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# Preparation and photocatalytic properties of ilmenite $NiTiO_3$ powders for degradation of humic acid in water

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**Abstract:** The powders of ilmenite structure $NiTiO_3$ were prepared by a modified Pechini process using tetrabutyl titanate and nickel acetate as raw materials, and using citric acid and ethanol as a chelating agent and a solvent respectively. The powder samples were characterized by thermogravimetric and differential thermal analysis (TG-DTA) and X-ray diffraction (XRD). The photocatalytic activity of $NiTiO_3$ under the irradiation of ultraviolet rays (UV) light was evaluated by degrading humic acid (HA) in water as a probe reaction. The possible photodegradation mechanism was studied by the examination of active species $\cdot OH$, $\cdot O_2^-$, and holes ($h^+$) through adding scavengers. The TG-DTA and XRD results indicated that the good crystal structure of ilmenite phase $NiTiO_3$ could be obtained when the Ni-Ti citrate complex was calcined at 600°C. The photocatalytic activity experiments indicated that $NiTiO_3$ had favourable photocatalytic activity under the irradiation of UV light, and the photocatalytic degradation rate of HA reached 95.3% after a 2.5 h reaction with the photocatalyst calcined at 600°C and a photocatalyst dosage of 0.4 g/L. The possible photocatalytic mechanism was deduced that holes ($h^+$) and $\cdot OH$ radicals are the major reactive active species in the photocatalytic reaction, and dissolved oxygen plays a weak role in the degradation of HA.

**Keywords:** photocatalysis; nickel titanate; degradation; humic acid; water treatment

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## 1. Introduction

As the part of natural organic matters, humic acid (HA) has brought great influences on natural water. For example, it affects the enrichment and migration of metal ions and trace elements in water and then results in the increased toxicity of natural water little by little [1]. In addition, it has been confirmed that humic substances are the major precursors of disinfectant byproducts during water chlorination processes and are difficult to be degraded [2]. Therefore, it is imperative to search for an effective and practical technique to remove HA from nature water.

Recently, some researchers were interested in discussing the photophysical, acoustic-optic, and catalytic properties of the ilmenite-type titanates, such as $CoTiO_3$, $NiTiO_3$, and $ZnTiO_3$ [3-5]. $NiTiO_3$ has an ilmenite structure in which both Ni and Ti prefer the octahedral coordination with alternating cation layers occupied by Ni and Ti alone [6]. This unique structure makes it to be used usually as a functional inorganic material in electrodes of solid oxide fuels cells [7], gas sensors [8], and metal air barriers [9] and as high-performance catalysts for the complete oxidation of hydrocarbons or CO and NO reduction [10]. At the same time, $NiTiO_3$ is a kind of semiconductor with a band gap of 2.18 eV. It should have some photocatalytic activity for the degradation of organics in water, but so far there is a lack of investigations for its application in water treatment. We tried to use $NiTiO_3$ as a photocatalyst for the removal of HA from water, and $NiTiO_3$ really expressed a good reaction activity. The obtained results are very interesting and worthy of further attention to the photocatalytic properties of ilmenite

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$NiTiO_3$. On the other hand, the properties of materials are closely related to the preparation methods. There are many methods used to prepare $NiTiO_3$ via different synthesis routes, such as Pechini process [6], coprecipitation [11], polymeric precursor [12], stearic acid gel method [13], emulsion [14], and the flux method [15]. Among them, Pechini process is a simpler method and can get fine powders with uniform structure.

The purpose of this study is first to prepare ilmenite structure $NiTiO_3$ powders by modified Pechini process using tetrabutyl titanate and nickel acetate as raw materials, and using citric acid and ethanol as a chelating agent and a solvent respectively, and then to investigate the photocatalytic activity of $NiTiO_3$ by the degradation of HA in water under the irradiation of UV light with a main wavelength of 365 nm and finally to build up a relationship between ilmenite structure $NiTiO_3$ powders and their photocatalytic activity. The possible photodegradation mechanism was also studied by the examination of active species $\cdot OH$, $\cdot O_2^-$, and holes ($h^+$) through adding their scavengers. The obtained results may provide valuable information leading to a better understanding of the photocatalytic performance of this ilmenite structure $NiTiO_3$.

## 2. Experimental

### 2.1. Preparation of $NiTiO_3$ powders

A stoichiometric amount of nickel acetate and tetrabutyl titanate (Ni/Ti= 1:1) was separately dissolved in ethanol to form two transparent solutions (marked as A solution and B solution, respectively). Then, citric acid of 1.5 times as many as $Ni^{2+}$ was added into the B solution under constant stirring. This solution was marked as C solution. When the A solution was mixed with the C solution, the tiny precipitates came out, and the mixed solution was stirred for 0.5 h at 70°C to insure that the precipitation reaction was conducted completely. Then, the precipitate suspension was further heated in an oven at 70°C to remove the excess solvent until light green agglomerates were formed. Furthermore, the agglomerates were calcined at different temperatures for 3 h, and $NiTiO_3$ powders were finally obtained.

Thermal behavior examination of the Ni-Ti-complexed precursor was performed by TG-DTA analyzer (America PERKEN ELMER 1700) in air to investigate the calcination temperature and possible phase transformation from 20 to 1000°C with a heating rate of 30°C/min. The crystal structure of the prepared powders was identified by Rigaku XRD (D/max-2500) with monochromated Cu $K_\alpha$ radiation at an accelerating voltage of 40 kV and an applied current of 100 mA, respectively. The data were collected with a scan rate of 8°/min in the range of $2\theta =$ 20-80°.

### 2.2. Preparation of HA solution

A HA suspension was first prepared by adding the HA chemicals into the deionized water and gently heating up to 60°C under magnetic stirring in order to accelerate the dissolution of HA. After the supersaturated HA suspension was cooled down to room temperature gradually, the suspension was filtered by millipore filter paper. The HA residue on the filter was dried in an oven at 85°C until its weight was unchanged. The HA concentration in the clear solution (filtrate) was calculated by the gravimetric method. The HA solution was stored as a stock solution in a refrigerator at 4°C for further use.

### 2.3. Photocatalytic activity experiments

The photocatalytic activity of $NiTiO_3$ powders was evaluated by the degradation of HA solution with an initial concentration of 10 mg/L in a cylindrical quartz glass reactor with an effective vessel volume of 50 mL. A 300 W UV light with a cooling water jacket acted as a side light source. During the reaction, the HA solution was irradiated by UV light and aerated with air through a mini-type pump to keep $NiTiO_3$ in fluidized state. At given time intervals, the samples of HA solution were analyzed periodically by Varian Cary 50 UV-vis spectrophotometer.

## 3. Results and discussion

### 3.1. TG-DTA analysis

In order to investigate the crystalline behaviour and find out the optimum calcining temperature of the citrate complex, the TG-DTA was conducted and the analytic spectra are illustrated in Fig. 1. The TG curve has two weight loss regions. The first weight loss region from room temperature to 180°C is mostly due to dehydration and evaporation of organic matters. The second weight loss region between 200 and 430°C seems to be associated with the evolution of carbonaceous materials. The DTA curve displays an obvious endothermic peak between 70 and 250°C, which might be the evaporation of the alcohol solvent. A remarkable exothermic peak is observed at 330°C, which might be the burnout and decomposition of the Ni-Ti citrate complex. The exothermic peak occurred in the temperature range of 470 to 600°C is assigned to form the ilmenite structure of $NiTiO_3$. The last exothermic peak about 750°C is due to the decomposition of certain $NiTiO_3$ into $Ni_2O_3$ and $TiO_2$.

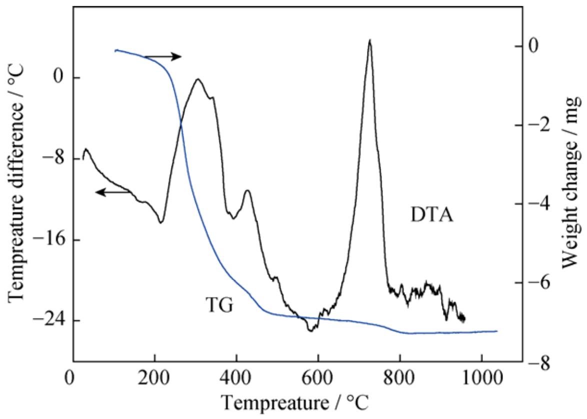

**Fig. 1. TG-DTA curves of the Ni-Ti citrate complex at a heating rate of 30°C/min.**

### 3.2. XRD patterns

XRD patterns of the prepared samples calcined at different temperatures for 3 h are shown in Fig. 2. The sample calcined at 500°C exhibits several broader small peaks as shown in Fig. 2(a), and the correspondence compounds are $TiO_2$, TiO, $Ni_2O_3$, and a small amount of $NiTiO_3$. When the temperature rises to 600°C, the major ilmenite reflections of $NiTiO_3$ are then clearly observed, which means that the transformation of the Ni-Ti citrate complex to ilmenite phase is almost complete. Some impurity peaks ($Ni_2O_3$ and $TiO_2$) occur when the temperature rises to 700°C. When the calcination temperature increases to 900°C, more nickel titanate decomposes due to the decomposition of a certain nickel titanate. Combining with the TG-DTA curves in Fig. 1, it can be seen that when the temperature is more than 750°C, nickel titanate will be decomposed. Based on the above TG-DTA and XRD analysis, the optimum calcining temperature of the Ni-Ti citrate complex is 600°C.

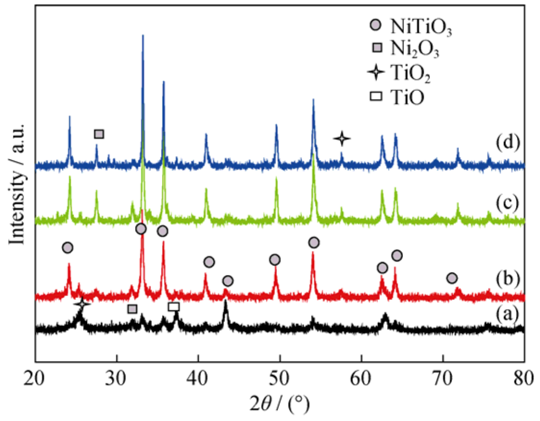

**Fig. 2. XRD patterns of the Ni-Ti citrate complex calcined at (a) 500°C, (b) 600°C, (c) 700°C, and (d) 900°C for 3 h.**

### 3.3. Effect of the calcined temperature of samples on the photocatalytic activity

In order to study the influence of calcined temperature for the Ni-Ti citrate complex on the degradation rate of HA, a set of experiments were performed under the same test conditions of photocatalyst 0.4 g/L and reaction time 2.5 h at different calcined temperatures of 500, 600, 700, and 900°C, and the results are shown in Fig. 3. Fig. 3 shows that the HA degradation rates under UV irradiation were 86%, 95.3%, 88.3%, and 67.2%, respectively. It is obvious that the photocatalyst calcined at 600°C exhibits the best photocatalytic activity among the four samples. These results demonstrate that the photocatalytic activity increases with the increase of heat treatment temperature below 600°C, and further increasing the heat treatment temperature leads to an obvious decrease in degradation rate. This feature indicates that the calcined temperature has an important influence on the photocatalytic activity of $NiTiO_3$. In consideration of the photocatalytic activity and catalyst structure, 600°C is chosen as calcined temperature for the Ni-Ti citrate complex in the following experiments.

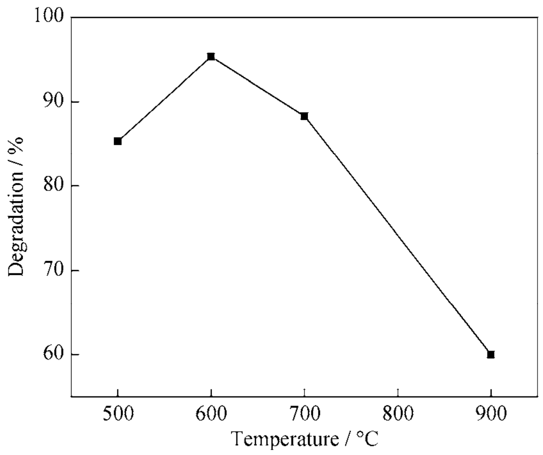

**Fig. 3. Effect of heat treatment temperature on the degradation of HA.**

### 3.4. Effect of active species on the photocatalytic process

In our case of photocatalytic degradation of HA, UV irradiation induces the formation of electrons ($e^-$) and holes ($h^+$) on the $NiTiO_3$ surface. The photogenerated holes ($h^+$) could react with the adsorbed $OH^-$ to produce high activity $\cdot$OH radicals. $\cdot$OH radicals can react with any substances non-selectively. The photogenerated holes ($h^+$) can also deprive the electrons of organic pollutants directly and oxidize them into radicals. Meanwhile, dissolved oxygen (DO) in water can capture electrons and produce $\cdot O_2^-$, which could react with HA or HA intermediates. Moreover, DO can further form into ·OH under protonation resulting in degradation of HA [16].

Therefore, in the photocatalytic degradation process of organics, the holes ($h^+$), $\cdot O_2^-$, and ·OH are considered to be the reactive active species, and ·OH hydroxyl radicals have been deemed to be the major active species and can be tested by different methods such as the photoluminescence (PL) technique [17] and sacrificial agents. To ascertain the role of the major reactive species in the degradation process of HA, a series of tests were conducted by adding some sacrificial agents, such as isopropanol ($C_{\text{isopropanol}}$ = 0.01 mol/L) [18], $NaHCO_3$ ($C_{NaHCO_3}$ = 0.01 mol/L) [19], and $N_2$ (in place of air) into the reaction solution to confirm the possible reaction mechanism. The results are shown in Fig. 4. From Fig. 4, it can be seen that when no scavenger was added to the reaction solution, about 95% HA was degraded by $NiTiO_3$. When $\cdot O_2^-$ scavenger, $N_2$, was introduced from the bottom of the photoreactor, about 87% HA was degraded. This shows that $\cdot O_2^-$ is not the major reactive species in this process. However, when the holes ($h^+$) and ·OH scavenger ($NaHCO_3$) were put into the photocatalytic reaction system, about 32% HA was degraded. This indicates that holes ($h^+$) and ·OH play an important role in the photocatalytic process. When ·OH scavenger (isopropanol) was put into the degradation system, about 58% HA was degraded. It suggests that ·OH radicals really play a major role in the photodegradation of HA. These results indicate that both photogenerated holes ($h^+$) and ·OH play an important role in the photodegradation of HA.

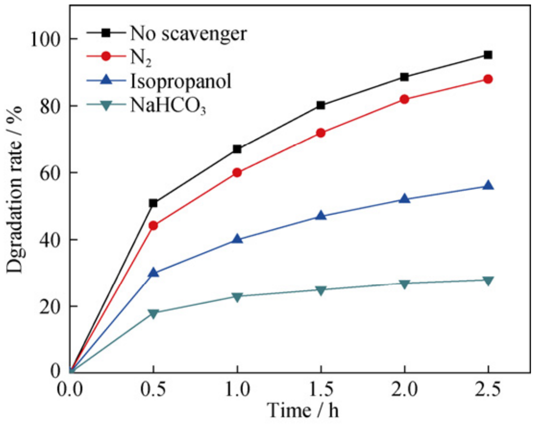

**Fig. 4. Effect of scavengers on the degradation rate.**

### 3.5. Effect of photocatalyst amount on the degradation rate

For economic removal of HA from nature water, it is necessary to find a favourite catalyst amount for photocatalytic degradation, and a set of experiments were performed under different $NiTiO_3$ dosages of 0.2, 0.4, and 0.6 g/L. Fig. 5 shows the degradation rate increased with the increase of photocatalyst dosage. However, when the photocatalyst amount exceeded 0.4 g/L, the degradation rate of HA decreased. It is well known that the less photo energy will be changed into chemical energy when the amount of photocatalyst is less. Therefore, the photocatalytic activity of the photocatalyst increased with the addition of photocatalyst. However, when the amount of the photocatalyst is excessive, the action of light scattering is aggravated by excessive catalyst suspending in aqueous solution. Additionally, for a larger catalyst amount, the catalyst particles screen mutually, which would reduce the surface area of the catalyst and lead to the decrease of photocatalytic activity [20]. Therefore, an appropriate catalyst amount is needed for the photocatalytic reaction. In our experiments, the favourite dosage of $NiTiO_3$ is 0.4 g/L.

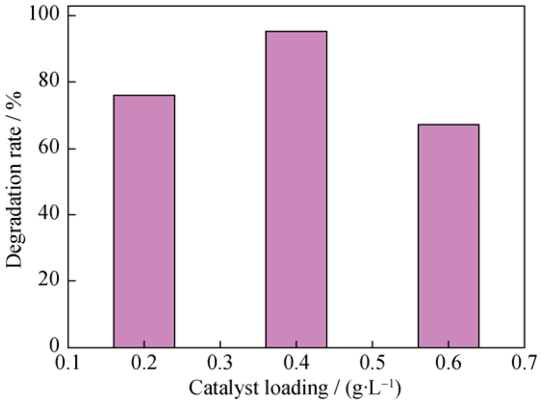

**Fig. 5. Effect of photocatalyst amount on the degradation rate.**

### 3.6. Comparison of photolysis, photocatalysis, and adsorption of HA

It is well known that the adsorption of organic pollutants on photocatalysts is very important for heterogeneous photocatalytic reactions [21]. In order to reveal some valuable information for a better understanding of the photocatalytic performance, Fig. 6 shows the comparative results of the degradation rate with reactive time in adsorption, photolysis, and photocatalytic process, respectively. The results showed that about 25% and 14.7% of HA were removed for adsorption and photolysis process, respectively. While after a 2.5 h reaction, 95.3% of HA was removed by photocatalytic process, and it can be seen the photocatalytic rate is higher within 0.5 h at the beginning. This is because the photocatalytic process of this period is composed of adsorption, photolysis, and photocatalysis at the same time, leading to the reaction rate at this period to be much higher than that at other periods. After some reaction time, both adsorption and photolysis achieved a relatively stable value, and the whole photocatalytic reaction rate increased slowly.

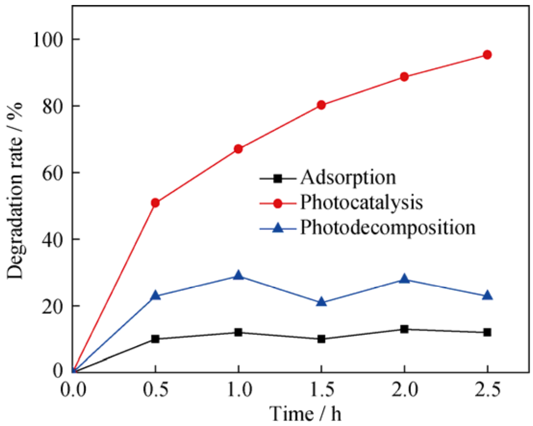

**Fig. 6. Comparison of photolysis, photocatalysis, and adsorption of HA.**

## 4. Conclusions

The powders of ilmenite structure $NiTiO_3$ were prepared successfully by a modified Pechini process and subsequent heat calcination treatment. The prepared $NiTiO_3$ powders exhibit good photocatalytic activity on the degradation of HA. The heat treatment temperature of the Ni-Ti citrate complex has a great effect on the crystal structure and photocatalytic activity of the prepared photocatalysts. When the heat treatment temperature is 600°C, $NiTiO_3$ expresses a higher photocatalytic activity in the degradation process of HA. The optimal amount of $NiTiO_3$ catalyst is 0.4 g/L. The photodegradation mechanism investigations demonstrate that the holes ($h^+$) and ·OH radicals are the major active species for the degradation reactions of HA under UV irradiation, but the $\cdot O_2^-$ oxidation plays a minor role.

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