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特约专栏

Photocatalytic Ceramic Foam Filter: Application Research Progress and Prospect

ZHOU Zhonghua, HUANG Yue
(College of Materials, Xiamen University, Xiamen 361005, China)

Abstract: Photocatalytic ceramic foam filter, the composite of high photoactive TiO_2 nano materials and three dimensional porous ceramic foam materials, has been widely applied in the field of air/water purification, owing to its characteristics of high photoactivity, large surface area, large flowing flux and ceramic heat/chemical resistance, recycling probability. Applications have been in the fields of industrial exhaust deodorization, agriculture pesticide degradation using sunlight, sterilization of laboratories and hospitals, high-speed train air purification, and so on. The application research progress, problem and future prospect of photocatalytic ceramic foam filter are summarized.

Key words: photocatalyst; ceramic foam filter; application; air/water purification

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光催化泡沫陶瓷过滤器的应用研究现状和展望

周忠华，黄 悦
(厦门大学材料学院，厦门 361005)

摘 要：高活性的光催化二氧化钛纳米材料与高气孔率的三维多孔泡沫陶瓷材料复合，得到的光催化泡沫陶瓷过滤器，具备高活性、大表面积、大通量、以及陶瓷的耐高温、耐化学腐蚀、循环适用性，在大气/水净化领域率先得到了广泛应用。在工业领域的废气脱臭处理、在农业领域的农药废水太阳光降解、在医疗卫生领域的实验室医院空气杀菌处理、在交通领域的高速列车空气净化等，已经展开应用。综述了国内外光催化泡沫陶瓷过滤器的应用研究现状、问题及其发展趋势。

关键词：光催化；泡沫陶瓷过滤器；应用研究；大气/水净化

1 Introduction

TiO_2 photocatalyst, due to its low price, high photoactivity and safety to human being and environment guaranteed by history, has been widely applied in the fields of air/water purification[1-5]. Among varieties of TiO_2 photocatalytic materials, photocatalytic ceramic foam filter, a composite of TiO_2 and ceramic foam by utilizing the high active performance of TiO_2 and the high resistance and large surface area of ceramic foam, has been commercialized recently and is getting more importance for industrial applications.

2 Applications in industrial deodorization

Experimental animal raising facility usually exhausts 24 hours everyday, and the odor complaint from residents is the main common problem for similar facilities. The exhaust contains several 10^{-6} degrees of ammonia, acetaldehyde, trimethylamine and organic acid such as n-butyric acid, etc. The condition is proper for photocatalytic deodorization treatment because the odor contaminations are low level, while the exhaust is at room temperature. Experimental animal raising facility exhaust deodorization is one of the success industrial applications for photocatalytic ceramic foam filter. One of the authors (Zhou) experienced the engineering of deodorization of 6 000 m^3/h experimental animal exhaust in Tokyo in 2005. The odor concentration was 130 before treatment and 32 after treatment, and deodorization effect reached about 75%.

Kitchen exhaust of shopping mall is usually deodorized by active carbon filter, and photocatalytic ceramic foam filter has already been applied in this field recently. Except oil substances, main odor contaminations of kitchen exhaust are several 10^{-6} degrees of ammonia and acetaldehyde, etc. Kitchen exhaust is necessary to be deoilingly treated before deodorization treatment by photocatalytic ceramic foam filter. One of the examples of 4 000 m^3/h shopping mall kitchen exhaust treatment in Tokyo in 2006 showed that the odor concentration was 3 200 before treatment, remained to be 3 200 after deoiling treatment, decreased to 790 after first pass photocatalytic deodorization and further decreased to 500 after second pass photocatalytic deodorization. This is another success example of photocatalytic ceramic foam filter for industrial use, and new-built shopping malls become to adopt photocatalytic deodorization system recently in Japan.

Rubbish odor of rubbish pressing and transiting facilities in

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Biography: Zhou zhonghua, Professor

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urban areas of China is one of the main problems needing to be deodorized. Rubbish pressing and transiting facilities are usually built near or inside resident areas, rubbish odor and noise bother residents. A field experiment of deodorization using photocatalytic ceramic foam filter was conducted by an equipment under the conditions of 4 passes, 0.09 m^2/pass, 300 m^3/h air treatment capacity, and the result showed the probability of applying photocatalytic technology in rubbish deodorization. Figure 1 showed the odor sensor's values of the air at the indoor (before deodorization) and the outdoor (after deodorization) of the equipment. The odor value before deodorization was not constant and varied largely during rubbish pressing process. The peak value reached about 4 to 5 times higher than the valley value. After deodorization by photocatalytic method, the odor value maintained low value which was much lowered than that before deodorization. The chemical substance concentrations before and after deodorization listed in Table 1 showed that main odor substances were ammonia and methyl mercaptan, and those degradations reached 88.2% and 67.9% after photocatalytic deodorization, respectively. From Table 2, odor concentration degraded 95.4% averagely after deodorization, comparing with odor concentration before treatment.

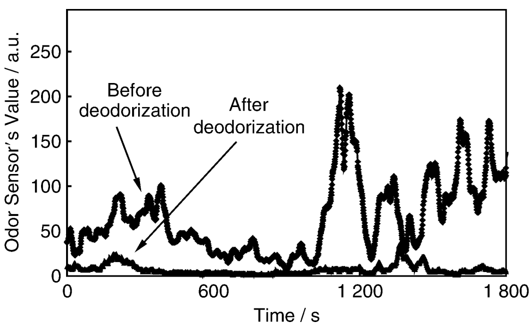

Fig. 1 Photocatalytic deodorization effect of the field test for rubbish pressing and transiting facility by using photocatalytic ceramic foam filters

Table 1 Chemical substance concentrations before and after deodorization of the field test

	Chemical substance concentration / 10^{-6}		
	H_2S	NH_3	CH_3SH
Indoor of testing equipment	0.001	17.3	0.002 8
Outdoor of testing equipment	ND	2.04	0.000 9
Degradation percent	–	88.2%	67.9%

Table 2 Odor concentrations before and after deodorization of the field test

		Odor concentration / a.u	Average
Indoor of testing equipment	Sample 1	1 738	1 694
	Sample 2	1 650	
Outdoor of testing equipment	Sample 1	81	78
	Sample 2	75	
Deodorization percent	Sample 1	95.3%	95.4%
	Sample 2	95.5%	

Pretreatment plays important role and is necessary in some industrial deodorization applications of photocatalytic ceramic foam filter. Oil particles, dust particles and moisture are particularly considered to be pre-filtered out during deodorization engineering processes, otherwise deodorization effects are affected largely. The affect of moisture on photocatalytic activity of photocatalytic ceramic foam filter has been tested in 40%, 60% and 90% relative humidity at 40 ℃ by degradation of acetaldehyde as a probe by our group, the result shows that the CO_2 forming rate under UV illumination of 40% humidity is the largest, that of 60% humidity is almost the same, and that of 90% humidity is the lowest and is only about half of that of 40% humidity, i.e., photoactivity of photocatalytic ceramic foam filter is restrained when humidity reaches a high level such as 90%. The result also shows that the adsorption of reaction substance of acetaldehyde drops with the increase of humidity, giving that the reason of that high humidity hinders photoactivity of photocatalytic ceramic foam filter can be reasonably connected with the drop of physical adsorption.

3 Applications in agriculture

Photocatalytic ceramic foam filter has been field tested to degrade pesticide of agriculture liquid waste and TOC (total organic carbon) of agriculture nutrient solution, reported by research groups of Tokyo University and Kanagawa Agriculture Techno-Center in Japan[6]. Rice seeds have to be disinfected by using pesticides and rinsed several times before cultivation, resulting in agriculture liquid waste containing pesticides. Treatment area of 2.25 m^2 of photocatalytic ceramic foam filter was used under sunlight to degrade 40 L pesticide liquid waste. The concentrations of ipconazole pesticide and TOC decreased largely when the treatment started. After 4 days, ipconazole pesticide was non-detected, and the degradation effect was confirmed by fish toxicity test[6]. The recycling nutrient solution was treated by photocatalytic ceramic foam filter under sun-light in tomato nutrient solution cultivation. The recycling system was consisted by treatment area of 1.2 m^2 of photocatalytic ceramic foam filter, reserving tank of 40 L and supplying tank of 100 L, and the batch treatment method was used. Among testing period of 10 months, the nutrient solution with photocatalytic treatment was transparent and TOC was 7~ 28 mg/L, while that without photocatalytic treatment was brown and TOC reached 21~ 777 mg/L. Tomato harvests of nutrient solution with photocatalytic treatment increased by 40.8% in the 1st harvest and by 34.0% in the 2nd harvest during the testing period, comparing with that without photocatalytic treatment.

4 Applications in sterilization

Photocatalytic ceramic foam filter has been applied in sterilization of laboratories and hospitals, related fundamental and applications reported by research groups of Tokyo University and some companies in Japan[7-9]. The fundamental of sterilizing mechanism of Cu/TiO_2 film under very weak UV irradiation was reported to consist of two steps[7-8]. The first step is the partial decomposition of the outer membrane in bacteria cell envelope by a photocatalytic process, the second step is the permeation of the copper ions into the cytoplasmic membrane to sterilize bacteria, which explain why Cu/TiO_2 showing high sterilization effect even under weak UV illumination. High porosity (about 80% ~ 90%) of photocatalytic ceramic foam filter was used in the test of sterilization of 30 m^3 SUS laboratory[8]. Airborne microbe decreases by 30% ~ 40% even in the absence of UV illumination, but in this case, microbe is only captured by the filter and will

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be released again with air flux. In the case of UV illumination, the survival rate of airborne microbe downs to 17% after 15 min, owing to that the microbe captured by the filter is sterilized by photocatalytic oxidization and can not be released again[8]. The practical applications of photocatalytic ceramic foam filter in laboratory raising rats and hospitals get satisfied effect of sterilization, and in the meantime, have also deodorization effect[8-9].

5 Applications in high-speed train

The development of deodorization equipment using photocatalytic ceramic foam filter for high-speed train was conducted, as reported by JREA[10]. The target is to decompose the chemical substances of tobacco odor and to apply for tobacco rooms in high-speed train. A new coating technology was developed and the oxidizing decomposition ability improved largely, comparing to ordinary coating method[10]. The equipment has been applied in the new series of N700 high-speed train in Japan[10]. In China, the application technology of photocatalytic ceramic foam filter in high-speed train has been developed by related companies in collaboration with Xiamen University.

6 High photoactive materials

The research of high photoactive materials of photocatalytic ceramic foam filter is always a technical challenge. Noble metal deposited TiO_2 has been intensively studied, and the photoactivity improves owing to that the recombination of photo induced electrons and holes are restrained by noble metal deposition. In practical applications, Ag deposition is applied instead of noble metal. Ag/TiO_2 photocatalytic ceramic foam filter is developed, as reported by research groups in Japan[11-12]. Ag nano particles are homogeneously dispersed into TiO_2, and the decomposition of H_2S improves largely, comparing to that without Ag deposition[11].

7 Conclusions

The industrial applications of photocatalytic ceramic foam filter have been widely extended recently, and the application research progress, problem and prospect are summarized mainly in the application fields of industrial deodorization, agriculture, sterilization and high-speed train. Meanwhile, the importance of Ag/TiO_2 photocatalytic ceramic foam filter is emphasized.

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973计划项目“水泥低能耗制备与高效应用的基础研究”进展顺利

我国水泥产量自 1985年以来一直位居世界第一， 2009年产量高达 16.4万吨。水泥行业具有能耗高、污染重、二氧化碳排放多等特点，尤其是生产过程中的烧、磨环节。如何降低水泥生产过程中的能量消耗，减少二氧化碳排放，对于节能减排具有重要意义。

973计划项目“水泥低能耗制备与高效应用的基础研究”由南京工业大学沈晓东教授为首席科学家，中国建筑材料研究院为依托单位。项目围绕水泥结构和熟料矿物组成、熟料分段烧成动力学及过程控制、水泥粉磨动力学及过程控制、水泥熟料和辅助性胶凝材料优化复合的化学和物理基础等重大科学问题开展研究，在降低能耗研究方面取得了多项进展。项目从提高水泥熟料胶凝性能、降低水泥熟料烧成的热耗入手，在研究熟料矿物质结构及形成机制基础上，建立熟料微结构与性能关系，研究熟料燃烧及快速冷却后能获得的阿利特高温介稳结构，提出的改进熟料烧制方法生产每吨水泥可节约 12 kg标准煤，节煤效率约 10% 以上，减少熟料使用量 20% 以上。同时，项目在熟料分段烧成动力学及过程控制研究中，通过不断尝试，把燃烧温度从原来的 1 400 ℃降低为 1 300 ℃，仅该环节就可降低烧成热耗 3% ~ 5%。此外，项目还从燃烧学、水泥结构、水泥浆体组成等不同方面进行降低能耗的基础研究。 （本刊通讯员）

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特约撰稿人薛群基


特约撰稿人吴以成


特约撰稿人闻海虎


特约撰稿人周忠华


特约撰稿人南策文


特约撰稿人孙　军


特约撰稿人黄学杰


特约撰稿人丁文江

薛群基：男，1942年生，中国工程院院士；1999~2003年任中科院兰州化学物理研究所所长；曾获香港“何梁何利奖”、中国摩擦学会“杰出成就奖”、中国化学会和中国石油化工公司“化学贡献奖”、国家发明二等奖、国家科技进步二等奖；发表论文300余篇，取得30余项国家发明授权专利。

吴以成：男，1946年生，理学博士，中国工程院院士，功能材料专家；在新型非线性光学材料探索、晶体生长及非线性光学特性研究、晶体结构与非线性光学性能的相互关系等方面取得多项成果；与合作者一起发明 LiB_3O_5，CsB_3O_5，$La_2CaB_{10}O_{19}$ 等多种非线性光学晶体；“新型非线性光学晶体三硼酸锂 – LiB_3O_5”发明获国家发明一等奖。

闻海虎：男，研究员，博导；2000~2009年任超导国家重点实验室主任，现任科技部超导973项目首席科学家、加拿大国家高等研究计划远东区代表，国内外多家知名杂志的编委。曾获国家杰出青年基金，曾获第7届中国青年科技奖、国家自然科学二等奖(1项，第一获奖人)、香港求是基金杰出成就集体奖，亚洲华人物理奖；发表论文220余篇，在国际会议做邀请报告50余场。

周忠华：男，1965年生，厦门大学材料学院教授；1998年在日本三重大学取得工学博士学位；1998~2007年为东芝陶瓷研发中心研究员，及主任研究员；中国化工学会无机化工行业学术带头人。

南策文：男，1962年生，教授、博导，清华大学材料科学与工程研究院院长，科技部973计划项目首席科学家；曾获国家杰出青年科学基金、美国陶瓷学会电子 Edward C. Henry 奖、国家自然科学二等奖等；发表论文300余篇；出版专著1部；获国家发明专利授权20项。

丁文江：男，1953年生，教授、博导，轻合金精密成型国家工程研究中心主任，国家重大基础研究项目技术首席；曾获国家科技进步二等奖、国家技术发明二等奖、国防科技进步二等奖和上海市技术发明奖一等奖各1次；发表论文321篇，SCI收录184篇，EI收录211篇；申请发明专利105项，其中美国专利1项，已授权75项。

黄学杰：男，1966年生，博导，中国科学院物理研究所研究员，清洁能源中心常务副主任，苏州星恒首席科学家；1993年在荷兰 Delft 技术大学获博士学位，1994~1995年在德国 Kiel大学做博士后研究；1996年起主持锂离子电池及其关键材料的研究、开发与产业化工作；曾获 ISI经典论文奖、求是杰出青年奖；发表论文140余篇，30余项发明专利获得授权。

孙　军：男，1959年生，工学博士、教授，博导，国家973计划项目首席科学家，金属材料强度国家重点实验室主任，西安交通大学材料科学与工程学院院长；1992~1995年获加拿大国家自然科学与工程研究理事会“国际研究员”研究奖学金，并在女王大学工作；1999年获国家杰出青年科学基金，长江学者特聘教授；已在 Nature, Nano Letters, Applied Physics Letter, Acta Materialia, Physical Review B等国际知名学术期刊上发表学术论文100余篇。

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