Investigation on Photocatalytic Removal of NO under Visible Light over Cr-Doped ZnO Nanoparticles

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ABSTRACT: Removal of nitrogen oxide pollution has attracted much attention, and photocatalysis is considered as an effective method to treat polluted gas. Currently, modified semiconductors with approximate band gap are used as visible-light-driven photocatalysts. Herein, this is the first investigation of photocatalytic removal of NO under visible light over Cr-doped ZnO nanoparticles (Cr–ZnO NPs). Furthermore, the trapping species experiment and electron spin resonance measurement were conducted to identify the primary reactive factor of the photocatalytic reaction. In this study, Cr–ZnO NPs were synthesized by the sol–gel method with a narrow band gap, enhanced NO photocatalytic degradation performance, low NO2 conversion yield, and high stability under visible light.

1. INTRODUCTION

Nowadays, the development of industries has led to increased emission of polluted gases into the air environment. Nitrogen oxide is one of the most popular emissions from factories and vehicles that is harmful to human, animals, and plants.1 In the environment, nitrogen oxide plays a role in producing acid rain, photochemical smog, and ozone destruction.2,3 Among many methods to remove nitrogen oxide, photocatalysis is considered as a “clean” and efficient approach.4,5 Among traditional and emerging photocatalysts such as TiO2, SnO2, Cu2O, g-C3N4, ZnO, Bi2WO6, BiPO4, etc.,6–12 ZnO exhibited superior properties such as unique optical and high chemical stability, as well as easy synthesis.13–15 However, ZnO has a large band gap (about 3.3 eV at room temperature); therefore, its photocatalytic activity is not really prominent in the visible light region.16–18 In the literature, there are many approaches to narrow the band gap, such as formation of oxygen-deficient structure, loading metal onto ZnO, and doping nonmetal or metal into ZnO.19–22 of which Cr doping into ZnO could be advantageous because Cr3+ can easily substitute the Zn2+ position, narrow the band gap, establish the magnetic property, etc.23,24 Recently, Li et al. have indicated that Cr3+ doping resulted in the generation of narrow band gap of SrTiO3 and in efficient decomposition of NO upon irradiation by low-intensity light.25 Wu et al. fabricated Cr–ZnO by the solvothermal method and indicated that the as-synthesized Cr-doped ZnO nanowires were a somewhat promising photocatalyst in remediation of water.26 Also, by the solvothermal method, Meng et al. used Cr–ZnO NPs with different Cr4+ contents, which is a somewhat novel and high-efficiency absorbent for the removal of acidic dye methyl orange from aqueous solution.27

There are many methods to synthesize Cr–ZnO NPs, such as solvothermal,27 hydrothermal,28 microwave-assisted,29,30 coprecipitation,31 combustion,32 magnetron sputtering,33 and sol–gel,34 of which the sol–gel route is considered as a facile and efficient approach compared to the others. The advantages of the sol–gel method include short synthetic time, use of green chemicals, low-cost synthesis, high-purity products, and ease of synthesis on the industrial scale.35–38

In this study, Cr–ZnO NPs have been synthesized by the sol–gel route and the NO degradation photocatalytic activity has been investigated under the visible light range. This is the first systematic study on the investigation of NO degradation photocatalytic activity. Moreover, the stability, photocatalytic mechanism, and NO2 yield have been discussed in this study.

2. EXPERIMENTAL SECTION

2.1. Materials. Chromium(III) nitrate nonahydrate (Cr(NO3)3·9H2O, 99%), zinc nitrate hexahydrate (Zn(NO3)2·6H2O, 99%), citric acid (C6H8O7·H2O, 99%), potassium iodide (KI, 99.99%), isopropyl alcohol (IPA; C3H8O, 99.99%), potassium dichromate (K2Cr2O7, 99.99%), 5,5′-dimethyl-1-pyrroline-N-oxide (DMPO; C6H11NO, 99%), sodium sulfate (Na2SO4, 99%), and acetone (C3H6O, 99%).

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NO and NO\(_2\) concentrations were measured after 30 min using a desorption equilibrium, the lamp was switched on. Finally, the prepared by coating their aqueous suspension onto a glass dish cut off rate under visible light irradiation (300 W xenon lamp with a UV concentration of 480 ppb, in a continuous Photocatalytic activity of samples was evaluated by measuring calcined at 400 \(^\circ\)C for 3 h. The removal ratio of NO (\(\eta\)) and the conversion of NO\(_2\) (\(\psi\)) over different photocatalysts were calculated from eqs 1 and 2.

\[
\eta = \frac{C_0 - C}{C_0} \times 100
\]

\[
\psi = \frac{C_{NO_2} - C}{C_0 - C} \times 100
\]

where \(C\) is the NO concentration of the outlet at any one time, \(C_0\) is the initial concentration of NO, and \(C_{NO_2}\) is the production of NO\(_2\).

2.4. Characterization of Materials. The crystalline structures of the samples were analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance 5000 diffractometer system. The morphology of samples was characterized by field emission scanning electron microscopy (FESEM, S-4800 at 10.0 kV) and transmission electron microscopy (TEM, JEOL JEM-1400 at 100 kV). Moreover, the lattice fringes of the as-prepared material were examined by selected area electron diffraction (SAED) patterns. The oxidation state and chemical compositions were analyzed by XPS (K-Alpha, Thermo Scientific) and energy-dispersive X-ray (EDX) mapping, respectively. The optical band gap properties were determined by UV−vis diffuse absorption spectroscopy (DRS) using a Jasco V-550 UV/VIS spectrophotometer. Photoluminescence (PL) spectra were recorded on a fluorescence spectrometer (HORIBA Jobin Yvon, Nanolong) at room temperature using excitation wavelength of 325 nm. To identify the main factor responsible for photocatalytic activity, KI, IPA, and K\(_2\)Cr\(_2\)O\(_7\) were used as photoreactive radicals of materials, such as superoxide anion radical (DMPO•−O\(_2^−\)) in methanol and hydroxyl radical (DMPO•−OH) in the aqueous state, under light-off and visible light-on for 6 min. The photocurrent of materials was controlled using an electrochemical workstation (BioLogic SP-240) with three electrodes including a Pt wire counter electrode, an Ag/AgCl (3 M KCl) reference electrode, and the working electrode of as-synthesized materials in 0.5 M Na\(_2\)SO\(_4\) electrolyte under visible light condition (100 mW/cm\(^2\) of 150 W xenon lamp).

3. RESULTS AND DISCUSSION

XRD patterns (Figure 1a) show that the as-synthesized materials, including ZnO NPs and Cr−ZnO NPs, exhibited diffraction peaks consisting of the standard diffraction pattern of the hexagonal wurtzite structure of ZnO (JCPDS 36-1451). In addition, no secondary phases existed in the XRD patterns of the Cr−ZnO NPs. However, Figure 1b shows that the typical peaks of the (002) and (101) planes of ZnO were shifted slightly to larger diffraction angels when Cr was doped into ZnO. This is because the ionic radius of the Cr\(^{3+}\) ion is smaller than that of the Zn\(^{2+}\) ion; therefore, it can easily penetrate and replace the original Zn atom of the host lattice, resulting in deformation of the ZnO lattice. Besides, according to previous publications, Cr easily replaces Zn in the ZnO lattice leading to a strong absorption in the visible-light region because of the intraband transition of the Cr 3d bands and the conduction band (CB). In addition, the morphology of the Cr−ZnO NPs shown in Figure 1c represents the spherical-like shape of the Cr−ZnO NPs with approximately 13−20 nm in diameter. Moreover, SAED diffraction patterns confirmed that the Cr−ZnO NPs exhibit well-defined crystallinity, as shown in Figure 1d. It is noteworthy that the prominent rings in the SAED patterns of Cr−ZnO NPs are consistent with the (100), (101), and (002) lattice planes of the wurtzite phase of ZnO.

Figure 2a shows the EDX spectrum of Cr−ZnO NPs, indicating the existence of Zn, O, and Cr atoms; herein, the content of Cr atoms in the sample is 1.38 wt % and 1.03 atom %. In addition, the surface of Cr−ZnO NPs (Figure 2b) is surveyed by EDX elemental mapping to determine the presence of atoms in the sample. Results confirmed the existence of Zn, O, and Cr atoms with their distribution as shown in Figure 2c−e, which demonstrates that Cr doped successfully into ZnO lattice.

To gain insight into the existence as well as oxidation states of as-synthesized materials, the XPS results were analyzed. The presence of Zn and O elements is observed in all samples, and the signal of Cr is detected in Cr−ZnO NPs as shown in Figure
3a. It is clearly observed that in the high-resolution XPS (HR-XPS) spectra of the Zn 2p region (Figure 3b), there are two symmetric peaks at binding energies (BE) of 1021.3 and 1044.4 eV for ZnO NPs, corresponding to Zn 2p3/2 and Zn 2p1/2 states, indicating a normal state of Zn2+ in the material. However, the positions of these peaks in Cr–ZnO NPs are slightly shifted. In detail, the BE values of Zn 2p3/2 and Zn 2p1/2 are located at 1022 and 1045 eV, respectively. This could be attributed to the substitution of Zn2+ by Cr3+, and an added Zn–O–Cr binding energy, which is consistent with the XRD pattern results.

Table 1. Gaussian Fitting Parameters for the HR-XPS Images

| Sample  | Region | Peak       | BE (eV) | FWHM (eV) | %  |
|---------|--------|------------|---------|-----------|----|
| ZnO     | Zn 2p  | Zn 2p3/2   | 1021.3  | 1.73      | 67.97|
|         |        | Zn 2p1/2   | 1044.4  | 1.78      | 32.03|
|         | Zn LMM | Zn LMM     | 577.2   | 6.02      | 44.05|
|         |        | Zn LMM     | 585.9   | 5.28      | 55.95|
| O 1s    |        | O_L        | 530     | 1.79      | 83.55|
|         |        | O_V        | 531.8   | 1.15      | 13.53|
|         |        | O_ads      | 532.9   | 1.04      | 2.92 |
| Cr–ZnO  | Zn 2p  | Zn 2p3/2   | 1022    | 1.79      | 68.13|
|         |        | Zn 2p1/2   | 1045    | 1.84      | 31.87|
|         | Zn LMM–Cr 2p | Zn LMM–Cr 2p3/2 | 576.3 | 5.41 | 47.06|
|         |        | Zn LMM–Cr 2p1/2 | 585.3 | 4.82 | 52.94|
| O 1s    |        | O_L        | 530     | 1.35      | 70.67|
|         |        | O_V        | 531.5   | 1.34      | 20.32|
|         |        | O_ads      | 532.5   | 1.54      | 9.01 |

*a* Binding energy. *b* Full width at half-maximum.
(Figure 1b). At a high content of Zn, the Cr 2p region overlaps strongly with Zn LMM Auger peaks. As shown in Figure 3c, the peaks centered at 577.1 and 585.9 eV correspond to Zn LMM states of ZnO. However, typical peaks of Cr$^{3+}$ were observed at 576.3 and 585.3 eV, which can be assigned to Cr 2p$^{3/2}$ and Cr 2p$^{1/2}$, respectively. Clearly, the presence of Cr$^{3+}$ has shifted the Zn LMM position to lower BE in the Cr$^{-}$ZnO sample. Figure 3d shows the HR-XPS spectra of O 1s of all doped and undoped samples. It could be fitted by a Gaussian distribution (Table 1) and shown that the asymmetric O 1s core spectrum deconvoluted with three peaks. The first peaks centered at $\sim$530 eV can be attributed to the coordination of \( \text{O}^{2-} \) ions in the wurtzite ZnO lattice (Zn$\rightarrow$O) (O$_L$). Meanwhile, the peaks at $\sim$531 and 532 eV are attributed to \( \text{O}^{-} \) in the oxygen-deficient regions/oxygen vacancy (O$_{\text{v}}$)$^{33,43}$ and the O$^{2-}$ ion of chemisorbed oxygen (O$_{\text{ads}}$) on the surface, respectively.$^{33,43}$ It is noteworthy that the percentage of O$_{\text{v}}$ in Cr$^{-}$ZnO NPs is higher than that of ZnO NPs (Table 1). It suggests that the oxygen vacancies on the as-synthesized ZnO NPs surface increased after doping, which could be partly explained via the band gap results.

For the optical properties, Cr is successfully doped into ZnO, and the DRS and PL spectra are obtained. Figure 4 shows that the absorption edge of the Cr$^{-}$ZnO NPs is red-shifted from a wavelength of 400–450 nm compared to the undoped ZnO (Figure 4a). Thus, we can conclude that the light absorption range of Cr$^{-}$ZnO NPs had transferred to the visible-light region. Besides, the optical band gaps of the ZnO NPs and Cr$^{-}$ZnO NPs were estimated to be 3.1 $\pm$ 0.2 and 2.76 $\pm$ 0.2 eV, respectively, as shown in Figure 4b. The emission of Cr$^{-}$ZnO NPs is also compared to that of ZnO NPs by the recognition of chemisorbed oxygen (O$_{\text{ads}}$) on the surface, respectively.$^{33,43}$ It is noteworthy that the percentage of O$_{\text{v}}$ in Cr$^{-}$ZnO NPs is higher than that of ZnO NPs (Table 1). It suggests that the oxygen vacancies on the as-synthesized ZnO NPs surface increased after doping, which could be partly explained via the band gap results.
PL spectra (Figure 4c). This indicates that the appearance of emission peaks in the 600–620 and 385–400 nm regions contributes to the donor states (Cr\textsuperscript{3+} and O\textsubscript{2}) and the band-to-band transition of materials, respectively. The intensity of typical peaks of Cr–ZnO NPs is lower than that of ZnO NPs, contributing to capture of donor states leading to an increase in the separation of the photogenerated electrons and holes, resulting in a higher photocatalytic performance.\textsuperscript{47–49} To confirm the efficient photoreponse ability of Cr doping into ZnO, the linear sweep voltammetry (LSV) of ZnO NPs and Cr–ZnO NPs with 0.5 M Na\textsubscript{2}SO\textsubscript{4} (Figure S1, Supporting Information) indicated the difference in the current density under dark and visible light condition; therein, the Cr–ZnO NPs greatly influence the current density. Further, the photocurrent density–time curves of materials were measured and are shown in Figure 4d. It is found that the photocurrent density of Cr–ZnO NPs (achieved 4.4 μA/cm\textsuperscript{2} at −0.3 V vs V\textsubscript{Ag/AgCl}) is approximately 14.7 times higher than that of ZnO NPs (0.3 μA/cm\textsuperscript{2} at −0.3 V vs V\textsubscript{Ag/AgCl}) under visible-light irradiation. Besides, the photocurrent density of Cr–ZnO NPs is kept stable after five light-on/light-off cycles. The combination of the PL and photocurrent density indicated that the Cr doping into ZnO has enhanced the separation and transfer the photogenerated charges.\textsuperscript{50}

The NO photocatalytic degradation of Cr–ZnO NPs is shown in Figure 5a. The results show that the NO photocatalytic removal over ZnO and Cr–ZnO NPs occurs quickly in the first 5 min, then decreases slightly, and finally reaches saturation for all of the catalysts after 30 min of visible light irradiation. The NO photocatalytic degradation efficiency of Cr–ZnO NPs achieved 24.44%, which was significantly higher than that of ZnO NPs (about 17.6%). Additionally, the stability of the Cr–ZnO NPs was tested via the recycling test with five repeat cycles. Figure 5b shows that the Cr–ZnO NPs have good stability, indicating that the NO degradation efficiency remained almost unchanged after five cycles. Moreover, the XRD patterns of as-synthesized Cr–ZnO after five cycles of photocatalytic test are shown in Figure S2 (Supporting Information), which indicate that the positions of all typical diffraction peaks of both samples are unchanged and the intensity of these peaks is slightly decreased. The combination of the photocatalytic ability of the recycling test and the XRD results demonstrates that the Cr–ZnO NPs have a good stability. The Langmuir–Hinshelwood model\textsuperscript{51} was used to describe the rate of the NO photocatalytic degradation of the materials. The initial photocatalytic degradation of NO gas was recognized to follow first-order kinetics; then, the obtained results are displayed by a linear plot of ln(C/C\textsubscript{0}) versus reaction time in Figure S3a (Supporting Information). The result shows that the reaction rate (k) of the Cr–ZnO NPs is 1.74 times higher than that of ZnO NPs. Besides, Figure S3b (Supporting Information) shows the NO degradation efficiency and NO\textsubscript{3} yield conversion of materials. Results show that the NO degradation efficiency over Cr–ZnO NPs is higher than that of undoped ZnO NPs and the NO\textsubscript{2} yield conversion is lower than that of undoped ZnO (7.5% for Cr–ZnO NPs and 17.3% for ZnO NPs). This demonstrated that Cr doping into ZnO not only improves the NO removal ability but also decreases the generation of NO\textsubscript{2} gas. Thus, Cr–ZnO NPs can be potential material for real-time application.

To clarify the NO photocatalytic degradation mechanism under visible light, trapping experiments were conducted to identify the active radical species. Figure 5c shows that the NO degradation photocatalytic activity of Cr–ZnO NPs decreased with the addition of scavengers. Furthermore, the NO degradation efficiency of Cr–ZnO NPs decreased from 24.44 to 15.18, 20.43, and 16.50% with the addition of KI, IPA, and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, respectively. This result indicated that the photocatalytic activity of Cr–ZnO NPs was contributed by h\textsuperscript{+}, *OH radicals, and e\textsuperscript{−}. However, the photocatalytic reaction rate (Figure 5d) indicated that the presence of IPA made the NO photocatalytic decomposition reaction rate the lowest. This means that *OH plays a primary role in the NO degradation ability of Cr–ZnO NPs via intermediate reactions. Furthermore, the DMPO-ESR results (Figure 5e) of the Cr–ZnO NPs indicated no signal in the dark. However, under visible light, the signals appeared clearly, demonstrating the existence of *O\textsubscript{2} and *OH radicals. Moreover, both in H\textsubscript{2}O and under light-on conditions, the strong signals prove that there are several *OH radicals that conform to the trapping test.

Based on the above results, a proposed mechanism of the photocatalytic activity of Cr–ZnO NPs for NO degradation under visible light is shown in Figure 6. First, the Cr–ZnO NPs are excited and electrons and holes are generated by visible light irradiation. Second, the photogenerated electrons generated in the valence band (VB) of the material transfer to the CB of the material or back and forth to the donor states (eq 3). Third, these electrons can either transfer to the surface of Cr–ZnO NPs or reduce adsorbed O\textsubscript{2} or oxygen gas to yield *O\textsubscript{2} \textsuperscript{−} superoxide radical anions (eq 4). Meanwhile, holes in the VB of Cr–ZnO NPs move to surface and oxidize OH\textsuperscript{−} radicals to yield *OH radicals (eq 5). During the reaction process, *O\textsubscript{2} produces H\textsubscript{2}O\textsubscript{2} hydroperoxyl (eq 6) and *OH radicals produce hydroxyl radical *OH (eqs 7–10). Finally, both *O\textsubscript{2} and *OH will react and degrade NO and NO\textsubscript{2} to NO\textsubscript{3} \textsuperscript{−} (eqs 11 and 12). As the trapping experiment results have concluded that *OH radicals are important (Figure 5c), in this step, *OH radicals will promote the photocatalytic activity of materials.\textsuperscript{52–55}

\[
\begin{align*}
\text{Cr} - \text{ZnO} + \text{hv} & \rightarrow \text{Cr} - \text{ZnO} (h\textsuperscript{+} + e\textsuperscript{−}) \\
\text{O}_2 + e\textsubscript{CB} & \rightarrow *\text{O}_2^- \\
\text{H}_2\text{O} + h\textsuperscript{+} & \rightarrow \text{HO}^\cdot + \text{H}^+ \\
*\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{HO}^\cdot + \text{OH}^- \\
2*\text{HO}_2 & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\end{align*}
\]
\[ \text{H}_2\text{O}^* + \text{H}_2\text{O} + e^-_{\text{CB}} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- \]  
(8)

\[ 2\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}_2 + \text{O}_2 \]  
(9)

\[ \text{H}_2\text{O}_2 + e^-_{\text{CB}} \rightarrow \text{OH}^- + \text{OH}^- \]  
(10)

\[ \text{NO} + \text{O}_2^- \rightarrow \text{NO}_2^- \]  
(11)

\[ \text{NO} + \text{HO}^* \rightarrow \text{NO}_2 + \text{H}_2\text{O} \]  
(12)

4. CONCLUSIONS

In summary, uniform spherical-like Cr–ZnO NPs with 13–20 nm diameter were synthesized via the sol–gel method. The results show that the Cr–ZnO NPs have good NO photocatalytic degradation activity (24.44% for 30 min under visible light), low NO\textsubscript{2} conversion yield, and high stability, as indicated in five measurement cycles with trivial change in performances. Moreover, *OH radical, the main active radical, was identified via trapping test and ESR analysis. The above-mentioned properties will open a promising application of Cr–ZnO NPs in visible-light-driven photocatalysis.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01628.

LSV sweep of ZnO NPs and Cr–ZnO NPs under dark and visible light conditions; XRD patterns of as-synthesized Cr–ZnO NPs and after five photocatalytic test cycles; and dependence of concentration on irradiation time, and NO removal efficiency and NO\textsubscript{2} conversion yield of ZnO NPs and Cr–ZnO NPs (PDF)

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**Notes**

The authors declare no competing financial interest.

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