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Article

Effect of N₂/Ar plasma treatment on the visible light photocatalytic activity of CuO/TiO₂

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ABSTRACT

The effect of N₂/Ar dielectric barrier discharge plasma on the photocatalytic activity of CuO/TiO₂ under visible light irradiation was studied. The photocatalysts were characterized by X-ray diffraction, ultraviolet-visible spectrophotometry, transmission electron microscopy, X-ray photoelectron spectroscopy, and electron paramagnetic resonance spectroscopy. The plasma parameters including gas composition, treatment time, and plasma power were investigated. The activities of the plasma-treated photocatalysts were evaluated by the photodegradation of methyl orange under visible light illumination. The optimal operation conditions were N₂:Ar = 8:2, treatment time of 20 min, and a discharge current of 1.0 A. Simulated mercury-containing wastewater was treated by the photocatalysts.

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1. Introduction

With the merits of photochemical stability, low cost, non-toxicity, and so on, TiO₂ has given high hopes in the areas of energy, environment protection, and organic synthesis and their many applications [1,2]. However, the efficiency of the photocatalyst is hindered by the high recombination rate of photo-generated electrons and holes and the narrow light response range. TiO₂ can only be excited by light with wavelength less than 387.5 nm, which comprise only 3%–5% of the solar spectrum, due to the intrinsic band gap (3.2 eV, anatase), that is, much of visible and infrared light cannot be utilized [3,4]. Because visible light response was achieved with N-doped TiO₂ by Asahi *et al.* [4] in 2001, N-doping has been recognized as one of the best strategies to extend the light response range of TiO₂. Meanwhile, the combination of nonmetal doping and co-catalyst deposition has been shown to give a better effect than the

single modification [5–7]. Cu_xO is one of the best co-catalysts for TiO₂ because of its nontoxicity, low cost, and unique optical and electrical properties [8,9].

Conventional methods of N-doping include sol-gel synthesis [10], calcination in a N-containing atmosphere [4], TiN oxidation [11], electrochemical anodic oxidation [12], ion implantation [13], and ultrasonic [14] and plasma treatments [7,15]. The plasma treatment method is easy to operate, there is no need for a high temperature, and it is rapid. So it has been widely used in the surface modification of materials. Pulsipher *et al.* [15] treated TiO₂ films with a NH₃/N₂ radio frequency discharge and obtained a series of N-doped samples, in which the highest N content reached 31.5%. Trejo-Tzab *et al.* [7] also prepared N-doped TiO₂ by N₂ plasma. Plasma treatment can enhance the photocatalytic performance of TiO₂ by both element doping and that it also induced the presence of oxygen vacancies and Ti³⁺ by the collision and spluttering of energetic

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species and materials during the plasma treatment [16–18]. Dielectric barrier discharge (DBD) is a kind of low temperature discharge plasmas. As compared with other kinds of discharges, the DBD apparatus is more compact in structure, more convenient to operate, and has a lower requirement of the reaction and low energy consumption [19,20].

In this work, CuO nanoparticles were deposited on the surface of P25-TiO₂, and the resulting CuO/TiO₂ was treated by a N₂/Ar DBD plasma. The samples were characterized by X-ray diffraction (XRD), ultraviolet-visible spectrophotometry (UV-Vis), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance spectroscopy (EPR). The effects of discharge parameters on the photocatalytic activity were evaluated by the photocatalytic degradation of methyl orange (MO). Mercury-containing wastewater was processed by the modified photocatalysts.

2. Experimental

2.1. Catalyst preparation and plasma treatment

CuO was deposited on the surface of P25-TiO₂ by the dipping method [21]. P25-TiO₂ (1 g) was added into 100 mL of 0.25 mol/L NaOH aqueous solution, and a 0.05 mol/L Cu(NO₃)₂ solution was added dropwise under vigorous stirring until the mass ratio of Cu:Ti was 0.01. After further stirring for 6 h, the precipitates were filtrated and washed with deionized water until the pH was 7, then dried at 80 °C for 12 h and subsequently calcined at 400 °C for 2 h in air. The resulting CuO/TiO₂ was then treated with N₂/Ar plasma in a DBD plasma reactor.

The experimental set-up for the plasma treatment is presented in Fig. 1. A molybdenum wire that served as the outer electrode was compactly wound around a 60 mm outer diameter corundum tube. A stainless steel rod (40 mm in diameter) was placed in the center of the corundum tube to act as the inner electrode, which was connected to the power supply (CP-8000P, Nanjing Suman Electronics Co., Ltd, China). The discharge gap between the corundum tube and inner electrode, where a quartz boat with the sample was placed, was 7 mm. A DBD plasma was generated between the steel electrode and the outer electrode that was attached to ground. N₂ (99.999%) and Ar (99.999%) were introduced into the reactor with the pressure and flow rates of N₂ and Ar controlled by mass flow controllers. Experiments were carried out using changes in the power delivered to the plasma, plasma treatment time, reaction pressure, and gas composition. The plasma treated catalyst was denoted as Cu₂O/N-TiO₂.

Fig. 1. DBD plasma treatment experimental setup.

2.2. Catalyst characterization

XRD analysis was carried out to verify the crystal structure of the photocatalysts using a Rigaku Smartlab3 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. The patterns were recorded in the range from 20° to 80° with a step size of 0.02°/s. UV-Vis absorption spectra were collected on a Perkin Elmer Lambda 950 scanning spectrophotometer using polytetrafluoroethene as the reference. The lattice structure was visualized by TEM using a JEOL JEM 2010F electron microscope equipped with a field emission gun electron source using an acceleration voltage of 200 kV. XPS analysis was performed on a PHI 5000 VersaProbe system to characterize the surface properties of the photocatalysts. All binding energies were referenced to the C 1s peak of adventitious carbon on the surface at 284.6 eV. EPR spectra were recorded at -196 °C on a Bruker EMX 10/12 spectrometer working in the X-band with 10 mg of the sample placed in an EPR quartz probe cell.

2.3. Photocatalytic evaluation

The photocatalytic activity was evaluated by monitoring MO degradation. A xenon light of 300 W (CEL-HXF 300) was used as light source, and visible light with wavelength above 400 nm was acquired by using a UVCUT-400 cut-off filter. A solution of 100 mL of MO (10 mg/L) and 0.10 g of catalyst were placed into a water-cooled jacket beaker (20 °C), and adsorption-desorption equilibrium was attained by stirring using a magnetic stirrer for 30 min before irradiation. The suspension was then irradiated for 120 min. Aliquots (5 mL) before (C_0) and after (C) irradiation was sampled. The aliquots were filtrated through a 0.45 μm syringe filter to remove the photocatalyst particles, and then the dye photodegradation was monitored by measuring the MO concentration using absorbance on a UV-Vis spectrometer (Spectrumbab 752s) at 464 nm. The decomposition efficiency was calculated as $(1 - C/C_0) \times 100\%$.

2.4. Treatment of Hg²⁺-containing wastewater

An HgCl₂-containing solution with a Hg²⁺ concentration of 50 mg/L was prepared, and three kinds of photocatalysts were used to process this simulated wastewater under visible light irradiation. The dosage of photocatalysts was 1 g/L, and the temperature was 20 °C. Before irradiation, the system was stirred in the dark for 60 min to give adsorption-desorption equilibrium. After the specified reaction time, an aliquot was sampled and filtered by a 0.45 μm syringe filter to remove the photocatalyst particles. Then inductively coupled plasma emission spectrometry (ICP, iCAP 6300, Thermo Fisher) was used to monitor the concentration of Hg²⁺.

3. Results and discussion

3.1. Characterization of the photocatalysts

XRD patterns of the TiO₂, CuO/TiO₂, and Cu₂O/N-TiO₂ catalysts are shown in Fig. 2. P25-TiO₂ is composed of 20% rutile

Fig. 2. XRD patterns of TiO₂ (1), CuO/TiO₂ (2), and Cu₂O/N-TiO₂ (3).

Fig. 3. UV-Vis spectra of TiO₂, CuO/TiO₂, and Cu₂O/N-TiO₂.

and 80% anatase. Signals corresponding to Cu species were not detected in the pattern after the deposition of CuO, which would be due to the low content and high dispersion of the Cu species [22]. The pattern of the plasma treated sample was unchanged, which means that the plasma treatment had no effect on the crystal structures of the TiO₂ phases.

As shown in Fig. 3, the UV-Vis absorption spectrum of TiO₂ was affected by the deposition of CuO and plasma treatment. The absorption below 400 nm was attributed to the intrinsic band gap. After TiO₂ modification, the absorption edges of CuO/TiO₂ and Cu₂O/N-TiO₂ were extended to the visible light range. The absorption in the range of 600–800 nm was due to the $d-d$ transition of Cu²⁺ ions [23]. The absorption of Cu₂O was

Fig. 4. TEM images of Cu₂O/N-TiO₂.

centered at 500–600 nm [24]. The small absorption near 400–500 nm originated from the interfacial charge transfer between TiO₂ and Cu_xO [25]. It is noteworthy that the absorption in the range of 500–600 nm was clearly increased after the plasma treatment, which was caused by the doped N and induced surface vacancies [16].

The structure of Cu₂O/N-TiO₂ was observed by TEM (Fig. 4), which clearly demonstrated that particles with the size of about 3 nm were uniformly supported on the surface of TiO₂. From the interplanar spacing (0.208 nm), the nanoparticles can be recognized as Cu₂O [26], which meant that the deposited CuO was reduced to Cu₂O during the plasma treatment.

Figure 5 shows the XPS spectra of Cu 2p, O 1s, N 1s, and Ti 2p of the Cu₂O/N-TiO₂ samples treated at different times. The ratio of N₂:Ar and discharge current were kept at 8:2 and 1.0 A, respectively. The atomic compositions of the samples treated for different times are shown in Table 1.

Fig. 5. XPS spectra of Cu 2p (a), O 1s (b), N 1s (c), and Ti 2p (d) for the Cu₂O/N-TiO₂ samples treated for different times.

Table 1Atomic compositions of Cu₂O/N-TiO₂ samples treated for different times.

Time (min)	Atomic composition (%)				O/Ti ratio
	N	O	Ti	Cu	
0	0	48.01	19.80	1.11	2.42
10	0	44.31	17.34	0.98	2.56
20	0.49	46.37	18.42	0.96	2.52
30	0.60	42.15	16.38	0.90	2.57
40	0.70	46.99	18.01	0.85	2.61

We can see from Fig. 5(a) that the binding energy of the Cu 2p_{3/2} level was shifted from ~933 to ~931 eV, which illustrated that CuO was reduced to Cu₂O by the plasma treatment. That was consistent with the TEM image. The O 1s and Ti 2p orbitals (Fig. 5(b) and (d)) showed the same trend as the Cu 2p_{3/2} orbital. This was explained by that N doping resulted from the plasma treatment, and electrons from the doped N species partially migrated to Ti and O. The electron density of Ti and O would increase, thus leading to the shifted binding energy [19].

As shown in Fig. 5(c), the peaks at 396, 400, and 407 eV appeared with the increase of treatment time in the N 1s spectra of the modified TiO₂. The content of N also increased with time (Table 1). The signal at 400 eV was assigned to N species in the interstitial of the TiO₂ lattice, such as NO and NH_x [27]. The signal at 396 eV was attributed to the formation of Ti-N, which resulted from the replacement of O by N [4]. The signal at 407 eV was assigned to NO₃ [28]. Asahi *et al.* [4] believed that the Ti-N bond formed led to the decrease of band gap and brought about the visible light response. However, this point of view has not been widely recognized, and the reason for induced photocatalytic activity is still under debate [29].

The EPR spectrum of Cu₂O/N-TiO₂ is shown in Fig. 6. A peak was shown at $g = 1.975$, which can be assigned to surface Ti³⁺ [16]. Surface Ti³⁺ can react with O and form O₂⁻ and/or O⁻, which would generate a signal around $g = 2.00$ [30], but this feature was not obvious in Fig. 6. The reason was that the signal was too weak and was screened by the signal of Ti³⁺ [31].

3.2. Effects of discharge parameters on the photocatalytic activity of the modified catalysts

The effect of the modification depended on the discharge

Fig. 6. EPR spectrum of the Cu₂O/N-TiO₂ sample.

parameters. N containing gases such as N₂ and NH₃ are usually used in N doping by gas phase methods, but the presence of the gas was not sufficient for doping. Huang *et al.* [17] modified TiO₂ by a N₂ radio frequency plasma, but N was not found in the product obtained. The doping is mainly affected by the gas composition, flow rate, delivered power, and treatment time. In our work, samples modified under different conditions were used to degrade MO by visible light irradiation for 120 min, and appropriate reaction conditions were optimized using the degrading efficiency.

In the experiments, the total gas flow was controlled at 1 L/min, and the ratio of N₂:Ar was selected as a variable. As shown in Fig. 7(a), the photocatalytic activity was enhanced with the increase of the proportion of N₂, but the modified sample obtained at the ratio of 8:2 was superior to that when only N₂ was used. The dissociation energy of N₂ is higher than that of Ar, so Ar is easier to excite. By the Penning effect of the plasma discharge process, the metastable particles of Ar can react with N₂ and promote the excitation and dissociation of N₂, and more N intermediates would be formed, such as N* and N₂⁺ [32,33]. So the increase of the proportion of N₂ increased the concentration of N, but the increase of the proportion of Ar led to the higher density of metastable species.

With regard to the treatment time, the concentration of doped N increased with the increase of treatment time. However, the results in Fig. 7(b) showed that an excessive treatment was detrimental to the activity of the modified sample. We can see from Table 1 that the Cu content decreased with

Fig. 7. Effects of N₂:Ar ratio (a), treatment time (b), and discharging current (c) on photocatalytic activity.

increasing treatment time. During the discharge, energetic metastable species strip the surface of TiO_2 continuously, so nano-sized Cu species may be stripped from the surface of the TiO_2 . The impairment of the p-n junction effect caused the loss of photocatalytic activity.

The power delivered to the reactor was crucial to the modification effect. Insufficient power cannot dissociate the gas, while excess power supplied to the system is converted into heat and causes overheating of the apparatus. In this work, the power was controlled by the adjustment of the discharge current. Figure 7(c) shows the influence of delivered power on the modification effect with the N_2 :Ar ratio of 8:2 and treatment time of 10 min. The results showed that the best discharge current was 1.0 A. In summary, the optimal operation conditions were N_2 :Ar at the ratio of 8:2, treatment time of 20 min, and discharge current of 1.0 A.

3.3. Hg^{2+} abatement by the modified photocatalyst

Figure 8 shows the results of the treatment of Hg^{2+} -containing wastewater by the catalysts. The simulated wastewater had a neutral pH. Under this circumstance, the adsorption of Hg^{2+} on the surface of the photocatalyst was negligible in the dark. We can see from Fig. 8(a) that the concentration of Hg^{2+} during the adsorption step showed no trend of decrease. Under visible light irradiation, the concentration of Hg^{2+} decreased significantly compared to that in the dark. The pristine TiO_2 showed a slight activity for Hg^{2+} treatment, but the photocatalytic activity of CuO/TiO_2 was much higher. The co-modified

Fig. 8. (a) Treatment of Hg^{2+} -containing wastewater using TiO_2 , CuO/TiO_2 , and $\text{Cu}_2\text{O}/\text{N-TiO}_2$. (b) Recycle runs for the photocatalytic treatment of Hg^{2+} -containing wastewater under visible light irradiation with $\text{Cu}_2\text{O}/\text{N-TiO}_2$.

Fig. 9. SEM image (a) and EDX spectrum (b) of $\text{Cu}_2\text{O}/\text{N-TiO}_2$ photocatalyst after reaction.

$\text{Cu}_2\text{O}/\text{N-TiO}_2$ gave the best performance and complete conversion in 20 min.

During the photocatalytic reduction of Hg^{2+} , photo-generated electrons reacted with Hg^{2+} adsorbed on the surface of the photocatalyst, and the heavy metal ions were reduced to a low valence state even to zero valence. The reactions are [34]:

The used photocatalyst was recovered with 5% HNO_3 and washed by deionized water. Then the dried photocatalyst was reused in the treatment of Hg^{2+} . As shown in Fig. 8(b), 4 recycling runs in the photocatalytic treatment of Hg^{2+} over $\text{Cu}_2\text{O}/\text{N-TiO}_2$ under visible light illumination were carried out. The reaction time was limited to 20 min for each run. The data showed that the photocatalyst exhibited almost no loss of activity after 4 cycles and was stable during the photocatalytic treatment of Hg^{2+} .

In order to verify the experimental results, the $\text{Cu}_2\text{O}/\text{N-TiO}_2$ photocatalyst was collected after reaction, and the surface was analyzed by SEM (JSM-6510, JEOL) and energy dispersive X-ray spectroscopy (EDX) after drying at 30 °C. As shown in Fig. 9, tiny particles were adsorbed on the surface of the photocatalyst. The EDX spectrum demonstrated the existence of Hg that was separate from O, Ti, and C. It can be concluded that the Hg^{2+} was reduced in the photocatalytic reaction and then adsorbed on the surface [35].

4. Conclusions

CuO/TiO_2 was modified by a N_2 /Ar DBD plasma treatment. Characterization of the obtained material demonstrated that N doping was achieved, and there was also the formation of sur-

Graphical Abstract

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N₂/Ar plasma treated CuO/TiO₂ gave better treatment of mercury-containing waste water under visible light irradiation than TiO₂ and CuO/TiO₂.

face defect states, such as Ti³⁺. The modifications induced by the plasma treatment led to the enhancement of visible light photoactivity. The discharge parameters were optimized using the degradation of MO by the samples under visible light irradiation. The appropriate treatment conditions were N₂:Ar at the ratio of 8:2, treatment time of 20 min, and discharge current of 1.0 A. The plasma-treated Cu₂O/N-TiO₂ catalyst showed superior performance to TiO₂ and CuO/TiO₂ for the treatment of Hg²⁺-containing wastewater, and it is expected to be a promising candidate for other applications.

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N₂/Ar等离子体改性对CuO/TiO₂可见光光催化活性的影响

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摘要: 研究了N₂/Ar介质阻挡放电处理对负载CuO的TiO₂可见光光催化活性的影响. 采用X射线衍射、紫外-可见分光吸收光谱、透射电镜、X射线光电子能谱和电子自旋共振进行了表征, 详细考察了等离子体改性参数包括气氛组成、处理时间和处理功率对改性效果的影响, 并通过降解甲基橙溶液考察了可见光光催化活性. 结果表明, 最佳等离子体处理条件为N₂与Ar比例为8:2, 处理时间为20 min, 放电电流为1.0 A. 最后, 使用改性后的光催化剂对模拟含汞废水进行了处理.

关键词: 二氧化钛; 等离子体; 改性; 氮掺杂; 汞

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1. 前言

TiO₂具有光化学稳定性好、成本低、无毒等优点, 广泛应用于能源、环境、合成以及其他光催化领域^[1,2]. 但是, 其光催化效果受限于较高的光生电子与光生空穴复合率和过于狭窄的光响应范围, 其本征禁带宽度(~3.2 eV, 锐钛矿)限制了它只能被波长387.5 nm以下的光线所激发, 而这一部分仅占太阳光谱的3%–5%, 大量的可见光甚至红外光线无法被利用^[3,4]. 自2001年Asahi等^[4]制备了可见光响应的N掺杂TiO₂以来, N掺杂改性被视为扩展其光响应范围的最佳途径之一. 同时, 非金属元素掺杂与助剂负载比单一的改性方法更有效^[5–7]. Cu_xO由于具有无毒、廉价和独特的光电特性已经成为TiO₂最好的助剂之一^[8,9].

通常的N掺杂方法包括溶胶凝胶法^[10]、含氮气氛焙烧^[4]、TiN氧化法^[11]、电化学阳极氧化法^[12]、离子注入法^[13]、超声法^[14]以及等离子体法^[7,15]等. 其中, 等离子体处理法具有操作简便、无需高温和处理时间短等优点, 已经被广泛运用于材料表面改性. Pulsipher等^[15]利用射频等离子体放电分别在NH₃和N₂气氛中对制备的TiO₂薄膜进行处理, 得到一系列N掺杂的样品, 最高含N量可达31.5%. Trejo-Tzab等^[7]使用N₂等离子体放电同样实现了N掺杂. 等离子体处理方法不仅能有效进行元素掺杂, 而且在处理过程中高能电子和基团与材料的表面碰撞、溅射所形成的氧空位和Ti³⁺缺陷, 也能显著提高TiO₂的光催化性能^[16–18]. 在多种等离子体放电方式中, 介质阻挡放电(DBD)作为一种低温等离子体放电方式, 相对于其他放电方式无需复杂的设备, 操作更简单, 反应条件要求更低,

耗能低, 更具有可操作性^[19,20].

本文采用浸渍法在TiO₂ (P25)表面负载CuO, 然后利用DBD放电装置在N₂/Ar气氛中对CuO/TiO₂进行处理, 运用X射线衍射(XRD)、紫外-可见吸收光谱(UV-Vis)、X射线光电子能谱(XPS)、透射电镜(TEM)和电子自旋共振(EPR)等手段对所得样品进行了表征, 并且通过它们对甲基橙的光催化降解考察了不同放电条件对其可见光光催化性能的影响. 最后将改性后的光催化剂用于处理模拟含汞废水.

2. 实验部分

2.1. 催化剂制备与等离子体改性

通过浸渍法将Cu负载在TiO₂ (P25, Degussa)表面^[21]. 将1 g TiO₂加入到100 mL NaOH溶液(0.25 mol/L)中搅拌均匀, 然后在剧烈搅拌下逐滴加入一定量Cu(NO₃)₂溶液(0.05 mol/L), 使得体系中Cu与Ti的质量比为1%. 搅拌6 h后, 过滤沉淀, 用水洗至pH = 7, 经80 °C干燥12 h后于400 °C焙烧2 h制得CuO/TiO₂.

将CuO/TiO₂置于自制的DBD等离子体发生器中进行处理. 如图1所示, 与地电极相连的钼丝紧密缠绕在外径60 mm的刚玉管外作为外电极, 直径40 mm的不锈钢与高压电源(CP-8000P, 南京苏曼电子有限公司)相连, 置于刚玉管中作为内电极, 内电极与刚玉管的间隙约为7 mm. 将样品盛放在厚约1 mm的石英舟上, 然后放置在刚玉管与内电极的间隙中, 通过电极之间的介质阻挡放电对TiO₂进行处理. N₂ (99.999%)与Ar (99.999%)通入反应器, 气体的压力和流速由压力表和流量计控制. 在处理过程中, 通过改变N₂与Ar的比例、等离子体处理时间和等

离子处理功率等考察不同处理条件对光催化剂的改性效果.

2.2. 催化剂表征

采用日本理学Smartlab3型X射线衍射仪($\text{Cu K}\alpha$ 靶, $\lambda = 1.5418 \text{ \AA}$)测定催化剂的晶型结构, 工作电压与电流分别为40 kV和30 mA, 扫描速度为 $0.02^\circ/\text{s}$, 扫描角度从 20° 到 80° . 催化剂的UV-Vis光谱通过Perkin Elmer Lambda 950型分光光度计测得, 以聚四氟乙烯作为参比. 晶格结构利用JEOL JEM 2010F型TEM表征, 扫描电压为200 kV. 使用PHI 5000 VersaProbe型电子能谱仪分析催化剂中各元素组分, 扫描结果以 284.6 eV 处的C 1s峰校正. 使用Bruker EMX-10/12型顺磁共振仪波谱仪测试10 mg样品在 -196°C 条件下的信号.

2.3. 光催化性能测试

将甲基橙溶液作为目标底物检验制备光催化剂的活性. 以氙灯作为光源(300 W, CEL-HXF300), 并且用UVCUT-400截止型滤光片滤掉 $\lambda < 400 \text{ nm}$ 的光线得到可见光. 将0.1 g光催化剂加入100 mL浓度为10 mg/L的甲基橙溶液中, 在光照前搅拌30 min以达到吸附-脱附平衡, 在整个反应过程中通过夹套中的循环水控制反应体系温度为 20°C . 达到一定反应时间后, 取样经 $0.45 \mu\text{m}$ 的滤头过滤, 滤液使用紫外可见分光光度计(Spectrumlab 752s)在464 nm处测试吸光值, 反应前的吸光值记为 C_0 , 反应后的吸光值为 C , 光催化降解效率表示为 $(1 - C/C_0) \times 100\%$.

2.4. 含汞模拟废水处理

将 Hg^{2+} 浓度为50 mg/L的 HgCl_2 溶液作为模拟含汞废水, 在波长 $> 400 \text{ nm}$ 可见光条件下分别用未改性 TiO_2 , CuO/TiO_2 和等离子改性的 $\text{Cu}_2\text{O}/\text{N}-\text{TiO}_2$ 进行处理. 光催化剂投加量为1 g/L, 反应温度维持在 20°C . 在光照反应之前避光搅拌60 min以达到吸附脱附平衡. 光照反应一定时间后, 取一定体积反应液经 $0.45 \mu\text{m}$ 滤头滤去催化剂颗粒, 用电感耦合等离子发射光谱(iCAP 6300, Thermo Fisher)检测滤液中 Hg^{2+} 含量.

3. 结果与讨论

3.1. 催化剂的表征

图2为 TiO_2 , CuO/TiO_2 和 $\text{Cu}_2\text{O}/\text{N}-\text{TiO}_2$ 的XRD图. P25的晶相组成约为80%的锐钛矿和20%的金红石相, 负载CuO之后, 并未出现Cu物种晶相, 可能是由于Cu含量较低且分散很均匀的缘故^[22]. 还可以看出, 等离子处理也没有改变催化剂的晶相结构, 说明等离子处理对 TiO_2

的晶体结构没有影响.

图3为等离子处理对 TiO_2 的UV-Vis光谱的影响. P25在400 nm处的吸收属于 TiO_2 本征吸收; 而负载了Cu和经过等离子处理之后, 其吸收边向可见光区域发生偏移. 其中600–800 nm范围内的吸收是由于 Cu^{2+} 上d-d轨道电子发生跃迁^[23]; 而 Cu_2O 的吸收光谱在500–600 nm处^[24]; 400–500 nm处的微弱吸收则源自于 TiO_2 与 Cu_xO 之间的界面载流子迁移^[25]. 等离子处理后, 掺杂的N元素和形成的氧空位使得样品在500–600 nm范围内的吸收明显增强^[16].

图4为等离子处理后 $\text{Cu}_2\text{O}/\text{N}-\text{TiO}_2$ 的TEM照片. 可以看出, 大小约为3 nm的微粒均匀地负载在 TiO_2 表面, 其晶面间距为0.208 nm, 可以确定为 Cu_2O ^[26]. 这说明经过等离子处理后, TiO_2 表面负载的CuO被活性中间产物和高能电子还原成 Cu_2O .

图5为不同时间等离子处理后样品的Cu 2p, O 1s, N 1s和Ti 2p XPS谱. 我们比较了气氛组成为 $\text{N}_2:\text{Ar} = 8:2$ 和电流1.0 A条件下不同处理时间对光催化剂表面元素组成的影响. 表1为等离子处理前后催化剂表面的元素组成与比例.

从图5(a)可见, 经等离子体处理后, Cu 2p_{3/2}信号峰向低结合能位移, 由 $\sim 933 \text{ eV}$ 移至 $\sim 931 \text{ eV}$, 说明 TiO_2 表面的CuO在等离子处理过程中被还原为 Cu_2O , 与TEM结果一致. 图5(b)和(d)分别为O 1s和Ti 2p谱图. 可以看出, O 1s和Ti 2p的峰都向低结合能偏移. 这可能是由于等离子处理造成N掺杂, 掺杂后N原子的部分电子转移给Ti和O, 引起Ti和O电子密度增加, 从而导致结合能偏移^[19].

如图5(c)所示, 随着处理时间的增加, 改性催化剂的N 1s在约396, 400和407 eV都出现峰, 另外其表面N含量逐渐增加(表1). 一般认为, 400 eV处峰的形成是由 TiO_2 晶格间隙的N化合物引起的, 如 NH_x 和NO等^[27]; 而396 eV处的峰则是 TiO_2 晶格中的O被N取代后所形成的Ti–N键导致的^[4]; 407 eV处峰说明可能存在 NO_3^- ^[28]. Asahi等^[4]首先认为, N取代晶格中的O后形成的Ti–N导致禁带宽度降低, 造成可见光响应. 但是也有许多不同观点^[29], 目前尚无定论.

图6为 TiO_2 等离子处理之后的EPR谱. 可以看出, TiO_2 在 $g = 1.975$ 处出现了一个峰, 可归属于表面 Ti^{3+} ^[16]. 一般情况下, 由于表面的 Ti^{3+} 会与氧分子反应, 生成 O_2^- 或者 O^- , 二者都可在 $g = 2.00$ 左右产生信号响应^[30]. 但是在图6中并不明显, 可能是由于氧空位信号太弱, 被 Ti^{3+} 的信号峰掩盖^[31].

3.2. 等离子处理条件对催化剂光催化性能的影响

不同反应条件对掺杂效果影响很大. 一般在气相掺杂方法中都是以含氮气体作为反应物, 如 N_2 和 NH_3 或其他一些易挥发的有机含氮物质. 但是仅仅在氮源存在的情况下, 并不一定能够实现N掺杂, 如Huang等^[17]利用 N_2 射频放电等离子体处理 TiO_2 后发现, 处理后的样品中并无N元素. 掺杂过程受到气体组分、气体流速、放电功率以及处理时间等条件的影响. 本文用不同条件下改性的光催化剂在可见光条件下降解甲基橙溶液, 通过比较改性后光催化剂的活性优化等离子改性条件.

控制气体总流量为1 L/min, 通过改变 N_2 :Ar比考察了气氛的影响. 由图7(a)可见, 随着 N_2 比例的增加, 改性后的光催化剂活性增大, 但是纯 N_2 改性后光催化剂可见光活性反而不如 N_2 :Ar为8:2条件下改性的催化剂. 在 N_2 与Ar的混合气体中, Ar的离解能低于 N_2 , 所以Ar更容易被激发. 由于潘宁效应的影响, 在等离子放电过程中, Ar的亚稳态粒子能够与 N_2 碰撞反应, 促进 N_2 的激发和离解, 更多的N中间化合态如 N^* 和 N_2^+ 能够提高表面处理及掺杂效率^[32,33]. 因此, N_2 :Ar比增加能够提高N活性中间物质的浓度, 而 N_2 :Ar比降低则提高了 N_2 处理的效率.

同样, 等离子处理时间也会影响改性效果. 如图7(b)所示, 随着处理时间的增加, TiO_2 中掺杂的N含量和表面的 Ti^{3+} 以及氧空位增加, 因此光催化效果逐渐增加, 但是处理时间超过20 min之后, 光催化活性开始降低. 从表1可以看出, Cu含量随着等离子处理时间增加而逐渐降低. 在等离子处理过程中, 高能亚稳态粒子不断剥蚀材料表面, 由于Cu粒径较小, 可能会逐渐从 TiO_2 表面脱落, TiO_2 与 Cu_2O 所形成的p-n半导体异质结的作用会慢慢降低, 影响整体复合结构的光催化活性.

输出功率对于整个反应至关重要, 输出功率太低则气体离解程度不够, 而功率太大则会导致过多的能量转化为热能, 造成整个反应装置温度升高. 本文通过控制电流大小来调节等离子发生装置的输出功率. 图7(c)为 N_2 :Ar比为8:2, 处理时间为10 min时不同输出电流对处理后光催化剂性能的影响, 可见输出电流1.0 A时最佳. 综上可确定最佳反应条件为 N_2 :Ar = 8:2, 放电处理时间20 min, 反应电流1.0 A.

3.3. 改性催化剂处理 Hg^{2+} 废水

图8示出了改性催化剂处理 Hg^{2+} 废水实验结果. 实验中模拟含 Hg^{2+} 废水是用 HgCl_2 配制的中性pH溶液, 在此环境中避光搅拌状态下 TiO_2 对 Hg^{2+} 吸附性能不佳. 从图8(a)可以看出, 在-60到0 min时间段内, 反应体系中 Hg^{2+} 浓度不稳定且无明显降低趋势. 结果表明, 未改性 TiO_2 对汞的处理效果很低, CuO的负载使其光催化效果明显增加, 而经等离子处理后的 $\text{Cu}_2\text{O}/\text{N}-\text{TiO}_2$ 的处理效果达到最佳, 20 min左右即处理完全. 在光催化还原 Hg^{2+} 的反应中, 光催化剂吸收光子产生光生电子, 然后光生电子将吸附在催化剂表面的 Hg^{2+} 还原^[34]:

将反应之后的光催化剂用5% HNO_3 回收 Hg^{2+} , 再经去离子水清洗和干燥, 重新用于 Hg^{2+} 的处理. 如图8(b)所示, 将 $\text{Cu}_2\text{O}/\text{N}-\text{TiO}_2$ 在可见光照射条件下重复使用4次, 反应时间为20 min, 经4次反应后光催化剂活性保持不变, 表现出良好的稳定性.

为了验证实验效果, 我们将反应结束后的光催化剂过滤收集, 30 °C烘干后用扫描电镜(SEM, JSM-6510, JEOL)观察催化剂表面形貌, 并且通过能量色散X射线光谱仪(EDX)分析表面的元素组成, 结果如图9所示. 由SEM照片可以看出催化剂表面有微小颗粒, 除了含有O, Ti以及C元素之外, 还存在Hg元素, 说明反应液中 Hg^{2+} 通过光催化还原之后吸附在光催化剂表面^[35].

4. 结论

采用 N_2 /Ar介质阻挡放电等离子体处理负载CuO的 TiO_2 . 结果表明, 等离子体不仅能够实现N掺杂, 而且能够在催化剂表面生成 Ti^{3+} 以及氧空位等缺陷态, 因而催化剂在可见光区的光吸收率与光催化活性增加. 通过可见光下甲基橙溶液的光催化降解实验, 优化了等离子体处理参数, 得到最佳处理条件为 N_2 与Ar比例为8:2、处理时间为20 min、放电电流为1.0 A. 最后, 模拟汞污染废水的处理实验表明, 光催化剂经等离子改性后性能明显改善, 可以应用于更多领域.