



THE INVESTIGATION ON THE ACTIVITY OF PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS ENCHANCED BY TiO₂ COMPOSITE WITH ANTIBACTERIAL PROPERTIES AGAINST *ESCHERICHIA COLI*

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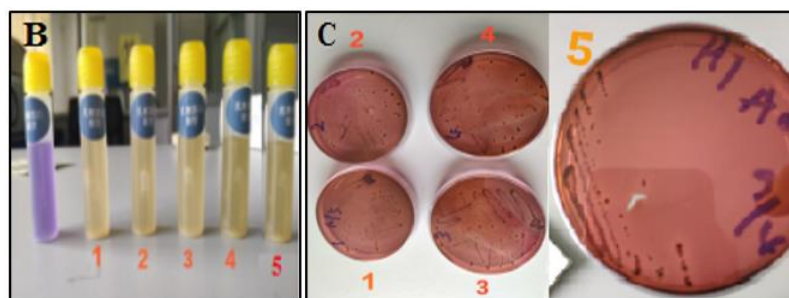
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Titanium dioxide composite (TiO₂/Cu, TiO₂/Ag, TiO₂/Au) was successfully fabricated by solvothermal method from tetrabutyl titanate and metallic salt of copper, silver, and gold elements. The crystal structure, surface topology, and morphology of TiO₂ composite were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), fluorescence spectrometer, etc. The results showed that the metallic ions doped TiO₂ composite possessed superior photocatalytic properties, and enabled rapid

degradation of methyl orange and other organic pollutants in untreated wastewater under simulated sunlight and/or nature solar. The photocatalytic degradation rates of methyl orange were up to 97.7%, 93.0%, and 83.6%, respectively, by using TiO₂/Cu, TiO₂/Ag, and TiO₂/Au as photocatalysts in comparison to the unmodified TiO₂ (63.1%). Further analyses via electron spin resonance spectrometer (ESR) and the temperature-programmed reduction of H₂ (H₂-TPR) revealed that metallic ions doped TiO₂ was conducive to promote the formation of free radicals, thereby increasing the photocatalytic activity. Moreover, the fabricated TiO₂ composite were found to have significant antibacterial properties against *Escherichia coli*, with the highest inhibition rate being observed with TiO₂/Ag (99.89%). Collectively, these findings highlighted the potential utility of such TiO₂ composite as photocatalysts for elimination of organic pollutants and microorganism in wastewater in parallel.



INTRODUCTION

The amount of micro-organism and organic pollutants are the most important parameters to decide whether the wastewater reaches to the discharging standard. Thus, a variety of methods are employed to eliminate micro-organism and organic

pollutants, generally, including biological technology, and physico-chemical approaches. Among these methods, the photocatalytic technology by using semiconductor material as photocatalyst is of particular significance for wastewater treatment, since the photocatalytic technology is often realizable under mild condition.

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In this sense, traditional semiconductor materials such as TiO_2 , ZnO , and Ag_3PO_4 are often utilized as the photocatalysts, due to their low cost, good stability, non-toxicity, and desired environmental acceptance.¹⁻⁴

TiO_2 has attracted the great attention of researchers since 1970s because of its stable chemical properties, high activity, good antibacterial performance, thermal stability, long-term effectiveness, low price, and no pollution [3]. Recently, TiO_2 becomes the core component of antibacterial material, moreover, also applies in decomposing organic pollutants and forming hydrogen from water splitting.³⁻⁵

Generally, TiO_2 is used for antibacterial agent and photocatalyst that takes effect by photo-generating electrons and holes in illumination process, by producing active free radicals including $\cdot\text{OH}$, $\cdot\text{HOO}$, or $\cdot\text{O}_2^-$ groups.⁶ However, the two defects of TiO_2 limit its large-scale application: (1) the narrow light response range to only the ultraviolet region greatly reduces the utilization efficiency of sunlight; (2) the recombination rate of electron-hole pairs seriously affects its photocatalytic rate.⁶⁻⁹

TiO_2 doped with metallic ions is an effective method to increase the efficiency of the photocatalytic process and antibacterial performance, mainly including noble metals and noble/transition metal ions.^{6,8-10} Transition metallic ions (Ag^+ , Au^+ , and Cu^{2+}) are usually used as dopants to induce the surface plasmon resonance (SPR) effect from transition metal to TiO_2 that are probably organized via two mechanisms, as called direct electron transfer (DET) and resonance energy transfer (RET).¹⁰ In another studies, Ag , Cu , Ni , and other transition metal doped TiO_2 composite have been employed as photocatalysts in decomposition of organic pollutants and the splitting water for H_2 production.^{9,10} Additionally, the relation between the free radical of semiconductor and photocatalytic activity is also very important to research the action mechanism of TiO_2 and the composite on photocatalytic degradation and antibacterial property.

Bear this thought in mind, the present research pays special attention to fabricate transition metal doped TiO_2 composite (TiO_2/Cu , TiO_2/Ag , TiO_2/Au), and their photocatalytic degradation performance and antibacterial property are studied. And then, the free radicals and the reducing temperatures of TiO_2 , TiO_2/Cu , TiO_2/Ag , and TiO_2/Au are characterized by ESR and TPR to explore the action mechanism.

MATERIALS AND METHODS

Reagents

Tetrabutyl titanate (TBT) was purchased from Tiancheng Chemicals Co., Ltd (Shandong province, China). Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), chloroauric acid (HAuCl_4), and silver nitrate (AgNO_3) were supplied by Kaitong chemicals Co., Ltd (Tianjin city, China). Methyl orange (MO), methylene blue (MB), *N,N*-dimethyl formamide (DMF), and phenol were bought from commercially available company. Wastewater was got from toilet wastewater for testing antibacterial property to *Escherichia coli*.

The fabrication of TiO_2 and transition metal doped TiO_2 composite

TiO_2 and transition metallic ions doped TiO_2 composite were fabricated by solvothermal synthesis. Specifically, TBT of 2 mL was added into absolute ethanol of 20 mL in a breaker of 50 mL and stirred by using a magnetic stirrer for 30 min. And then, the resultant solution was transferred to a hydrothermal reactor of 30 mL and heated in Muffle furnace of 210 °C for 24 h. Upon completion of the reaction, as-obtained sample was washed thrice with distilled water and absolute ethanol, respectively, furtherly dried in the oven of 80 °C for 24 h to afford TiO_2 . Transition metal ions doped TiO_2 composite was prepared in the same manner while a proper amount of transition metallic salt was simultaneously introduced into the hydrothermal reactor together with the ethanol solution of TBT. As-obtained transition metal ions doped TiO_2 composite contained doped transition metallic ions of 1.0% (atomic ratio).

The photocatalytic degradation properties of TiO_2 and TiO_2 composite on organic pollutants

The photocatalytic degradation properties of TiO_2 and transition metal doped TiO_2 composite on organic pollutants were tested under the irradiation of simulated sunlight and/or nature sunlight by monitoring the concentration of organic pollutants in solution. The typical procedure for evaluating the photocatalytic degradation performance of TiO_2 or TiO_2 composite was as following: 0.05 g TiO_2 or TiO_2 composite and 50 mL organic pollutant of 100 mg/L were mixed into a 100 mL breaker. The resultant

solution was stirred by using a magnetic stirrer for 1 h under dark environment to achieve adsorption saturation, then illuminated by simulated or nature solar light at room temperature condition for proper time. Upon completion of the illumination, about the aqueous solution of 2 mL was taken from the breaker and added into a 10-mL centrifugal tube and centrifuged for about 30 min. Then supernatant was recorded at a pre-set wavelength by UV-Vis absorbance spectrometer so as to estimate its content of residual organic pollutants.

The antibacterial properties of TiO₂ and its composite

The antibacterial properties of TiO₂ and TiO₂ composite toward to *Escherichia coli* were tested by using toilet wastewater as microbial source. The typical representative was as follows: firstly, fermentation process was carried out for microbial growth. Upon completion of fermentation, toilet wastewater was inoculated into a small catheter with lactose bile culture solution in fecal coliform test kit, and cultured in a constant temperature incubator at 44 °C for 24 h. Then, 1 mL, 0.1 mL, and 0.01 mL of inoculation solution were put into 5 inoculation tubes, respectively. Followed plate separation and identification of *Escherichia coli*, and then the culture medium in the color changing tube was scribed and inoculated on the eosin methylene blue agar (EMB agar) which was set in 37 °C constant temperature incubator for 24 h. Subsequently, the coliform community was selected for Gram staining.¹¹ Most probable number (MPN) of coliforms was obtained according to Chinese national standard (GB 18466 2005) to count number distribution of positive tubes in coliform test kit.¹²

Characterization of TiO₂ and its composite

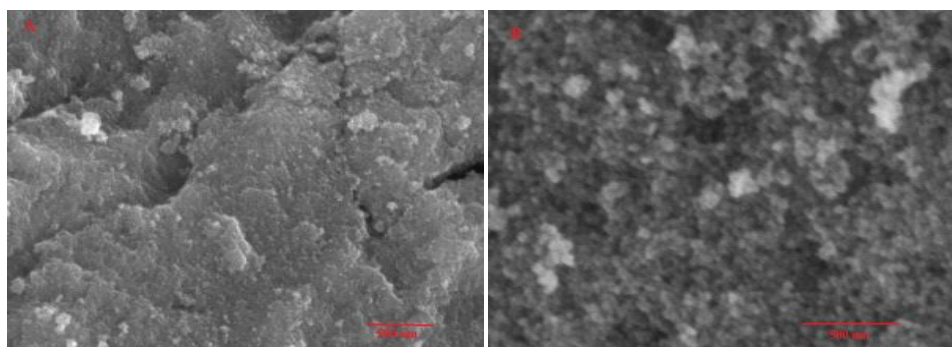
A scanning electronic microscope (SEM, JSM 5600LV, Japanese Electronics, Japan) was employed

at an accelerating voltage of 30 kV to test the morphology of TiO₂ and metal doped TiO₂ composite. The X-ray diffraction (XRD) patterns of as-prepared TiO₂ and its composite were gotten with a D/max 2550VX-ray diffractometer (Rigaku, Japan; Cu K_α radiation, $\lambda = 1.54178 \text{ \AA}$). The ultraviolet-visible (UV-vis) absorbance spectrum of as-fabricated sample was obtained over 200~800 nm of the wavelength range with a UV-Vis absorbance spectrometer (Varian Cary 100, Varian company, American). The fluorescent performance of TiO₂ and its composite were measured by a fluorescence spectrometer (F-2700, Hitachi Company, Japan) in the wavelength range of 220~730 nm. The three free radicals including superoxide free radical (O₂⁻), singlet oxygen (¹O₂), and hydroxyl radical ($\cdot\text{OH}$) were detected by using an ESR spectrometer (ESR-221) under dark and irradiation, respectively. Furthermore, the reduction behavior of Ti element and metallic ions in TiO₂ and its composite were evaluated by monitoring the temperature- programmed reduction of H₂ with H₂-TPR.

RESULTS AND DISCUSSION

Characterization of TiO₂ and transition metal doped TiO₂ composite

SEM photos of TiO₂ and metal doped TiO₂ composite were shown in Fig. 1. The TiO₂ nanoparticles formed aggregates and presented uneven sizes. However, doping of metallic into TiO₂ changed the fine structure of the latter by forming fluffy structure with particles gradually adhered to the surface of the TiO₂ matrix. This structure is beneficial to improve the specific surface area of as-prepared samples thereby increasing the contact area between the photocatalyst and organic compounds, and in turn, improving the photocatalytic degradation activity.⁸⁻¹⁰



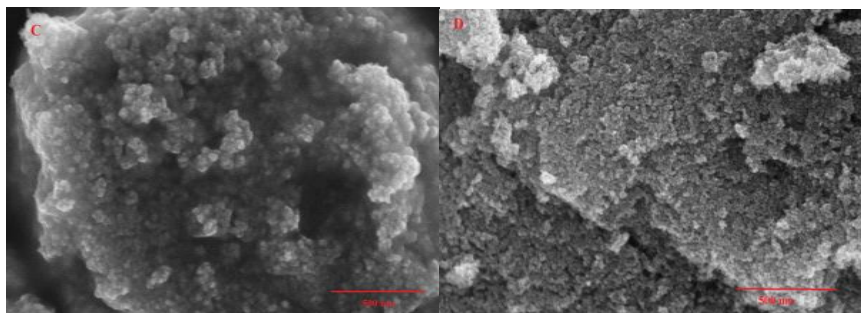


Fig. 1 – SEM photos of TiO₂(A), TiO₂/Cu(B), TiO₂/Ag(C), and TiO₂/Au(D).

XRD patterns of TiO₂ and metal doped TiO₂ composite were showed in Fig. 2. It could be seen that the peaks of 25.3°, 38°, 47.7°, 54.8°, 62.8°, and 68.8° corresponded to the (101), (004), (200), (105), (104), and (200) crystal faces of nano-TiO₂, respectively.^{5-7,13} The presence of these peaks indicated that the TiO₂ nanoparticles featured the anatase structure. Doped with metal ions did not change the crystal structure of TiO₂. Moreover, the

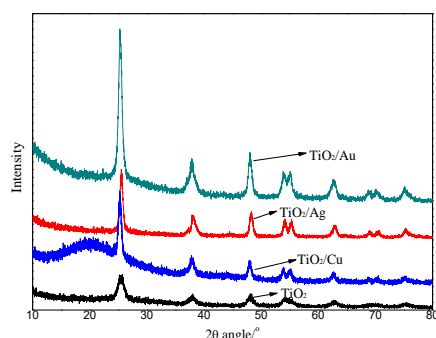


Fig. 2 – XRD curves of TiO₂ and TiO₂ composite.

UV-Vis absorption could indicate the optical response range of inorganic materials. Figure 3 showed UV-Vis absorption of TiO₂ and TiO₂ composite. It could be seen that the absorption of TiO₂ composite was remarkably changed by embedding metal elements. At about 277 nm, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au showed a wider optical response range and stronger visible optical absorption effects that was beneficial for increasing

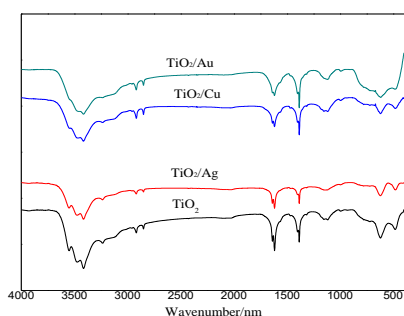


Fig. 4 – FTIR spectra of TiO₂ and its composite.

diffraction peaks of Ag and Au elements were not found in the XRD patterns of TiO₂ composite, likely because its doped amount was very low. However, Cu signal was found in XRD patterns, it might be that Cu element processed background signal. Besides, the peak width of TiO₂ was obviously wider than that of TiO₂ composite, there was because that metal ions embedded the crystal structure of TiO₂ and formed the interaction between metal element and TiO₂.⁶

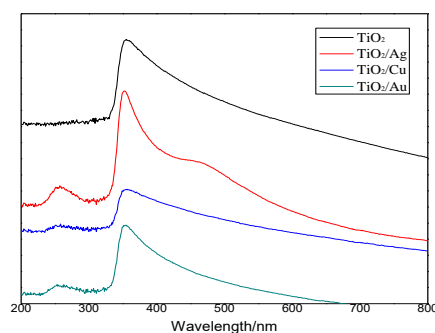


Fig. 3 – UV-Vis absorption of TiO₂ and TiO₂ composite.

SPR, thereby enhancing photon capture at the UV region. These results revealed that the light response range of the photocatalysts were improved and the ability to degrade organic pollutants.¹⁴⁻¹⁶ Interestingly, an obvious visible optical absorption at about 425 nm was appeared in the UV curve of TiO₂/Ag, which indicated that TiO₂/Ag possessed the stronger optical response ability thereby improving its photocatalytic activity.¹⁵

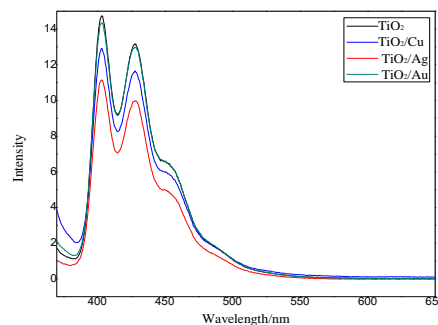


Fig. 5 – Fluorescence spectra of TiO₂ and its composite.

TiO₂ composites formed by transition metal doped TiO₂ would affect the structure of TiO₂. Figure 4 showed the FTIR spectra of TiO₂ and its composites. The absorption peak at 3400 cm⁻¹ belonged to the adsorption peaks of hydroxyl groups (-OH) on the surface of TiO₂. Additionally, the peaks at 2925 cm⁻¹ and 2850 cm⁻¹ represented methyl and methylene (-CH₃ and -CH₂), which were owned to residue of the organic chains of tetrabutyl titanate.^{13,14} However, the FTIR relative intensity of TiO₂/Cu, TiO₂/Ag and TiO₂/Au appeared at the range of 400–1000 nm. And the adsorption peak at 1700 cm⁻¹ belonging to carbonyl groups (C=O) were weaker than that of TiO₂. The main reason might be the strong adsorption properties of metallic Cu, Ag, and Au to light, which enhanced the intensity of response light of photocatalyst thereby improving photocatalytic degradation rate.^{13–15}

The other issues about the recombination rate of holes and electrons, as well as the adsorption behavior of photocatalyst, are considered to be the main factors.^{16,17} The electron recombination rates of the photocatalysts were tested by fluorescence

spectrometry, and the results were shown in Fig. 5. Among the emission intensities observed, that of TiO₂ was the strongest whereas that of TiO₂/Cu, TiO₂/Ag, and TiO₂/Au was obviously weak, suggesting that metal doped TiO₂ had a low recombination rate of electron-hole pairs. The possible reasons owned to that the excited electrons from TiO₂ were translated to the conductive bond of transition metal, thereby preventing the recombination of holes and electrons and leaving holes with strong oxidation capacity. Moreover, the enhancing amounts of holes improved the oxidation capacity of TiO₂, and then increased its photocatalytic degradation abilities.¹⁶

The photocatalytic degradation performances of TiO₂-based composite

Methyl orange was as typical representative organic pollutants, the photocatalytic degradation properties of TiO₂, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au under irradiation of simulated sunlight were studied, as seen in Fig. 6.

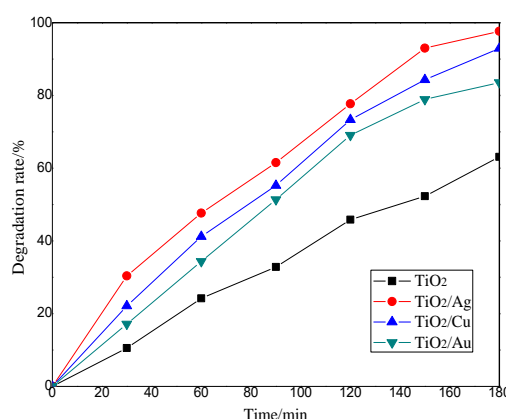


Fig. 6 – Photocatalytic degradation efficiency of TiO₂, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au on methyl orange.

The degradation rate of methyl orange gradually increased with extending irradiation time. After irradiation of 3 h, the photocatalytic efficiencies of TiO₂/Ag, TiO₂/Cu, and TiO₂/Au were up to 97.7%, 93.0%, and 83.6%, respectively, which were significantly higher than that of TiO₂ (63.1%) under the same circumstances, among these, TiO₂/Ag possessed highest photocatalytic efficiencies. The results showed that metal doped TiO₂ composite obviously possessed better photocatalytic degradation performance that might own to the metallic ions doped into TiO₂ lattice thereby expanding the light response range and decrease the recombination of electrons-holes, which

was agreement with the results of fluorescence spectrometry. Additionally, introducing defects or changing the crystallinity of TiO₂ by doped metallic ions could prolong the lifetime of carriers, thereby improving the photocatalytic performance.^{13–16}

Table 1 listed the photocatalytic degradation performances of methyl orange catalyzed by TiO₂, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au without illumination (in the dark) and under the irradiation of simulated (Xe lamp) or nature sunlight. It was found that without illumination, the degradation rate of methyl orange was very low, possibly due to highly retarded adsorption of methyl orange

thereunder. Besides, under the simulated sunlight and nature sunlight irradiation conditions, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au all exhibited enhanced

photocatalytic properties for degradation of methyl orange, with TiO₂/Ag and TiO₂/Cu being the superior ones.¹⁵

Table 1

Degradation rates of methyl orange catalyzed by photocatalysts under the conditions of no illumination, irradiation of simulated sunlight (Xe lamp), and nature sunlight

Photocatalyst	Degradation rate of methyl orange		
	No light	Xenon light ^a	Nature sunlight ^b
TiO ₂	6.5%	65.1%	52.8%
TiO ₂ /Cu	6.0%	90.3%	73.0%
TiO ₂ /Ag	7.2%	94.5%	75.4%
TiO ₂ /Au	5.8%	81.6%	60.3%

Notes: a represents the Xenon light conditions (simulated sunlight of 500 W and the current of 15 A), b represents nature sunlight, and the times are all 1.5 h.

Table 2

Photocatalytic degradation rates of different pollutants by TiO₂ and its composite

No.	Photocatalyst	Organic pollutant	Adsorption rate/% ^a	Degradation rate/% ^b
1	TiO ₂	DMF	6.1	52.7
2	TiO ₂ /Cu	DMF	7.2	65.4
3	TiO ₂ /Ag	DMF	6.0	73.7
4	TiO ₂ /Au	DMF	6.9	70.6
5	TiO ₂	Methyl orange	6.5	63.1
6	TiO ₂ /Cu	Methyl orange	6.0	93.0
7	TiO ₂ /Ag	Methyl orange	7.2	97.7
8	TiO ₂ /Au	Methyl orange	5.8	83.6
9	TiO ₂	Methylene blue	6.0	90.9
10	TiO ₂ /Cu	Methylene blue	6.3	94.3
11	TiO ₂ /Ag	Methylene blue	7.9	100
12	TiO ₂ /Au	Methylene blue	6.4	92.7
13	TiO ₂	Phenol	5.1	83.6
14	TiO ₂ /Cu	Phenol	5.3	90.7
15	TiO ₂ /Ag	Phenol	5.7	98.6
16	TiO ₂ /Au	Phenol	5.5	90.0

Note: "a" represents the adsorption of the organic compounds by photocatalysts in the dark environment; "b" represents the photocatalytic degradation rate of the organic compounds catalyzed by the photocatalysts under the irradiation of Xe lamp light.

In parallel, the photocatalytic degradation behaviors of TiO₂, TiO₂/Cu, TiO₂/Ag, and TiO₂/Au

toward to other organic pollutants in the wastewater were also investigated under the simulated sunlight

irradiation conditions, which including DMF, methyl orange, methylene blue, rhodamine B, and phenol, as showed in Table 2. The results indicated that metallic ion doped TiO₂ composite, especially TiO₂/Ag possessed excellent photocatalytic degradation properties to these organic pollutants.¹⁴

The antibacterial properties of TiO₂ and its composite

One apparent determinant that decides whether the wastewater reaches to the discharging standard is the levels of micro-organism. Therefore, the

antibacterial properties of metallic ion doped TiO₂ composite against *Escherichia coli* were determined. It proved that there would be *Escherichia coli* if the color of the testing solution became yellow from purplish red by using eosin-methylene blue indicator (Fig. 7A), and the corresponding sample tube was noted as positive tube, the tube without *Escherichia coli* was noted as negative one. In the following, every positive tube was diluted 10, 100, and 1000 times, respectively, and the dilution solution was inoculated in 5 tubes respectively (Fig. 7B), then inoculated into EMB medium and cultured in 37 °C incubator for 24 h continually (Fig. 7C).

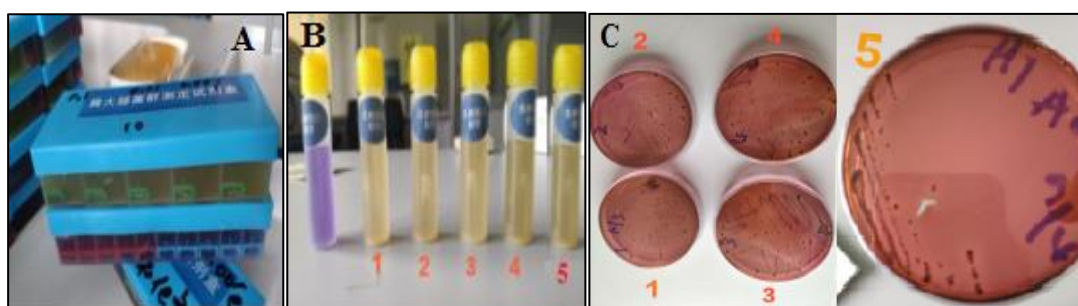


Fig. 7 – Fecal coliform fermentation experiment (A: *E. coli* kit; B: inoculation tube; C: EMB medium).

Usually, most probable number (MPN) of coliforms was very important to obtain the number of bacteria thereby evaluating the antibacterial property of the samples. *Escherichia coli* in this work was from toilet wastewater and stained for Gram dyeing and used as representative to evaluate the antibacterial property of TiO₂, TiO₂/Ag, TiO₂/Cu, and TiO₂/Au. MPN was gotten according to Chinese

national standard (GB 18466-2005),¹² as seen in Table 3. It could be seen that MPN of the *Escherichia coli* in toilet wastewater was above 80000/L. The bacteriostasis rates of TiO₂, TiO₂/Ag, TiO₂/Cu, and TiO₂/Au were all over 98% that displayed strong antibacterial properties of TiO₂ and its composite to *Escherichia coli*, particularly, TiO₂/Ag possessed best antibacterial performance with antibacterial rate of 99.89%.

Table 3

The testing results of fecal coliform

No.	Composite	Diluted times	MPN level(L ⁻¹)	Antibacterial rate (%)
1	--	1:5	>80000	--
2	TiO ₂	1:5	1100	98.84
3	TiO ₂ /Ag	1:5	100	99.23
4	TiO ₂ /Au	1:5	550	99.42
5	TiO ₂ /Cu	1:10	200	99.89

(The antibacterial rate in comparison with 80000 of original solution)

Mechanism analysis of photocatalytic activity on TiO₂ and its composite

Usually, the free radical intensity directly affects the photocatalytic activity of photocatalyst, as related to the light response range of photocatalyst.^{18,19}

Generally, the intensity of three free radicals, superoxide free radicals (O₂⁻), singlet oxygen (¹O₂), and hydroxyl radicals (·OH), were utilized for evaluating photocatalytic activity of photocatalyst. The intensities of O₂⁻, ¹O₂, and ·OH of TiO₂, TiO₂/Ag, TiO₂/Cu, and TiO₂/Au were tested by ESR, as shown

in Fig. 8. It could be seen that the O_2^- intensities of TiO_2/Ag and TiO_2/Au were obviously higher than TiO_2 and TiO_2/Cu . Meanwhile, TiO_2/Ag possessed the highest intensity of the 1O_2 and $\cdot OH$ that explained TiO_2/Ag had best photocatalytic degradation and

antibacterial property. Additionally, the results indicated that Ag and Au elements possessed strong SPR effect, thus transition metal doped TiO_2 could increase the light response range of the photocatalysts, thereby improving the photocatalytic activity.

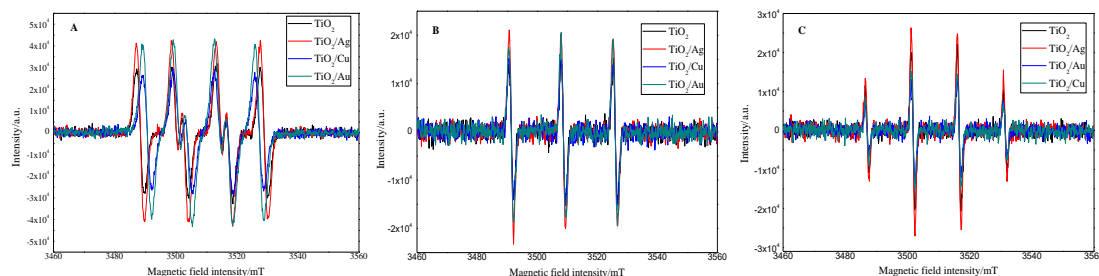


Fig. 8 – ESR spectra of: A) superoxide free radical (O_2^-); B) singlet oxygen (1O_2); C) hydroxyl radical ($\cdot OH$) in TiO_2 , TiO_2/Cu , TiO_2/Ag , and TiO_2/Au .

Additionally, the H_2 -TPR results confirmed that the reducing temperature of Ti element from TiO_2 composite by hydrogen was obviously lower than that of TiO_2 , as seen in Fig. 9. There was because that metallic ion doped into TiO_2 increased the activity of the photocatalyst and produced more free radicals,⁶ as evidence by relevant ESR results. Furthermore, metal ions (such as Ag, Au, Cu elements) typically replace Ti^{4+} sites, introducing impurity energy levels or altering band structures. In addition, the band-gap of TiO_2 , TiO_2/Cu ,

TiO_2/Ag , and TiO_2/Au were calculated by TP method, as seen in Fig. 10. The results showed that the slit width of TiO_2 was obviously higher than TiO_2/Cu , TiO_2/Ag , and TiO_2/Au , the slit width of TiO_2/Ag evenly reached about 2.75 eV. Further, silver doping TiO_2 indicated more activity that was consistent with the results of photocatalytic degradation on organic pollutants and antibacterial properties on *Escherichia coli*. These results owned to the metal doping TiO_2 thereby improving the optical response range of TiO_2 .¹⁵⁻¹⁷

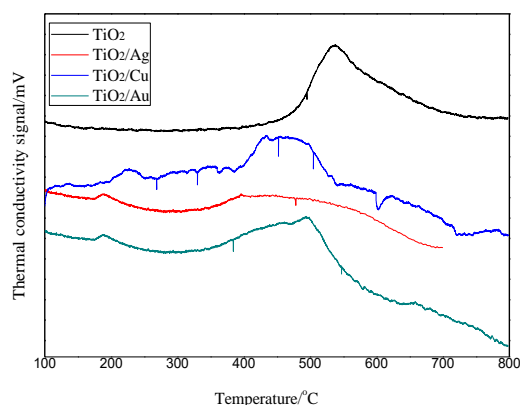


Fig. 9 – H_2 -TPR curves of TiO_2 and its composite.

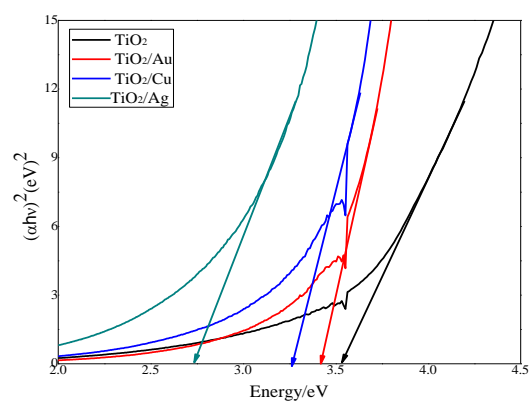


Fig. 10 – The slit width of TiO_2 and its composite.

CONCLUSION

The photocatalysts of metallic ions doped TiO_2 composites were prepared readily by solvothermal method and characterized by using UV-Vis, FTIR, XRD, SEM, ESR, TPR, and fluorescence spectrometer. The results showed that as-prepared photocatalysts had thermal stable performance, uniform size of metal doped TiO_2 , and stable crystal structure, and low recombination rate of holes and electrons. Additionally, the photocatalysts

possessed superior photocatalytic degradation properties towards

a wide range of organic pollutants, including methyl orange, DMF, methylene blue and phenol. Among which, TiO_2/Ag was found to exhibit the highest degradation rates for photocatalysis of these contaminants, which also demonstrated potent antibacterial properties against *Escherichia coli* in wastewater. Collectively, these results suggested that these metallic ions doped TiO_2 composite,

especially TiO₂/Ag, could be used as promising photocatalysts for elimination of organic pollutants in the wastewater.

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REFERENCES

1. M. Aslam, A. Z. Abdullah, M. Rafatullah, *Environ. Sci. Pollut. R.*, **2022**, *29*, 41053–41064.
2. C. Lyu, L. Ju, X. Yang, *J. Mater. Sci.-Mater. El.*, **2020**, *31*, 4797–4807.
3. J. Li, X. Liu, G. Zhao, *Sci. Total Environ.*, **2023**, *869*, 161767.
4. J. Cheng, L. Liu, G. Liao, *J. Mater. Chem. A*, **2020**, *8*, 5890.
5. Y. Nam, J. H. Lim, K. C. Ko, *J. Mater. Chem. A*, **2019**, *7*, 13833–13859.
6. Q. Xu, Y. Wang, M. Chi, *Catalysts*, **2020**, *10*, 310.
7. H. Sopha, L. Hromadko, M. Motola, *Electrochem. Commun.*, **2020**, *111*, 106669.
8. J. V. Hernández, S. Coste, A. G. Murillo, *J. Alloys Compd.*, **2017**, *710*, 355–363.
9. Y. Li, P. Zhang, D. Wan, *Appl. Surf. Sci.*, **2020**, *504*, 144361.
10. X. T. Zhou, X. H. Liu, X. J. Huang, *J. Hazard. Mater.*, **2022**, *422*, 126869.
11. C. Barbas Arribas, D. Rojo Blanco, *Sci. Rep.*, **2014**, *4*, 4134.
12. GB 18466-2005. Discharge standard of water pollutants for medical organization [S]. Beijing China, China Environmental Science Press, 2005.
13. S. Garcíagarcía, A. Lopezortega, Y. Zheng, *Chem. Sci.*, **2019**, *10*, 2171–2178.
14. L. Zhang, B. Han, P. Cheng, *Catal. Today*, **2020**, *341*, 21–25.
15. A. Gnanaprakasam, V. M. Sivakumar, P. L. Sivayogavalli, *Ecotox. Environ. Safe.*, **2015**, *121*, 121–125.
16. T. D. Pham, B. K. Lee, C. H. Lee, *Appl. Catal. B: Environ.*, **2016**, *182*, 172–183.
17. K. Ishibashi, A. Fujishima, T. Watanabe, *J. Photochem. Photobiol. A*, **2000**, *134*, 139–142.
18. C. Kütahya, P. Wang, S. Li, *Angew. Chem. Int. Edit.*, **2020**, *59*, 3166–3171.
19. J. Di, J. Xia, X. Li, *Carbon*, **2016**, *107*, 1–10.

