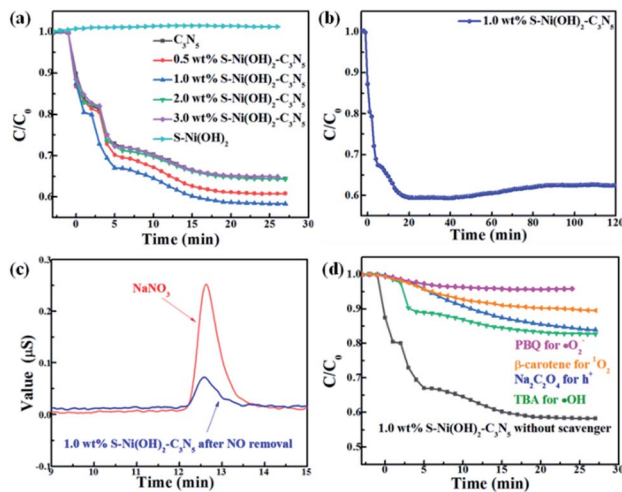


Fig. 7 (a) Influence of S-Ni(OH)<sub>2</sub> loading amount on NO removal ratio over the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid. (b) Durability of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> for NO removal. (c) Detection of NO<sub>3</sub><sup>-</sup> by ion chromatography. (d) Photocatalytic NO removal performance of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> in the presence of a series of trapping agents.

for NO removal, and only a slight decrease in NO removal ratio is observed during 120 nm light irradiation, demonstrating the good stability of the hybrid. Generally, the main products of photocatalytic NO oxidation are NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> according to literature reports.<sup>58–60</sup> The detection of NO<sub>2</sub> is carried out on the present NO<sub>x</sub> analyzer, and the concentration of NO<sub>2</sub> along with NO oxidation is shown in Fig. S5.† It is found that most NO is converted to NO<sub>3</sub><sup>-</sup> based on the amount of NO removal and NO<sub>2</sub> production. Therefore, the confirmation of produced NO<sub>3</sub><sup>-</sup> in the reaction is shown in Fig. 7c with NaNO<sub>3</sub> as a reference by ion chromatography, in which a clear signal corresponding to NO<sub>3</sub><sup>-</sup> is observed for the sample prepared with 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> experiencing photocatalytic NO oxidation reaction.

It has been reported that activation of molecular O<sub>2</sub> and generation of a series of ROS (*i.e.* <sup>•</sup>OH, <sup>•</sup>O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub>) play the main role in the procedure of photocatalytic NO oxidation.<sup>61–63</sup> In addition, photogenerated h<sup>+</sup> residual in the VB of the semiconductor is also of great importance.<sup>64,65</sup> Thus, the photocatalytic NO removal performance of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> in the presence of a series of trapping agents for different active species is compared in Fig. 7d. As displayed, when Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, *tert*-butanol (TBA), *p*-benzoquinone (PBQ) and β-carotene are used as scavengers for h<sup>+</sup>, <sup>•</sup>OH, <sup>•</sup>O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub> respectively, the photocatalytic performance of 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is seriously restrained, demonstrating that NO is removed by these ROS and residual h<sup>+</sup> in the VB of C<sub>3</sub>N<sub>5</sub>. The NO<sub>2</sub> concentration during the photocatalytic NO removal on 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> was also monitored with the NO<sub>x</sub> analyzer (see Fig. S8†). The corresponding residual ratio of NO<sub>2</sub> is provided in Table S2.† From these results, it can be seen that the <sup>•</sup>OH and <sup>1</sup>O<sub>2</sub> play important roles in the conversion of NO<sub>2</sub> to NO<sub>3</sub><sup>-</sup>. Electron spin-resonance spectroscopy (ESR) tests are conducted to monitor the change of signals corresponding to <sup>•</sup>OH, <sup>•</sup>O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub>. As revealed in Fig. 8, almost no signals are detected in

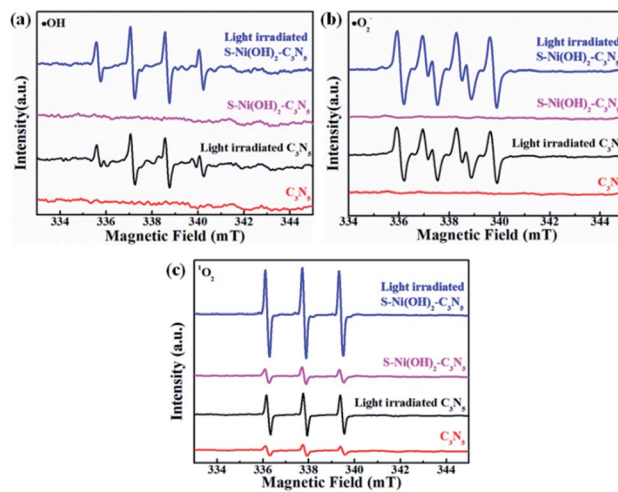
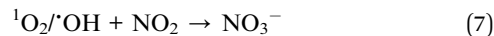
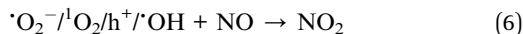
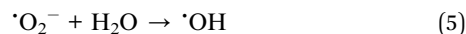
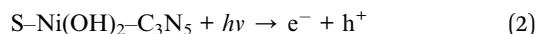


Fig. 8 ESR spectra of DMPO-<sup>•</sup>OH (a), DMPO-<sup>•</sup>O<sub>2</sub><sup>-</sup> (b) and TEMPO (c) for ROS detection.

the dark on both 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> and C<sub>3</sub>N<sub>5</sub>, but strong peaks corresponding to distinct DMPO-<sup>•</sup>OH, DMPO-<sup>•</sup>O<sub>2</sub><sup>-</sup> and TEMPO (product of TEMP oxidized by <sup>1</sup>O<sub>2</sub>) signals are detected,<sup>3,7,64</sup> demonstrating that the generation of these ROS is light controllable. Moreover, the light induced ESR signal intensity on 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is higher than that of C<sub>3</sub>N<sub>5</sub>, revealing that more amount of ROS is generated on S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> due to the quick internal charge transfer. So, the process of photocatalytic NO removal on 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> should be as follows:



Based on all of the above results, the mechanism for photocatalytic H<sub>2</sub> production or NO oxidation over the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid is proposed. Under visible light irradiation, C<sub>3</sub>N<sub>5</sub> is excited and generates e<sup>-</sup>/h<sup>+</sup> pairs. S-Ni(OH)<sub>2</sub> can promote the internal charge separation and harvest the e<sup>-</sup> on the CB of C<sub>3</sub>N<sub>5</sub>, and then the trapped electrons participate in subsequent surface reactions. For photocatalytic H<sub>2</sub> production (Fig. 9a), the collected electrons on S-Ni(OH)<sub>2</sub> react with adsorbed H<sub>2</sub>O molecules and H<sub>2</sub> is produced. The residual h<sup>+</sup> on the VB of C<sub>3</sub>N<sub>5</sub> is consumed by TEOA, and then the whole photocatalytic H<sub>2</sub> production procedure is accomplished. However, the situation for photocatalytic NO oxidation is different (Fig. 9b). O<sub>2</sub> is firstly activated and a series of ROS (<sup>•</sup>O<sub>2</sub><sup>-</sup>, <sup>1</sup>O<sub>2</sub> and <sup>•</sup>OH) can be generated. Generally, <sup>•</sup>O<sub>2</sub><sup>-</sup> is produced by reaction between e<sup>-</sup>





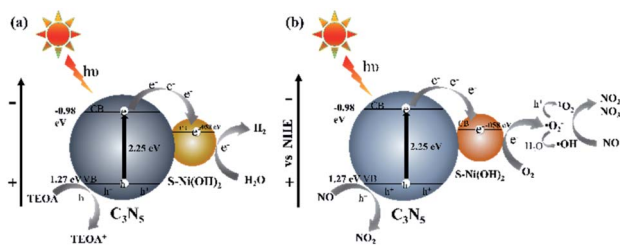


Fig. 9 The supposed mechanism of photocatalytic H<sub>2</sub> production (a) and NO removal (b) on 1.0 wt% S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub>.

and adsorbed O<sub>2</sub>, while the reaction between <sup>•</sup>O<sub>2</sub><sup>-</sup> and h<sup>+</sup> can generate <sup>1</sup>O<sub>2</sub>.<sup>3,61</sup> <sup>•</sup>OH should originate from the oxidization of H<sub>2</sub>O by <sup>•</sup>O<sub>2</sub><sup>-</sup> since the VB position of C<sub>3</sub>N<sub>5</sub> cannot satisfy the requirement of <sup>•</sup>OH generation based on our previous work.<sup>33,66</sup> In addition, the generation of these ROS is enhanced by S-Ni(OH)<sub>2</sub>, as discussed in the above section. And then, these ROS and the residual h<sup>+</sup> on the VB of C<sub>3</sub>N<sub>5</sub> participate in the NO oxidation procedure along with the formation of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub>.

## Conclusions

In summary, near-zero-cost 2D S-Ni(OH)<sub>2</sub> active sites are planted on wide visible light responsive C<sub>3</sub>N<sub>5</sub> ultrafast within 30 min at room temperature by reaction between Ni(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S in aqueous solution. The loading of S-Ni(OH)<sub>2</sub> can greatly enhance the photogenerated e<sup>-</sup>/h<sup>+</sup> separation efficiency of C<sub>3</sub>N<sub>5</sub> after light excitation. Due to the quick internal charge transfer, the S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> hybrid is highly efficient as a multifunctional catalyst in various photocatalytic applications: H<sub>2</sub> production from water and NO removal. Most impressively, the H<sub>2</sub> production activity on S-Ni(OH)<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> is even higher than that of Pt-C<sub>3</sub>N<sub>5</sub> and an AQY value of 30.9% at 420 nm is achieved. This work brings new insights into the design of low-cost noble-metal-free co-catalysts on semiconductors for photocatalytic applications.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21703075, 51872107, 52073110, and 22002047), Natural Science Foundation of Hubei Province (2020CFB694 and 2020CFB394) and Fundamental Research Funds for the Central Universities (2662020LXPY005 and 2662019QD018).

## Notes and references

- 1 T. Banerjee, F. Podjaski, J. Kröger, B. P. Biswal and B. V. Lotsch, *Nat. Rev. Mater.*, 2021, **6**, 168–190.
- 2 Q. Wang and K. Domen, *Chem. Rev.*, 2020, **120**, 919–985.

- 3 X. Yang, S. Wang, T. Chen, N. Yang, K. Jiang, P. Wang, S. Li, X. Ding and H. Chen, *Chin. J. Catal.*, 2021, **42**, 1013–1023.
- 4 M. Rahman, M. Kibria and C. Mulins, *Chem. Soc. Rev.*, 2020, **49**, 1887–1931.
- 5 Y. Wang, B. Gao, Q. Yue and Z. Wang, *J. Mater. Chem. A*, 2020, **8**, 19133–19155.
- 6 X. Zou, Z. Sun and Y. Hu, *J. Mater. Chem. A*, 2020, **8**, 21474–21502.
- 7 S. Wang, X. Ding, N. Yang, G. Zhan, X. Zhang, G. Dong, L. Zhang and H. Chen, *Appl. Catal., B*, 2020, **265**, 118585.
- 8 Z. Wang, C. Li and K. Domen, *Chem. Soc. Rev.*, 2019, **48**, 2109–2125.
- 9 B. Zhang and L. Sun, *Chem. Soc. Rev.*, 2019, **48**, 2216–2264.
- 10 W. Yang, R. Prabhakar, J. Tan, S. Tilley and J. Moon, *Chem. Soc. Rev.*, 2019, **48**, 4979–5015.
- 11 Y. Wang, A. Vogel, M. Sachs, R. Sprick, L. Wilbraham, S. Moniz, R. Godin, M. Zwijnenburg, J. Durrant, A. Cooper and J. Tang, *Nat. Energy*, 2019, **4**, 746–760.
- 12 Q. Xu, L. Zhang, B. Cheng, J. Fan and J. Yu, *Chem*, 2020, **6**, 1543–1559.
- 13 J. Fu, J. Yu, C. Jiang and B. Cheng, *Adv. Energy Mater.*, 2018, **8**, 1701503.
- 14 X. Yang, Z. Hu, Q. Yin, C. Shu, X. Jiang, J. Zhang, X. Wang, J. Jiang, F. Huang and Y. Cao, *Adv. Funct. Mater.*, 2019, **29**, 1808156.
- 15 D. Zhao, Y. Wang, C. Dong, Y. Huang, J. Chen, F. Xue, S. Shen and L. Guo, *Nat. Energy*, 2021, **6**, 388–397.
- 16 K. Gottschling, G. Savasci, H. Vignolo-Gonzalez, S. Schmidt, P. Mauker, T. Banerjee, P. Rovo, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2020, **142**, 12146–12156.
- 17 X. Zhang, J. Xiao, M. Hou, Y. Xiang and H. Chen, *Appl. Catal., B*, 2018, **224**, 871–876.
- 18 F. Xu, K. Meng, B. Cheng, S. Wang, J. Xu and J. Yu, *Nat. Commun.*, 2020, **11**, 4613.
- 19 J. Wang, L. Xu, T. Wang, R. Li, Y. Zhang, J. Zhang and T. Peng, *Adv. Energy Mater.*, 2021, **11**, 2003575.
- 20 J. Wang, M. Kuo, P. Zeng, L. Xu, S. Chen and T. Peng, *Appl. Catal., B*, 2020, **279**, 119377.
- 21 T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T. Hisatomi and K. Domen, *Nature*, 2020, **581**, 411–414.
- 22 X. Wang, K. Maeda, A. Thomas, K. Takane, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76–80.
- 23 L. Lin, Z. Lin, J. Zhang, X. Cai, W. Lin, Z. Yu and X. Wang, *Nat. Catal.*, 2020, **3**, 649–655.
- 24 G. Zhang, G. Li, T. Heil, S. Zafeirotos, F. Lai, A. Savateev, M. Antonietti and X. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 3433–3437.
- 25 Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, *J. Am. Chem. Soc.*, 2019, **141**, 2508–2515.
- 26 T. H. T. Vinh, C. M. Thi and P. V. Viet, *Mater. Lett.*, 2020, **281**, 128637.
- 27 V. V. Pham, D. Q. Mai, D. P. Bui, T. V. Man, B. Zhu, L. Zhang, J. Sangkaworn, J. Tantirungrotechai, V. Reutrakul and T. M. Cao, *Environ. Pollut.*, 2021, **286**, 117510.



- 28 P. V. Viet, T. D. Nguyen, D. P. Bui and C. M. Thi, *J. Materiomics*, 2021, DOI: 10.1016/j.jmat.2021.06.006.
- 29 L. Zhang, R. Long, Y. Zhang, D. Duan, Y. Xiong, Y. Zhang and Y. Bi, *Angew. Chem., Int. Ed.*, 2020, **59**, 6224–6229.
- 30 X. Jiang, L. Zhang, H. Liu, D. Wu, F. Wu, L. Tian, L. Liu, J. Zou, S. Luo and B. Chen, *Angew. Chem., Int. Ed.*, 2020, **59**, 23112–23116.
- 31 P. Kumar, E. Vahidzadeh, U. K. Thakur, P. Kar, K. M. Alam, A. Goswami, N. Mahdi, K. Cui, G. M. Bernard, V. K. Michaelis and K. Shankar, *J. Am. Chem. Soc.*, 2019, **141**, 5415–5436.
- 32 J. Zhang, B. Jing, Z. Tang, Z. Ao, D. Xia, M. Zhu and S. Wang, *Appl. Catal., B*, 2021, **289**, 120023.
- 33 M. Li, Q. Lu, M. Liu, P. Yin, C. Wu, H. Li, Y. Zhang and S. Yao, *ACS Appl. Mater. Interfaces*, 2020, **12**, 38266–38274.
- 34 I. Y. Kim, S. Kim, X. Jin, S. Premkumar, G. Chandra, N. S. Lee, G. P. Mane, S. J. Hwang, S. Umapathy and A. Vinu, *Angew. Chem., Int. Ed.*, 2018, **57**, 17135–17140.
- 35 G. P. Mane, S. N. Talapaneni, K. S. Lakhi, H. Ilbeygi, U. Ravon, K. Al-Bahily, T. Mori, D. H. Park and A. Vinu, *Angew. Chem., Int. Ed.*, 2017, **56**, 8481–8485.
- 36 C. Peng, L. Han, J. Huang, S. Wang, X. Zhang and H. Chen, *Chin. J. Catal.*, 2021, **42**, DOI: 10.1016/S1872-2067(21)63813-5.
- 37 T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrović, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Susha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk and J. Feldmann, *Nat. Mater.*, 2014, **13**, 1013–1018.
- 38 X. Zhao, J. Feng, J. Liu, W. Shi, G. Yang, G. C. Wang and P. Cheng, *Angew. Chem., Int. Ed.*, 2018, **57**, 9790–9794.
- 39 Z. Sun, H. Zheng, J. Li and P. Du, *Energy Environ. Sci.*, 2015, **8**, 2668–2676.
- 40 L. Yu, L. Wu, B. McElhenny, S. Song, D. Luo, F. Zhang, Y. Yu, S. Chen and Z. Ren, *Energy Environ. Sci.*, 2020, **13**, 3439–3446.
- 41 X. Jin, R. Wang, L. Zhang, R. Si, M. Shen, M. Wang, J. Tian and J. Shi, *Angew. Chem., Int. Ed.*, 2020, **59**, 6827–6831.
- 42 H. Zou, B. He, P. Kuang, J. Yu and K. Fan, *Adv. Funct. Mater.*, 2018, **28**, 1706917.
- 43 A. Yan, X. Shi, F. Huang, M. Fujitsuka and T. Majima, *Appl. Catal., B*, 2019, **250**, 163–170.
- 44 L. Yu, L. Wu, B. McElhenny, S. Song, D. Luo, F. Zhang, Y. Yu, S. Chen and Z. Ren, *Energy Environ. Sci.*, 2020, **13**, 3439–3446.
- 45 J. Zhang, H. Tao, S. Wu, J. Yang and M. Zhu, *Appl. Catal., B*, 2021, **296**, 120372.
- 46 G. S. Gund, D. P. Dubal, S. B. Jambure, S. S. Shinde and C. D. Lokhande, *J. Mater. Chem. A*, 2013, **1**, 4793.
- 47 G. Zhang, Y. S. Feng, W. T. Lu, D. He, C. Y. Wang, Y. K. Li, X. Y. Wang and F. F. Cao, *ACS Catal.*, 2018, **8**, 5431–5441.
- 48 J. Fu, Q. Xu, J. Low, C. Jiang and J. Yu, *Appl. Catal., B*, 2019, **243**, 556–565.
- 49 Y. Ren, Y. Li, X. Wu, J. Wang and G. Zhang, *Chin. J. Catal.*, 2021, **42**, 69–77.
- 50 Y. Luo, J. Qin, G. Yang, S. Luo, Z. Zhao, M. Chen and J. Ma, *Chem. Engineer. J.*, 2021, **410**, 128394.
- 51 G. X. Zhao, W. Zhou, Y. B. Sun, X. K. Wang, H. M. Liu, X. G. Meng, K. Chang and J. H. Ye, *Appl. Catal., B*, 2018, **226**, 252–257.
- 52 Q. Lin, Y. H. Li, M. Y. Qi, J. Y. Li, Z. R. Tang, M. Anpo, Y. M. A. Yamada and Y. J. Xu, *Appl. Catal., B*, 2020, **271**, 118946.
- 53 P. Xia, M. Antonietti, B. Zhu, T. Heil, J. Yu and S. Cao, *Adv. Funct. Mater.*, 2019, **29**, 1900093.
- 54 B. Chai, T. Peng, J. Mao, K. Li and L. Zan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16745–16752.
- 55 K. Li, B. Chai, T. Peng, J. Mao and L. Zan, *ACS Catal.*, 2013, **3**, 170–177.
- 56 G. Zuo, Y. Wang, W. Teo, A. Xie, Y. Guo, Y. Dai, W. Zhou, D. Jana, Q. Xian, W. Dong and Y. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 11287–11292.
- 57 J. Ran, J. Zhang, J. Yu, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2014, **43**, 7787–7812.
- 58 P. Chen, H. Liu, Y. Sun, J. Li, W. Cui, L. a. Wang, W. Zhang, X. Yuan, Z. Wang, Y. Zhang and F. Dong, *Appl. Catal., B*, 2020, **264**, 118545.
- 59 Y. Geng, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Appl. Catal., B*, 2021, **280**, 119409.
- 60 H. Shang, S. Huang, H. Li, M. Li, S. Zhao, J. Wang, Z. Ai and L. Zhang, *Chem. Engineer. J.*, 2020, **386**, 124047.
- 61 M. Kou, Y. Deng, R. Zhang, L. Wang, P. K. Wong, F. Su and L. Ye, *Chin. J. Catal.*, 2020, **41**, 1480–1487.
- 62 X. Shi, P. Wang, W. Li, Y. Bai, H. Xie, Y. Zhou and L. Ye, *Appl. Catal., B*, 2019, **243**, 322–329.
- 63 W. Huo, T. Cao, W. Xu, Z. Guo, X. Liu, H. C. Yao, Y. Zhang and F. Dong, *Chin. J. Catal.*, 2020, **41**, 268–275.
- 64 J. Hu, D. Chen, Z. Mo, N. Li, Q. Xu, H. Li, J. He, H. Xu and J. Lu, *Angew. Chem., Int. Ed.*, 2019, **58**, 2073–2077.
- 65 D. Liu, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Angew. Chem., Int. Ed.*, 2020, **59**, 4519–4524.
- 66 S. Wang, X. Ding, X. Zhang, H. Pang, X. Hai, G. Zhan, W. Zhou, H. Song, L. Zhang, H. Chen and J. Ye, *Adv. Funct. Mater.*, 2017, **27**, 1703923.

