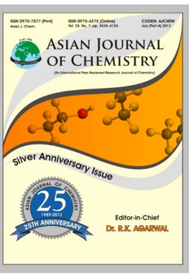
Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5719-5723

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH72



Preparation and Characterization of Electroless Deposited Ni-Zn-P-TiO_2(N) Composite Coating†

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AJC-13315

Nitrogen doped nano anatase TiO_2 particles were prepared by nitriding treatment. The Ni-Zn-P-TiO_2(N) composite coatings were prepared by adding nano TiO_2(N) to electroless plating Ni-Zn-P alloy bath. The composite coatings were characterized and tested. The results show that, the maximum deposition rate occurs at 1 g dm^{-3} content of TiO_2(N). The as-plated Ni-Zn-P-TiO_2(N) composite coating consists face-centered-cubic Ni-Zn-P alloy and anatase type TiO_2(N). The percentage weight of zinc, phosphorus and titanium in the composite are 6.94, 8.15 and 2.56 % respectively. The Ni-Zn-P-nano TiO_2(N) composite coatings have higher hardness value, better erosion property and photodegradation effect than those of Ni-Zn-P-TiO_2 composite coatings.

Key Words: Electroless deposite, Nanocomposites, Erosion, Photocatalytic, Hardness.

INTRODUCTION

Nano titanium dioxide suspension system has good photocatalytic properties. Its application fields were restricted because of the difficulties of separating and recycling nano titanium dioxide powders[1,2]. Many researchers have employed various methods to develop loading nano titanium dioxide photocatalysis system. Pilkenton and Herrmann[3,4] have loaded nano titanium dioxide by glass and gained good photocatalytic effect owing to good translucency of glass. But the capacity is restricted because of glass has low specific surface. Nano titanium dioxide has poor adhesive force due to glass having smooth surface. Zhe and Jin[5] developed a method to load titanium dioxide film on silica gel by chemical vapour deposition. The test results show that titanium dioxide particles distribute on the external surface of silica gel and have good stability. Takenori and Kiyohisa[6] have prepared TiO_2-Zn film on steel surface. Then the samples were annealing treated in the air at 673 K to produce ZnO whiskers. The results show that TiO_2-ZnO film have better photocatalytic property than TiO_2-Zn film.

One or more kinds of insoluble solid particles can be mixed with metal deposition uniformly by chemical deposition or electrodeposition. The composite coatings have comprehensive performance of matrix metal and solid particles. So the solid particles can be loaded by this method. Novakovic and Vassiliou[7] have prepared Ni-P-TiO_2 composite coating on steel samples by electroless plating. The coatings have higher hardness value and better corrosion resistance than Ni-P alloy coatings at as-plated state or after heat treated. Song *et al.*[8] have prepared Ni-P/TiO_2 composite coatings on NdFeB permanent magnet. The results show that, the composite coatings have good corrosion resistance in 0.5 mol/L H_2SO_4 and 0.5 mol/L NaCl solutions. Xinming *et al.*[9] have obtained composite coatings contained nano titanium dioxide particles by electroless deposition. The composite coatings have good magnetic and photocatalytic properties. Feng *et al.*[10] added nano titanium dioxide particles into electro plating nickel bath directly and obtained Ni-P-nano TiO_2 composite coatings on metallic substrates. Nano titanium dioxide particles are well-distributed in nickel matrix which is confirmed by scanning electron microscope. Nano titanium dioxide particles are loaded in Ni-P alloy on metallic substrates.

It is a good method to modify TiO_2 by nitrogen doping[11]. Radius of nitrogen ionic and oxygen ionic have little difference. Ionic nitrogen is easy to occupy the position of ionic oxygen. So nitrogen doped nano titanium dioxides have great superficial area and higher absorbance in the range of longer wavelength. The corrosion resistance of the alloy was enchanced by perfect the microstructure of the coating through adding nonmetallic element phosphous into Ni-Zn alloy[12]. In this paper, Ni-Zn-P-TiO_2(N) composite coatings were prepared by adding nitrogen doped nano titanium dioxides into electroless plating Ni-Zn-P alloy bath.

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†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

EXPERIMENTAL

Titanium dioxide powders used for test are anatase-type structure of cubic system and the mean particle diameter is 20 nm. A certain amount of TiO_2 powders were mixed with urea and then put into a airtight container. The mixture was heated to 300 ºC in muffle furnace and holded for 5 h. They were grinded after cooled. Then nitrogen doped TiO_2 powders were obtained. They were characterized by means of X-ray diffraction, infrared spectrometer and X-ray photoelectron spectroscopy respectively.

The dimensions of copper matrix samples are 20 mm × 30 mm × 1.5 mm. They were activated in 30 % hydrochloric acid solution and put into the bath after being washed with distilled water. Basic bath composition and process conditions are: $NiSO_4.6H_2O$ 30 g dm^{-3}, $ZnSO_4.7H_2O$ 5 g dm^{-3}, $NaH_2PO_2{\cdot}H_2O$ 25 g dm^{-3}, bath stabilizer 0.002 mg dm^{-3}, appropriate amount of complexing agent. The bath temperature was 80-90 ºC and the pH value of the bath was adjusted to 7.0-9.0. The bath was agitated with magnetic stirrer.

The morphology and composition of the composite coatings were tested by scanning electron microscope (SEM) and energy dispersed spectrometer (EDS). The structure of the composite coatings was analyzed by X-ray diffracter. The micro-hardness values of the coatings were determined by micro hardness tester of 71 type. The test load was 0.98 N and the loading time was 10 sec.

The erosion tester was shown in the paper has been published[13]. The substrate material is 20 steel, the dimension of 20 steel samples is 15 mm × 25 mm × 3 mm. The flowing media is 0.05 M hydrochloric acid solution. The mass loss of the coatings was calculated from the weight of the sample before and after the erosion test.

50 mL of 10 mg/L methyl orange solution was placed in petri dish. Then, samples were put into the solution. The samples were directly irradiated under UV lamp of 30 watts. The distance between the samples and the lamp was kept 30 cm. The solutions were adjusted to volume of 50 mL by distilled water after that they had been irradiated for certain period. The absorbency of yhe solutions was tested under illuminating light of 465 nm wavelengths by device of model 721 spectrophotometer. The photocatalytic effect was characterized by the absorbency difference before and after the experiment.

$$\eta = (A_0 - A)/A_0 \times 100\ \% \qquad (1)$$

RESULTS AND DISCUSSION

Characterization of N doped nano TiO_2 powder: Fig. 1 is XRD partens of nano TiO_2 powders before and after nitriding. It can be seen that the structure of N doped nano TiO_2 is still anatase-type structure of cubic system. There are no diffraction peaks of impurity in XRD pattern of N doped nano TiO_2. The (101) characteristic peak of anatase shifted. This may be the result of nitrogen atoms having entered TiO_2 lattice to repalce some oxygen atoms and forming Ti-O-N atomic bonding.

Fig. 2 is infrared spectrum of pure TiO_2 and N doped TiO_2. It can be seen that Ti-O stretching vibration center shifts to lower wavenumber. A new peak around 1320 cm^{-1} appears because of a new bond formed by titanium atom and oxygen atom. Nitrogen atoms repalce some oxygen atoms of TiO_2 lattice and form Ti-N atomic bonding.

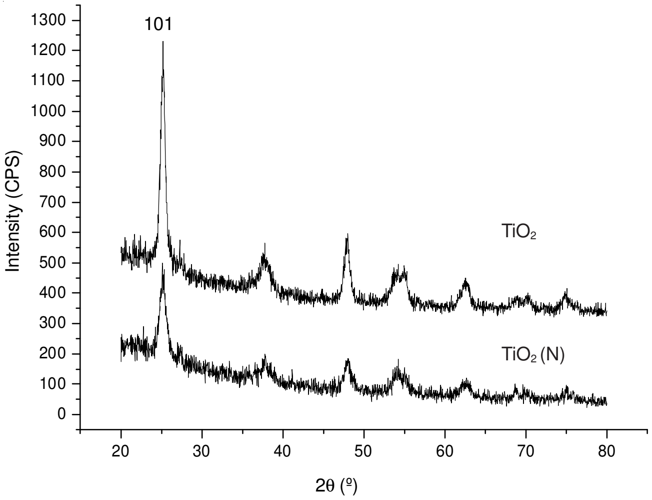

Fig. 1. XRD parttern of TiO_2 and TiO_2(N)

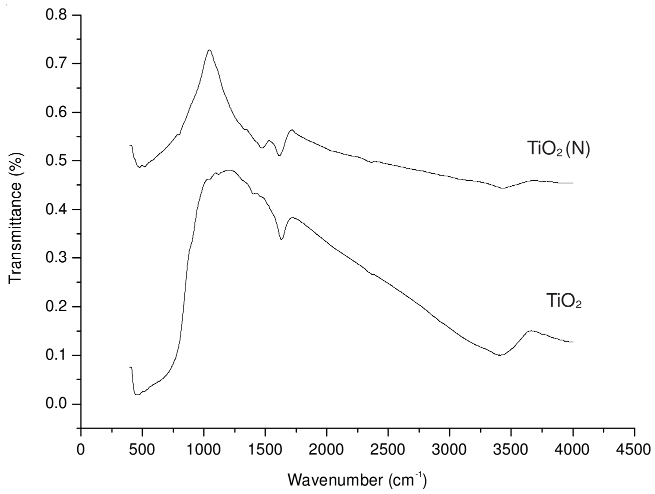

Fig. 2. Infrared spectra of TiO_2 and TiO_2(N)

Fig. 3 is the degradation rate curves of TiO_2(N) and TiO_2 powders degradating methyl orange under UV light. It can be seen that TiO_2(N) powders has higher degradation rate than TiO_2 powders. When ionic nitrogen replaces ionic oxygen in TiO_2 crystal lattices, the 2p orbital of nitrogen interacts with titanium atomic orbitals, so band gap of titanium dioxide becomes narrow. The photocatalytic property of TiO_2(N) is improved. The 2*p* orbital of nitrogen hybridizates with 2*p* orbital of oxygen. This effect can improve photocatalytic property of TiO_2(N) too.

Preparation of electroless deposited Ni-Zn-P-TiO_2(N) composite coatings: Figs. 4 and 5 show the effect of nano particle content in the bath on deposition rate and composition of titanium dioxide in the coatings. It can be seen that the maximum deposition rate occurs at the content of 1 g/L. The amount of TiO_2(N) in the composite coatings increased with TiO_2(N) content in the bath increased. But when TiO_2(N) content in the bath is more than 1 g/L, the amount of TiO_2(N) in the composite coatings increased slowly. The amount of suspended nano TiO_2(N) particles increased with TiO_2(N) content in the bath increased. The chance of sample surface adsorbing nano TiO_2(N) particles is increased. This causes deposition rate and composition of TiO_2(N) in the coatings being increased. When TiO_2(N) content in the bath is too high, the amount of nano TiO_2(N) particles adsorbed on the surface of the sample is too many. This will reduce the catalytic surface of the samples. The deposition rate of Ni-Zn-P alloys will slow down. When TiO_2(N) content in the bath exceeds a specific value, the adsorbed particles on the surface of the sample changed hardly. So the amount of TiO_2(N) in the composite coatings increased slowly when TiO_2(N) content in the bath is more than 1 g/L.

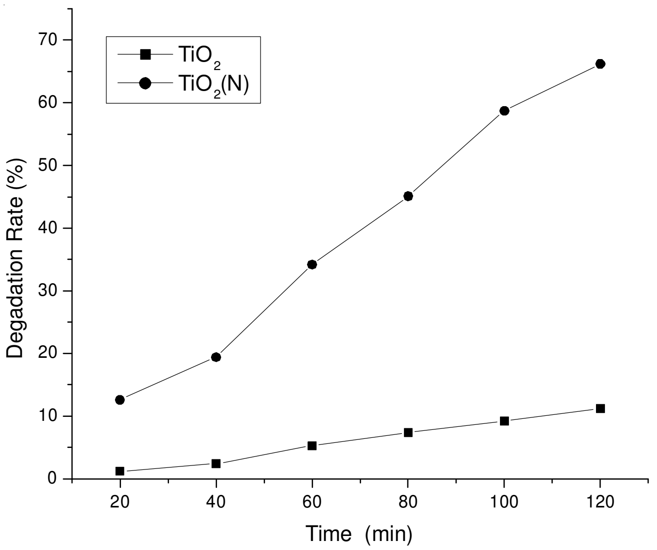

Fig. 3. Degradation rate curves of TiO_2(N) and TiO_2 powders

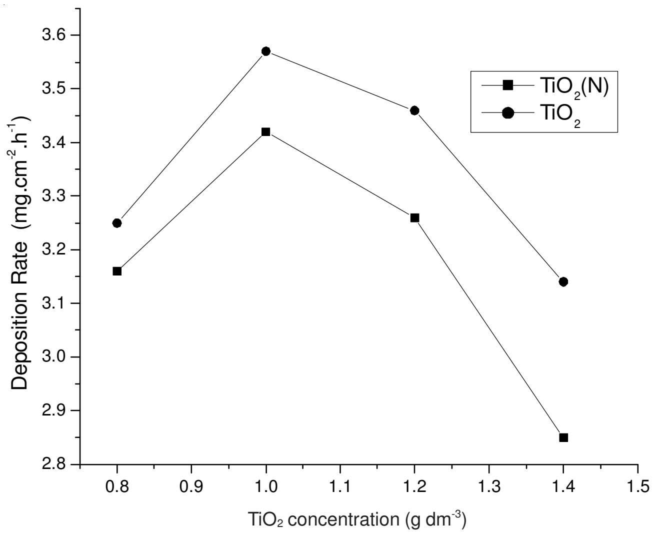

Fig. 4. Effect of TiO_2(N) concentration on deposition rate

Due to the introduction of element nitrogen and formation of Ti-O-N bond, TiO_2(N) particles have greater polarity than that of pure TiO_2 particles. So the deposition rate and the amount of TiO_2(N) in the composite are lower than that of pure TiO_2 under the same condition.

Fig. 6 is XRD pattern of Ni-Zn-P-nano TiO_2(N) composite coating. The as-plated Ni-Zn-P-nano TiO_2(N) composite consists face-centered-cubic Ni-Zn-P alloy and TiO_2(N) of anatase type. It can be seen from Fig. 7 that, TiO_2(N) particles are distributed uniformly in matrix alloy. Fig. 8 is the EDS pattern of the composite coating. The percentage weight of zinc, phosphorus and titanium in the composite are 6.94, 8.15 and 2.56 % respectively.

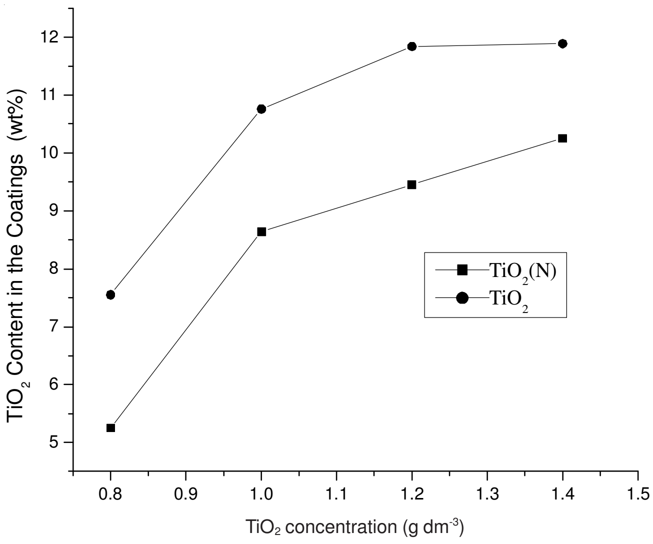

Fig. 5. Effect of TiO_2(N) concentration on deposition content

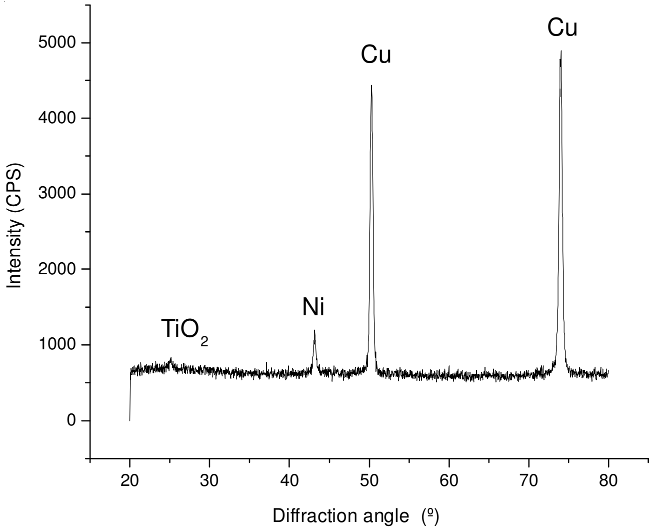

Fig. 6. XRD pattern of the composite coating

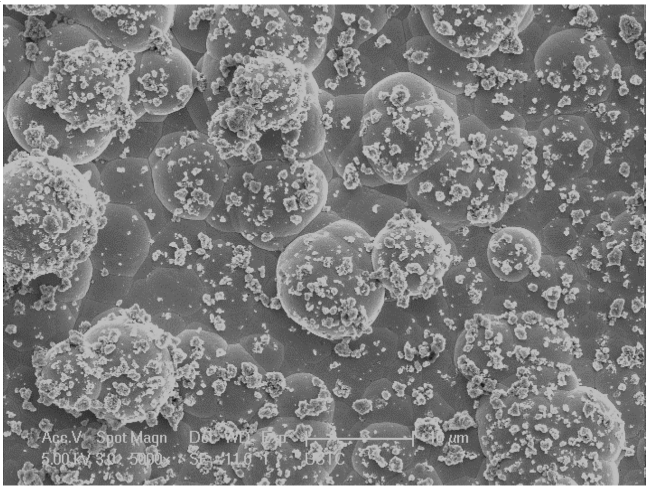

Fig. 7. Morphology of the composite

Microhardness of Ni-Zn-P-TiO_2(N) composite coatings: Fig. 9 shows the microhardness value curves of Ni-Zn-P, Ni-Zn-P-TiO_2 and Ni-Zn-P-TiO_2(N) after heat treated for 1 h at varied temperatures and as-plated. The microhardness values of composite coatings are higher than that of Ni-Zn-P alloy coatings at the same condition. The highest hardness values of the coatings occurr when the coatings have been heat treated for 1 h at 400 ºC.

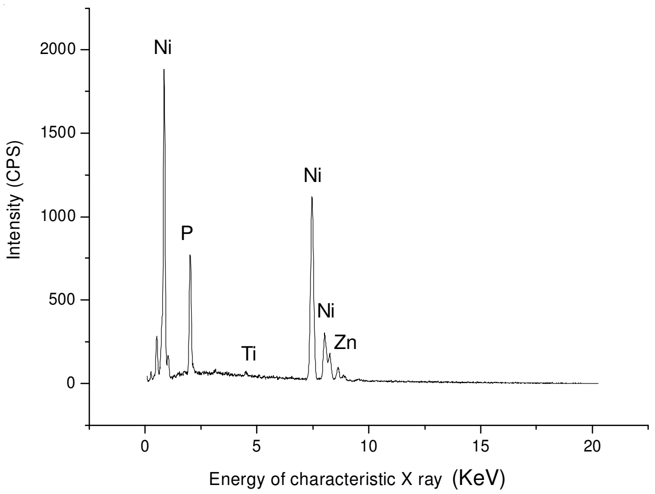

Fig. 8. EDS parttern of Ni-Zn-P-TiO_2(N) composite coatings

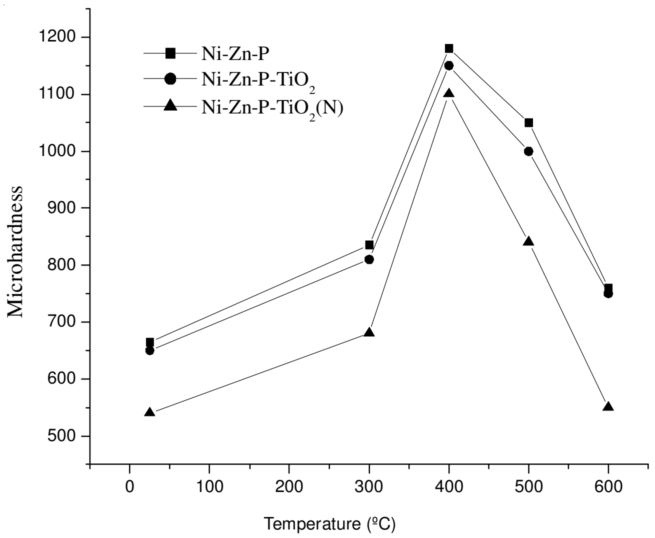

Fig. 9. Effect of heat treatment on microhardness of the coatings

Erosion property of Ni-Zn-P-TiO_2(N) composite coatings: Fig. 10 shows the mass loss of the coating at different impact angles. The mass loss of the coatings is increasing with impact angle decreasing. The mass loss of Ni-Zn-P-TiO_2(N) composite coatings are the lowest among the tested coatings. The nano particles refine grain size of Ni-Zn-P alloys and enhance microhardness values of the composite coatings. On the other hand, nano particles can improve the corrosive potential and corrosion resistance of the composite coating.

Photocatalytic property of Ni-Zn-P-TiO_2(N) composite coatings: Table-1 summarizes the photodegradation effect of the coatings tested in methyl orange solution. It can be seen that, Ni-Zn-P alloy coatings have no photocatalytic effect on degradation of methyl orange solution. Ni-Zn-P-TiO_2(N) and Ni-Zn-P-TiO_2 composite coatings have photocatalytic effect on degradation of methyl orange solution. The photodegradation effect of the coatings is related to the state of nano particles in the composite. A portion of TiO_2(N) or TiO_2 nanoparticles in composite coating distribute on the surface of Ni-Zn-P alloy which can be seen from surface morphology of the composite coating. Because TiO_2(N) powders has higher degradation rate than TiO_2 powders and the content of particles in the coatings have little difference, Ni-Zn-P-TiO_2(N) composite coatings have better photocatalytic effect than Ni-Zn-P-TiO_2 composite coatings.

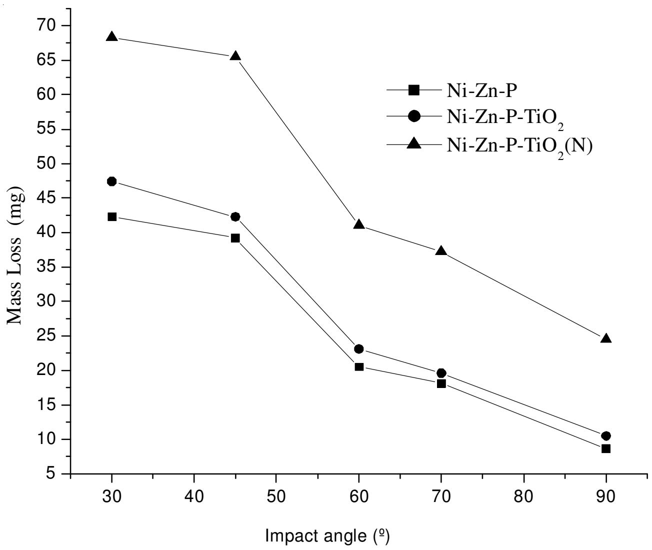

Fig. 10. Effect of impact angle on the mass loss of the coatings

TABLE-1
RELATIONSHIP OF ABSORBANCE AND IRRADIATED TIME

Test condition	Rate of absorbance change (%)	
	12 h	24 h
Ni-Zn-P coating	0	0
Ni-Zn-P-TiO_2 coating	8.5	14
Ni-Zn-P-TiO_2(N) coating	15.5	22.5
TiO_2 coating	26	32

Conclusion

(1) Nitrogen doped nanometer TiO_2 powders were prepared by nitriding treanment, which are anatase-type structure of cubic system and have the same size with raw materials.

(2) The maxim deposition rate occur at the content of TiO_2(N) at 1 g/L. The as-plated Ni-Zn-P-nano TiO_2(N) composite consists face centered cubic Ni-Zn-P alloy and TiO_2(N) of anatase type. The percentage weight of zinc, phosphorus and titanium in the composite are 6.94, 8.15 and 2.56 %, respectively.

(3) Ni-Zn-P-nano TiO_2(N) composite has higher hardness valure and better erosion property than that of Ni-Zn-P-nano TiO_2 composite. Ni-Zn-P-nano TiO_2(N) composite has better photodegradation than Ni-Zn-P-nano TiO_2 composite.

ACKNOWLEDGEMENTS

This work was supported by the sustentation fund from National Natural Science Foundation of China (Grant No. 20571022), Key Scientific Research Project Supported by Ministry of Education of Anhui Province (Grant No. KJ2010A064).

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