High photocatalytic activity in nitrate reduction by using Pt/ZnO nanoparticles in the presence of formic acid as hole scavenger

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In this work, the photocatalytic reduction of nitrate in water was examined using zinc oxide loaded with platinum nanoparticles and formic acid as a hole scavenger (electron donor). The data obtained in the structural characterization and in the nitrate photoreduction experiments showed that 1wt% Pt/ZnO photocatalyst had the highest photocatalytic activity and selectivity toward nitrogen. Selectivity and conversion were higher than 98 and 70%, respectively. This system effectively promoted the photocatalytic reduction of NO_3^- to N_2. Nitrite ions were not observed during the reaction and a negligible amount of ammonia was formed.

INTRODUCTION

Increased groundwater contamination by nitrate has received attention all over the world [1–3] due to the intensive use of fertilizers from agricultural activities [4, 5], the disposal of massive amounts of livestock manure [5], and the discharge of poorly treated wastewater [6]. Nitrate has been known to be hazardous to human health, which can cause methaemoglobinaemia and blue baby syndrome, fatal disease to babies under 6 months of age [7], and leads to the formation of carcinogenic nitrosamine in the human body [8]. In the efforts to control nitrate contamination in groundwater, United States Environmental Protection Agency (USEPA) set regulations on maximum contaminant level of nitrate at 10 mg/L nitrate-nitrogen (NO_3^--N) [9]. Remediation technologies such as advanced biological nutrient treatment, electro-kinetic denitrification, reverse osmosis, and chemical reduction [10–15] have been developed to solve compelling issues of nitrate contamination in groundwater. However, these technologies suffer from sludge generation [11], high operational cost [12–14], and undesirable by-product formation [15].

Catalytic reduction of nitrate to harmless nitrogen gas has drawn attention as a promising alternative for nitrate treatment since Vorlop and Tacke [16] demonstrated the effectiveness of bimetallic catalysts in 1989. Enormous efforts to find out the most effective metal combination in catalytic nitrate reduction have been made by loading Cu, Sn, Ni, Pd, Pt, Au, and Rh on diverse supporting materials [17–21]. At present, supported catalysts have been investigated and widely applied in many industrial fields [22–24].

Photocatalytic denitrification (photoreduction of nitrate to innocuous nitrogen gas through the action of a photocatalyst) is an economically viable process having also environmental benefits compared to other treatments available for the removal of nitrogen from aqueous media, such as advanced filtration and biological denitrification [25-27].

There are several reports on the successful photoreduction of nitrate promoted by metal catalysts supported on TiO_2 [28-36], SnO_2 [37], and ZnS [38, 39]. However, there are limited reports on the photocatalytic reduction of nitrate over a metal-loaded ZnO catalyst system so far [40-41]. In our previous published research works [42-48], we synthesized several catalytic systems and described the catalytic activities of the prepared catalysts in different reactions. In the present work, we were interested in exploring the utility of Pt/ZnO (NPs) as a reusable, economical and commercially available catalyst for the photoreduction of nitrate to nitrogen gas. The effect of different operating parameters such as content of metal and hole scavenger, catalyst amount and initial nitrate concentration, was investigated.

EXPERIMENTAL

Instrumentation

X-ray diffraction (XRD) patterns were obtained on a Philips pw 1840 powder diffractometer using Cu Kα (λ = 1.54178Å) radiation (2θ from 0° to 70°)

at a scanning rate of 2.4°/min. Transmission electron microscopy (TEM) was carried out on a Philips CM-10 model instrument operating at 100 keV. Before photographing, the samples were dropwise added onto the surface of a carbon membrane and dried at ambient temperature.

Preparation of the photocatalyst Pt/ZnO (NPs)

Pt-doped ZnO nanoparticles were prepared by a direct precipitation method using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and platinum (IV) chloride ($PtCl_4$) as the precursors of zinc and platinum, respectively. First, $Zn(CH_3COO)_2.2H_2O$ and Na_2CO_3 were dissolved separately in distilled water to obtain 0.5 mol/L solutions. Zinc acetate solution (50 ml, 0.5 mol/L) was slowly added to 50 ml of 0.5 mol/L Na_2CO_3 solution under vigorous stirring. Afterwards, platinum (IV) chloride in the required stoichiometry was slowly added to the mix under stirring for 30 min yielding a yellow precipitate. The latter was filtered, rinsed repeatedly with distilled water and washed twice with ethanol. The resultant solid product was dried at 100ºC for 12 h and calcined at 300ºC for 2 h. ZnO nanoparticles were prepared by the same procedure without the addition of platinum (IV) chloride solution. The doping concentrations of Pt are expressed in wt%.

Photocatalytic reduction test

In order to investigate the effect of platinum doping on the photocatalytic activity of ZnO, the photocatalytic reduction of nitrate was carried out in a ZnO or Pt/ZnO suspension under UV irradiation. The photocatalytic experiments were performed in a reactor at ambient temperature and atmospheric pressure. A 400 W high-pressure mercury lamp was used as a light source. The reaction suspensions were prepared by adding 25 mg of catalyst and 3 ml of 0.008 M formic acid to 25 ml of aqueous nitrate solution with an initial NO_3^- concentration of 60 mg/l. Prior to illumination, the reaction suspension was stirred in the dark for 15 min to ensure adsorption/desorption equilibrium. The aqueous suspension containing nitrates and photocatalyst was then irradiated by UV. The reaction mixture was magnetically stirred to maintain the catalyst in suspension. The sample solution was periodically withdrawn and the powdered catalyst was immediately separated from the aqueous phase by centrifugation. The remaining solution was divided in three portions and the concentration of nitrate, nitrite and ammonium was determined by measuring the absorption in the

presence of brucine, Griess and Nessler reagents at 410, 520, and 392 nm, respectively, as shown in Figs. 1 - 3. At the end of the reaction, no nitrite ions and very small amounts of ammonium ions were detected, therefore, the selectivity towards nitrogen according to Eq. 1 was estimated to be about100%. [49-51].
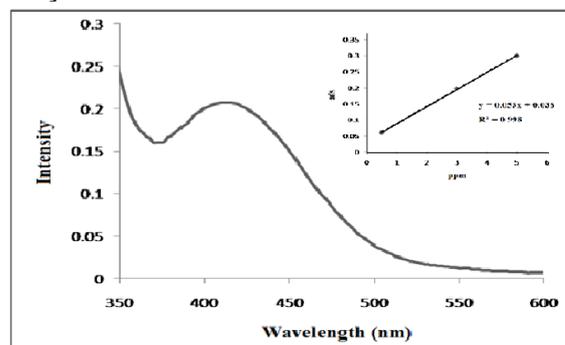

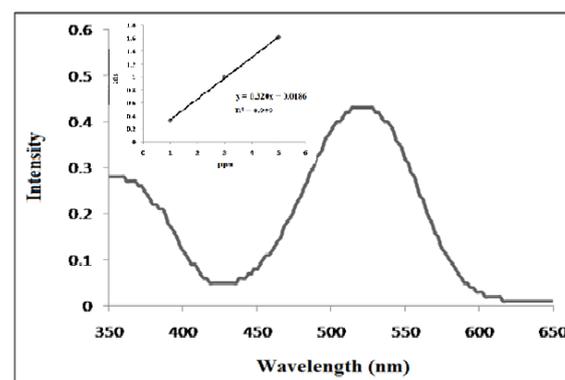**Fig. 1.** Absorption spectrum and calibration curve of brucine - nitrate at 410 nm

Fig. 2. Absorption spectrum and calibration curve of Griess-nitrite at 520 nm
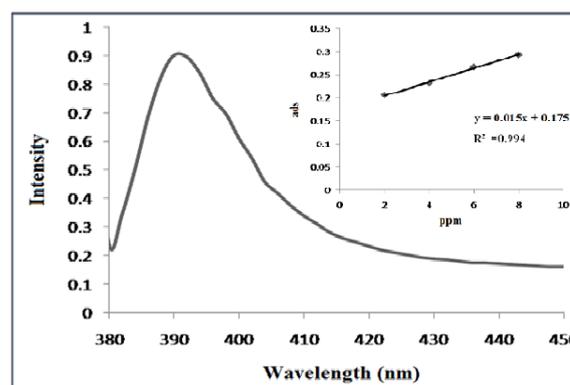

Fig. 3. Absorption spectrum and calibration curve of Nessler - ammonium at 392 nm

Determination of catalytic activity and selectivity

The catalytic activity for the reduction of nitrate is defined as the amount of reduced nitrate ions per time and catalyst weight (mmol g_{cat}^{-1} h^{-1}). The selectivity to nitrogen is defined as the ratio of the

amount of formed nitrogen to the amount of reduced nitrate, based on the assumption that no products other than nitrite and ammonium are formed. N_2 selectivity is calculated according to Eq. (1):

$$S_{N2} = \frac{[nitrate]_0 - [nitrate]_t - [nitrite]_t - [ammonia]_t}{[nitrate]_0 - [nitrate]_t} \times 100 \quad (1)$$

where S_{N2} is N_2 selectivity, $[nitrate]_0$ is the initial nitrate concentration, and $[nitrate]_t$, $[nitrite]_t$ and $[ammonia]_t$ are the residual concentrations of nitrate, nitrite and ammonia after reaction for 1 h, respectively [31].

RESULTS AND DISCUSSION

Photocatalytic nitrate reduction over metal-modified catalysts

Various metal-modified catalysts were tested for the reduction of nitrate to nitrogen. It can be seen that under the given conditions (initial concentration of nitrate = 60 ppm, photocatalyst = 25 mg and reaction time = 60 min), pure ZnO has low activity (18.5%). The experimental results shown in Fig. 4 demonstrate that after 60 min of reaction time, the concentration of nitrate in all suspensions was reduced. Among these catalysts, 1 wt% Pt/ZnO showed the maximum photocatalytic activity and thereby was selected as a model catalyst in this study.
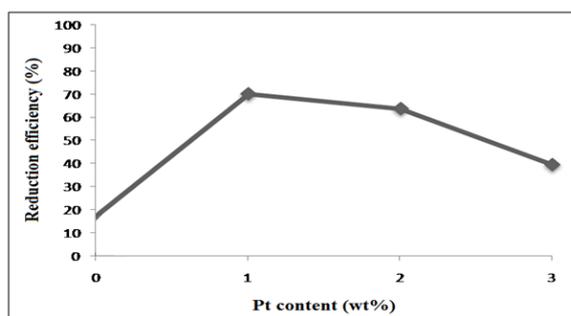

Fig. 4. Influence of metal content on the photocatalytic reduction activity of nitrate ions over Pt/ZnO catalysts (initial concentration of nitrate = 60 ppm, photocatalyst = 25mg and reaction time = 60min).

Effect of total metal content

As shown in Fig. 4, high metal content (2 wt% and 3 wt%) is not beneficial to the reduction of nitrate and the optimum reduction is obtained at a metal content of 1 wt%. This suggests that active atomic arrangement and active particle size on the surface of the catalyst may have a greater influence on the removal of nitrate than the amount of loaded metal. Several research groups have suggested that, at a metal content higher than the optimal one, the overaccumulation of electrons on the metal deposits could attract photogenerated holes to the metal sites [52, 53]. This may promote the recombination of charge carriers, the metal deposits reversely behaving as recombinant centers. In addition, higher surface loadings of metal deposits may decrease the catalytic efficiency of the semiconductor due to the reductive availability of semiconductor surface for light absorption and pollutant adsorption [54].

XRD analysis of 1 wt% Pt/ZnO photocatalyst

Fig. 5 shows the XRD pattern of 1 wt% Pt/ZnO. There are two sets of diffraction peaks for each sample, indicating that the synthesized samples are composite materials. As shown, the diffraction peaks at $2\theta = 31.7°$, $34.4°$, and $36.2°$ are indexed to diffractions of hexagonal structured ZnO (wurtzite) (JCPDS Card No. 36-1451). The peaks located at $2\theta = 40.5°$ and $47°$ are characteristic to diffractions of Pt [55]. XRD test shows the presence of ZnO and Pt phases in the samples. Its average crystal size is determined to be 41 nm according to the Debye-Scherrer formula ($L = 0.89\lambda/\beta\cos\theta$).
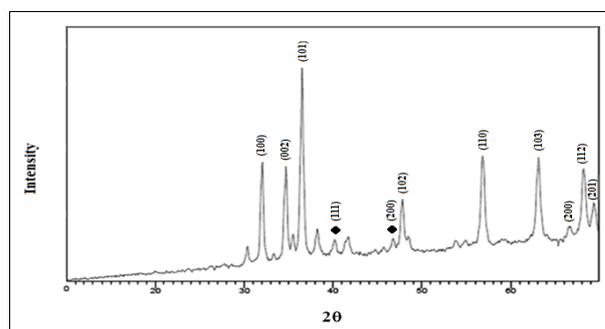

Fig. 5. XRD pattern of 1 wt% Pt/ZnO

TEM micrograph of 1 wt% Pt/ZnO photocatalyst

In order to further observe the morphology of ZnO and 1 wt% Pt/ZnO catalyst, TEM images of the catalysts were taken and representative photographs are shown in Fig. 6. TEM images show that the size of ZnO particles is larger than that of zinc oxide loaded with platinum nanoparticles and the size of most of the nanoparticles of 1 wt% Pt/ZnO is about 40-50 nm. The results are consistent with the results of XRD.
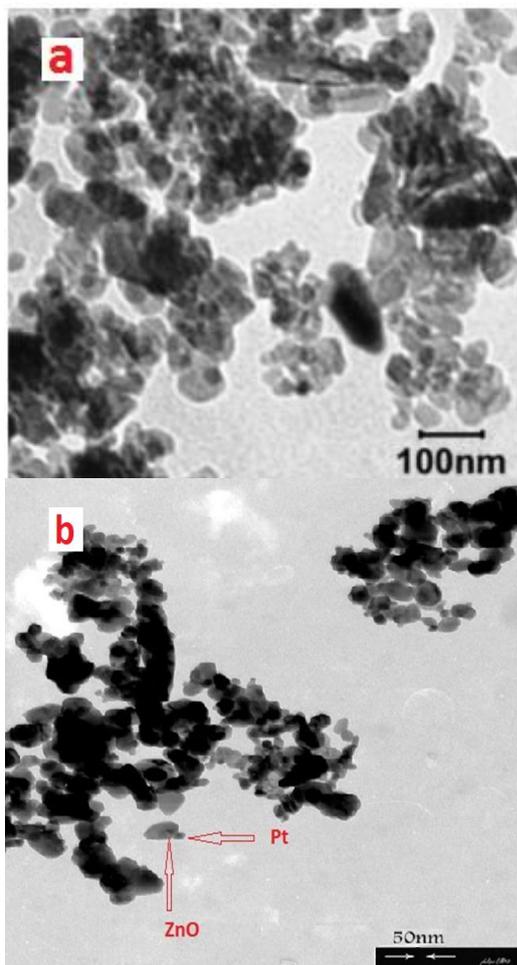
Fig. 6. TEM image of a) ZnO b) 1wt% Pt/ZnO

Effect of catalyst amount

As shown in Fig. 7, pure ZnO (0 % Pt) has low catalytic activity (18.5%) and the optimum catalyst amount for NO_3^- removal is 25 mg. However, further increase in catalyst dosage decrease the photo-degradation efficiency of nitrate. The photo-decomposition rates of pollutants are influenced by the active site and the photo-absorption of the catalyst used. Adequate loading of the semiconductor increases the generation rate of electron–hole pairs for promoting the degradation of pollutants. However, the addition of a high dose of the semiconductor decreases the light penetration through the photocatalyst suspension [56].

On the other hand, additional experiments were carried out to evaluate the efficiency of nitrate degradation by 1 wt% Pt/ZnO at higher initial nitrate concentrations (e.g., 100 ppm). The reduction of nitrate ions at concentrations of 60 and 100 ppm with 1 wt% Pt/ZnO with time is shown in Figure 8. The maximum percentages of nitrate removal from water were observed at 69.5% and 50% respectively.
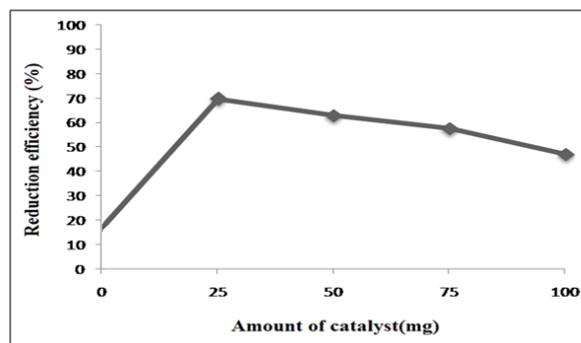
Fig. 7. Influence of catalyst amount on the photocatalytic reduction activity of nitrate ions over 1 wt% Pt/ZnO catalyst (initial concentration of nitrate = 60 ppm, reaction time = 60 min).
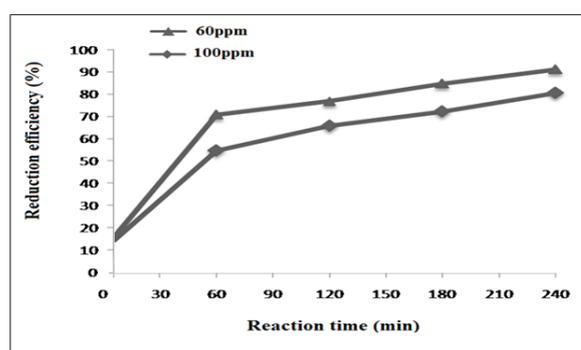

Fig. 8. Influence of initial nitrate concentration on the photocatalytic reduction activity over 1 wt% Pt/ZnO catalyst
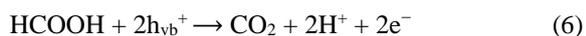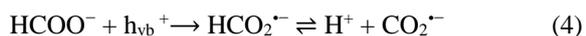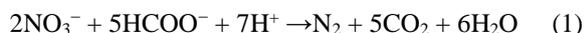
Mechanism and role of Pt

Loading a small amount of Pt (1 wt%) on ZnO leads to the enhancement of its photocatalytic activity. With 1 wt% Pt loading, the photocatalytic activity reaches a maximum. Increasing the amount of Pt loading to 3 wt% decreases the photocatalytic activity. Under UV irradiation, the electrons in the valence band of ZnO can be excited to their corresponding conduction band, thus, the efficient separation of photoinduced electrons and holes leads to the generation of photocurrent. Compared with the pure ZnO photocatalyst, loading a small amount of Pt on ZnO leads to an enhancement of its photocurrent. However, the further increase in the Pt loading to 3% results in a considerable decrease in its photocurrent. This observation reveals that the presence of excess Pt lowers the separation efficiency of photogenerated electrons and holes in the 3 % Pt/ZnO photocatalyst because the possibility of hole capture increases by the large number of negatively charged Pt particles on ZnO when Pt loading is above the optimum [57]. This process of hole capture probably takes place in a nonradiative pathway. Therefore, the lowest

photocatalytic activity of the 3 % Pt/ZnO photocatalyst is attributed to its lowest separation efficiency of photogenerated electrons and holes. This result indicates that the modification of ZnO with an appropriate amount of Pt can increase the separation efficiency of photogenerated electrons and holes in ZnO, which results in enhancement of its photocatalytic activity.

Effect of hole scavenger

When formic acid and nitrate are mixed in dark, no nitrate reduction occurs in the absence of a photocatalyst. Therefore, formic acid does not act as a direct reductant under these experimental conditions; it rather acts as a hole scavenger. It has been proved that a sacrificial reagent is necessary for the reduction of nitrate ions, and the different sacrificial reagents have distinct redox characteristics [58]. From Fig. 7 it can be seen that nitrate conversion is appreciably high when formic acid is used as the hole scavenger. Experimental parameters including pH, nitrate concentration, formate concentration, photocatalyst concentration, and metal loading were varied to demonstrate their effect on product selectivity. Under acidic conditions, nitrogen gas was the final product. However, under neutral pH conditions, only nitrite was formed [59].

In this work, the results have shown that the product was only nitrogen gas, so the reaction takes place according to Eq. (1). Consequently, two holes would have to be reduced by one formic acid molecule (Eq. 6). Formic acid first adsorbs on the surface of ZnO and disproportionates to a formate anion and a proton (Eq. 3). Formate reacts with one $h_{vb}+$ to form the carbon dioxide anion radical, $CO_2^{\bullet-}$ (Eq. 4) After $CO_2^{\bullet-}$ forms, it reacts with an $h_{vb}+$ (Eq. 5). So the total reaction for formic acid can be expressed as Eq. (6). [34, 60, 61]

$$2NO_3^- + 5HCOO^- + 7H^+ \rightarrow N_2 + 5CO_2 + 6H_2O \quad (1)$$

$$ZnO(Pt) + h\nu \rightarrow e^- + h^+ \quad (2)$$

$$HCOOH \rightarrow H^+ + COOH^- \quad (3)$$

$$HCOO^- + h_{vb}{}^+ \rightarrow HCO_2{}^{\bullet-} \rightleftharpoons H^+ + CO_2{}^{\bullet-} \quad (4)$$

$$CO_2{}^{\bullet-} + h_{vb}{}^+ \rightarrow CO_2 \quad (5)$$

$$HCOOH + 2h_{vb}{}^+ \rightarrow CO_2 + 2H^+ + 2e^- \quad (6)$$

CONCLUSIONS

In the present work, the enhancement of the photocatalytic activity of ZnO catalyst by doping with Pt was confirmed in the reaction of nitrate reduction in the presence of formic acid. It was found that a suitable amount (1 wt%) of the Pt

dopant effectively increases the photocatalytic activity of ZnO. The Pt particles doped on the ZnO surface behave as sites where electrons accumulate. Better separation of electrons and holes on the modified ZnO surface allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions. The experiments demonstrated that nitrate was degraded in aqueous Pt/ZnO suspension by more than 70% within 60 min. The reduction of nitrate eventually releases nitrogen gas.

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ВИСОКА ФОТОКАТАЛИТИЧНА АКТИВНОСТ НА НАНОЧАСТИЦИ ОТ Pt/ZnO ПРИ РЕДУКЦИЯТА НА НИТРАТИ В ПРИСЪСТВИЕ НА МРАВЧЕНА КИСЕЛИНА КАТО ДОНОР НА ЕЛЕКТРОНИ

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(Резюме)

В тази работа е изследвана фотокаталитичната редукция на нитрати във вода при използването на цинков оксид, зареден с наночастици от платина и мравчена киселина като донор на електрони. Получените данни за структурното охарактеризиране и фоторедукцията на нитрати показват, че фотокатализаторът с 1t% (тегл.) Pt/ZnO има най-висока активност и селективност спрямо азота. Селективносттта и конверсията са по-високи от 98 и 70% съответно. Тази система повишава фотокаталитичната редукция на NO_3^- до N_2. Не са наблюдавани нитритни йони и пренебрежимо количество амоняк.