# **Energy** Advances



View Article Online PAPER



Cite this: Energy Adv., 2024, 3.2604

Received 26th July 2024, Accepted 3rd September 2024

DOI: 10.1039/d4ya00476k

rsc.li/energy-advances

# Construction of organic-inorganic hybrid composites derived from C<sub>3</sub>N<sub>5</sub> incorporated with CeO<sub>2</sub> for enhanced photocatalytic hydrogen evolution\*

Ashil Augustin, Da Manova Santhosh Yesupatham, Da M. D. Dhileepan, Ashil Augustin, Da Manova Santhosh Yesupatham, Da M. D. Dhileepan, Ashil Augustin, Da Manova Santhosh Yesupatham, Da M. D. Dhileepan, Ashil Augustin, Da Manova Santhosh Yesupatham, Da Wanova Santhosh Yesupatham, Sanguk Son, (D) Ezhakudiyan Ravindran, Bernaurdshaw Neppolian, a Hyoung-il Kim \*\* and Karthikeyan Sekar \*\* \*\*

Energy scarcity and environmental issues can be effectively addressed via photocatalytic hydrogen production. The effective combination of semiconductor materials can prevent exciton recombination, making it a highly effective method for enhancing photocatalytic activity. This study details the synthesis of a conjugated polymer encapsulated with a metal oxide photocatalyst using a simple ex situ method. The encapsulation of the polymer with CeO<sub>2</sub> nanoparticles resulted in exceptional performance in H<sub>2</sub> production, exhibiting improved visible light absorption and a significant increase in charge transfer efficiency. This is attributed to the high charge transfer and reduced recombination in the composite. Moreover, photogenerated holes led to a substantial decline in the recombination rate of excitons and concomitant enhancement in the rate of photocatalytic H2 production. Markedly, the observed hydrogen evolution for 10 wt% of  $CeO_2$  doped  $C_3N_5$  composites is 1256  $\mu$ mol  $g^{-1}$   $h^{-1}$ , whereas for  $C_3N_{5r}$ , it is 125 µmol  $g^{-1}$   $h^{-1}$ . Electrochemical analysis showed that the optimized composites exhibit a low electron-hole recombination rate, and UV-vis spectroscopic analysis showed improved visible light absorption resulting in excellent photocatalytic activity. Notably, the proposed system offers a novel strategy for hydrogen evolution via photocatalysis using CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> composites. Consequently, this research offers a new perspective on the design of organo-inorganic heterostructures and introduces a novel pathway to explore their catalytic capabilities.

## Introduction

Fossil fuels, including crude oil, natural gas, and coal, play an essential role in satisfying the world's energy needs.<sup>1,2</sup> It is anticipated that global energy consumption will increase by nearly 55% and CO<sub>2</sub> emissions by 20% by 2024–2050.<sup>3,4</sup> Global warming and fuel shortages that have resulted from the significant increase in the emission of greenhouse gases and the accelerated depletion of fossil fuels have compelled humanity to identify alternative renewable and pure energy sources. 5 It is anticipated that the consumption of renewable energy will increase and reach approximately 247 exajoules by 2050. In contrast, the total consumption of renewable energy was 96 exajoules in 2024.6 Photocatalytic water splitting using semiconductors has been recognized as a sustainable and prospective green technology that has garnered significant attention owing to its ability to effectively convert sustainable solar energy into environmentally friendly hydrogen. A sustainable method for producing green hydrogen fuel is through photocatalytic water splitting, which utilizes pure solar energy.7-9

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, 603203, India.

E-mail: karthiks13@srmist.edu.in

<sup>&</sup>lt;sup>b</sup> Department of Civil & Environmental Engineering, Yonsei University, Seoul 03722, Republic of Korea. E-mail: hi.kim@yonsei.ac.kr

<sup>†</sup> Electronic supplementary information (ESI) available: Fig. S1. Rietveld analysis of the CeO<sub>2</sub> photocatalyst and composition of the CeO<sub>2</sub> photocatalyst. Fig. S2. FTIR spectra of C<sub>3</sub>N<sub>5</sub>, CeO<sub>2</sub> and C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> composites. Fig. S3. (a) SEM image (b) and (c) respective energy-dispersive spectroscopy ratio of the CeO2/C3N5 composite (Ce, O, C, and N elements). Fig. S4. Survey XPS spectra of CeO2, C3N5 and  $C_3N_5/\text{CeO}_2$  composites. Fig. S5. High resolution XPS spectra of  $\text{CeO}_2$  and  $C_3N_5$ pristine materials: (a) C 1s, (b) N 1s, (c) Ce 3d, and (d) O 1s. Fig. S6. Photoluminescence spectra of the samples. Fig. S7. Mott-Schottky analysis of the samples: (a) CeO2 and (b) C3N5. Fig. S8. XRD analysis of the C3N5/CeO2 composite after and before the reaction study. Table S1. Physiochemical properties of the pristine catalyst used for photocatalytic application. Table S2. Elemental composition of  $C_3N_5$ ,  $CeO_2$  and  $C_3N_5/CeO_2$  composites. Table S3. Activity comparison of some representative photocatalysts for photocatalytic hydrogen production. See DOI: https://doi.org/10.1039/d4ya00476k

Paper

Owing to its environmentally friendly and sustainable nature, photocatalysis has garnered significant interest among many other potential technologies. It is based on the photosynthesis process occurring in plants to transform low-density solar energy into high-density energy fuels. 10-12 To achieve this, research communities are working extremely hard to investigate effective, reliable, affordable, and visible-light sensitive materials. Innovation based on photocatalysis is useful as a viable, sustainable, cost-effective, reliable and steady solution to the world's power issues. 13-15 Solar energy can be converted into sustainable hydrogen energy via photocatalytic water splitting using semiconductors irradiated by visible light, which is a safe and environmentally friendly process. Goodeve and Kitchener (1938) discovered that TiO2 could enhance dye removal efficiency under both vacuum and air conditions, and TiO2 remained stable after the completion of the reaction; this marked the beginning of semiconductor-based photocatalysts. 16,17 Fujishima and Honda (1972) noticed photoelectrical water splitting on TiO<sub>2</sub> films when solar light was being irradiated and the door to semiconductorbased photocatalyst innovation was opened as soon as the world became aware of this amazing accomplishment.<sup>18</sup> However, the activity of the majority of photocatalysts is still constrained by the absence of active sites, severe recombination of photogenerated excitons, and diminished light-harvesting efficiency. 19,20 Therefore, it is imperative to investigate novel photocatalysts with a broad spectral response that are extremely active to achieve sustainable hydrogen production. The modifiable band diagram, low toxicity, good thermal stability, and chemical stability of graphite carbon nitride (g-C<sub>3</sub>N<sub>5</sub>) have all been the subject of extensive research. In addition to that, the visible light absorption can be expanded and a rapid electron movement can be facilitated by the narrow band gap of g-C<sub>3</sub>N<sub>5</sub>. <sup>21-26</sup> CeO<sub>2</sub> is a type of rare earth metal oxide that is non-toxic and low-cost having a cubic crystalline n-type material with a 2.5 eV band gap. In the CeO<sub>2</sub> unit cell, every Ce(IV) is linked in the octahedral interstitial with eight adjacent O2-, and each O2- is linked with four adjacent Ce(IV), forming a tetrahedral structure; here, Ce<sup>3+</sup> and Ce<sup>4+</sup> are capable of coexisting indefinitely and converting to each other effortlessly.<sup>27-29</sup> The efficacy of photocatalysts will be improved, resulting in the multivalence property of CeO2, which enables the generation of robust interactions with other catalyst components for photocatalytic hydrogen production. Zou et al. have developed a CeO<sub>2</sub> hybridised g-C<sub>3</sub>N<sub>4</sub> composite, which produced a hydrogen yield of 860 μmol g<sup>-1</sup> h<sup>-1</sup>.30 Sha et al. have discussed about the charge separation in CeO2/MnO2 nanoflakes with an efficiency of 540 μmol g<sup>-1</sup> h<sup>-1</sup> of hydrogen.<sup>31</sup> Liu et al. have modified C<sub>3</sub>N<sub>5</sub> with nickel oxide for improving the activity, which shows a yield of 357  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of hydrogen production.<sup>32</sup> Still, there are no pertinent reports regarding the formation of a heterojunction between C<sub>3</sub>N<sub>5</sub> and CeO<sub>2</sub> for photocatalytic hydrogen evolution. The heterostructures obtained by the chemical binding of C<sub>3</sub>N<sub>5</sub> and CeO2 composites effectively segregate and constrain the charge carrier recombination. As anticipated, the well-designed CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> heterojunction, substantially improves the photocatalytic hydrogen evolution, without the need of additional co-catalysts.

## **Materials**

All chemicals and reagents 3-amino-1,2,4-triazole (C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>)  $(\geq 98\%)$ , cerium(III) nitrate hexahydrate  $(Ce(NO_3)_3 \cdot 6H_2O)$ ( $\geq$ 98%), methanol (CH<sub>3</sub>OH) ( $\geq$ 98%), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) ( $\geq$ 99.5%), triethanolamine ( $C_6H_{15}NO_3$ ) ( $\geq$ 98%), lactic acid  $(C_3H_6O_3)$  ( $\geq 98\%$ ), ascorbic acid  $(C_6H_8O_6)$  ( $\geq 99\%$ ), sodium sulfide (Na<sub>2</sub>S) ( $\geq$ 98%), and sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) ( $\geq$ 98%) were obtained from Sigma Aldrich, TCI, and SRL India.

#### Synthesis of C<sub>3</sub>N<sub>5</sub>

C<sub>3</sub>N<sub>5</sub> was synthesized using a thermal polymerization method in a muffle furnace, as described in the literature by Wu et al. In a typical synthesis, 2 g of 3-amino-1,2,4-triazole was placed in a porcelain crucible and was gradually calcined at 550 °C with a heating rate of 2  $^{\circ}$ C min<sup>-1</sup> for a period of 3 h. Bulk C<sub>3</sub>N<sub>5</sub> is a darkyellowish product that was collected and crushed into a powder after naturally cooling to room temperature<sup>33</sup> (Scheme 1a).

#### Synthesis of CeO<sub>2</sub>

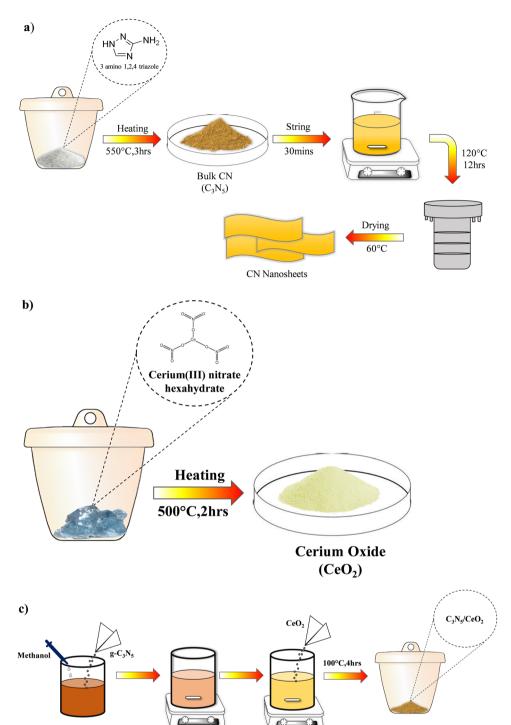
CeO<sub>2</sub> was synthesized by a thermal polymerization method in a muffle furnace, as described in the literature by Song et al. Briefly, 2.0 g cerium(III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) was calcined at 500 °C for 2 h in the muffle furnace with a heating rate of 2 °C min<sup>-1</sup>. CeO<sub>2</sub> is a light-yellowish product that was collected and crushed into a powder after naturally cooling to room temperature<sup>34</sup> (Scheme 1b).

#### Synthesis of C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> composite

The C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> heterostructures were synthesized as follows: 100 mg of C<sub>3</sub>N<sub>5</sub> was mixed in 25 mL of methanol under an ultrasonic setting for 30 min, and then a sufficient amount of CeO<sub>2</sub> was immersed into the suspensions. The mixture was vigorously stirred at room temperature, followed by half an hour of ultrasonic treatment to remove the organic solvent. The resultant dark yellowish powder was then calcined for 4 h at 100 °C with a 2 °C min<sup>-1</sup> heating rate. The composite catalysts were designated as 5 wt% C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub>, 10 wt% C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub>, 15 wt% C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub>, and 20 wt% C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> by various weight percentages of the polymer content (5, 10, 15, 20 wt%) in the composite (Scheme 1c). The term "C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub>" refers to 10 wt% C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> in the subsequent text.

#### Characterisation

The phase purity and crystallinity of the prepared photocatalysts were assessed through X-ray diffraction utilizing a PANalytical X'Pert particle diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 A). Shimadzu IRTracer-100 was used to carry out the Fourier-transform infrared spectroscopy (FT-IR). The morphology of the nanocomposites was examined utilizing high-resolution transmission electron microscopy (HRTEM, JEOL Japan, JEM-2100 Plus) and field emission scanning electron microscopy (FE-SEM) (FEI Quanta FEG 200). UV-vis diffuse reflectance (UV-DRS) data were acquired through the utilization of a Shimadzu UV-3600i Plus UV-vis spectrophotometer. The photoluminescence (PL) spectra were analysed using a fluorescence spectrophotometer (Horiba, Fluorolog-QM).



Scheme 1 (a). Schematic representation of the synthesis of  $C_3N_5$ . (b) Schematic representation of the synthesis of  $CeO_2$ . (c) Schematic representation of the synthesis of the  $C_3N_5$ /CeO<sub>2</sub> composite.

#### Photoelectrochemical measurements

The CHI 760E electrochemical workstation was employed to acquire the Mott–Schottky, impedance and transient photocurrent responses. Ag/AgCl and a platinum wire serve as the reference and counter electrode, respectively. As an electrolyte, a  $0.5~M~Na_2SO_4$  aqueous solution is utilized. The slurry was prepared through the deposition of 2.5~g of the catalyst

dispersed in a mixture of deionized water and anhydrous ethanol (1:1) and coated on the working electrode (glassy carbon electrode) for electrochemical studies.

C<sub>3</sub>N<sub>5</sub>/CeO<sub>2</sub> composite

#### Photocatalytic studies

The photocatalytic hydrogen generation reaction was performed in direct sunlight. The reaction was carried out in a

Kjeldhal flask containing 5 mg of the catalyst dispersed in 50 ml of 5% sacrificial agent. The dissolved gases were eliminated from the reaction solution by purging with nitrogen gas for 15 minutes. The reaction setup was kept under sunlight, and an offline gas chromatograph (Shimadzu GC-2014 equipped with a Molecular Sieve [5 Å column]) analysed hydrogen generation with a TCD detector after the reaction setup was kept in sunlight for a period of 3 hours. The mean solar light intensity was ascertained to be 80 000 lux using a lux meter. While the pH of the reaction mixture was adjusted using solutions of NaOH and H<sub>2</sub>SO<sub>4</sub>, various sacrificial agents were employed when necessary.

## Results and discussion

Fig. 1 shows the crystal structures of CeO<sub>2</sub>, C<sub>3</sub>N<sub>5</sub>, and the 10 wt% CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> nanocomposite revealed by the XRD patterns (Fig. 1a). The CeO<sub>2</sub> peaks in the XRD pattern can be found at 28.6°, 33.1°, 47.5°, 56.4°, and 59.1°, 69.2°, 76.6° and 79.2°, which correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) planes, respectively, of the fluorite crystal

structure (ICPDS 34-0394) (Fig. 1b). The large peak (002) in the C<sub>3</sub>N<sub>5</sub> XRD pattern, which is centered at 27.5 degrees, reveals the material's amorphous nature (JCPDS 87-1526). The XRD pattern of the CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> nanocomposites reveals peaks that correlate to the synthesis of both CeO2 and C3N5. Rietveld analysis of CeO<sub>2</sub> is obtained to understand the atomic percentage of the elements (Fig. S1, ESI†) composition. In the nanocomposite, the peak intensities of CeO2 increased and the C<sub>3</sub>N<sub>5</sub> peak intensity decreased, indicating some degree of crystallographic disorder brought on by the addition of C<sub>3</sub>N<sub>5</sub>. The stretching vibration of the surface free amino group and the hydroxyl group of water is represented by the wide peak of pure  $C_3N_5$  at 3000–3600 cm<sup>-1</sup> in (Fig. S2, ESI†). The typical stretching vibration of C-N and C-N heterocycles is responsible for the peaks at 1235 cm<sup>-1</sup>, 1316 cm<sup>-1</sup>, 1411 cm<sup>-1</sup>, 1571 cm<sup>-1</sup>, and 1637 cm<sup>-1</sup>. The characteristic stretching vibration of the s-triazine ring unit is represented by the peak at 805 cm<sup>-1</sup>. The characteristic peaks of C<sub>3</sub>N<sub>5</sub> and CeO<sub>2</sub> remained unaltered in the composite, as evidenced by the presence of all characteristic vibration peaks in the corresponding CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> composites.

The UV-Vis diffuse reflectance spectra of the modified samples are illustrated in Fig. 1(c). The CeO<sub>2</sub> shows an absorption

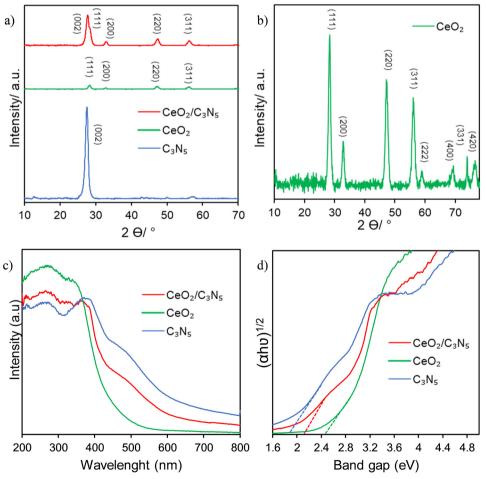


Fig. 1 (a) XRD patterns of  $C_3N_5$ ,  $CeO_2$  and  $CeO_2/C_3N_5$  composites. (b) XRD patterns of  $CeO_2$ . (c) UV-vis absorbance spectra and (d) optical band gap using relative Tauc plots.

below 500 nm. Nevertheless, the photo response of exposed  $CeO_2$  is expanded to the visible region when it is combined with  $C_3N_5$ . The band gap positions of  $CeO_2$  and  $g-C_3N_5$  are calculated as 2.5 eV and 1.9 eV, respectively, using the Tauc plot, as illustrated in Fig. 1(d). This may be attributed to the fact that  $C_3N_5$  effectively functions in absorbing significant quantities of visible light particles. This confirms the efficacy of  $C_3N_5$  for visible light harvesting.

The morphologies of CeO<sub>2</sub>, C<sub>3</sub>N<sub>5</sub> and CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> have been closely observed using SEM analysis. The SEM images show the presence of both CeO<sub>2</sub> incorporated into C<sub>3</sub>N<sub>5</sub>. The impact of CeO<sub>2</sub> on the morphological structure of C<sub>3</sub>N<sub>5</sub> is clearly visible in the composite (Fig. 2(a-c)). The TEM images reveal the composite formation between CeO<sub>2</sub> and C<sub>3</sub>N<sub>5</sub> in Fig. 2(e-g). As demonstrated, the micromorphology of g-C<sub>3</sub>N<sub>5</sub> sheets is clearly observed, and the presence of CeO<sub>2</sub> particles is confirmed. The influence of CeO<sub>2</sub> decoration on the structure of C<sub>3</sub>N<sub>5</sub> is clearly visible in the TEM images. Fig. 2(e) shows clear (111) and (220) crystal planes with lattice fringes with a spacing of 0.21 nm and 0.27 nm, respectively. The crystallite size of CeO<sub>2</sub> and C<sub>3</sub>N<sub>5</sub> is calculated as 7.13 nm and 8.55 nm (Table S2, ESI†). The acquired images confirmed the existence of crystallized CeO2 nanoparticles encircled by an exceedingly thin layer of C<sub>3</sub>N<sub>5</sub>, which reflects the composite's extremely low concentration. (Fig. S3, ESI†). The images show that the CeO<sub>2</sub> nanoparticles were evenly distributed on the host photocatalyst, which shows that the CeO<sub>2</sub> nanoparticles were evenly distributed on the host photocatalyst, which is a sign of a good deposition process.

By employing X-ray photoelectron spectroscopy (XPS), the electronic chemical states and surface elemental composition of  $CeO_2$ ,  $C_3N_5$  and  $CeO_2/C_3N_5$  were ascertained (Fig. 3). The

CeO<sub>2</sub>, C<sub>3</sub>N<sub>5</sub> and CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> composite, as indicated by the XPS survey spectra presented in Fig. S4 (ESI†), comprise the elements Ce, O, C and N. The C 1s spectra of C<sub>3</sub>N<sub>5</sub> depict the binding energies at 284.9 eV, 287.6 eV and 288.3 eV, corresponding to C-C/C=C, N=C and C-NH bonds, respectively. In the high resolution of N 1s spectra, two main peaks at 402.3 eV and 404.1 eV are attributed to CN=C and C-N=N-C groups, respectively. In addition, the peak at 406.9 eV is generated by N-H bonds. In the O 1s spectra, the peak labelled at 528.8 eV is attributed to the lattice oxygen in CeO2. Apart from this, a broad peak is deconvoluted at 532.3 eV and 538 eV, which is attributed to oxide defects and adsorbed oxygen, respectively. The high-resolution Ce 3d spectrum of CeO<sub>2</sub> is deconvoluted. Ce<sup>4+</sup> is the dominant state, and its characteristic spectrum is represented by the peak with high intensity at 914.2 eV. Furthermore, the Ce 3d<sub>5/2</sub> spin-orbit is represented by the peaks at 879.8 eV, 884.7 eV and 887.1 eV. The Ce 3d<sub>3/2</sub> spinorbit is shown by the peaks at 903.7 eV, 900.4 eV, 899.3 eV, and 895.4 eV (Fig. S5, ESI†). The sample surface is not completely oxidized, as evidenced by the presence of Ce<sup>3+</sup>/Ce<sup>4+</sup> oxidation states on the surface of CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> composites (Table S2, ESI†).

The  $CeO_2/C_3N_5$  composite is more mobile and has a greater resistance to charge recombination, as indicated by the reduced arc radius of the electrochemical impedance spectroscopy (EIS) Nyquist plot in comparison to that of  $CeO_2$  and  $C_3N_5$  (Fig. 4a). Mott–Schottky analyses were performed on  $CeO_2$  and  $g-C_3N_5$  to clarify the flat band potential of the pristine materials. Possibly, the positive slope represented an n-type semiconductor (Fig. 4c and d). In contrast to the redox potential of  $H^+/H_2$ , the flat band positions of  $C_3N_5$  and  $CeO_2$  concerning the Ag/AgCl electrode were -1.42 eV and -1.08 eV, respectively,

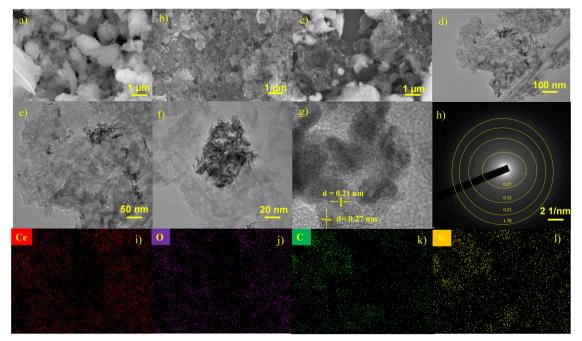


Fig. 2 SEM images of (a)  $CeO_2$ , (b)  $C_3N_5$ , and (c)  $CeO_2/C_3N_5$  composites; (d)–(g) high-resolution TEM (HRTEM) images of  $CeO_2/C_3N_5$  composites; (h) clear fringes with lattice spacings. (i)–(l) EDS mapping images of Ce, O, C, and N elements.

Paper

N<sub>1</sub>s C<sub>1</sub>s b) a) C-C C=N-C Intensity (a.u) Intensity (a.u) N=C-N C-N=C-N 290 287 284 281 278 402 399 396 393 390  $3d_{3/2}$ Binding energy (eV) Binding energy (eV)  $3d_{5/2}$ d) c) 01s Ce3d 3d<sub>5/2</sub> Intensity (a.u) ntensty (a.u) Adsorbed attice oxygen oxygen

538

Fig. 3 High-resolution XPS spectra of  $CeO_2/C_3N_5$  composites: (a) C 1s, (b) N 1s, (c) Ce 3d, and (d) O 1s

Binding energy (eV)

both of which were more negative (eqn (S1), ESI†). The conduction band potential (CB) and flat band in n-type semiconductors are well established. Additionally, as demonstrated by the transient photocurrents in Fig. 4(b), CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> demonstrates a significantly higher photocurrent density than the pristine materials when subjected to intermittent light irradiation. The improved charge transfer and separation efficacy of the CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> nanocomposite is illustrated by its increased photocurrent response, which is accompanied by a decreased rate of photogenerated charge carrier recombination. The PL intensity of the composite is lower than that of individual counterparts, which implies that it has a higher charge carrier separation efficiency (Fig. S6, ESI†). In summary, the photoelectrochemical data indicated that the photoelectron transport efficacy of the catalyst can be enhanced through the formation of a CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> nanocomposite.

925

#### Photocatalytic activity

In the presence of a hole scavenger in deionized water, the photocatalytic efficiency was evaluated in response to direct sunlight (Fig. 5).

The optimization of the CeO<sub>2</sub>-C<sub>3</sub>N<sub>5</sub> composite, exhibiting notable photocatalytic activity, has been carried out using pristine CeO<sub>2</sub>, C<sub>3</sub>N<sub>5</sub>, 5 wt% CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub>, 10 wt% CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub>,

15 wt%  $CeO_2/C_3N_5$ , and 20 wt%  $CeO_2/C_3N_5$  composites. The 10 wt% CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> composite produced an efficiency of 1256 μmol  $g^{-1} h^{-1}$  (Fig. 5a). This value is considerably greater than that of the pristine material (125  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>) and other composites. With increasing CeO2, the rate of H2 evolution initially increases and then decreases. Under visible-light irradiation, the H<sub>2</sub> evolution rate of the 10 wt% CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> heterojunction can reach its maximum value with the loading amount of CeO<sub>2</sub>. The values obtained are comparatively higher than those of the published articles in the field of photocatalytic hydrogen production, which is discussed in Table S1 (ESI†). The photocatalytic hydrogen evolution is carried out using different scavengers, including methanol, TEOA, glycerol and lactic acid, producing yields of 1290, 510, 1032, and 227  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, respectively (Fig. 5b). In order to demonstrate the stability of the catalyst, the CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> sample was subjected to four consecutive cycles (Fig. 5c), and the outcomes show that the sample exhibits high stability and hydrogen production. XRD characterization studies confirm the structural integrity of the catalyst after repeated use (Fig. S8, ESI†).

528

Binding energy (eV)

518

Finally, the electronic charge transfer, advantages of C<sub>3</sub>N<sub>5</sub> integrating with CeO<sub>2</sub> and formation of type II heterojunctions were understood based on the aforementioned results and prior experimental investigations. A potential mechanism for

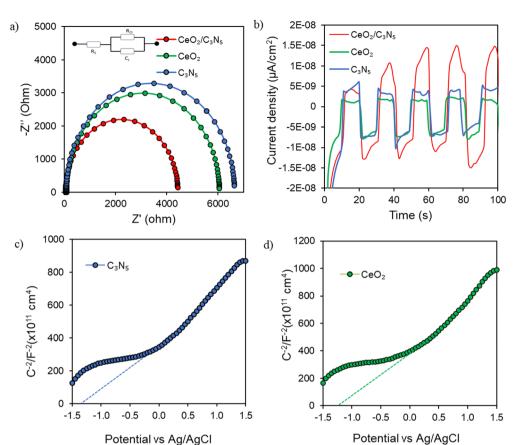


Fig. 4 (a) Impedance spectra plots, (b) photocurrent response, and (c) and (d) Mott–Schottky analysis of the samples.

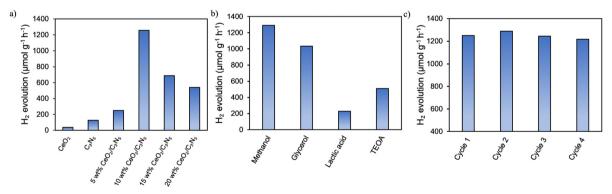


Fig. 5 (a) Photocatalytic  $H_2$  evolution rates of the  $CeO_2/C_3N_5$  composite. (b) Photocatalytic  $H_2$  evolution rate with different scavengers. (c) Stability study.

the 10 wt%  $CeO_2/C_3N_5$  composite is suggested in (Fig. 6) based on the observed results.  $e^-$  is excited from the valence band (VB) to the conduction band (CB) of  $C_3N_5$  and  $CeO_2$  by high-energy photons under light irradiation. Using the Mott Schottky analysis, the flat band positions of  $C_3N_5$  and  $CeO_2$  with respect to the Ag/AgCl electrode were -1.42 eV and -1.08 eV, respectively, in contrast to the redox potential of  $H^+/H_2$ . The relationship between the flat band and the conduction band potential (CB) in n-type semiconductors is well-established. The conduction band edges were -0.81 eV and -0.47 eV, as calculated from the Tauc plot analysis (eqn (S2), ESI $^+$ ). Therefore, a type II heterojunction

mechanism was suggested for the  $CeO_2/C_3N_5$  composite in response to the band levels of  $C_3N_5$  and  $CeO_2$ . The conduction band accumulates excited electrons (e<sup>-</sup>) in response to photon irradiation, while the valence band of  $C_3N_5$  and  $CeO_2$  accumulates holes (h<sup>+</sup>). Due to variations in energy levels, the accumulated electrons migrate from the CB of  $C_3N_5$  to the CB of  $CeO_2$ . At the same time, the holes from the valence band of  $CeO_2$  are transferred to the valence band of  $C_3N_5$ . At the CB of  $CeO_2$ , the reduction of H<sup>+</sup> to hydrogen occurs concurrently, while the oxidation of the hole scavenger occurs at the VB of  $C_3N_5$ . Consequently, the synergistic effect of  $C_3N_5$  and  $CeO_2$  can

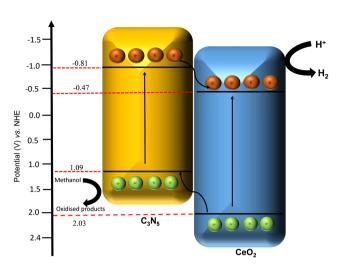


Fig. 6 Plausible mechanism of the CeO<sub>2</sub>/C<sub>3</sub>N<sub>5</sub> catalyst

effectively separate photoelectron-hole pairs, enticing a greater number of carriers to participate in the photodegradation process, thereby improving the photocatalytic activity.

## Conclusion

**Paper** 

In summary, the CeO<sub>2</sub> dopedC<sub>3</sub>N<sub>5</sub> composite is the product of a straightforward synthesis method, which led to the successful development of CeO<sub>2</sub>-incorporated C<sub>3</sub>N<sub>5</sub>. The primary goal of this research is to investigate the impact of organic-inorganic hybrid photocatalysts by optimizing the catalyst to enhance the reaction performance. According to the results of the morphological investigation, the composition and morphological transformation of the synthesized samples are significantly affected by CeO<sub>2</sub> dispersed on C<sub>3</sub>N<sub>5</sub>. Moreover, the optical band gap decreased, leading to an increased absorption of the visible spectrum. In addition, photoelectrochemical methods have consistently exhibited an effective ability to prevent the recombination of photogenerated electron-hole pairs. Notably, the photocatalytic hydrogen evolution for the 10 wt% CeO2 doped C<sub>3</sub>N<sub>5</sub> catalyst is 1256 μmol g<sup>-1</sup> h<sup>-1</sup>, which is 10 times greater than that of  $C_3N_5$  alone (125  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>). Due to the efficient transfer of photogenerated holes, the recombination rate of excitons has been significantly reduced with the simultaneous enhancement of the rate of photocatalytic H<sub>2</sub> production. This study offers a unique perspective that aids in creating innovative photocatalysts for efficient solar energy conversion into fuel.

## Data availability

The data supporting this article have been included within the manuscript and as part of the ESI.†

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

The authors appreciate the support from the SRM Institute of Science and Technology, India. S. K. would like to thank the Royal Society-Newton International Fellowship Alumni follow-on funding support AL\211016 and AL\221024. S. K. is also grateful to the SERB Start-up Research Grant (SRG/2023/000658). We acknowledge SRMIST for the fellowship and SRM-SCIF and Nanotechnology Research Centre (NRC) for the research facilities.

### References

- 1 S. Chu and A. J. Majumdar, Nature, 2012, 488, 294-303.
- 2 T. Hisatomi and K. J. Domen, Nat. Catal., 2019, 2, 387-399.
- 3 L. Wang, S. Duan, P. Jin, H. She, J. Huang, Z. Lei, T. Zhang and Q. J. Wang, *Appl. Catal.*, B, 2018, 239, 599–608.
- 4 A. Naldoni, M. Altomare, G. Zoppellaro, N. Liu, S. Kment, R. Zboril and P. J. Schmuki, *ACS Catal.*, 2018, 9, 345–364.
- 5 X. Yin, X. Zhao and W. J. Zhang, Energy, 2018, 158, 1204-1212.
- 6 M. I. Alhamid, Y. Daud, A. Surachman, A. Sugiyono, H. Aditya, T. J. R. Mahlia and S. E. Reviews, *Renewable Sustainable Energy Rev.*, 2016, 53, 733–740.
- 7 C. Xia, H. Wang, J. K. Kim and J. J. Wang, Adv. Funct. Mater., 2021, 31, 2008247.
- 8 W. Zhou, W. Li, J.-Q. Wang, Y. Qu, Y. Yang, Y. Xie, K. Zhang, L. Wang, H. Fu and C. S. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 9280–9283.
- 9 D. Ma, D. Sun, Y. Zou, S. Mao, Y. Lv, Y. Wang, J. Li and J.-W. Shi, J. Colloid Interface Sci., 2019, 549, 179–188.
- 10 A. Augustin, C. Chuaicham, M. Shanmugam, B. Vellaichamy, S. Rajendran, T. K. Hoang, K. Sasaki and K. J. Sekar, *Nanoscale Adv.*, 2022, 4, 2561–2582.
- 11 L. Yu, G. Zhang, C. Liu, H. Lan, H. Liu and J. J. A. C. Qu, ACS Catal., 2018, 8, 1090–1096.
- Y. Zhang, D. Ma, J. Li, C. Zhi, Y. Zhang, L. Liang, S. Mao and J.-W. J. C. C. R. Shi, *Coord. Chem. Rev.*, 2024, 517, 215995.
- 13 M. Shanmugam, C. Chuaicham, A. Augustin, K. Sasaki, P. J. Sagayaraj and C. Sekar, New J. Chem., 2022, 46, 15776–15794.
- 14 M. S. Yesupatham, A. Augustin, N. Agamendran, B. H. Honnappa, M. Shanmugam, P. J. Sagayaraj, T. Ganesan, N. C. S. Selvam and K. J. Sekar, *Sustainable Energy Fuels*, 2023, 7, 4727–4757.
- 15 D. Ma, J. Chen, J. Li, X. Ji and J.-W. Shi, *J. Mater. Chem. A*, 2024, **12**, 12293–12324.
- 16 C. Goodeve and J. J. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 570–579.
- 17 Y. Zou, S. Li, D. Zheng, J. Feng, S. Wang, Y. Hou and G. J. Zhang, *Sci. China Chem.*, 2024, 1–9.
- 18 A. Fujishima and K. J. n Honda, Nature, 1972, 238, 37-38.
- 19 C. Hu, Y.-H. Lin, M. Yoshida and S. J. Ashimura, ACS Appl. Mater., 2021, 13, 24907–24915.
- 20 D. Ma, Z. Zhang, Y. Zou, J. Chen and J.-W. J. Shi, Coord. Chem. Rev., 2024, 500, 215489.
- 21 B. Debnath, S. Singh, S. M. Hossain, S. Krishnamurthy, V. Polshettiwar and S. J. L. Ogale, *Langmuir*, 2022, **38**, 3139–3148.

- 22 H. Wang, M. Li, Q. Lu, Y. Cen, Y. Zhang and S. J. Yao, *ACS sustainable Chem.*, 2018, 7, 625–631.
- 23 P. Kumar, E. Vahidzadeh, U. K. Thakur, P. Kar, K. M. Alam, A. Goswami, N. Mahdi, K. Cui, G. M. Bernard and V. K. Michaelis, *J. Am. Chem. Soc.*, 2019, **141**, 5415–5436.
- 24 Q. Wang, S. Li, D. Zheng, S. Wang, Y. Hou and G. J. Zhang, *ACS Appl. Energy Mater.*, 2024, 7, 6090–6095.
- 25 Q. Wang, G. Zhang, W. Xing, Z. Pan, D. Zheng, S. Wang, Y. Hou and X. J. Wang, *Angew. Chem.*, 2023, 135, e202307930.
- 26 B. K. Raja, M. Govindaraj, M. K. Muthukumaran and S. J. Ramar, New J. Chem., 2024, 48, 15324–15337.
- 27 D. Gao, Y. Zhang, Z. Zhou, F. Cai, X. Zhao, W. Huang, Y. Li, J. Zhu, P. Liu and F. J. Yang, J. Am. Chem. Soc., 2017, 139, 5652–5655.

- 28 Y. Wang, Z. Chen, P. Han, Y. Du, Z. Gu, X. Xu and G. J. A. C. Zheng, *ACS Catal.*, 2018, **8**, 7113–7119.
- 29 J. Tian, Y. Sang, Z. Zhao, W. Zhou, D. Wang, X. Kang, H. Liu, J. Wang, S. Chen and H. J. Cai, *Small*, 2013, 9, 3864–3872.
- 30 W. Zou, Y. Shao, Y. Pu, Y. Luo, J. Sun, K. Ma, C. Tang, F. Gao and L. J. Dong, *Appl. Catal., B*, 2017, **218**, 51–59.
- 31 M. A. Sha, G. Mohanan, L. Elias, T. Bhagya and S. J. Shibli, Mater. Chem. Phys., 2023, 294, 127019.
- 32 M.-Y. Liu, J.-Y. Wang, D. Lian, L. Xian and L. J. Zhang, *J. Fuel Chem.*, 2022, **50**, 243–249.
- 33 B. Wu, T. Sun, N. Liu, L. Lu, R. Zhang, W. Shi and P. J. Cheng, *ACS Appl. Mater. Interfaces*, 2022, **14**, 26742–26751.
- 34 J. Song, F. Wu, Y. Lu, X. Zhang and Z. J. Li, *ACS Appl. Nano Mater.*, 2021, 4, 4800–4809.