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Preparation of Silver and Copper Co-impregnated Nano-ZnO Immobilized on Mesoporous SiO_2 and its Photocatalytic Performance

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ABSTRACT

To improve light usage, Ag and Cu were co-impregnated with nano-ZnO, and the mesoporous silica gel (meso-SiO_2) was chosen as the carrier. The sol-gel method was used to successfully construct a composite photocatalyst with 3 percent Ag/0.1 percent Cu/nano-ZnO/meso-SiO_2. For the evaluation of the photocatalytic activity of the as-prepared catalysts, Reactive Black 5 was used as a simulated organic pollutant in aqueous. The results revealed that uniform spherical nano-ZnO particles with a diameter of 10 nm were attached to the surface and mesopore of meso-SiO_2. The average pore width and specific surface area of this composite were 7.06 nm and 305 $m^2.g^{-1}$, respectively. The optimal amount of loaded Ag and Cu were 3% and 0.1%, respectively, which resulted in around 100% removal of Reactive Black 5 after 280 min UV-light irradiation. The degradation process followed pseudo-first-order kinetics. Ag and Cu-loaded nano-ZnO/SiO_2 could be advantageous for suppressing the recombination of photo-generated holes and electrons, thus improving the degradation efficiency. The constant of degradation rate and adsorption equilibrium of 3%Ag/0.1%Cu/nano-ZnO/meso-SiO_2 were 0.049 min^{-1} and 2.14 $L.g^{-1}$, respectively. After three reuses, the Ag/Cu/ZnO/meso-SiO_2 photocatalyst remained very stable during the photocatalytic process with no loss of photocatalytic activity. According to the GC-MS results, a probable degradation mechanism was estimated.

INTRODUCTION

Over the last half-century, photocatalytic semiconductors have piqued the interest of an increasing number of scientists. Because of its exciton binding energy of 60 meV (Waag et al. 2004) and bandgap energy of 3.3 eV (Xu et al. 2017) at room temperature, zinc oxide (ZnO) is one of the stellar n-type photocatalytic semiconductors that has been used in organic degradation.

The nano-ZnO, on the other hand, has two disadvantages as a photocatalyst: low light usage and poor recyclability and reusability. Metal was used to modify nano-ZnO to minimize bandgap and thus increase the photocatalytic activity of ZnO to improve light-harvesting efficiency. Cu-doped ZnO nano-photocatalyst was developed for the increase of photocatalytic activity in the treatment of methyl orange wastewater, according to the literature (Kadam et al. 2017). In addition, Ag also could improve the photocatalytic activity of ZnO to decompose phenol, which was more efficient than P25-TiO_2 (Jaramillo-Paez et al. 2017). Modwi et al. (made Ag (1%) and Cu (5%) doped ZnO nanoparticles that successfully cured malachite green in an aqueous solution. The bandgap energy of Cu/ZnO was moved from 2.95 to 2.79 eV (pure ZnO 3.3 eV) by the Ag/Cu/ZnO nano-composite, indicating that Ag and Cu were suitable options for improving photocatalyst activity (Modwi et al.2018). Furthermore, the nano-sized ZnO could not be recycled or reused. The nanoparticles loaded on some supporters, on the other hand, may be able to solve this problem. However, the nanopowders loaded on some supporters could alleviate this problem. Sarah et al. developed a composite photocatalyst in which nano-ZnO was immobilized on bentonite clay to improve the reusability of the catalyst (Sarah et al. 2013). In addition, porous activated carbon loaded nano-ZnO was proved more efficient than ZnO alone for removing alizarin cyanin green from aqueous (Muthirulan et al. 2013). In our preliminary work, the composite photocatalysts of Ag and Fe bi-metals doped quantum-sized ZnO immobilized on micro-pore ZSM-5 (Xu et al. 2017) were prepared to decompose Rhodamine B in aqueous and exhibited satisfactory photocatalytic activity.

Sol-gel technology was one of the most extensively used methods to synthesize inorganic materials in the preparation of nanomaterials (Xu et al. 2018, Wu et al. 2019). The sol-gel method was used to generate Ag and Cu bi-metals loaded nano-ZnO immobilized mesoporous SiO_2 composite photocatalysts, which were then evaluated by XRD, SEM, TEM, and BET. For assessing photocatalytic performance, Reactive Black 5 was chosen as a pollutant in an aqueous

solution. The contents of Ag and Cu in photocatalysts were studied and optimized.

MATERIALS AND METHODS

Preparation of Ag/Cu/nano-ZnO/Mesoporous SiO_2 Photocatalyst

$Zn(CH_3COO)_2$ (0.01 mol), $Cu(NO_3)_2$ (0.005-0.02 mmol), and $AgNO_3$ (0.1-0.5 mmol) were dissolved in 50 mL anhydrous ethanol. Then, 1.6 g meso-SiO_2 was added to form a hybrid solution. A solution of 0.58 g lithium hydroxide in 50 mL anhydrous ethanol and 100 mL of *n*-hexane were added to the hybrid system at room temperature. A white gel was obtained after standing overnight at 4°C. The precursor was obtained by centrifugation and drying at 100°C. The Ag/Cu/nano-ZnO/mesoporous SiO_2 composite powder was prepared by calcination at 200°C for 4 h. The mass ratio of ZnO and SiO_2 was 1:2.

Characterization of Materials

The crystal phase of the sample was analyzed by XRD using a PANalytical X-ray diffractometer (X'Pert Pro MPD, Netherlands) using Cu Kα radiation. SEM was performed using a Nova NanoSEM (FEI, USA) with EDX. TEM was carried out using JEM-2010 (JEOL, Japan). N_2 sorption isotherms were measured using a Mocromeritics ASAP2020 system (USA).

Photocatalytic Activity Tests

Reactive Black 5 was selected as a simulated pollutant to investigate the photocatalytic performance and its main information was shown in Table 1. The maximum absorption wavelength of Reactive Black 5 was 553 nm.

To evaluate the photocatalytic activity, 200 mL of 20 $mg.L^{-1}$ Reactive Black 5 and 0.1 $g.L^{-1}$ photocatalyst were added to a 250 mL beaker under magnetic stirring. A 10 cm long mercury UV lamp (10 W Guangdong Bright Star) was used as the radiation source with a wavelength of 245 nm. The lamp was fixed above the reaction liquid. After a certain reaction interval of 40 min, a 10 mL sample was removed and centrifuged at 12,000 rpm to remove the catalyst. The dyestuff absorbance of Reactive Black 5 was analyzed using a UV-2102PC UV-visible spectrophotometer (UNICO, China). The degradation rate of Reactive Black 5 was calculated using Eq. (1):

$$\text{Removal} = [(C_0 - C_t)/C_0] \times 100\% \quad \ldots(1)$$

Where, C_0 is the initial concentration of Reactive Black 5, and C_t is the concentration of Reactive Black 5 at time t.

GC-MS Analysis

The organic substance in the sample should be extracted by dichloromethane before the GC-MS test. The separation was carried out on a DB-5 MS fused quartz capillary chromatographic column (J&W Scientific, Folsom, CA, USA) with a 30 m 0.25 mm i.d. and 0.25 m phase thickness in a Finnigan Trace GC 2000 chromatograph. Using a Trace MS 2000 mass spectrometer (Thermo-Quest, Finnigan, USA) in EI+ mode, coupled to the chromatograph, the analytes were examined by mass spectrometry.

RESULTS AND DISCUSSION

XRD Analysis

Fig.1 shows the XRD results of pure-SiO_2, pure-ZnO, ZnO/SiO_2, 3%-Ag/ ZnO/SiO_2 and 3%-Ag/0.1%-Cu/ZnO/SiO_2. It could be seen clearly from Fig.1 that the XRD pattern of pure-SiO_2 displayed a wide diffraction peak located at around 22°. The diffraction peaks of pure ZnO at 2θ values of 31.7°, 34.4°, 36.2° and 47.5° were attributed to (100), (002), (101), and (102) crystal planes, respectively. All the peaks could be well indexed to standard patterns (JCPDS 36-1451) without any impurity phase (Dou et al. 2015). From the XRD pattern of ZnO/SiO_2, all the characteristic peaks of ZnO and SiO_2 could be found. The half peak width of ZnO in ZnO/SiO_2 became bigger than pure ZnO which meant SiO_2 could decrease the particle size of ZnO. In the XRD pattern of 3%-Ag/ZnO/SiO_2, the diffraction peaks of AgO at 2θ values of 39.4° and 53.9° were found. However, according to the standard patterns of AgO (JCPDS 74-1750), the major peaks of AgO at 2θ values of 32.3°, 34.2°, and 37.2° did not appear. This could be attributed to the low content of sliver in the composite catalyst (only 3%). The amount of Cu was rather low that no diffraction peak was observed in the XRD pattern of 3%-Ag/0.1%-Cu/ZnO/SiO_2. The average particle sizes of ZnO in Ag/Cu/ZnO/ SiO_2 and pure ZnO were obtained using the Scherrer equation $D = K\lambda/\beta\cos\theta$, where, D was the average crystallite size, λ was the X-ray wavelength, θ was the Bragg angle, β was the corrected half-peak width of the experimental sample, and K was the shape factor with a value of 0.9 (Bechambi et al. 2015). The average crystal sizes of ZnO in Ag/Cu/ZnO/SiO_2 and pure ZnO were 10.1 nm and 15.7 nm, respectively.

Table 1: Identified intermediates of degradation of Reactive Black 5.

RT[min]	Authentic chemical formula
6.81	1,2-diacetylenzene*
7.40	3,5,5-trimethylhexanoic acid
14.08	2-butenedicarboxylate
16.53	phthaic acid, diisobutylester
17.46	1,4-dinitrobenzoic acid*
19.15	phthalic acid*

*main products

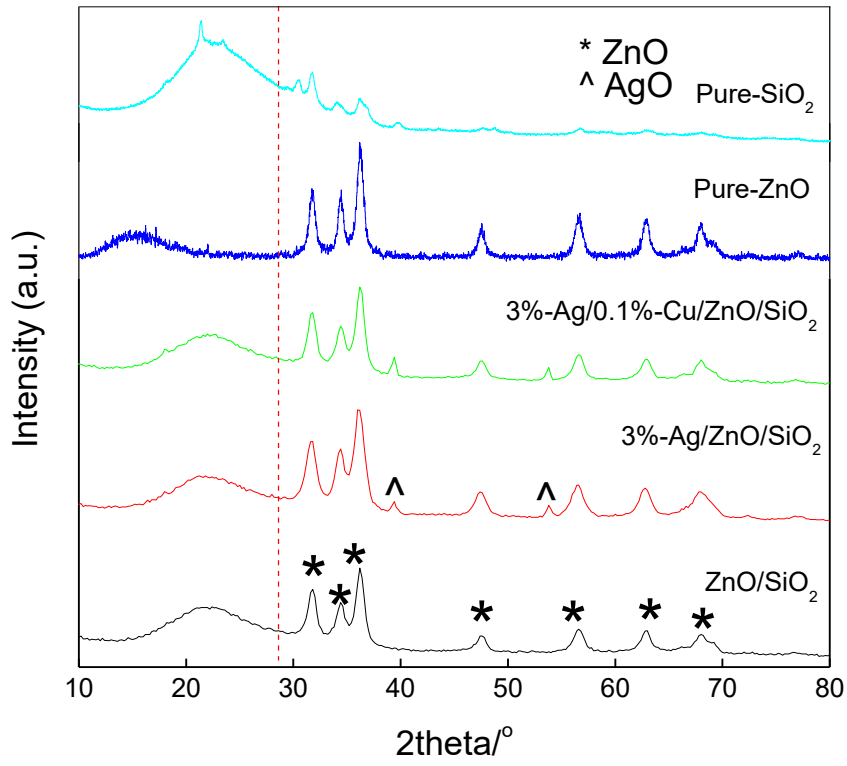


Fig. 1: XRD of 3%-Ag/0.1%-Cu/ZnO/ SiO_2, 3%-Ag/ZnO/SiO_2, ZnO/SiO_2, pure ZnO and pure SiO_2

N_2-Adsorption and Desorption Analysis

Fig. 2 showed the nitrogen isotherm data for Ag/Cu/ZnO/ meso-SiO_2. The type IV isotherm indicated this composite had a mesoporous structure (Fu et al. 2015). The average pore width and surface area of this material were 7.06 nm and 305 $m^2.g^{-1}$, respectively. In a preliminary study (Xu et al. 2015a), ZnO/mesoporous SiO_2 and pure mesoporous SiO_2 exhibited 318 and 330 $m^2.g^{-1}$ surface areas along with average pore sizes of 7.9 and 8.6 nm, respectively. It suggested that the

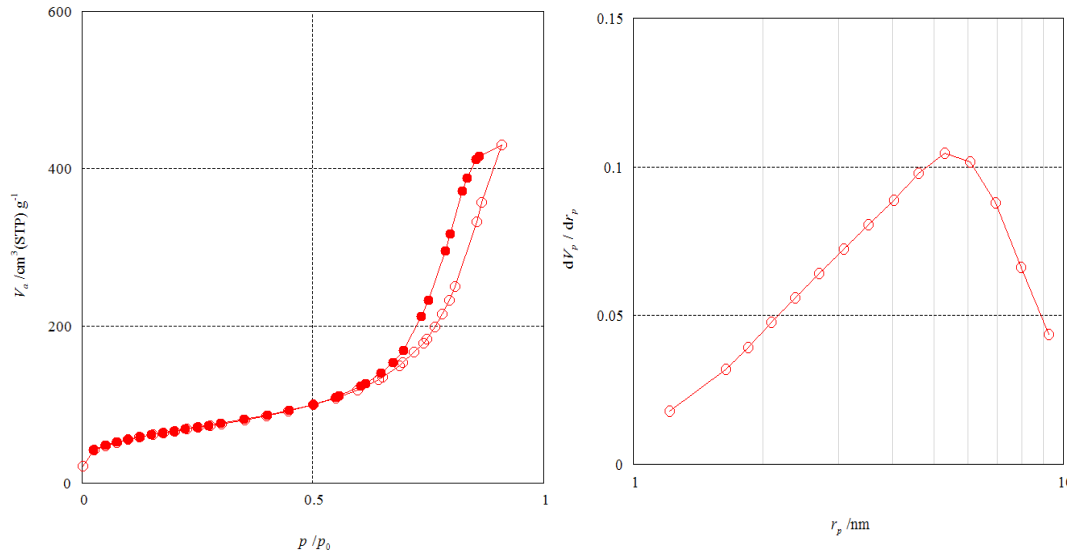


Fig. 2: Nitrogen isotherm adsorption-desorption curve (a) and pore size distribution (b) for 3%-Ag/0.1%-Cu/ZnO/meso-SiO_2.

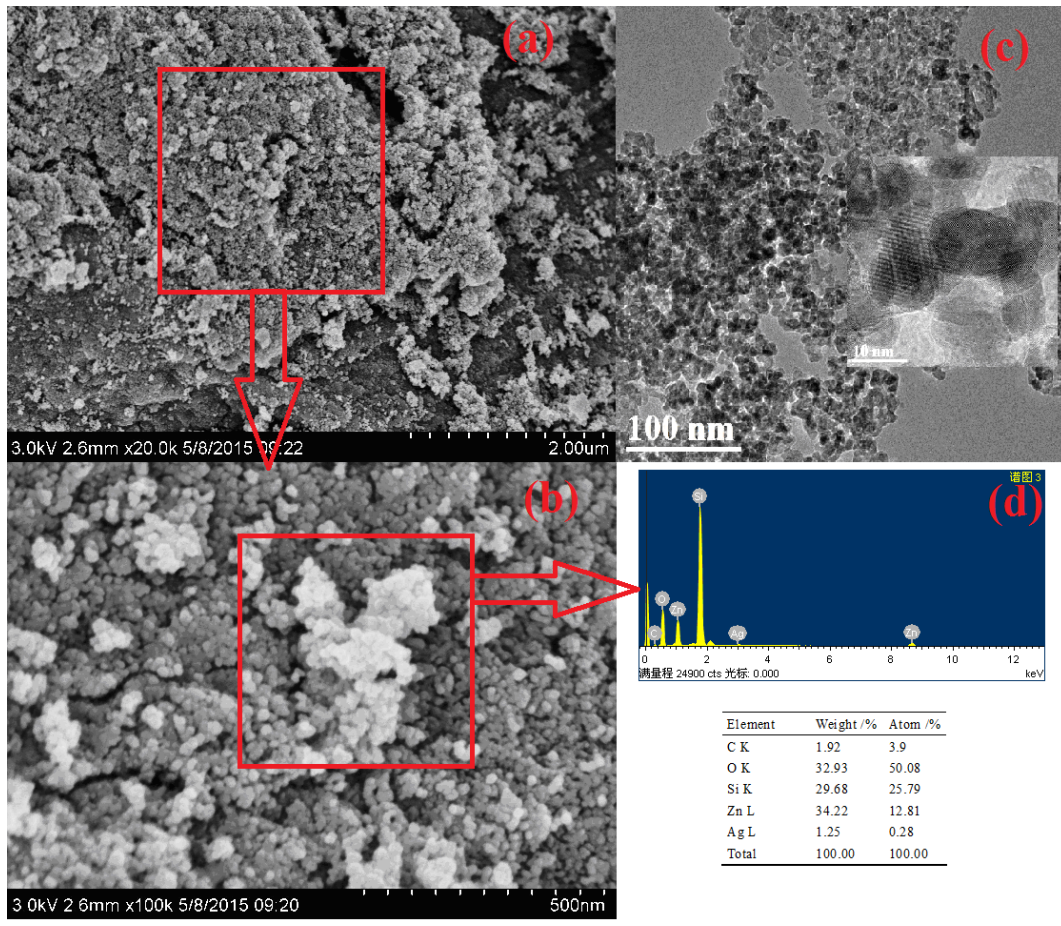
metal had been successfully doped on ZnO/mesoporous SiO_2 and affected its surface area and pore width, which resulted in the reduction of 13 $m^2.g^{-1}$ and 0.8 nm, respectively.

Morphological Analysis

The morphological study of 3 percent -Ag/0.1 percent Cu/ ZnO/SiO_2 was shown in Fig. 3. A considerable number of nano-sized ZnO particles agglomerated on the surface of SiO_2 as seen in SEM images (Fig. 3a & 3b). The particle size of ZnO was consistent in the TEM picture (Fig.3c). The average particle size was around 8 nm, which was similar to the theoretical XRD finding (15.7 nm). EDX was used to determine the presence of Cu and Ag in the Ag/Cu/ZnO/SiO_2 composite. The catalyst has five elements, as shown in Fig.3d. For the C element, 1.92 wt% C could be attributed to the incomplete cleaning of the composite or the contamination during the measuring process. The content of the O element was about 50%. The element ratio of Si and Zn was nearly 2.01:1 which was consistent with the experimental dosage. Moreover, the content of Ag was only 0.28% which was lower than Ag dosage and Cu metal was not found in the EDX results. The reason was that only the red square zone of the catalytic surface in Fig. 3b was scanned to obtain the EDX result. The red square zone sometimes could not represent the surface properties of the entire material. The content of Cu was only 0.1% which was difficult to be detected.

Effect of Ag Content in $Ag/ZnO/SiO_2$

Fig. 4 showed the effect of Ag contents in $Ag/ZnO/SiO_2$ on the decomposition of Reactive Black 5 during irradiation time from 0 to 280 min. It could be seen clearly from Fig.4 that there was a low photocatalytic efficiency when the composite catalyst was free from silver. After 280 min, only 22.6% Reactive Black 5 was decomposed. When the Ag content increased from 1% to 3%, the degradation rate of Reactive Black 5 exhibited a great improvement. The color removals were 60.5% and 78.9% at 280 min, respectively. However, when the Ag-loaded amount reached 5%, the dye removal



Element	Weight /%	Atom /%
C K	1.92	3.9
O K	32.93	50.08
Si K	29.68	25.79
Zn L	34.22	12.81
Ag L	1.25	0.28
Total	100.00	100.00

Fig. 3: SEM images (a and b), TEM image (c), and EDX (d) of 3%-Ag/0.1%-Cu/ ZnO/SiO_2.

decreased to 65.1% at 280 min. Therefore, the optimal Ag-loaded amount was 3% in this experimental condition.

Based on the experimental results, the reason could be analyzed as follow. When ultraviolet light illuminated the photocatalyst (ZnO/SiO_2), electrons were promoted from the valence band to the conduction band, forming electron (e^-)—hole (h^+) couples (Chang et al. 2015). Meanwhile, the electrons and holes were able to quickly recombine, releasing heat. The holes at the ZnO surface could oxidize H_2O_{ads} and OH^-_{ads}, adsorbed in the ZnO surface, to produce $\cdot OH_{ads}$. The $\cdot OH_{ads}$ was a powerful oxidizing agent which would attack the organic compounds and generate intermediates (Int_{ads}). These intermediates could further react with $\cdot OH_{ads}$ to produce final products (P). In the meantime, the $\cdot OH_{ads}$ could be also be consumed by inactive species which leads to lower degradation efficiency. The appropriate Ag impregnation aided in the division of electrons and holes as well as the rate of electron transport to dissolved oxygen, boosting photocatalytic efficiency even more. Excess Ag, on the other hand, could fill the surface of ZnO, resulting in insufficient UV light utilization and so being detrimental to photocatalytic activity. Excess Ag, on the other hand, could create electron-hole recombination centers, reducing dye removal.

Effect of Cu Content in $Cu/ZnO/SiO_2$

Fig. 5 shows the effect of Cu amount in $Cu/ZnO/SiO_2$ photocatalyst on Reactive Black 5 degradation. From Fig.5, when the Cu-loaded amount was increased from 0% to 0.1%, the Reactive Black 5 removal increased significantly from 22.6% to 70.4% after 280 min. However, with more Cu impregnation (exceeded 0.1%), the Reactive Black 5 removal dramatically decreased. Among which, only 41.4% removal was observed after 280 min at 0.2% Cu-loaded amount. Therefore, the optimal Cu-loaded amount was 0.1% with 70.4% dye removal which was lower than that of 3% Ag-loaded catalyst.

Cu impregnation significantly increased the ZnO photocatalytic activity. Metallic Cu consumed the photo-generated electrons, which could suppress the recombination of photo-generated holes and electrons. As a result, more active holes reacted with H_2O molecules adsorbed on the surface of the catalyst, producing more hydroxyl radicals. In contrast, the catalytic activity was reduced when the Cu-loaded amount exceeded the best dosage. Cu may also act as an electron-hole recombination center, thus decreasing the photocatalytic activity of ZnO.

Comparison of Different Photocatalysts

Fig. 6 shows a comparison of Reactive Black 5 degradation on ZnO/SiO_2, 0.1% $Cu/ZnO/SiO_2$, 3%$Ag/ZnO/SiO_2$, and 3%Ag/0.1%$Cu\text{-}ZnO/SiO_2$ under UV-lamp. From Fig. 6, 3%Ag/0.1%$Cu/ZnO/SiO_2$ was the most efficient photocatalyst in the presence of UV irradiation with 91.5% Reactive Black 5 removal at 280 min. Ag and Cu could

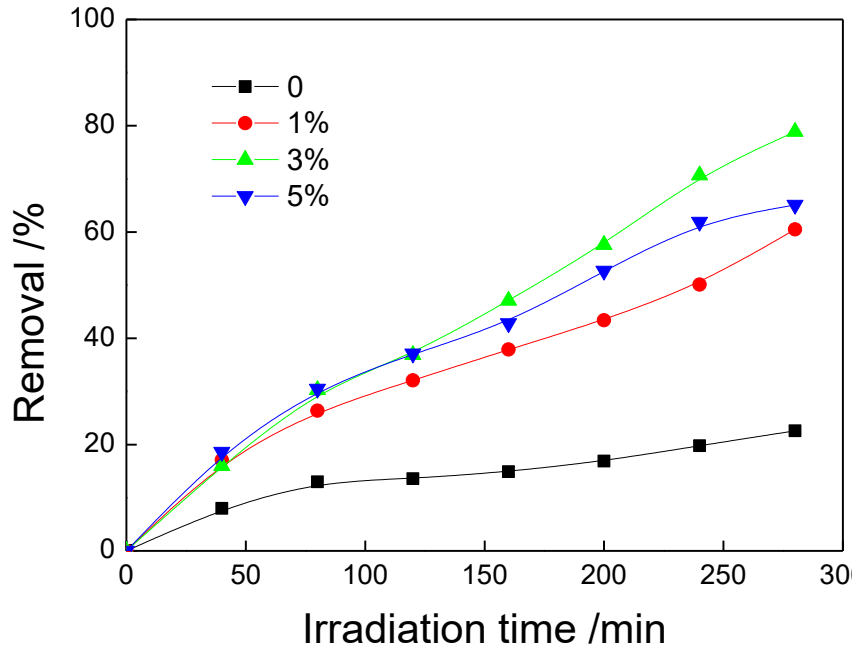


Fig. 4: Reactive Black 5 removal at different Ag contents in Ag/ZnO/ SiO_2.

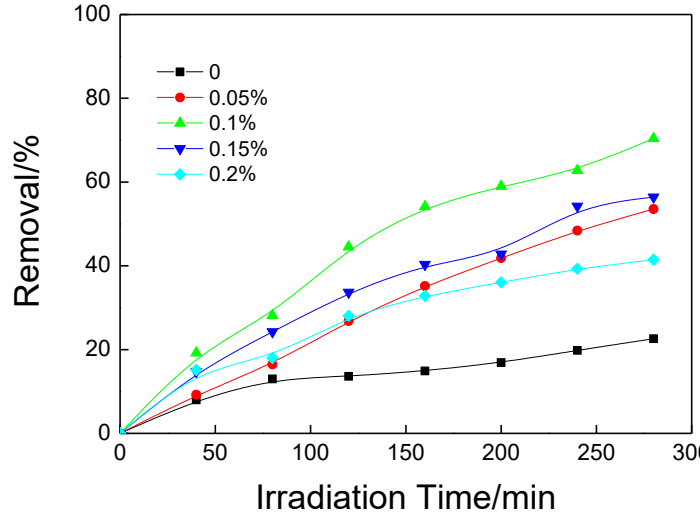


Fig. 5: Reactive Black 5 removal at different Cu contents within Cu/ZnO/ SiO_2.

capture the photo-generated electrons, and prevent hole–electron recombination, which improved the photocatalytic efficiency. The Ag and Cu co-loaded nano-ZnO decreased the band-gap energy of nano semiconductor photocatalyst. Therefore, 3%Ag/0.1%Cu-ZnO/SiO_2 displayed a remarkable activity under this experimental condition.

Effect of Ag/Cu/ZnO/SiO_2 Dosage

The dosage of 3%Ag/0.1%Cu/ZnO/SiO_2 should be optimized to avoid waste during degradation. A series of experiments were carried out with varying composite catalyst concentrations from 0.05 to 0.3 $g.L^{-1}$ to determine the optimal Ag/Cu/ZnO/SiO_2 dosage. Reactive Black 5 removals at different catalyst dosages were shown in Fig.7. Accordingly, the removal after 280 min were 73.4%, 91.5%, 99.3%, 100%, 98.7% and 80.2% corresponding to different catalyst dosages of 0.05 $g.L^{-1}$, 0.1 $g.L^{-1}$, 0.15 $g.L^{-1}$, 0.2 $g.L^{-1}$, 0.25 $g.L^{-1}$ and 0.3 $g.L^{-1}$, respectively. The removal of Reactive Black 5 increased with the increase of Ag/Cu/ZnO/SiO_2 dosages from 0.05 $g.L^{-1}$ to 0.2 $g.L^{-1}$. Nevertheless, even the catalyst was increased to 0.25 $g.L^{-1}$, the removal was almost unchanged. Moreover, the removal was further reduced when the catalyst was added to 0.3 $g.L^{-1}$. Thus, the optimum catalyst dosage was 0.2 $g.L^{-1}$ with nearly 100 % removal of Reactive Black 5 after 280 min.

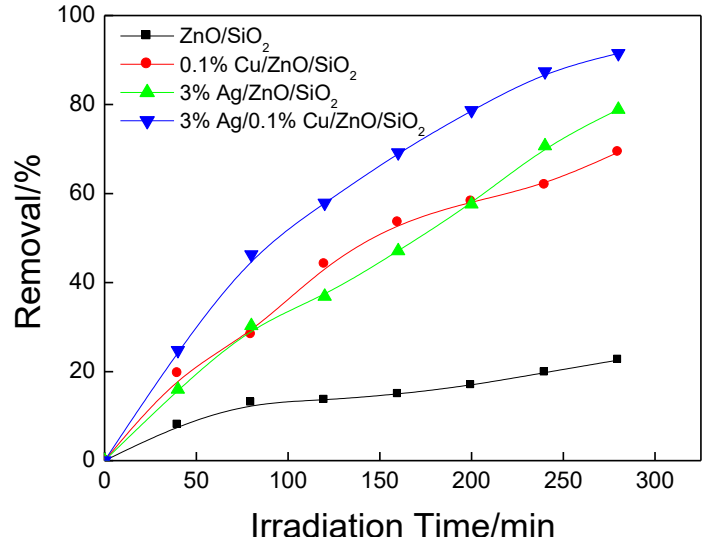


Fig. 6: Reactive Black 5 removal at different catalysts.

According to the references (Xu et al. 2015 b), the photocatalytic process followed pseudo-first-order kinetics, $\ln(C_t/C_0)=k_{ap}t$. Here, the slope represents the apparent reaction rate constant (k_{ap}). The fitting results at different Ag/Cu/ZnO/SiO_2 dosages were shown in Fig. 8. In general, the fitting coefficients were above 0.99 when the catalyst dosages were between 0.05 g/L to 0.2 g/L, which means the Reactive Black 5 degradation process by UV/Ag/Cu/ZnO/SiO_2 perfectly followed the first-order kinetics. When the catalyst dosages were 0.25 g/L and 0.3 g/L, the fitting coefficient values were lower than 0.99, which meant excessive catalyst had a negative effect on first-order degradation kinetics. According to the slope of fitting line equation, the reactive rate constants were 0.0047 min^{-1}, 0.00871 min^{-1}, 0.0123 min^{-1}, 0.0140 min^{-1}, 0.0139 min^{-1} and 0.00756 min^{-1} at different catalyst dosages 0.05 $g.L^{-1}$, 0.1 $g.L^{-1}$, 0.15 $g.L^{-1}$, 0.2 $g.L^{-1}$, 0.25 $g.L^{-1}$ and 0.3 $g.L^{-1}$, respectively. The biggest k_{ap} at 0.2 g/L catalyst dosage was 0. 0140 min^{-1}.

The experimental results indicated that the more catalysts were added, the more photons from the UV-lamp were harvested, which could promote the valence band electron excitation to the conduction band. Reactive Black 5 was degraded by photo-generated holes in the valence band, which were active sites with a high oxidation capacity. At higher concentrations, the catalyst particles, on the other hand, could reflect, screen, and scatter the UV lamp's light, reducing the photonic flux within the irradiated solution. Another reason was the efficient catalyst surface probably became smaller for photoabsorption because of the agglomeration and sedimentation of catalyst particles. Therefore, there was an optimal catalyst dosage.

Effect of Ag/Cu/ZnO/SiO_2 amount on pseudo-first-order rate constant (k_{ap}) were fitted with a Langmuir type expresesion (Xu et al. 2014):

$$k_{ap}=\frac{k_o KC}{1+KC}$$

Here, k_0, K, and C were the catalyst surface reaction rate constant, the adsorption equilibrium constant, and the catalyst concentration, respectively. Values of k_0 *K* could be calculated according to the Langmuir type formula, as k_0 was 0.049 min^{-1} and K was 2.14 $g.L^{-1}$, respectively. The correlation coefficient is 0.9981.

Photocatalyst Recovery

Fig.7 showed the recovery test of Ag/Cu/ZnO/SiO_2 under UV-light irradiation. The photocatalyst could be used five times. Almost no obvious declination of the photoactivity was observed after four times. At the fifth time, the dye removal decreased by about 5%. The results demonstrated that Ag/Cu/ZnO/SiO_2 catalyst was stable during the photocatalytic process.

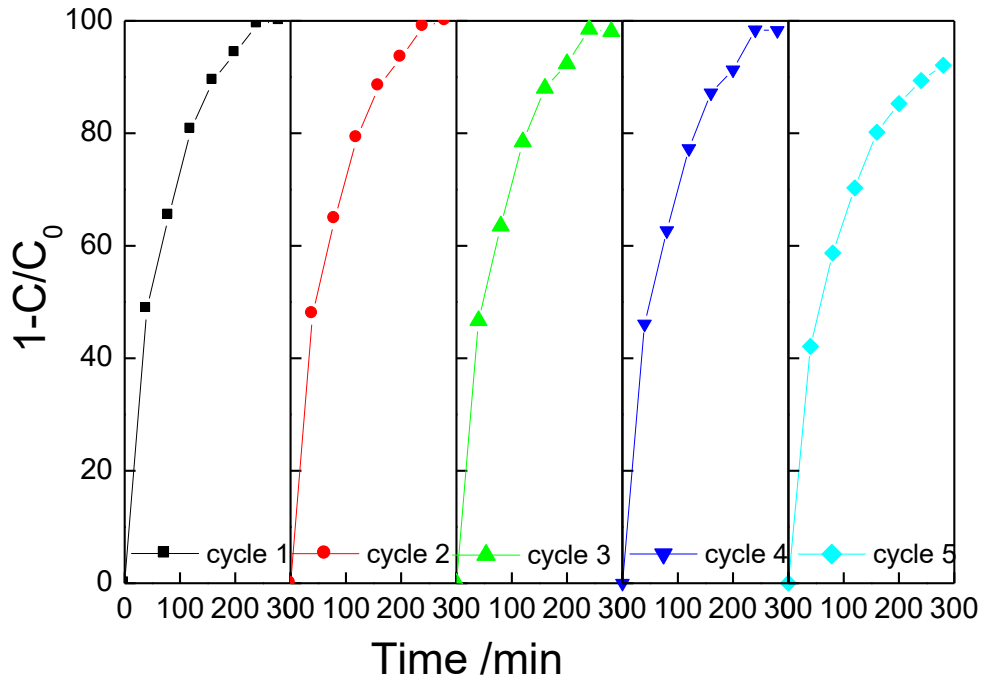


Fig. 7: Recyclability of 3%-Ag/0.1%-Cu/ZnO/SiO_2 for the photo-degradation.

Possible degradation pathway of Reactive Black 5

Although the photocatalytic process exhibited nearly 100% removal, the intermediate products should also be considered. The intermediate products were obtained by dichloromethane extraction and the sample was analyzed by GC-MS. The results were shown in Table 1. From Table1, there were many colorless intermediate products. The main by-products were 1,2-diacetylenzene (RT: 6.8 min), 2-butenedicarboxylate (RT: 14.08 min), 1,4-dinitrobenzoic acid (RT: 17.46 min), and phthalic acid (RT: 19.15 min). According to the GC-MS results, a lot of organic acids could be generated when the structure of Reactive Black 5 was decomposed by the photocatalytic process.

The probable deconstructed pathway of Reactive Black 5 was indicated in Fig. 8 based on the MS results. Reactive Black 5 had an anthracene ring, benzene ring, sulfonic group, group, and so on in its chemical structure. Because of their low bond energy, the sulfonic and amino groups were quickly eliminated. As a result, the very active hydroxyl radical attacked and oxidized these bonds first, causing the chemical structure to decompose. The anthracene and benzene rings were difficult to break down since cleaving them required a lot of energy. The benzene ring oxidation produced the 2-butenedicarboxylate. Decomposition of the anthracene ring yields 1,2-diacetylenzene, 1,4-dinitrobenzoic acid, and phthalic acid.

CONCLUSION

A composite photocatalyst 3%-Ag/0.1%-Cu/nano-ZnO/mesoporous SiO_2 was successfully prepared and applied to effectively degrade Reactive Black 5 in aqueous under UV light irradiation. The uniform spherical nano-ZnO particles with a size of ~10 nm are attached to the surface and mesopore of meso-SiO_2. The Ag/Cu/ZnO/meso-SiO_2 exhibited the classical type IV isotherm during the N_2 adsorption and desorption process, which signified an excellent mesoporous structure. The average pore width and surface area of this material were 7.06 nm and 305 $m^2.g^{-1}$, respectively. The optimal Ag and Cu-loaded amounts were 3% and 0.1%, respectively, which contributed nearly 100% Reactive Black 5 removal at 280 min under UV-light irradiation. Doping with Ag and Cu could significantly reduce the recombination of photo-generated holes and electrons, resulting in a faster deterioration rate. Furthermore, the photocatalyst Ag/Cu/ZnO/meso-SiO_2 displayed perfect stability during the photocatalytic process, with no visible fading of photocatalytic activity after five reuses. Based on the GC-MS results, a plausible degradation mechanism was hypothesized.

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REFERENCES

Bechambi, O., Chalbi, M., Najjar, W. and Sayadi S. 2015. Photocatalytic activity of ZnO loaded with Ag on the degradation of endocrine disrupting under UV irradiation and the investigation of its antibacterial activity. Appl. Surf. Sci., 347: 414-420.

Chang, C.T., Wang, J.J., Tong, O.Y., Zhang, Q. and Jing, Y.H. 2015. Photocatalytic degradation of acetaminophen in aqueous solutions by TiO_2/ZSM-5 zeolite with low energy irradiation. Mater. Sci. Eng., 196: 53-60.

Dou, P.T., Tan, F.T., Wang, W., Sarreshteh, A., Qiao, X.L., Qiu, X.L. and Chen, J.G. 2015. One-step microwave-assisted synthesis of Ag/ZnO/graphene nanocomposites with enhanced photocatalytic activity. Photochem. Photobiol. A- Chem., 302: 17-22.

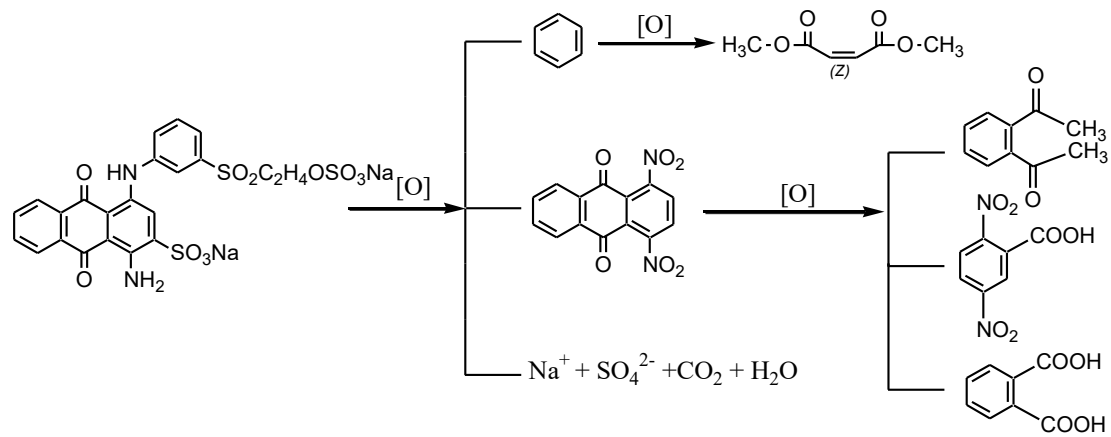

Fig. 8: Possible degradation pathway of Reactive Black 5.

Fu, J.R., Zheng, J., Fang, W.J., Chen, C., Cheng, C., Yan, R.W., Huang, S.G. and Wang, C.C. 2015. Synthesis of porous magnetic Fe_3O_4/Fe@ ZnO core-shell heterostructure with superior capability for water treatment[J]. Alloys Comp., 650: 463-469.

Jaramillo-Paez, C., Navio, J.A., Hidalgo, M.C. and Macias, M. 2017. High UV-photocatalytic activity of ZnO and Ag/ZnO synthesized by a facile method. Catal. Today, 284: 121-128.

Kadam, A.K., Kim, T.G., Shin, D.S., Garadkar, K.M. and Park J. 2017. Morphological evolution of Cu doped ZnO for enhancement of photocatalytic activity. J. Alloys Comp., 710: 102-113,

Modwi, A., Ghanem, M.A., Al-Mayouf, A.M. and Houas, A. 2018. Lowering energy bandgap and enhancing photocatalytic properties of Cu/ZnO composite decorated by transition metals. Mol. Struct., 1173: 1-6.

Muthirulan, P., Meenakshisundararam, M. and Kannan, N. 2013. The beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in an aqueous solution. Adv. Res., 4: 479-484.

Sarah, C.M., Suprakas, S.R., Maurice, S.O., and Maggie, N.B. 2013. Microwave-assisted synthesis, characterization and antibacterial activity of Ag/ZnO nanoparticles supported bentonite clay. J. Hazard. Mat., 262: 439-446.

Waag, A., Gruber, T., Thonke, K., Sauer, R., Kling, R., Kirchner, C. and Ress, H. 2004. ZnO metal-organic vapor phase epitaxy: Present state and prospective applications. Alloys Comp., 371: 77-81,

Wu, F.M., Wang, X.W., Li, M. and Xu, H. 2019. Synthesis of Alpha-Fe_2O_3 nanospheres and its dark-degradation for organic dye pollutions. Environ. Prog. Sustain. Energy, 38: 1-5

Xu, H., Yu, T.L. and Liu, J.F. 2014. Photo-degradation of Acid Yellow 11 in aqueous on nano-ZnO/Bentonite under ultraviolet and visible light irradiation. Mater. Lett., 117: 263-265.

Xu, H., Yu, T.L. and Liu, Y. 2015a. Characteristics and performance of nano zinc oxide/mesoporous silica gel photocatalytic composite prepared by a sol-gel method. Nanomaterials, 65: 1-5.

Xu, H., Yu, T.L., Wang, J.X., Li. M. and Liu, Y.N. 2015b. Online monitoring of Fenton-mediated reactive Red 6B oxidation kinetics. Environ. Prog. Sustain. Energy, 34: 1019-1027.

Xu, H., Zhang, D.D. and Wu, F.M. 2017 Photocatalytic activity of nano-ZnO loaded with Ag and Fe immobilized on ZSM-5. Desalin. Water Treat., 74: 308-315.

Xu, H., Zhang, D.D. and Wu, F.M. 2018. Effect of the template on the hydrothermal synthesis of mixed molecular sieves for methanol dehydration. Environ. Prog. Sustain. Energy, 37: 2132-2138.