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1. Introduction

Sustainable development of technology is essential to solve the increasingly imminent energy crisis and the accompanying associated environmental issues with pollution.^{1,2} Photocatalysis technology based on semiconductor photocatalysts is one of the most promising strategies to meet the increasing global energy and environmental demand.3-5 Among the existing semiconductor photocatalysts, TiO_2 has been most frequently used due to its easy availability, lowprice, high stability and non-toxicity.^{6,7} However, sluggish surface reaction kinetics, response to only the UV fraction of solar spectra, and the fast recombination of charge carriers result in the low photocatalytic activity of pure TiO₂ in solar energy conversion.^{8,9} Thus, significant research efforts have been focused on the modification of TiO₂ for improving its photocatalytic efficiency.^{10,11} The loading of co-catalysts has

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A size tunable bimetallic nickel-zinc nitride as a multi-functional co-catalyst on nitrogen doped titania boosts solar energy conversion[†]

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To enable high-efficiency solar energy conversion, rational design and preparation of low cost and stable semiconductor photocatalysts with associated co-catalysts are desirable. However preparation of efficient catalytic systems remains a challenge. Here, N-doped TiO_2 /ternary nickel-zinc nitride (N-TiO_2-Ni_3ZnN) nanocomposites have been shown to be a multi-functional catalyst for photocatalytic reactions. The particle size of Ni_3ZnN can be readily tuned using N-TiO_2 nanospheres as the active support. Due to its high conductivity and Pt-like properties, Ni_3ZnN promotes charge separation and transfer, as well as reaction kinetics. The material shows co-catalytic performance relevant for multiple reactions, demonstrating its multifunctionality. Density functional theory (DFT) based calculations confirm the intrinsic metallic properties of Ni_3ZnN. N-TiO_2-Ni_3ZnN exhibits evidently improved photocatalytic performances as compared to N-TiO_2 under visible light irradiation.

been considered to be one of the most efficient methods of modification. Generally, noble metals, such as Pt, Ag, and Au, are considered to be preeminent co-catalysts for effective enhancement of photocatalytic activity.^{12–14} However, their rare reserves and high prices greatly limit their applications. Thus, the exploration of high performance and low-cost co-catalysts has become a pivotal research area in the field of photocatalysis.

Transition metal nitrides (TMNs) are metallic interstitial compounds with high melting points, hardness, and corrosion resistance.15 They show significant catalytic activity, selectivity, and resistance to poisoning compared to their parent metals.¹⁶ The introduction of nitrogen results in the extensive deformation of the metal lattice (when compared to the corresponding oxide) and causes a change in the density of states (DOS) associated with the metal d_0 band.¹⁷ Contraction of the d-band improves the DOS near the Fermi level and results in better conductivity when compared to the corresponding oxides.¹⁸ Due to these advantages, TMNs have found promising applications in the field of catalysis.^{19,20} However, there are limitations too; agglomeration is an unavoidable problem in the traditional synthesis process of TMNs. The large particle size of TMNs deleteriously affects their catalytic activity.^{21,22} Therefore, regulation of the size of TMNs remains a challenge. Thanks to the development of materials synthesis technology, nano-sized TMN materials have been prepared recently and have been used as efficient co-catalysts and as noble metal alternatives in the field of photocatalysis.²³⁻²⁵ Nevertheless,



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compared with other non-noble-metal co-catalysts like transition metal oxides, phosphides, and sulfides,^{26–28} studies on TMN-based photocatalysis are still insufficient.²⁹ In particular, bimetallic nitrides, which exhibit desirable catalytic performance as compared with single-metal nitrides,^{19,30} hold great promise in the field of photocatalysis but are rarely reported.

Here, for the first time, we report the application of a bimetallic nickel-zinc nitride (Ni₃ZnN) as a co-catalyst for effectively improving the photocatalytic activity of N-TiO₂ for different photocatalytic reactions. Notably, the size of Ni₃ZnN can be well tuned to approximately 60 nm by using the N-TiO₂ support while the size of pure Ni₃ZnN is larger than 300 nm. Experimental and density functional theory (DFT) calculation results confirm the intrinsic metallic properties of Ni₃ZnN, which are beneficial for charge carrier separation and transfer as well as reaction kinetics of the catalysts. Thus, N-TiO2-Ni₃ZnN nanocomposites exhibit an evidently enhanced H₂ generation rate (55.3 μ mol g⁻¹ h⁻¹) when compared to pure N-TiO₂ (1.7 μ mol g⁻¹ h⁻¹). Moreover, as a multi-functional photocatalyst, N-TiO2-Ni3ZnN also exhibits better photocatalytic performances for 4-nitrophenol and Cr(vi) reduction as compared to pure N-TiO₂.

2. Experimental section

2.1 Materials and reagents

1-Hexadecylamine ($C_{16}H_{35}N$, HDA), titanium tetra-isopropanolate ($C_{12}H_{28}O_4Ti$, TIP), triethanolamine ($C_6H_{15}NO_3$, TEOA), 4-nitrophenol ($C_6H_5NO_3$, 4-NP), potassium dichromate ($K_2Cr_2O_7$), chloroplatinic acid hexahydrate ($H_2PtCl_6\cdot 6H_2O$, Pt 37.5%) and ammonium formate (HCOONH₄) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and anhydrous ethanol (C_2H_6O) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). NH₃ (99.999%) was purchased from Zhengzhou Xingdao Chemical Technology Co., Ltd (Zhengzhou, China). Deionized water used in the processes was obtained from local sources. All chemicals used throughout this work were of analytical grade or better and were used as received without any further purification.

2.2 Preparation of photocatalysts

Preparation of N–TiO₂–Ni₃ZnN nanocomposites. 4.362 g of Ni(NO₃)₂·6H₂O and 1.487 g of Zn(NO₃)₂·6H₂O were dissolved in 250 mL of ethanol to get the NiZn-precursor salt solution. 0.1 g of pure TiO₂ nanospheres and different volumes of the NiZn-precursor salt solution (0.2, 0.6, 1, 1.4, 2 mL) were added into 200 mL of ethanol and dispersed using ultrasonication for 30 min. Then the liquid was dried at a constant temperature of 90 °C. The powder was left in a beaker and dried in an oven at 60 °C overnight. The dried TiO₂–NiZn precursor samples were transferred into a quartz boat after grinding and spread thinly on the boat. The samples were prepared in a NH₃ flow (99.999%) of 100 sccm at 550 °C with a heating rate of

5 °C min⁻¹ and maintained for 1 h. The obtained grey sample is the N–TiO₂–Ni₃ZnN nanocomposites. The detailed syntheses of the TiO₂ precursor, TiO₂ and N–TiO₂ nanospheres are shown in the ESI.†

Preparation of the pure Ni₃**ZnN sample.** 0.872 g of Ni $(NO_3)_2 \cdot 6H_2O$ and 0.297 g of $Zn(NO_3)_2 \cdot 6H_2O$ were added into 200 mL of ethanol and dispersion was ensured using ultrasonication for 30 min. Then the liquid was dried at a constant temperature of 90 °C. The NiZn-precursor sample was dried in an oven at 60 °C overnight. The dried NiZn-precursor sample was transferred into a quartz boat after grinding and spread thinly on the boat. The samples were prepared in a NH₃ flow (99.999%) of 100 sccm at 550 °C with a heating rate of 5 °C min⁻¹ and maintained for 1 h. The pure Ni₃ZnN sample was successfully prepared after grinding.

2.3 Materials characterization

The crystal structures of the solid samples were characterized using an X-ray diffractometer (XRD, Rigaku Miniflex 600, Japan) in the 2θ range of 10–80° at a scan rate of 1° min⁻¹. The diffuse reflectance spectra of the samples were recorded in the range of 200-800 nm using a UV-vis spectrophotometer (UVvis DRS, Hitachi U-3900, Japan) equipped with an integrating sphere attachment. The photoluminescence (PL) spectra of the solid samples were recorded using a spectrophotometer (PL, Horiba Jobin Yvon Fluoromax 4C-L, France) with an excitation wavelength of 360 nm. The Brunauer-Emmett-Teller (BET, Micromeritics ASAP 2010, USA) surface areas were determined at 77 K. The morphologies of the samples were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai F20 instrument. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD (Shimadzu, Japan) spectrometer with Al K_{α} excitation (1486.6 eV). The electrochemical measurement details are shown in the ESI.[†]

2.4 Calculation method

The details of density functional theory (DFT) calculations are shown in the ESI. \dagger

2.5 Photocatalytic tests

Photocatalytic H₂ production measurements. Photo-catalytic water splitting to H₂ was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. H₂ evolution analysis was performed by dispersing 20 mg of photocatalyst powder in an aqueous solution (80 mL) containing TEOA (8 mL) as the sacrificial electron donor. A 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd) was used as the light source, and visible light irradiation was realized by using a 400 nm cutoff filter. Continuous magnetic stirring was done in order to keep the photocatalyst in suspension during the whole experiment. The temperature of the reaction solution was maintained at 278 K by a flow of cooling water during the reaction. The evolved H₂ was *in situ*

monitored periodically using an online gas chromatograph with a thermal conductivity detector (FULI GC9790II, Ar as a carrier gas).

Photocatalytic reduction of nitroaromatic compounds. 30 mg of the catalyst and 40 mg of HCOONH₄ (hole scavenger) were added into 40 mL of 4-nitrophenol solution (10 mg L^{-1}) in a quartz vial. The suspension was stirred in the dark for 1 h to establish the adsorption-desorption equilibrium between the sample and reactant. The same Xe arc lamp was used as the light source ($\lambda > 400$ nm). 2 mL of the suspension was collected at a certain time interval during the process of the reaction and centrifuged to remove the catalyst completely at 10 000 rpm. Afterward, the solution was analyzed on a Varian ultraviolet-visible light (UV-Vis) spectrophotometer (Hitachi U-3900). The whole experimental process was conducted under N₂ bubbling at a flow rate of 50 sccm. The measurement process of the photocatalytic reduction of Cr(vi) was similar to that of the photocatalytic reduction of 4-nitrophenol. The detailed process is shown in the ESI.[†]

3. Results and discussion

Scheme 1 shows the synthesis process of the N-TiO₂-Ni₃ZnN nanocomposites. Firstly, the TiO2-NiZn precursors are prepared by adding different volumes of nickel nitrate and zinc nitrate mixture to the suspension of TiO₂. Then, the as-prepared TiO₂-NiZn precursors are heated at 550 °C under an NH₃ atmosphere for 1 h; this results in the formation of the N-TiO₂-Ni₃ZnN nanocomposites. The blank Ni₃ZnN sample is synthesized through a similar process, except for not adding the TiO₂ support. The Rietveld refined X-ray diffraction (XRD) pattern of the pure Ni₃ZnN sample is presented in Fig. 1a. It can be clearly seen that all the diffraction peaks of the as-prepared blank Ni₃ZnN sample are indexed to the cubic structure (space group $Pm\bar{3}m$, no. 221) without any impurity phase.^{31,32} The Rietveld analysis General Structure Analysis System (GSAS) gives the lattice parameter of the pure Ni₃ZnN sample as a =3.766 Å. It is comparable to that of the anti-perovskite-type nitride Ni₃ZnN ($Pm\bar{3}m$), a = 3.756 Å, reported before.³² Using the Bragg equation and XRD data, the calculated lattice distance d_{hkl} of the (111) plane is found to be 0.217 nm. The morphology of the pure Ni₃ZnN sample is shown in Fig. 1b. It exhi-



ethanol

Ni(NO₃)₂·6H₂O + Zn(NO₃)₂·6H₂O

distillation

TiO₂-NiZn precurso

NH₃ 1h 550 °C

N-TiO₂-Ni₃ZnN



Fig. 1 (a) Rietveld refined XRD pattern and (b) SEM image of the $\rm Ni_3ZnN$ sample.

bits an irregular block morphology with an average size of 330 nm (Fig. S1†). The optical and electrochemical properties of the pure Ni₃ZnN sample are studied using UV-vis absorption spectra (Fig. S2a†) and electrical impedance spectra (Fig. S2b†). After the nitridation of the NiZn precursor, pure Ni₃ZnN exhibits a full band absorption and excellent conductivity. This in fact bodes well for the enhancement of light absorption intensity and electron transfer efficiency of the material when used as a co-catalyst.³³

The crystal structures of TiO₂ based samples are illustrated in Fig. S3.[†] The TiO₂ precursor sample is amorphous because of the low synthesis temperature. After the calcination of the TiO₂ precursor, the crystalline TiO₂ sample exhibits both anatase (JCPDS no. 021-1272, a = b = 3.785 Å, c = 9.514 Å) and rutile phases (JCPDS no. 021-1276, *a* = *b* = 4.593 Å, *c* = 2.959 Å). Moreover, after calcining under an ammonia atmosphere, the crystal structure of TiO2 still remains. Fig. 2a exhibits the XRD patterns of a series of N-TiO2-Ni3ZnN nanocomposites. The composites show the typical diffraction peaks of TiO₂, which indicates that loading Ni3ZnN does not change the crystalline structure of TiO₂. Notably, compared with the pure N-TiO₂ samples, a new diffraction peak can be observed at 41.6°, which is attributed to the (111) facet of the cubic structure Ni₃ZnN (Fig. 2b). Meanwhile, with the increase of the loading amount of Ni₃ZnN in the N-TiO₂-Ni₃ZnN nanocomposites, the intensity of the diffraction (111) peak of Ni₃ZnN obviously increases. The analysis of the XRD pattern proves that the N-TiO₂-Ni₃ZnN nanocomposites are successfully synthesized.

X-ray photoelectron spectroscopy (XPS) is employed to further analyze the surface elemental components and chemical states of the N–TiO₂–Ni₃ZnN sample. The survey spectrum of the N–TiO₂–Ni₃ZnN nanocomposite (Fig. 2c) confirms the existence of Ti, O, Ni, Zn and N elements. For the high-resolution spectrum of Ti 2p (Fig. 2d), two peaks at 458.4 and 464.1 eV are observed which can be ascribed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively.^{34,35} Fig. 2e shows the O 1s XPS spectrum; two peaks found at 529.6 and 531.3 eV correspond to the Ti–O and Ti–O–N bonds respectively.^{36–38} For the Ni 2p spectrum in Fig. 2f, the peaks at 854.9 and 872.6 eV correspond to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, while the two broad peaks at 860.3 and 878.1 eV are assigned to the corresponding satellite peaks.^{39–41} A couple of weak peaks are also observed at 851.9 and 860.3 eV which are ascribed to the Ni–N bond. This in fact further confirms

TiO

NH₃ 1h 550 °C

N-TIO

TiO₂ precursor

HDA

H₂N

550°C



Fig. 2 (a) XRD pattern and (b) high-resolution XRD pattern of the N–TiO₂ based samples. (c) The X-ray photoelectron survey spectrum of the N–TiO₂–Ni₃ZnN sample. High-resolution spectrum of (d) Ti 2p, (e) O 1s, (f) Ni 2p, (g) Zn 2p and (h) N 1s for the N–TiO₂–Ni₃ZnN sample.

the formation of transition metal nitride.³¹ Fig. 2g shows the Zn 2p XPS core level spectrum, in which binding energy peaks at 1019.6 and 1042.1 eV are observed, and these peaks are assigned to the electronic orbitals of Zn $2p_{3/2}$ and Zn $2p_{1/2}$.^{42,43} The high-resolution spectra of N 1s (Fig. 2h) show four peaks. The three peaks located at 396.1, 397.4 and 400.2 eV can be ascribed to the Ti–N, Ti–O–N and N–O bonds, suggesting that the nitrogen atom is successfully doped in the TiO₂ lattice.^{25,44–46} Meanwhile, the other peak located at 398.7 eV belongs to the metal–N bond (including two chemical bonds

Ni–N and Zn–N), further confirming that Ni_3 ZnN is loaded on the surface of N–TiO₂.^{47,48} On the basis of these results, it is reasonable to infer that the N–TiO₂–Ni₃ZnN nanocomposites have indeed been formed.

The morphologies and microstructures of a series of samples are observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As displayed in Fig. 3a, the TiO_2 precursor has a uniform and spherical morphology with diameters of around 480–630 nm (Fig. S5a[†]) and with fairly smooth surfaces. After the calcina-



Fig. 3 SEM images of (a) the TiO₂ precursor, (b) TiO₂, (c) N-TiO₂ and (d) N-TiO₂-7%Ni₃ZnN. TEM images of (e) N-TiO₂ and (g) N-TiO₂-7%Ni₃ZnN. HRTEM images of (f) N-TiO₂ and (h) N-TiO₂-7%Ni₃ZnN.

tion procedure in air, as revealed in Fig. 3b, TiO₂ continues to have a spherical morphology but the surface of the nanospheres becomes relatively rough. Meanwhile, the average size of the TiO₂ nanospheres shrinks to 280-390 nm (Fig. S5b[†]) due to the decomposition of surfactants.⁴⁹ After being treated in an NH₃ atmosphere, the morphology and size of the N-TiO₂ sample are found to be almost the same as those of the TiO₂ sample (Fig. 3c and Fig. S5c[†]). Fig. 3d and Fig. S4[†] show the morphology of the N-TiO₂-Ni₃ZnN nanocomposites with different weight ratios of Ni₃ZnN. It is clear that the Ni₃ZnN nanoparticles are loaded on the surface of the N-TiO₂ nanospheres and the distribution density increases with the increase of the mass ratio (the inset images of Fig. 3d and Fig. S4[†]). Notable is the fact that, compared with the pure Ni₃ZnN sample whose average size is about 330 nm, the size of the Ni₃ZnN nanoparticles loaded on the N-TiO₂ nanospheres' surface is significantly reduced (Fig. S6[†]). Moreover, with the increase of Ni₃ZnN content, the nanoparticle size of Ni₃ZnN increases slightly. Therefore, it can be considered that N-TiO₂ as a carrier effectively regulates the size of ternary Ni₃ZnN.

The TEM image of the pure N-TiO₂ sample reveals its spherical morphology which is composed of small nanoparticles (Fig. 3e). The high-resolution TEM (HRTEM) image of the pure N-TiO₂ sample shows only one lattice fringe with a spacing of 0.352 nm; this corresponds to the (101) facet of anatase TiO₂ (Fig. 3f). The TEM image (Fig. 3g) indicates the successful loading of the Ni₃ZnN nanoparticles and the intimate contact between the Ni₃ZnN nanoparticles and TiO₂ nanospheres. The size of the Ni₃ZnN nanoparticles in the TEM image is about 50-60 nm, which is consistent with the SEM image. In addition, the HRTEM image of the nanocomposite is shown in Fig. 3h. An interplanar distance of 0.352 nm corresponds to the (101) facet of anatase TiO₂ and an interplanar distance of 0.217 nm can be assigned to the (111) facet of the Ni₃ZnN nanoparticles (Fig. 3g). These results also clearly indicate that Ni₃ZnN is successfully loaded on the surface of N-TiO₂.

UV-Vis diffuse reflectance spectra (DRS) are recorded to determine the optical absorption properties of the samples (Fig. S7^{\dagger}). It can be seen that the TiO₂ sample exhibits intrinsic band gap absorption with an absorption edge onset at 410 nm. This corresponds to a band gap (E_{α}) of about 3.02 eV. It is evident that after being treated in an NH₃ atmosphere the N-TiO₂ sample exhibits increased optical absorption compared to the pure TiO₂ sample, with an obvious red shift in the absorption edge (from 410 nm to 455 nm). The corresponding band gaps are reduced from 3.02 eV to 2.72 eV. All N-TiO2-Ni₃ZnN nanocomposites show a marked enhancement in the visible-light region as compared to the pure N-TiO₂ sample, suggesting that the loading of Ni₃ZnN resulted in advantageous optical absorption. With the increased weight addition of Ni₃ZnN, the visible light absorption of the nanocomposites is enhanced gradually and the absorption edge is red shifted gradually (from 455 nm to 491 nm). The corresponding band gaps are reduced from 2.72 eV to 2.52 eV. This result is due to

the formation of a close contact between $\rm Ni_3ZnN$ and $\rm N-TiO_2$ which is in agreement with the TEM image. 50

To investigate the photocatalytic performance of a series of N-TiO₂ based samples, their photocatalytic H₂ evolution performance under visible light irradiation ($\lambda \ge 400$ nm) is evaluated with triethanolamine (TEOA) as a sacrificial electron donor. The control experiment shows that H₂ evolution is not detected without irradiation or a catalyst, suggesting that H₂ evolution is a light driven catalytic reaction (Fig. S8[†]). Meanwhile, the pure Ni₃ZnN sample due to its property of being a metal conductor shows no H₂ generation under visible light irradiation. As shown in Fig. 4a, the pure N-TiO₂ sample shows a quite low hydrogen production rate (1.7 μ mol g⁻¹ h⁻¹) under visible light irradiation owing to the rapid recombination of photo-generated electrons and holes. Obviously, the photocatalytic H₂ evolution rate is prominently enhanced when the Ni₃ZnN nanoparticles are loaded on the surface of the N-TiO₂ sample. This indicates that the Ni₃ZnN nanoparticles can effectively improve the photocatalytic activity. The optimum loading content of the Ni3ZnN nanoparticles is found to be about 7 wt% and the H₂ generation rate is 55.3 μ mol g⁻¹ h⁻¹, which is 33-fold higher than that of the pure N-TiO₂ sample. The optimal turnover number (TON) is 0.2 for Ni_3ZnN in one hour. Notably, the excess Ni_3ZnN nanoparticles (more than 7 wt%) loaded on the N-TiO2 surface will lead to relative reduction in the photocatalytic H₂ generation rate. This may be due to the fact that a high amount of Ni₃ZnN nanoparticles not only shields the incident light but also induces the formation of recombination centers for the photogenerated electron-hole pairs.33,51,52 Notably, Ni3ZnN as a high-efficiency co-catalyst has a comparable or superior



Fig. 4 (a) The average rates of H₂ evolution under visible-light ($\lambda \ge 400 \text{ nm}$) over N-TiO₂ based samples. (b) Stability examination of H₂ production (evacuation every 4 h) by the N-TiO₂-7%Ni₃ZnN sample. The photocatalytic performance of the N-TiO₂ and N-TiO₂-7%Ni₃ZnN samples for the reduction of (c) 4-nitrophenol and (d) Cr(v).

efficiency to those of Pt and most previously reported non-noble-metal co-catalysts (Fig. S9 and Table S1[†]).

The photocatalytic stability of the N–TiO₂–7%Ni₃ZnN sample for H₂ generation has been confirmed by long-duration experiments (Fig. 4b), which is as important as photocatalytic activity from the perspective of practical application. The nanocomposite shows a linear increase in the rates of H₂ evolution during the photocatalytic reaction. After six consecutive reaction recycles (24 h in total), there is no significant decrease observed in H₂ production, which indicates the superior stability of the N–TiO₂–Ni₃ZnN nanocomposites. The morphologies and crystal structures of the fresh and used N–TiO₂–7%Ni₃ZnN sample have been researched comparatively in Fig. S10.† The crystal structure and morphology of the nanocomposite show no change before and after the photocatalytic reaction. All the above results suggest the photo-stability of the N–TiO₂–Ni₃ZnN nanocomposites under visible light irradiation.

In order to further examine the co-catalytic efficiency of Ni₃ZnN, other typical photocatalytic reactions such as photocatalytic reduction of 4-nitrophenol and Cr(vi) are researched under visible light irradiation. Fig. 4c reveals the photocatalytic activities of the pure N-TiO2 and N-TiO2-7%Ni3ZnN samples toward the photocatalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). After 120 min of visible light irradiation, the 4-NP conversion rate of the N-TiO₂-7%Ni₃ZnN sample reaches 73%, much higher than that of the pure N-TiO₂ (trace). A similar trend is achieved toward the photocatalytic reduction of Cr(vi) to Cr(iii) for the N-TiO₂ and N-TiO₂-7%Ni₃ZnN samples. As shown in Fig. 4d, the Cr(vi) reduction rate of N-TiO2-7%Ni3ZnN reaches 75% after 240 min of visible light irradiation, while the reduction rate of pure N-TiO₂ is only 43%. Such results indicate that Ni₃ZnN can be used as a multi-functional co-catalyst to effectively enhance the activity of photocatalysts in different photocatalytic reactions.

The N₂ adsorption–desorption isotherms and pore size distribution curves of the N–TiO₂ and N–TiO₂–7%Ni₃ZnN samples are shown in Fig. S11 and Table S2.† The type III isotherms with type H3 hysteresis loops are observed for both samples, suggesting the existence of mesoporous structures in the as-prepared samples.⁵³ Notably, the specific surface area of the N–TiO₂–7%Ni₃ZnN sample (5.78 m² g⁻¹) is similar to that of the pure N–TiO₂ sample (6.45 m² g⁻¹). This means that the specific surface area hardly contributes to the enhanced photocatalytic H₂ evolution performance of N–TiO₂–Ni₃ZnN.

To decipher the reason for the promoted photocatalytic activity of the N–TiO₂–Ni₃ZnN nanocomposites, a series of photoluminescence and photo-electrochemical studies are conducted. Fig. 5a shows the periodic on/off transient photo-current response (*I*–*t* curves) of the pure N–TiO₂ and N–TiO₂–7%Ni₃ZnN samples under intermittent visible light irradiation. The N–TiO₂–7%Ni₃ZnN nanocomposite shows an about 2.5 fold enhancement of photocurrent density compared to the pure N–TiO₂ sample, indicating that a higher separation efficiency of the photon-generated carriers has been achieved after loading Ni₃ZnN on the N–TiO₂ sample.^{52,54} The cyclic vol-



Fig. 5 (a) Transient photocurrent response, (b) cyclic voltammetry curves, (c) photoluminescence spectra ($\lambda_{ex} = 360$ nm), (d) electrochemical impedance spectra, (e) Specific capacitance performance and (f) polarization curves of N–TiO₂ and N–TiO₂–7%Ni₃ZnN samples.

tammogram (CV) curves (Fig. 5b) of the N-TiO₂ and N-TiO₂-7%Ni₃ZnN samples show two reversible anodic and cathodic peaks corresponding to the one-electron redox process. Because the preparation of the electrodes and electrolyte is identical for the measurements, the current density of the electrodes (and differences thereof) is related to the electron transfer rate of the electrode materials.55,56 That the N-TiO2-7% Ni₃ZnN nanocomposite shows a higher current density than the pure N-TiO₂ sample means that promoted electron transfer efficiency has been achieved due to the introduction of Ni₃ZnN.⁵⁷ The photoluminescence (PL) spectra of the pure and nanocomposite samples at an excitation wavelength of 360 nm are shown in Fig. 5c. The loading of Ni₃ZnN on the surface of N-TiO₂ can decrease the PL intensity, indicating the beneficial roles of Ni₃ZnN in the efficient inhibition of the recombination process of photo-generated carriers.58,59 The electrochemical impedance spectra (EIS) are used to research the charge carrier transfer properties of the electrode materials at solid/electrolyte interfaces (Fig. 5d). Obviously, the semicircle radius of the N-TiO2-7%Ni3ZnN nanocomposite is much smaller than that of the pure N-TiO₂ sample, demonstrating that the Ni₃ZnN co-catalyst can greatly reduce the interfacial charge transfer resistance and enhance the migration efficiency of charge carriers.^{60,61}

The specific capacitance performance test of the as-prepared samples has been performed to further understand the

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underlying reason for the enhanced separation efficiency of charge carriers. As shown in Fig. 5e, the area of curves of the N-TiO₂-7%Ni₃ZnN sample is obviously larger than that of the pure N-TiO₂ sample, indicating that the nanocomposite has a much larger capacitance. The enhanced specific capacitance of the pure N-TiO₂ sample by Ni₃ZnN is better for storing electrons from the excited N-TiO₂ constituent, thus enhancing the separation of the electron-hole pairs and finally improving the photocatalytic efficiency.^{62,63} Moreover, the electrochemically active surface area of the pure N-TiO₂ and N-TiO₂-7%Ni₃ZnN samples is studied by measuring the electrochemical doublelayer capacitance (Fig. S12[†]). The results reveal that loading Ni₃ZnN on the N-TiO₂ sample increases the electrochemical surface area and results in more active sites for the reaction, which contribute to improving the photocatalytic activity.⁴¹ The polarization curves of the pure N-TiO₂ and N-TiO₂-7% Ni₃ZnN samples are researched to further understand the function of Ni₃ZnN for improving the photocatalytic activity (Fig. 5f). The evidently higher current density of the N-TiO₂-7%Ni₃ZnN nanocomposite than that of the pure sample indicates that ternary Ni₃ZnN as a co-catalyst can effectively decrease the H₂ evolution over-potential and enhance the charge transfer kinetics.64,65

Density functional theory (DFT) calculations are carried out to further pinpoint the origin of the excellent co-catalytic performance of Ni_3ZnN for the photocatalytic reaction. The atomic structure model of Ni_3ZnN is shown in Fig. 6a; it possesses a simple cubic structure. Fig. 6b exhibits the densities of states (DOS) of Ni_3ZnN . It is clear that the d orbitals of the Ni atoms make a major contribution to the total DOS near the Fermi level. Successive contribution of the p orbitals of the N atoms to the partial DOS is also observed, suggesting a covalent interaction among Ni, Zn, and N in the energy region between -5 and -8 eV.^{66} On the other hand, the band struc-



Fig. 6 (a) Total and partial electronic density of states (TDOS and PDOS) calculated for Ni₃ZnN. The Fermi level is set at 0 eV. (b) The atomic structure model of Ni₃ZnN. (c) Mott–Schottky plots of the N–TiO₂–7%Ni₃ZnN sample. (d) Schematic illustration of the photo-induced charge separation process in the N–TiO₂–Ni₃ZnN samples.

ture of Ni₃ZnN is consecutive near the Fermi level, which demonstrates the metallic nature of Ni₃ZnN.^{67,68} Therefore, the superior activity of the N–TiO₂–Ni₃ZnN nanocomposite sample might be due to the metallic characteristics of Ni₃ZnN, which enhance its electrical conductivity and accordingly promote the charge carrier transport, thus enhancing the charge transfer kinetics and further improving the photocatalytic activity.^{68,69}

The relative band positions of the as-prepared sample are investigated using Mott–Schottky plots. As shown in Fig. 6c, the flat-band potential of the N–TiO₂–7%Ni₃ZnN sample is estimated to be around –0.79 V vs. Ag/AgCl (*i.e.* –0.19 V vs. NHE). The N–TiO₂–7%Ni₃ZnN sample exhibits a positive slope of the linear plots, and thus it is an n-type semiconductor.⁷⁰ Generally the conduction band (CB) potentials of an n-type semiconductor are considered to be more negative than its flat-band potential by –0.2 V, and thus the $E_{\rm CB}$ of the nanocomposite is speculated to be –0.39 V vs. NHE.^{33,71} Combined with the band-gap energy of the N–TiO₂–7%Ni₃ZnN sample (Fig. S7b†), the valence band (VB) potential is found to be 2.18 V vs. NHE ($E_{\rm VB} = E_{\rm CB} + E_{\rm g}$).⁷²

Based on all the above discussions, a tentative reaction mechanism and charge transfer process of the N-TiO2-Ni3ZnN photocatalytic system are illustrated in Fig. 6d. Under the illumination of visible light, the active constituent N-TiO₂ is excited to produce the electron-hole pairs. Due to the metalliclike properties and conductivity of the ternary transition metal nitride Ni₃ZnN, the photo-generated electrons readily transfer to Ni₃ZnN from the conduction band of N-TiO₂ by a close interfacial contact between N-TiO₂ and Ni₃ZnN and catalyze the photocatalytic reduction reactions (reduction of H₂O, 4-nitrophenol and Cr(vi)). Simultaneously, the photo-generated holes from the valence band of the N-TiO₂ sample are trapped by the hole scavenger. Ni₃ZnN with the low Fermi level and excellent electronic storage capability can continually trap the electrons, thus efficiently promoting the separation and transfer of the photo-generated electrons. Taken together, such a ternary transition metal nitride Ni₃ZnN with a variety of excellent properties as a multi-functional co-catalyst can dramatically improve the photocatalytic activity in different photocatalytic reactions over N-TiO2-Ni3ZnN systems.

4. Conclusions

In summary, we reported a novel anti-perovskite-type bimetallic transition metal nitride Ni_3ZnN as a multi-functional non-noble-metal co-catalyst for improving the photocatalytic activity of N–TiO₂ in different photocatalytic reactions. This N– TiO₂– Ni_3ZnN nanocomposite shows a much higher photocatalytic activity than the pure N–TiO₂ sample toward not only photocatalytic water splitting hydrogen evolution but also the reduction of 4-nitrophenol and Cr(v₁). Both experimental results and DFT calculations show that Ni_3ZnN effectively enhances the charge transfer kinetics and promotes the separation of photo-generated electrons and holes, thus obviously improving the photocatalytic activity. In addition, the N-TiO₂-Ni₃ZnN nanocomposite also exhibits excellent stability and recyclability. This work opens up new vistas for development and deployment of novel low-cost, multi-functional, co-catalysts to enhance the photocatalytic activity in solar energy conversion.

Conflicts of interest

The authors declare that they have no conflict of interest.

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