Enhancement of photocurrent and photocatalytic activity of ZnO hybridized with graphite-like C\textsubscript{3}N\textsubscript{4}†

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A ZnO photocatalyst was hybridized with graphite-like C\textsubscript{3}N\textsubscript{4} via a monolayer-dispersed method. After hybridization with C\textsubscript{3}N\textsubscript{4}, the photocurrent of ZnO was enhanced by 5 times under UV irradiation and a photocurrent under visible light irradiation was observed. The photocatalytic activity of C\textsubscript{3}N\textsubscript{4}/ZnO under UV irradiation was increased by 3.5 times, the visible light photocatalytic activity was generated and the photocorrosion of ZnO was suppressed completely after ZnO was hybridized with C\textsubscript{3}N\textsubscript{4}. The enhancement in performance and photocorrosion inhibition under UV irradiation was induced by the high separation efficiency of photoinduced holes from ZnO to the HOMO of C\textsubscript{3}N\textsubscript{4}. Under visible light irradiation, the electron excited from the HOMO to the LUMO of C\textsubscript{3}N\textsubscript{4} could directly inject into the CB of ZnO, making C\textsubscript{3}N\textsubscript{4}/ZnO present visible light photocatalytic activity. The optimum synergetic effect of C\textsubscript{3}N\textsubscript{4}/ZnO was found at a weight ratio of 3%, which corresponded to a monolayer dispersion of C\textsubscript{3}N\textsubscript{4} on the surface of ZnO.

Introduction

In recent years, photocatalysis has attracted much attention in water treatment due to its total destruction ability of pollutants and broad compound applicability. Among various semiconductor materials in present research, although TiO\textsubscript{2} has been extensively investigated and widely employed, ZnO appears to be a suitable alternative to TiO\textsubscript{2}. ZnO is also relatively inexpensive and its photodegradation mechanism is similar to that of TiO\textsubscript{2}. Moreover, some studies have highlighted that ZnO exhibits a higher efficiency than TiO\textsubscript{2} in the photocatalytic degradation of some dyes in water and photoelectric conversion. However, the high recombination ratio of photoinduced electron–hole pairs, very poor response to visible light and the photocorrosion have hindered the application of ZnO in photocatalysis. Some effort has been devoted to reducing the recombination of photogenerated electron–hole pairs and improving the utilization of solar light of ZnO, such as doping, deposition of metals, or combining ZnO with another semiconductor. It is anticipated that ZnO could become an excellent photocatalyst if the photocorrosion can be suppressed. However, few reports have focused on this topic. It has been reported by He and co-workers that a ZnO/reduced graphite oxide composite exhibited higher photocatalytic activity and a photocorrosion improvement. Comparelli and co-workers found that surface organic coating of ZnO could provide the oxide with photocorrosion resistance and pH variation.

Materials with delocalized conjugated \pi structures have been extensively studied in electron-transfer processes due to their rapid photoinduced charge separation and a relatively slow charge recombination. A delocalized conjugated \pi structure material combined with a semiconductor may act as a novel “dyade” type structure which could form a common conjugated...
Opaque powder was obtained after drying at 100 °C in a fume hood for 24 h. After volatilization of the methanol, an ZnO powder was added into the above solution and stirred in an ultrasonic bath for 30 min to completely disperse the C3N4. The photocatalytic activity of ZnO was enhanced via dye-sensitization, and metal-modification, and combination of C3N4 with a metal to form heterojunctions.

C3N4 has a conjugated π structure and the combination of ZnO and C3N4 may be an ideal system to achieve an enhanced charge separation in electron-transfer processes and suppress the photocorrosion. To the best of our knowledge, there has been no report regarding the introduction of C3N4 to ZnO to enhance the photocatalytic activity and suppress the photocorrosion. Herein, we present the first example of a C3N4-hybridized ZnO photocatalyst fabricated by the chemisorption method and demonstrate that a hybrid effect exists between ZnO and C3N4. The possible mechanisms of photocorrosion inhibition and enhancement of photocatalytic activity via hybridization were also investigated.

**Experimental section**

**Preparation of the C3N4/ZnO photocatalyst**

Melamine (C3H6N6) was purchased from Sinopharm Chemical Reagent Corp, P. R. China; ZnO (particle diameter 20 nm, surface area 37.741 m² g⁻¹) was obtained from Nanjing Haitai Nanometer Materials Corp, P. R. China. All other reagents used in this research were analytically pure and used without further purification. The C3N4 used in this study was prepared by heating melamine to 550 °C for 2 h in N2 atmosphere according to the literature. The typical preparation of C3N4/ZnO photocatalysts was as follows: firstly, an appropriate amount of C3N4 was added into methanol then the beaker was placed in an ultrasonic bath for 30 min to completely disperse the C3N4. The ZnO powder was added into the above solution and stirred in a fume hood for 24 h. After volatilization of the methanol, an opaque powder was obtained after drying at 100 °C in N2 atmosphere. According to this method, different mass ratios of C3N4/ZnO photocatalysts from 1% to 8% were synthesized.

To investigate the transition of photogenerated electrons before and after C3N4 hybridization, ZnO and C3N4/ZnO electrodes were prepared as follows: 5 mg of the as-prepared photocatalyst was suspended in 5 mL ethanol to produce a slurry, which was then dip-coated onto a 2 cm × 4 cm indium-tin oxide (ITO) glass electrode. Electrodes were exposed to UV light for 12 h to eliminate ethanol and subsequently calcined at 200 °C for 30 min under N2 flow (rate = 60 mL min⁻¹). All investigated electrodes were of similar thickness (0.8–1.0 μm).

**Characterization**

Fourier transform infrared (FT-IR) spectra were measured by a Perkin Elmer System 2000 infrared spectrometer with KBr as the reference sample. The morphologies and structure of the as-prepared samples were examined with transmission electron microscopy (TEM) by a JEM 1010 electron microscope operated at an accelerating voltage of 100 kV. The high-resolution transmission electron microscopy (HRTEM) images were obtained by Tecnai TF20 transmission electron microscope operated at an accelerating voltage of 200 kV. UV-Vis diffuse reflectance spectroscopy (DRS) was carried out on a Hitachi U-3010 UV-Vis spectrophotometer. BaSO4 was the reference sample. The Brunauer-Emmett-Teller (BET) surface area was measured by ASAP 2010 V5.02H. The crystallinity of the as-prepared sample was characterized by X-ray diffraction (XRD) on Bruker D8-advance diffractometer using Cu-Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TG) was performed in air at a heating rate of 10 °C min⁻¹ on a Dupont 1090 thermal analyzer. The concentration of Zn²⁺ in the solution of ZnO and the C3N4/ZnO photocatalytic system was measured as follows: at certain time intervals, 10 mL aliquots were sampled and centrifuged 5 times to remove all the particles. The filtrates were determined on a Thermofisher IRIS Intrepid II XSP ICP-OES instrument. The total organic carbon (TOC) was measured with a Tekmar Dohrmann Apollo 9000 TOC analyzer. The photocurrents were measured on an electrochemical system (CHI-660B, China). UV light was obtained from an 11 W germicidal lamp and visible irradiation was obtained from a 500 W xenon lamp (Institute for Electric Light Sources, Beijing) with a 450 nm cutoff filter. A standard three-electrode cell with a working electrode (as-prepared photocatalyst), a platinum wire as counter electrode, and a standard calomel electrode (SCE) as reference electrode were used in the photoelectric studies. 0.1 M Na₂SO₄ was used as the electrolyte solution. Potentials are given with reference to the SCE. The photoresponses of the photocatalysts as light on and off were measured at 0.0 V.

**Photocatalytic experiments**

The photocatalytic activities were evaluated by the decomposition of MB under UV light (λ = 254 nm) and visible light irradiation. The radial flux was measured by a power meter from the Institute of Electric Light Sources, Beijing. UV light was provided by an 11 W UV-light lamp (Institute of Electric Light Sources, Beijing) and the average light intensity was 0.8 mW cm⁻². An aqueous solution of MB (100 mL, 10 mg L⁻¹) was placed in a vessel, and 50 mg photocatalyst was added. Prior to irradiation, the suspensions were magnetically stirred in the dark for about 30 min. At certain time intervals, 2 mL aliquots were sampled and centrifuged to remove the particles. The filtrates were analyzed by recording variations of the maximum
absorption peak (663 nm for MB) using a Hitachi U-3010 UV-vis spectrophotometer. To estimate the photostability of the photocatalysts, 96 h persistent MB degradation of ZnO and C$_3$N$_4$/ZnO-2% were performed. At certain time intervals (24 h, 48 h and 96 h), the MB degradation performance of ZnO and C$_3$N$_4$/ZnO-2% was determined. The visible light was obtained by a halogen-tungsten lamp (provides visible light in the range of 400–800 nm; the main wavelength is about 550 nm) and the average visible light intensity was 1.2 mW cm$^{-2}$. The method was similar with the UV light degradation. The active species generated in the photocatalytic system could be detected through trapping by tert-butyl alcohol (t-BuOH) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na).

**Results and discussion**

**Enhancement of photocatalytic activity and photocurrent**

Fig. 1 shows the photocatalytic activity of ZnO and the C$_3$N$_4$/ZnO photocatalysts with different loading amounts of C$_3$N$_4$ under UV light and visible light irradiation, respectively. The mechanically blended C$_3$N$_4$ and ZnO (3%) were used as a reference. The photocatalytic degradation process was fitted to pseudo-first-order kinetics, and the value of the rate constant $k$ is equal to the corresponding slope of the fitting line. As can be seen in Fig. 1A, the photocatalytic activity of the blended C$_3$N$_4$ and ZnO sample was almost the same as that of the pure ZnO, whereas all of the C$_3$N$_4$/ZnO photocatalysts exhibited higher photocatalytic activity than the pure ZnO sample under UV light irradiation. The photocatalytic activity was enhanced gradually with the increasing proportion of C$_3$N$_4$. When the proportion of C$_3$N$_4$ reached 3%, the as-prepared photocatalyst exhibited the highest photocatalytic activity. The apparent rate constant $k$ was 0.0379 min$^{-1}$ and was almost 3.5 times as high as that of pure ZnO. However, further increasing the proportion of C$_3$N$_4$, the degradation rate decreased gradually though it remained higher than that of ZnO. It can also be seen from the insert graph of Fig. 1A that the loading amount of C$_3$N$_4$ had a great influence on the photocatalytic activity of the as-prepared photocatalysts. The optimal loading amount of C$_3$N$_4$ on the surface of ZnO was 3%.

To further understand the mineralization property of the as-prepared photocatalyst, the decrease of TOC in the photo-degradation of MB by ZnO and C$_3$N$_4$/ZnO-3% photocatalysts was determined (see supplementary data Figure S1†). It was found that the TOC removal percentage is 64% and 32% for C$_3$N$_4$/ZnO-3% and ZnO after 2 h photocatalytic reaction, respectively. After C$_3$N$_4$ modification, the mineralization property of ZnO was evidently enhanced. Under visible light irradiation, since ZnO could not be excited by visible light irradiation, the pure ZnO played no role in degrading MB. After modification with C$_3$N$_4$, ZnO possessed excellent visible light photocatalytic activity (see Fig. 1B), and the photocatalytic activity is much higher than that of pure C$_3$N$_4$. The C$_3$N$_4$/ZnO-3% photocatalyst could degrade MB by 72.3% in 5 h. It was notable that the mechanical blend did not obviously enhance the photocatalytic activity of ZnO, implying that there may be some interaction between ZnO and C$_3$N$_4$ that plays an important role in improving the photocatalytic activity.

Photocurrents were measured for C$_3$N$_4$/ZnO-3% and ZnO electrodes to investigate the electronic interaction between C$_3$N$_4$ and ZnO (Fig. 2). It was clear that fast and uniform photocurrent responses were observed in both electrodes and the photocurrent enhancement of the as-prepared photocatalyst showed a noticeable photocurrent under visible light irradiation (Fig. 2B). Under visible light irradiation, ZnO showed almost no photocurrent response. On the contrary, C$_3$N$_4$/ZnO-3% photocatalyst showed a noticeable photocurrent under visible light irradiation (Fig. 2B). The photocurrent enhancement of the C$_3$N$_4$/ZnO photocatalyst indicated an enhanced photoinduced electrons and holes separation, which could be attributed to the synergetic effect of C$_3$N$_4$ and the ZnO semiconductor.

**Photocorrosion suppression**

To estimate the photostability of the photocatalysts, 96 h persistent MB degradation of ZnO and C$_3$N$_4$/ZnO-2% was performed, and the rate constant $k$ at a certain reaction time is shown in Fig. 3. Under UV light irradiation, 72% of MB could be degraded in 2 h when ZnO was used for the first time. After 24 h of photocatalytic reaction, a sharp decrease of photocatalytic activity of pure ZnO can be seen from Fig. 3 and the reaction rate constant $k$ decreased from 0.0107 min$^{-1}$ to 0.0052 min$^{-1}$. After
To further investigate the suppression of photocorrosion, XRD patterns, TEM images and ICP-OES were determined before and after photocatalytic reaction. Figure S2 shows the XRD patterns of ZnO and C3N4/ZnO-2% before and after 48 h photocatalytic reaction. For pure ZnO, after 48 h photocatalytic reaction, new diffraction peaks appeared at 27.7°, 32.8°, and 60.1°, which could be attributed to the Zn3(OH)2(CO3)2 phase. The crystalline phase structure of ZnO was obviously destroyed, indicating that severe photocorrosion had taken place. However, the XRD patterns of C3N4/ZnO-2% showed no notable differences before and after 48 h photocatalytic reaction. The TEM images of ZnO and C3N4/ZnO-2% photocatalysts before and after 48 h reaction are shown in Figure S3. Before reaction, the ZnO and C3N4/ZnO-2% samples consisted of agglomerated approximately spherical particles with diameters of 20 nm. After 48 h photocatalytic reaction, for pure ZnO, only loose floccule existed, indicating that the structure of the ZnO crystal had been seriously destroyed. In contrast, for the C3N4/ZnO-2% sample before and after 48 h photocatalytic reaction, it had not exhibited any great changes in morphology, revealing that C3N4-hybridized ZnO was photostable and the photocorrosion was successfully suppressed.

The concentrations of Zn2+ in the solution of ZnO and the C3N4/ZnO-2% photocatalytic system before and after photocatalytic reaction are shown in Table 1. After 4 h of reaction, the concentration of Zn2+ was 9.485 µg mL−1 and 7.264 µg mL−1 in ZnO and C3N4/ZnO-2% photocatalytic solution, respectively. After 24 h of photocatalytic reaction, the concentration of Zn2+ was 389.500 µg mL−1 in the solution of the ZnO photocatalytic system, indicating that the structure of ZnO was destroyed and a large amount of ZnO particles was dissolved in the solution. Interestingly, after 24 h of photocatalytic reaction, the concentration of Zn2+ was 8.078 µg mL−1 in the solution of C3N4/ZnO-2% photocatalytic system which was not evidently different from that after 4 h reaction. The ICP results were in good agreement with the results of TEM and XRD, further revealing that the presence of C3N4 on the ZnO surface could effectively suppress the photocorrosion of ZnO during the photocatalytic reaction.

### Structure and morphology of C3N4/ZnO photocatalysts

Fig. 4 shows an HRTEM image of C3N4/ZnO-3% photocatalyst. As can be seen from Fig. 4, the lattice structure of ZnO was very orderly and the outer boundary of the as-prepared sample was distinctly different from the ZnO core. The measured interplanar spacing is 0.136 nm which corresponds to the ZnO (201) plane. The thickness of the C3N4 layer coated on the C3N4/ZnO-3% sample was about 0.354 nm, which is close to the scale of ZnO.

### Table 1  The concentrations of Zn2+ in the solutions of ZnO and the C3N4/ZnO-2% photocatalytic system before and after different times of photocatalytic reaction

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Before reaction (µg mL−1)</th>
<th>After 4 h reaction (µg mL−1)</th>
<th>After 24 h reaction (µg mL−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1.940</td>
<td>9.485</td>
<td>389.500</td>
</tr>
<tr>
<td>C3N4/ZnO-2%</td>
<td>1.247</td>
<td>7.264</td>
<td>8.078</td>
</tr>
</tbody>
</table>
monolayer C₃N₄ (about 0.325 nm). Therefore, it can be inferred that the C₃N₄ molecule was dispersed on the surface of ZnO with an approximately monolayer structure.

The amount of C₃N₄ could be obtained by TG analysis (Figure S4†). For pure ZnO, a weight loss occurring from 200 °C to 500 °C could be attributed to the desorption of surface bound water. For pure C₃N₄, two weight loss regions could be seen in the TG curve. The first weight loss could also be attributed to the desorption of surface bound water. The second weight loss occurring from 500 °C to 720 °C could be assigned to the burning of C₃N₄. These two weight loss regions could be seen in all C₃N₄/ZnO samples. The amount of C₃N₄ hybridized on the surface of ZnO could be calculated from the second weight loss and is shown in the insert of Figure S4. Except for the C₃N₄/ZnO-8% sample, the amount of C₃N₄ was nearly consistent to the dosage of C₃N₄ added.

The XRD patterns of ZnO, C₃N₄ and various C₃N₄/ZnO photocatalysts are shown in Fig. 5. As can be seen from Fig. 5 the crystal phase of ZnO did not change after hybridization. All the diffraction peaks of the ZnO can be exactly indexed as the zincite structure (JCPDS 89-1397). There was no crystalline C₃N₄ in the C₃N₄/ZnO photocatalysts with low C₃N₄ loadings, whereas the as-prepared samples with higher C₃N₄ loadings (>3%) exhibited a crystalline C₃N₄ peak; the peak intensities increased with the increase in C₃N₄ loading. Thus, it can be inferred that C₃N₄ was dispersed uniformly on the ZnO surface with low C₃N₄ loadings, while crystalline C₃N₄ appeared only if its loading exceeded a threshold value (3%).

The UV-vis DRS spectra of ZnO and different mass ratios of C₃N₄/ZnO photocatalysts are shown in Fig. 7. As expected, a sharp fundamental absorption edge rises at 410 nm for ZnO. Compared with that of pure ZnO, the C₃N₄/ZnO photocatalysts show the same absorbance edge, but extend the absorbance to the visible region due to the presence of C₃N₄ on the ZnO surface. The absorption edge does not shift for all C₃N₄/ZnO samples, indicating identical band gap energies. The absorption intensity of the prepared samples increases with increasing amounts of C₃N₄.

Mechanism of enhancement of photoactivity and photocorrosion suppression under UV irradiation

It is well known that the photocatalytic activity is mainly governed by phase structure, adsorption ability, and separation efficiency of photogenerated electrons and holes. As can be seen from the XRD spectra, the crystal phase structure of ZnO was not changed during the hybridization. An adsorption experiment was performed to evaluate the adsorption ability of the ZnO and C₃N₄/ZnO photocatalysts in the dark (see Figure S5†). As can be seen from Figure S5† after equilibration in the dark for 10 min, 89.2% and 74.9% of MB remained in the solution with pure ZnO and C₃N₄/ZnO-3% photocatalyst, respectively. However, there were no significant changes in the BET surface area (37.741 and 37.832 m² g⁻¹ for ZnO and C₃N₄/ZnO-3% photocatalyst, respectively.

Fig. 4 HRTEM image of C₃N₄/ZnO-3% photocatalyst.

Fig. 5 XRD of ZnO, C₃N₄ and C₃N₄/ZnO photocatalysts.

Fig. 6 FT-IR spectra of ZnO, C₃N₄ and C₃N₄/ZnO photocatalysts.

Fig. 7 UV-vis DRS spectra of ZnO and various C₃N₄/ZnO photocatalysts.
indicating the MB adsorption should not just originate from simply physical adsorption. The enhancement of adsorption could be contributed to the π–π stacking between MB and C$_3$N$_4$, which was similar to the conjugation between aromatic molecules and graphene. MB molecules could be adsorbed on the C$_3$N$_4$ surface with offset face to face orientation via π–π conjugation until an adsorption–desorption equilibrium is reached. The enhanced adsorptivity was a good supplement for the high photocatalytic activity of the hybridized C$_3$N$_4$/ZnO photocatalyst.

It is important to detect the main oxidative species in the photocatalytic process for revealing the photocatalytic mechanism. The main oxidative species in the photocatalytic process could be detected through the trapping experiments of radicals and holes by using t-BuOH (radical scavenger) and EDTA-2Na (hole scavenger), respectively. As shown in Fig. 8A, in the ZnO system, the addition of a scavenger of radicals (t-BuOH) only caused a small change in the photodegradation of MB. On the contrary, the photocatalytic activity of ZnO could be greatly suppressed by the addition of a scavenger for holes (EDTA-2Na). This result suggested that the photogenerated holes were the main oxidative species of the ZnO system. In the C$_3$N$_4$/ZnO system (see Fig. 8B), the photocatalytic activity was greatly prevented by the EDTA-2Na, indicating the main oxidative species is the same as that of ZnO.

As discussed above, the crystal phase structure and surface area was not evidently changed and the limited adsorptivity enhancement was not the major factor of the significant enhancement of the photocatalytic activity of ZnO (enhanced about 3.5 times). The significant enhancement of photocatalytic activity was mainly due to the high efficiency of charge separation induced by the hybrid effect of C$_3$N$_4$ and ZnO. A schematic for electron–hole separation and transportation at the C$_3$N$_4$/ZnO photocatalyst interface is shown in Fig. 9. ZnO can be excited by UV light and produce photogenerated electron–hole pairs, showing photocatalytic activity. Since the valence band (VB) position of ZnO is lower than the highest occupied molecular orbital (HOMO) of C$_3$N$_4$, the photogenerated holes on ZnO could directly transfer to C$_3$N$_4$, making charge separation more efficient and reducing the probability of photogenerated electron–hole recombination, leading to an enhanced photocatalytic activity.

As shown above, beyond the higher photocatalytic activity, the presence of C$_3$N$_4$ could effectively enhance the photostability of ZnO photocatalyst. Many reports have suggested that ZnO semiconductor suffers from a significant decrease in photocatalytic activity due to the photoinduced dissolution.

\[ \text{ZnO} + 2h^+ + n\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_{2-n}^{(2-n)+} + \frac{1}{2}\text{O}_2 + n\text{H}^+ \]  

(1)

where $n$ depends on the pH of the solution. As can be seen from eqn (1), the photoinduced holes participate in the photocorrosion process of ZnO can be presented as follows:
and destroy the crystal structure of ZnO. As a result, the photocatalytic activity of ZnO is greatly decreased. After introduction of C3N4 to ZnO, the photogenerated holes on ZnO could transfer to C3N4, and then effective photocorrosion inhibition is achieved.

**Mechanism of visible photoactivity**

As it is well known that ZnO itself can not be excited by visible light, the trapping experiments of radicals and holes were only performed on C3N4/ZnO-3% photocatalyst. As can be seen from Fig. 10, the photodegradation of MB was obviously suppressed after the injection of t-BuOH. This result suggests that radicals are the main oxidative species in this system. On the basis of the results of photodegradation and photogenerated carrier trapping test, a proposed schematic mechanism of the visible light activity of the C3N4/ZnO photocatalyst is shown in Fig. 11. C3N4 absorbs visible light to induce \( \pi-\pi^* \) transition, transporting the excited-state electrons from the HOMO to the lowest unoccupied molecular orbital (LUMO). The LUMO potential of C3N4 (−1.12 eV) is more negative than the conduction band (CB) edge of ZnO (−0.5 eV),\(^8\) so the excited electron on C3N4 could directly inject into the CB of ZnO. C3N4– would accept electrons from fragments of MB degradation and return to the ground state. The electrons would subsequently transfer to the photocatalyst surface to react with water and oxygen to generate superoxide and hydroxyl radicals. The radicals are able to oxidize the pollutant due to their high oxidative capacity, producing visible light photocatalytic activity.

**Conclusion**

A C3N4/ZnO photocatalyst was successfully synthesized via a facile chemisorption. After introduction of C3N4, the photocurrent of ZnO was enhanced by 5 times under UV light irradiation and a noticeable photocurrent was observed under visible light irradiation. The C3N4/ZnO photocatalyst possessed significantly enhanced UV light photocatalytic activity, visible light photocatalytic activity and excellent antiphoto-corrosion ability. The performance enhancement and photocorrosion inhibition under UV light irradiation were induced by the high separation efficiency of photoinduced charges. The visible photocactivity originated from the injection of excited electrons from the LUMO of C3N4 to the CB of ZnO. C3N4 hybridization is demonstrated to be a promising approach to design highly active and stable ZnO photocatalysts.

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**References**