

## Preparation of TiO<sub>2</sub>/AmPAM Composite Materials with Improved Photocatalytic Performance and Flocculation Effect

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**Abstract:** A novel TiO<sub>2</sub>/AmPAM composite material was successfully synthesized using AmPAM as carrier. Nanostructured TiO<sub>2</sub> was prepared via sol-gel process by infiltrating nanostructured TiO<sub>2</sub> into methacryloyloxyethyltrimethyl ammonium chloride (DMC), acrylic acid (AA) and acrylamide (AM) followed by its gelation, drying and calcinations. The TiO<sub>2</sub>/AmPAM composite material was determined by fourier transformation infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). The results showed that the optimal parameters were as follows: monomer mass fraction 35%, initiator dosage 0.06%, reaction temperature 35 °C, TiO<sub>2</sub> dosage 3%. Compared with AmPAM, the TiO<sub>2</sub>/AmPAM composite material has better flocculation effect. The light transmittance of the clear water on the slime water from Wangfenggang Coal Preparation Plant is up to 99.5%, and the sedimentation speed of the slime is up to 21.2cm/min. Moreover, TiO<sub>2</sub>/AmPAM composite shows an enhanced photocatalytic performance compared with the pure TiO<sub>2</sub> sample, for the degradation of methylene blue (MB) under UV light.

**Keywords:** Photo-initiation; AmPAM; TiO<sub>2</sub>; Composite; Wastewater treatment; Photocatalytic performance.

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### Introduction

With the continuous development of industrialization, water pollution and prevention has become a key and difficult problem in today's society. It is an urgent problem to explore and study efficient, low energy consumption and no secondary pollution water treatment methods [1, 2]. Semiconductor photocatalytic technology is widely considered as an ideal green technology to solve the global energy crisis and environmental problems [3, 4], which has attracted great attention of scholars and researchers [5].

As a kind of chain like water-soluble composite material with special properties, AmPAM has anion and hydrophilic groups, good water solubility and photochemical stability, which widely used in fine solid material papermaking process, mineral separation, water treatment and soil remediation [6, 7]. At present, polyacrylamide is the

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most commonly used water-soluble polymer surfactant. The new polyacrylamide flocculant can be used in a wide range of fields by introducing nanoparticles to expand its application path and improve its properties<sup>[8]</sup>. Nanostructure TiO<sub>2</sub> is a kind of semiconductor inorganic functional material with unique photocatalytic performance, however, the powdered TiO<sub>2</sub> is easy to aggregate, easy to inactivate, and difficult to recycle, which limits the practical application effect. In order to solve this problem, people usually solve it by loading TiO<sub>2</sub>, so it is more and more important to modify TiO<sub>2</sub> and improve its photocatalytic performance<sup>[9,10]</sup>. Research and development of supported TiO<sub>2</sub> and TiO<sub>2</sub> composite materials has become an inevitable trend in the field of photocatalysis<sup>[11]</sup>.

Based on the above considerations, this paper developed a facile and environment-friendly aqueous solution polymerization route to fabricate AmPAM. The as-prepared AmPAM was used as a carrier of nanostructure TiO<sub>2</sub> photocatalyst to prepare TiO<sub>2</sub>/AmPAM composite. As expected, the TiO<sub>2</sub>/AmPAM presented a strong photocatalytic performance and exhibit the significantly improved photocatalytic efficiency in the photodegradation of methylene blue (MB) compared with the nanostructure TiO<sub>2</sub>.

### Experimental Section

Titanium alkoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, ≥98%), methacryloyloxyethyltrimethyl ammonium chloride (DMC, 78%), acrylic acid (AA, 99%), acrylamide (AM, 98%), absolute ethyl alcohol (99.7%), nitric acid (HNO<sub>3</sub>, 68%), diphenyl ketone kind photoinitiator and methylene blue (MB, ≥82%). All reagents were of analytical grade, and used without further purification.

Ubbelohde viscometer with inner diameter of 0.54 mm was used to measure the intrinsic viscosity of the sample, the FT-IR spectra were recorded on a Nicolet 380 from 400 to 4000 cm<sup>-1</sup> using KBr pellets that were prepared by pressing pellets containing 100 mg KBr and 1 mg of sample, thermal gravimetric analyses (TGA) of the samples using about 5 mg for every sample were carried out on a Shimadzu TA-50 thermal analyzer at a heating rate of 10 °C/min from room temperature to 600 °C in air, the UV-vis absorption spectra were recorded on a DUV-3700 DUV-vis-near-IR recording spectrophotometer from Shimadzu Corp.

Preparation of TiO<sub>2</sub> the sol-gel process was used by imixing n (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>): n (C<sub>2</sub>H<sub>5</sub>OH): n (H<sub>2</sub>O): n (HNO<sub>3</sub>) = 1: 15: 4: 0.35, the sol was aged, dried, ground, calcined, and then subjected to secondary grinding to obtain nanostructure TiO<sub>2</sub>. The TiO<sub>2</sub>/AmPAM composite material were successfully synthesized by aqueous solution polymerization. A certain molar ratio AM, DMC, AA and nanostructure TiO<sub>2</sub> were dissolved in deionized water, then magnetic stirring for 2h at room temperature, subsequently small amount photoinitiator was dropped into the solution, vigorous stirring was maintained throughout the entire process. After purging with nitrogen (N<sub>2</sub>) for 10min then sealed and placed it under the UV light irradiation for 4 hours, after completion of the reaction, and then dried at 80 °C for 4 h and grinded.

## Results and Discussion

Chemical compositions of the samples were characterized by FT-IR spectroscopy (Figure 1). In transmission spectra of samples, the peak at 3400 cm<sup>-1</sup> is characteristic absorption peak of N-H stretching mode of the amide; The peaks at around 2950cm<sup>-1</sup> corresponded to the -CH<sub>2</sub> telescopic vibration absorption; The peaks at 1630 and 1400cm<sup>-1</sup> correspond to the carbonyl group of COO<sup>-</sup> are 1630 and 1400cm<sup>-1</sup>; The peak at 1450cm<sup>-1</sup> correspond to the bending vibrations of methylene; The peak at 950cm<sup>-1</sup> correspond to the quaternary ammonium group absorption; The peaks at 1370 and 1060cm<sup>-1</sup> are ascribed to the deformation vibration of C-O-H causes Ti-O-C vibration. All of peaks in FT-IR spectrum were in agreement with the experimental monomer [12, 13].

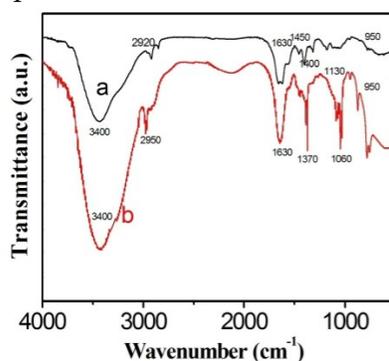


Figure 1

The thermal stability and weight loss percentage of TiO<sub>2</sub>, AmPAM, and TiO<sub>2</sub>/AmPAM composite were studied by TGA measurements, and the TGA curves are shown in Figure 2. For TiO<sub>2</sub> the weight loss is about 4% below 600 °C, which can be ascribed to the removal of absorbed water. In the TGA curve of the AmPAM and TiO<sub>2</sub>/AmPAM composite, the weight loss at temperatures below 150 °C is typically associated with the evaporation of residual solvent and began to lose weight obviously at 350 °C. At 550 °C, AmPAM and TiO<sub>2</sub>/AmPAM composite basically stabilized and no longer lost weight. The weight loss percentage corresponding to the removal of TiO<sub>2</sub> in the composite is about 31.5%, which is the loading content of TiO<sub>2</sub> in the TiO<sub>2</sub>/AmPAM composite. It meaning that the TiO<sub>2</sub> can improve the thermal stability of the composite.

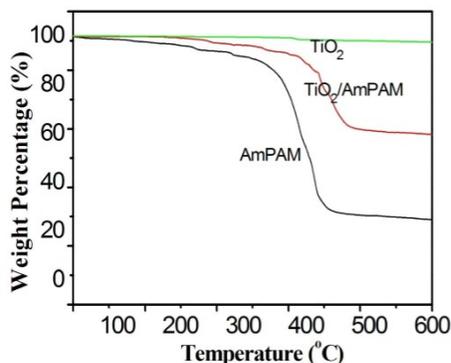


Figure 2

Table 1 shows the results of the single factor test using  $n(\text{AM}):n(\text{DMC}):n(\text{C}_3\text{H}_3\text{O}_2\text{Na}) = 1:0.16:0.65$  [14]. Table 2 shows the optimal solution for exploring polymerization using four-factor and three-level orthogonal experiments. The result indicates that the order of the factors is as follows: monomer mass fraction, initiator dosage, reaction temperature and  $\text{TiO}_2$  dosage, which influence of the characteristic viscosity of the composite material, and the optimum conditions when monomer mass fraction 35%, initiator dosage 0.06%, reaction temperature 35 °C, and  $\text{TiO}_2$  dosage 3%. Table 3 shows that the final samples were tested with  $n(\text{AM}):n(\text{DMC}):n(\text{C}_3\text{H}_3\text{O}_2\text{Na}) = 1:0.16:0.65$ , monomer mass fraction 35%, initiator dosage 0.06%, reaction temperature 35!,  $\text{TiO}_2$  dosage 0 and 3%, respectively. The result indicates that under the optimum conditions, the products were basically consistent with the orthogonal test in terms of appearance, solubility and characteristic viscosity, which could reach 795mL/g.

Table 1

Level	Monomer mass fraction (%)	Initiator dosage(%)	$\text{TiO}_2$ dosage(%)	Reaction temperature°C
1	30	0.02	1	30
2	35	0.06	2	35
3	40	0.09	3	40

The slime water flotation was used to examine the flocculation property of (a) 572mL/g, (b) 656mL/g, (c) 735mL/g, (d) AmPAM (786 mL/g ) and (e)  $\text{TiO}_2/\text{AmPAM}$  (795mL/g). In the experiment, the slime water used come from Huainan Wangfenggang coal preparation plant [15]. As shown in Figure 3, The  $\text{TiO}_2/\text{AmPAM}$  composite material has a good flocculation effect on the slime water, and the larger the characteristic viscosity number, the higher the light transmittance of the supernatant liquid during the flocculation process, and the faster the sedimentation speed of the slime. This is because the  $\text{TiO}_2/\text{AmPAM}$  composite has a chain structure, which not only has the basic characteristics of the flocculant, but also has the electronic structure and photocatalytic characteristics of the nanostructure  $\text{TiO}_2$ . For polymers , the larger the intrinsic viscosity of the polymer, the longer the chain structure and the charge, the stronger the neutralization ability, the better the bridging ability of the coal bridging molecules with more bridging groups, and the more obvious the flocculation effect. With the addition of excessive composite materials, the formation of bridge structure is easily prevented, which is not conducive to the settlement of coal slime. In conclusion, the  $\text{TiO}_2/\text{AmPAM}$  composite material of the test site has a good effect on the application test of Wangfenggang slime water. The highest supernatant liquid transmittance can reach 99.5%, and the slime sedimentation speed can reach 21.2cm/min.

Table 2

NO	Monomer mass fraction A	Initiator dosage B	Reaction temperature C	TiO <sub>2</sub> dosage D	Intrinsic viscosity [η]
1	1	1	1	1	621
2	1	2	2	2	781
3	1	3	3	3	656
4	2	1	2	3	649
5	2	2	3	1	767
6	2	3	1	2	735
7	3	1	3	2	615
8	3	2	1	3	609
9	3	3	2	1	572
K <sub>1</sub>	2058	1885	1965	1960	T=6005
K <sub>2</sub>	2151	2157	2002	2131	
K <sub>3</sub>	1796	1963	2038	1914	
k <sub>1</sub>	686	628.3	655	653.3	
k <sub>2</sub>	717	719	667.3	710.3	
k <sub>3</sub>	598.7	654.3	679.3	638	
Range	118.3	90.7	24.3	72.3	

Table 3

Test Item	Result analysis (no TiO <sub>2</sub> )	Result analysis (TiO <sub>2</sub> .3%)	national standard
Appearance	white transparent colloid	white transparent colloid	GB17514-98
solubility	stir and dissolve completely	a small amount of sediment after stirring	-----
solid content	40.72%	41.05%	GB12005.3-89
Intrinsic viscosity	786mL/g	795mL/g	GB12005.1-89

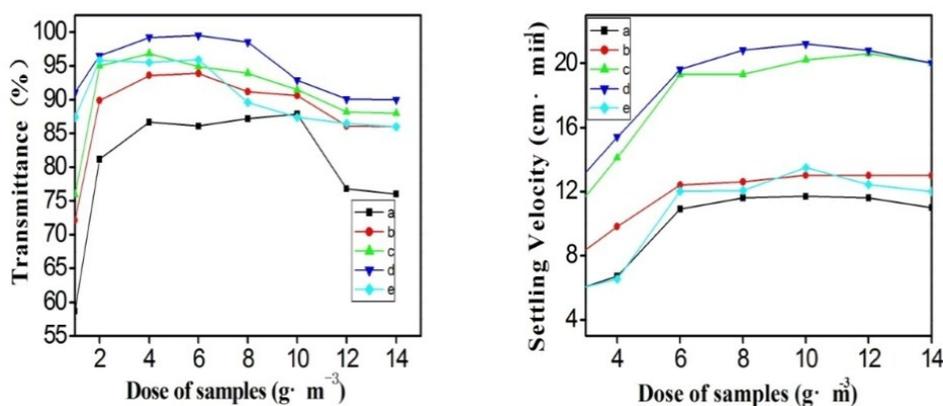


Figure 3

The results of the MB degradation in a series of experimental conditions are summarized in Figure 4. The photocatalytic rate of the TiO<sub>2</sub>/AmPAM composite material is better than that of the corresponding pure TiO<sub>2</sub> sample, and the greater the intrinsic viscosity number, the better the photodegradation rate of the MB solution. This is because

the TiO<sub>2</sub>/AmPAM composite has a chain structure, which makes the surface of TiO<sub>2</sub> hydrophobic and dispersible, and can sufficiently receive ultraviolet light and increase the probability of contact with MB blue molecules in solution, thereby improving the photocatalytic degradation rate. The larger the intrinsic viscosity, the longer the chain structure, the higher the ratio of nanostructure TiO<sub>2</sub> supported by the composite. From the photodegradation performance, it can be seen that the introduction of AmPAM inhibits the agglomeration of TiO<sub>2</sub> and improves the light of TiO<sub>2</sub> and AmPAM.

## Conclusion

In conclusion, a simple and efficient aqueous solution polymerization route was demonstrated to synthesize TiO<sub>2</sub>/AmPAM. According to the experimental results, it was found that the optimum reaction conditions: monomer mass fraction 35%, initiator dosage 0.06%, reaction temperature 35 °C, and TiO<sub>2</sub> dosage 3%. The TiO<sub>2</sub>/AmPAM displayed an enhanced flocculation effect and photocatalytic performance compared with nanostructure TiO<sub>2</sub> and AmPAM. Moreover, this work further hints that this facile and economical approach can be extended to synthesize other metal-oxide materials.

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