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Photocatalyst Technology for Deodorization in Household Refrigerator Based on Odor Removal

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This paper describes what the sources of odor gas are in the refrigerator and analyzes how well the existing deodorization technology seems like. Here comes the TiO_2-based photocatalyst for refrigerator deodorization. As for its work principle, this is an elaboration in details. It is also discussed how various types of factors such as carrier type, humidity and temperature affect the odor removal effect of photocatalyst materials in the refrigerator. A test is also cited for application of this technology to deodorize the refrigerator and the test results are analyzed. This test reveals that the deodorization device in the refrigerator has an odor removal rate of more than 90%. In the end, in view of the defects of photocatalyst used for the odor gas purification in the refrigerators, the prospect is visualized herein in order to provide the clues to subsequent studies in the field.

1. Introduction

Contemporary consumers more and more concern the green, environmentally friendly and healthy products. When purchasing the refrigerators, those that can effectively and auto remove odors will be popular among consumers. In view of this, refrigerator manufacturers who focus on brand quality are committed to developing new technologies in an attempt to reduce or even eliminate the odor components of the refrigerator.
The odor in the refrigerator mainly derives from oxidized amines, ammonia and lower fatty acids generated by food protein putrefaction. The sources of odor components in the refrigerator include two types (Nychas et al., 2008): the first is fat oxidation, mainly including aldehydes, ketones, low molecular fatty acids, alcohols, and esters; the second type is protein putrefaction, which produces the odor components such as thiols, trimethylamine, ammonia, and indole hydrogen sulfide. The amines produced during the decay process are decomposed by the bacterial amine oxidase into NH_3, CO_2 and H_2O. Trimethylamine oxides in fish and meat can be reduced by trimethylamine oxidoreductase of bacteria into trimethylamine.
Currently, there are 4 types of deodorization technologies used in the refrigerators (Ochiai et al., 2012). (1) Masking deodorization: the main component of such technology is a fragrance, which is usually processed on its monomer or by loading it on a carrier. In the use, the fragrance volatilizes a kind of constituent that can mask the odor. The aromatic taste evaporates quickly. When it is exhausted, it no longer plays an odor-masking role, so that it has a limited service life, and the odor cannot be removed from the root. (2) Physical deodorization: In the refrigerator, the odor gas is mainly adsorbed by a solid adsorption material such as activated carbon to achieve the effect of removing harmful gases. There are clay mineral and zeolite deodorants, and the like. (3) Biological antibacterial deodorization: the deodorization effect is achieved mainly by antibacterial active ingredients such as tea polyphenols, ketones and the like. (4) Chemical antibacterial deodorization: it is the ozone oxidation antibiosis deodorization technology which oxidizes odor molecules, but excessive ozone is harmful to humans. Therefore, it is not applicable for household refrigerators.
Due to a short service life and hidden dangers of traditional deodorization technology, the study introduces the TiO_2-based photocatalyst antibiosis deodorization technology instead (Xu and Xu, 2018). Under the action of ultraviolet light, the energy of photocatalyst is excited to decompose odor gas, thus exerting a good antibacterial deodorization performance.

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2. Basic principle

Among the current technologies for removing food odors in the refrigerator, photocatalyst is a new, safe, non-toxic, low-energy consumptive deodorization technology (Fujishima et al., 1999; Paz, 2010; Ochiai et al., 2012).

Since it was discovered by the Japanese scholar Fujishima in the 1970s that single crystal TiO_2 electrodes can catalyze the oxidation water under the action of light to produce hydrogen, the TiO_2 photocatalytic oxidation susceptibility has aroused common concern. Thanks to its non-toxic, harmless and stable properties, it is increasingly applied to the atmosphere and sewage purification. The energy gap of TiO_2 is 3.2 ev (anatase). Under the exposure to the light (ultraviolet light) with a wavelength less than or equal to 387.5 nm, the electrons of the valence band will gain the photon energy and jump to the conduction band to form a photo-induced electron (e-); while in the valence band, photogenerated holes (h+) are formed accordingly.

If each TiO_2 particle dispersed in the solution is approximate to small short-circuit photoelectrochemical cell, the photo-induced electrons and holes generated by the photoelectric effect migrate to different positions on the surface of the TiO_2 under the action of the electric field, where the photo-induced electrons e- are easily trapped by oxidizing substances such as dissolved oxygen in water to generate superoxide radicals O2-; the holes h+ can oxidize the organic substances adsorbed on the surface of TiO_2 or OH- and H_2O molecules thereon first into hydroxyl radical OH; OH and O_2- have strong oxidization capacity, which can almost break the chemical bonds of various organic substances, thus to oxidize most of the organic and inorganic pollutants and mineralize them into inorganic molecules, CO_2 and H_2O. The reaction process is given as follows:

$TiO_2+hv \rightarrow h^+ + e^-$

$h^+ + OH^- \rightarrow \bullet OH$

$h^+ + H_2O \rightarrow \bullet OH + H^+$

$e^- + O_2 \rightarrow \bullet O_2^-$

$H_2O + \bullet O_2^- \rightarrow HO_2\bullet + OH^-$

$2HO_2\bullet + e^- + H_2O \rightarrow H_2O_2 + OH^-$

$H_2O_2 + e^- \rightarrow \bullet OH + OH^-$

$H_2O_2 + \bullet O_2^- \rightarrow \bullet OH + H^+$

$\bullet OH + VOC + O_2 \rightarrow nCO_2 + mH_2O$

Naturally, the photo-induced electrons are also bound with holes:

$h^+ + e^- \rightarrow$ heat energy

Since photocatalysis technology originated in Japan and had the best development in Japan, general photocatalyst products are called photocatalysts.

The individual photocatalyst nano powder can be diluted with water or organic solvent into the solution for spraying, which runs dry to form a film as the photocatalyst layer. This method has been widely used for indoor decoration gas purification and sewage treatment, but it is not applicable to the odor removal in the refrigerator due to the easy wear of the film layer and poor photocatalytic activity. The photocatalyst material used for deodorization inside the refrigerator needs to be cured on the carrier by the recombination. Now, the carrier adsorbent material (activated carbon) is bonded on the support to form an adsorption layer, and then the nano-TiO_2 is loaded on the particles of the adsorption layer to form the outermost photocatalytic layer (Arconada et al., 2011; Warheit et al., 2007)

3. Analysis of impact factors

The deodorization effect of photocatalyst materials in the refrigerator is subjected to some factors as follows (Fang et al., 2014; Obee et al., 1995).

3.1 TiO_2 crystal form and particle size

TiO_2 includes three types, i.e. anatase, rutile and brookite, among which, anatase has the best TiO_2 catalytic activity. The smaller the particle size of nano-TiO_2, the wider the energy gap of the conduction and the forbidden bands; the stronger the oxidation and reduction capacities of the photo-induced electrons and holes excited; the higher the photocatalytic activity; moreover, the faster the photo-induced electrons migrate to the surface of the catalyst, thereby reducing the probability of recombination with photogenerated holes and increasing the photocatalysis activity. Nowadays, some air purification products are labeled with nominal photocatalyst, but in fact, it does not reach the nanometer particle size at all, only micron level. The photocatalytic activity is very poor.

3.2 Carrier type

The photocatalytic property greatly depends on the carrier types. In general, the carrier belongs to inorganic substance, and there are glass, ceramic, metal, and carbon-based adsorbents. The glass surface looks too smooth and flat, but has a poor adhesion. During the preparation process, sodium and silicon ions implant in the lattice of TiO_2 to reduce the catalytic activity. Ceram is a porous material with good adhesion, but the above gap also exists. Metal ions also undermine the lattice structure of TiO_2. Activated carbon as a commonly used adsorbent carrier features large specific surface area (Dias et al., 2018), ultrastrong adsorption capacity, especially for organic substances in gases. Moreover, it has more active functional groups on the surface and good regenerability, so is widely applied as a carrier for photocatalysts. In particular, the activated carbon fiber developed in recent years applies to the adsorption and enrichment of odor gases with low-concentration. The synergy of absorption with photocatalysis can realize the original taste regeneration and self-cleaning of the carrier. It has found wider application in the odor removal of the refrigerator. It is proved that activated carbon fiber as a union of carrier and photocatalyst has an excellent deodorization effect on the refrigerators.

3.3 Specific surface area

The size of specific surface area of the loaded TiO_2 determines how strong its adsorption of pollutants is, the stronger adsorption capacity and the higher initial concentration of pollutants, the faster the reaction rate and the better the photocatalytic property.

3.4 Relative humidity

The higher relative humidity (RH) in the gas phase generally facilitates the photocatalytic reaction of the gas phase since the interaction of water vapor with the photogenerated holes on the surface of the catalyst will generate more active hydroxyl radicals (•OH), further improving the photocatalytic degradation efficiency, which is also in compliance with the development trend of efficient moisturizing of refrigerators.

3.5 Temperature

The temperature matters not only the photocatalytic reaction kinetics but also the adhesion of catalyst surface to gaseous organic pollutants. For the adsorption process, the contaminant coverage of the photocatalyst surface decreases with the temperature rise. Studies have shown that the photocatalytic reaction rates of various gases vary with temperature rise, such as acetaldehyde, toluene, whose photocatalytic reaction rate decreases, whilst ethylene reaction rate increases. Since the types of odor gases inside the refrigerator are very complicated, the temperature effects vary each other.

3.6 Modification of TiO_2

Due to the wide band gap between the forbidden and the conduction bands of pure TiO_2, the utilization of visible light is low; the photo-induced electrons and holes are easily recombined, resulting in poor catalytic effect. The modification technology of TiO_2 can expand its spectral response extent so that the response wavelength is red-shifted to the visible light band. In the past decades, scholars had hammered at the TiO_2 modification, doping and surface finish. They have also made a lot of fruitful works in an attempt to improve catalytic activity, increase visible light utilization, and provide quantum yield. There are several common modification methods including precious metal deposition, transition metal ion doping, N doping, recombination of photosensitive dyes with semiconductor materials at a narrow band gap, and surface modification finish, etc.

3.7 Initial concentration of odor gas

The relationship between initial concentration of pollutants, i.e. the odor gas in the refrigerator and the photocatalytic efficiency coincides with the Langmiur-Hinshelwood (L-H) model. In general, when other parameters are given, each odor gas (contaminant) has a specific initial concentration that maximizes the reaction rate. In fact, there is a ppm (10^{-6}) concentration of VOCs in the refrigerator. In this range, the correlation between initial concentration and the photocatalytic reaction rate can be approximately linear, and the higher the concentration, the faster the reaction. This provides the clues to the selection of the carrier for the adsorption capacity, that is, the better the adsorption capacity, the higher the initial concentration of the contaminant, and the more conducive it is to the photocatalytic degradation.

3.8 Gas flow rate

The reaction that the photocatalytic material degrades the odor gas belongs to the gas-solid photocatalytical type, and in the whole process, there are two stages, i.e. mass transfer and catalytic reaction. Mass transfer is caused by the deviation in the concentration between the catalyst reaction surface and the gas flow. If the reaction is mass transfer control, the reaction rate will increase as the flow rate increases. When the gas concentration gets close to that on the surface of the catalyst, the effect of mass transfer weakens. The photocatalytic reaction itself controls the reaction process. As the flow rate increases, the reaction rate does not grow. Since the carrier of the photocatalyst material features absorption and enrichment of the odor gas, it is inevitable that there is difference in the odor gas concentration between the catalyst surface and the gas flow, so that the increased gas flow rate will greatly raise the rate and the efficiency of the photocatalytic reaction. Therefore, the photocatalyst material is preferably installed at the air inlet and outlet of the refrigerator to increase the gas flow rate (Lim et al., 2015; Xiao et al., 2017)

4. Deodorization test method (Bai et al., 2012; Mo et al., 2009)

4.1 Test equipment and reagents

(1) Gas chromatography (Shimadzu)
(2) BCD-301 electronically controlled and air-cooled refrigerator, BCD-181 electronically controlled and direct-cooled refrigerator
(3) Trimethylamine (analytical pure), ethanethiol (analytical pure)

4.2 Acquisition position

Air inlet and gas collection hole are drilled in the door of refrigerator chamber for inputting and collecting the gases to be tested. The opening method is given as follows: at horizontally three halved points, two collection holes of 2cm in diameter are drilled, respectively.

4.3 Photocatalyst position

With the odor removal feature of TiO_2 photocatalyst, it organically recombines with the active honeycomb block to significantly improve the sterilization and fresh-keeping efficiencies. The fan can absorb and exhaust the air to make the air in freezer chamber flow, and the odor gas will be absorbed from the air inlet onto the honeycomb activated carbon.

4.4 Test environment

The ambient temperature to be tested in the refrigerator vessel is -20°C~5°C, the relative humidity inside the tank is greater than 55%.

4.5 Test procedure

The refrigerator door is tightly closed, and the odor gas for test is input from the air inlet into the inner cavity of the refrigerator; the air inlet is then closed to circulate the gas in the inner cavity, so that the odor gas will be evenly distributed therein. After the gas flow formed by the circulation is stabilized, the odor gas is sampled from the gas collection hole. The sampling result is recorded as the initial concentration of the odor gas; the refrigerator is turned on to make it operate normally; after the test time preset for normal operation of it, the odor gas in the inner cavity is sampled from the gas collection hole, and the sampling result is recorded as the final concentration of the odor gas; the decomposition rate used for evaluating the deodorization effect in the refrigerator is calculated according to the formula.
In the test, trimethylamine or ethanethiol at an initial concentration of 3 mg/m^3~9mg/m^3 is input. The residual concentrations of trimethylamine and ethanethiol are tested after 1 hour.

4.6 Concentration calculation

The gas adsorption and decomposition rate are calculated by: A=(C1-C2)/C1×100%
Where, A is the gas decomposition rate; C1 is the gas concentration at the start of the test, mg/m^3; C2is the gas concentration at the end of the test, mg/m^3.

5. Test results and analysis

It is tested what are the effects of it on the odor removal in the electronically controlled direct-cooled refrigerator and air-cooled refrigerator. Compare gas concentrations at the beginning of the test and after 1 h of the test, the results are shown in Tables 1 and 2. The decomposition rates of trimethylamine and ethanethiol in the electronically controlled direct-cooled refrigerator are 95% and 97%, respectively; while the decomposition rates of the two in the electronically controlled air-cooled refrigerator are 90% and 92%, respectively. Analyze the cause: the air-cooled refrigerating chamber and freezer chamber are connected via the air duct, where the number of wind cycles per unit time is less than that of the direct-cooled refrigerator, so that the odor removal rate is lower than that of the direct-cooled refrigerator.

Table 1: Test results of odor removal in direct-cooled refrigerator

Pollutant	Initial concentration (mg/m^3)	Final concentration (mg/m^3)	Odor decomposition rate (%)
Trimethylamine	4.0	0.19	95
Ethanethiol	6.8	0.221	97

Table 2: Test results of odor removal in air-cooled refrigerator

Pollutant	Initial concentration (mg/m^3)	Final concentration (mg/m^3)	Odor decomposition rate (%)
Trimethylamine	3.5	0.35	90
Ethanethiol	8.4	0.70	92

6. Conclusion

In this test, the odor removal device in the direct-cooled refrigerator has an odor decomposition rate of 95% or above, but that in the air-cooled refrigerator is 90% or above. Therefore, it can be inferred that the technology has an obvious effect on odor removal in the refrigerator so as to play a certain purification effect on microorganisms in the refrigerator.

7. Prospect forecast

In relation to the traditional deodorization technologies for existing refrigerators, TiO_2 as a photocatalyst features mild reaction conditions, low investment, low energy consumption, and easy to react, that is, the photocatalytic chemical reaction can occur only if irradiated with ultraviolet light; the organic pollutants can also be oxidized and then degraded into CO_2 and H_2O non-toxic to the human body, so that there is no secondary pollution. At the moment, it is undeniable that, however, photocatalyst technology still has certain gaps in the field.

(1) Passivity of effect (Nakata et al., 2012; Park et al., 2013). Currently, the active factors generated when producing the photocatalyst products cannot actively capture the particles in the air, and function only when they are in direct contact with the microbial particles and the odor gases. It is proved by tests that the photocatalyst shows no effect on bacteria if applied to a smooth surface and then irradiated by a fluorescent lamp for 12 h. Based on the above fact, the photocatalyst technology will not play a better effect until it integrates air purification system. The photocatalyst sprayed on the surface of the object can only oxidize and decompose the microorganisms and organic substances adsorbed on the surface.

(2) There must be a light source with a UV component. It is impossible for the photocatalyst to exert a clean effect in the absence of light source, and an ultraviolet light is preferable. The light source containing a trace of ultraviolet light component allows the photocatalyst to function, such as daylight, natural light, incandescent light, etc. It is required to further test in practices whether it plays a good effect.

(3) Limitations of killing microbe. The effect of photocatalysts on the killing of microorganisms is not too high, and its microbial activity is weaker than chemical disinfectants. Photocatalyst is nothing but a cleaner in the environment when it works well. In this case, its role should be properly promoted.

The deodorization effect of the photocatalyst material in the refrigerator is attributed to various factors such as the crystal form of TiO_2 and particle size, light wavelength, carrier type, carrier specific surface area, relative humidity, temperature, initial concentration of odor gas, and gas flow rate. Further study should focus on how to coordinate the relationship between various factors and how to improve the photocatalytic efficiency, so as to develop a more effective and cost-effective odor removal program for refrigerators.

There is no appropriate standard issued for evaluating the degradation effect of photocatalyst material on various complex components, as well as its catalytic performance and longevity. The existing products are hybrid and urgently need to standard specifications on them. Photocatalyst deodorization technology integrated with the traditional refrigerator odor removal, air filter and adsorption, plasma and other technologies organically will significantly improve the purification effect of odor gas, and push forward the upgrade of refrigerator deodorization technology.

References

Arconada N., Castro Y., Durán A., Héquet V., 2011, Photocatalytic oxidation of methyl ethyl ketones over sol–gel mesoporous and meso-structured TiO_2 films obtained by EISA method, Applied Catalysis B: Environmental, 107(1-2), 52-58, DOI: 10.1016/j.apcatb.2011.06.036

Bai L.S., Wei B., Wei B., Li M., Hu H., 2012, A study on food freshness retaining techniques in refrigerator by deodorization and eliminating bacterial, Electric appliance S1, 108-111, DOI: 10.3969/j.issn.1672-8823.2012.z1.022

Dias D., Bernardo M., Lapa N., Pinto F., Matos I., Fonseca I., 2018, Activated carbons from the co-pyrolysis of rice wastes for cr(iii) removal, Chemical Engineering Transactions, 65, 601-606, DOI: 10.3303/CET1865101

Fang F., Lu J., Pan S.W., Zhang M.M., 2014, The application of loaded composite photocatalyst in refrigerators and the impact analysis of its performance, Proceedings of the 2014 China Household Appliance Technology Conference, 71-74.

Fujishima F., Hashimoto K., Watanabe T., 1999, TiO_2 photocatalysis fundamentals and applications, A Revolution in cleaning technology, 14-21.

Lim E., Yamamoto K., Sumiyoshi E., Yamaguchi T., Ito K., 2015, Small test chamber experiment and modeling of photocatalytic oxidation for CFD simulation part 1–CFD modeling of photocatalytic oxidation and numerical prediction of concentration reduction performance in indoors, Trans Soc Heat Air Condit Sanit Eng Jpn, 224, 19-27.

Mo J., Zhang Y., Xu Q., Lamson J.J., Zhao R., 2009, Photocatalytic purification of volatile organic compounds in indoor air: a literature review, Atmospheric Environment, 43, 2229-2246, DOI: 10.1021/ja063550r

Nakata K., Fujishima A., 2012, TiO_2 photocatalysis: Design and applications, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 13, 169-189, DOI: 10.1016/j.jphotochemrev.2012.06.001

Nychas G.J.E., Skandamis P.N., Tassou C.C., Koutsoumanis K.P., 2008, Meat spoilage during distribution, Meat Science, 78, 77-89.

Obee T.N., Brown R.T., 1995, TiO_2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene, Environmental Science & Technology, 29, 1223-1231, DOI: 10.1021/es00005a013.

Ochiai T., Fujishima A., 2012, Photoelectrochemical properties of TiO_2 photocatalyst and its applications for environmental purification, Journal of Photochemistry and photobiology C: Photochemistry reviews, 13(4), 247-262, DOI: 10.1016/j.jphotochemrev.2012.07.001

Ochiai T., Hayashi Y., Ito M., Nakata K., Murakami T., Morito Y., Fujishima A., 2012, An effective method for a separation of smoking area by using novel photocatalysis-plasma synergistic air-cleaner, Chemical engineering journal, 209, 313-317, DOI: 10.1016/j.cej.2012.07.139

Park H., Park Y., Kim W., Choi W., 2013, Surface modification of TiO_2 photocatalyst for environmental applications, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 15, 1-20, DOI: 10.1016/j.jphotochemrev.2012.10.001

Paz Y., 2010, Application of TiO_2 photocatalysis for air treatment: Patents' overview, Applied Catalysis B: Environmental, 99(3), 448-460, DOI: 10.1016/j.apcatb.2010.05.011

Warheit D.B., Hoke R.A., Finlay C., Donner E.M., Reed K.L., Sayes C.M., 2007, Development of a base set of toxicity tests using ultrafine TiO_2 particles as a component of nanoparticle risk management, Toxicology letters, 171(3), 99-110, DOI: 10.1016/j.toxlet.2007.04.008

Xiao J., Breitung W., Kuznetsov M., Zhang H., Travis J.R., Redlinger R., Jordan T., 2017, GASFLOW-MPI: A new 3-D parallel all-speed CFD code for turbulent dispersion and combustion simulations: Part I: Models, verification and validation. international journal of hydrogen energy, 42(12), 8346-8368, DOI: 10.1016/j.ijhydene.2017.01.215

Xu J., Xu H., 2018, Study on photoelectric properties of surface tio2 nanoparticles doped with sn4+ ion, Chemical Engineering Transactions, 66, 1345-1350, DOI: 10.3303/CET1866225