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Research Progress on photocatalytic treatment of uranium waste liquid with ZnO Quantum Dots

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Abstract: Aiming at the difficult problem of radioactive nuclear waste liquid treatment, this paper summarizes the principle and development of a new photocatalytic technology for removing uranium waste liquid, several preparation methods of ZnO quantum dots and its applications in biomedicine, catalysis and light shielding, and summarizes its research on radioactive uranium waste liquid. In the future, it is expected that ZnO quantum dots with better properties can be modified and put into commercial production for the treatment of radioactive uranium-containing waste liquid.

Keywords: Radioactive uranium waste liquid, Photocatalysis, ZnO quantum dots.

1. Introduction

With the continuous development and utilization of nuclear energy, the waste liquid containing uranium is increasing day by day, and its treatment has become an internationally recognized problem. In view of this environmental pollution problem, researchers have conceived a variety of treatment ideas, such as changing the existing form of radiation ions in radioactive waste liquid by various physical and chemical methods, so as to achieve the purpose of removing radioactivity. These methods include precipitation method [1], evaporation method[2], ion exchange method[3], adsorption method, membrane treatment method[4] and so on. However, these methods have a variety of defects, such as expensive equipment, long experimental cycle, secondary treatment of reactants, safety risks and so on.

In recent years, the treatment of nuclear waste liquid by photocatalysis technology has gradually become a hot topic. Compared with traditional biochemical treatment methods, photocatalysis technology is a green technology with high treatment efficiency, low energy consumption and harmless to the environment. Its basic principle is to reduce soluble U (VI) to insoluble U (IV) by photogenerated electrons excited by semiconductors under light conditions, so as to achieve the effect of removing uranium from radioactive wastewater, which has the advantages of high catalytic activity, low treatment cost and no harm to the environment. In this paper, the principle and development of photocatalysis technology are described, the preparation and application of ZnO quantum dots as photocatalyst are introduced in detail, and its application in the treatment of waste liquid containing uranium is reviewed.

2. Photocatalysis Technology

Photocatalysis technology is a new green environmental protection technology, which has great potential in the removal of harmful ions and air pollutants in water. At present, photocatalysis technology is not only becoming more and more mature in theory, but also has made great progress in practical application. The well-known photocatalytic materials are TiO_2, CdS, SnO_2 and so on [5]. At present, the widely used semiconductor photocatalyst is TiO_2, which has good stability, non-toxic and harmless, and high catalytic efficiency. Photocatalysis, popularly speaking, refers to the catalytic reaction carried out under the condition of light. According to the energy band theory, the internal structure of semiconductor atoms consists of three parts: conduction band (CB), valence band (VB) and forbidden band (FB). Among them, the difference between valence band potential and conduction band potential is the width of band gap (also known as band gap, E_g). According to the research of scientists, the performance of the catalyst is mainly determined by the band gap width (E_g), and the relationship between them is as follows:

$$E_g=1240/\lambda_g$$

λ_g is the threshold of light absorption wavelength, unit: nm, E_g is the width of forbidden band, unit: eV.

Because the positive and negative charges of the photocatalyst are the same, it is normally electrically neutral. When the semiconductor photocatalyst is irradiated by incident light, and the radiation energy is higher than its own band gap energy ($hv \geq E_g$), the electron (e^-) in the valence band absorbs energy and shifts to the conduction band, while a hole (h^+) is produced in the valence band, forming a photogenerated electron-hole pair (e^-/h^+). The photogenerated hole has a strong oxidizing ability, which occurs when it comes into contact with the substance adsorbed on the semiconductor surface, and it can also react with water (H_2O) or hydroxyl group (OH^-) to form hydroxyl radical (·OH). ·OH can also oxidize the organic compounds adsorbed on the surface of the catalyst, while the corresponding photogenerated electron (e^-) has a strong reducibility and can reduce the material on the surface of the photocatalyst. Many researchers use the strong redox properties of photogenerated electrons and photogenerated holes to carry out photocatalytic treatment of printing and dyeing waste liquid and radioactive waste liquid to achieve the purpose of removing pollutants. Yu used titanium isopropanol (TTIP) as titanium source, and the adsorption rate of methylene blue dye was the highest in TiO_2 and its modified samples prepared under alkaline conditions, and the adsorption rate was 9 times of P_{25}[6].

3. ZnO Quantum Dots

ZnO is an II B-IV A group n-type semiconductor oxide, white solid, insoluble in water, with good luminous property[7]. Compared with the traditional photocatalyst TiO_2, the band gap of ZnO is similar to that of traditional photocatalyst, and the band gap of 25ºC is 3.37 eV, which can respond to ultraviolet light, and the preparation cost is relatively low, so it is a good photocatalytic material. However, due to the low utilization of sunlight by zinc oxide, its commercial use is greatly limited. By doping metal or non-metal elements and building heterojunctions with other semiconductor materials, researchers reduce the band gap of ZnO and expand the light response spectrum, so as to improve the catalytic efficiency. For example, Zhuang modified ZnO quantum dots with mercaptoacetic acid (MAA), the ultraviolet exciton luminescence properties of the modified ZnO quantum dots were obviously enhanced, and the fluorescence emission of surface defects almost disappeared[8]. The ZnO@SnO2 heterojunction nanotube composite (HDNs) obtained by Gao by two-step solvothermal method has good photocatalytic activity, and the removal rate of methylene blue, eosin and other printing and dyeing waste liquor can reach 95% under the condition of 60 minutes of illumination[9]. Li prepared ZnO/g-C3N4 composite photocatalyst by gel method, which was proved by experiments to have good catalytic activity, stability and reusability[10].

3.1. Hydrothermal method

Hydrothermal method is a method to prepare materials under the condition of high temperature and high pressure, using water as solvent to dissolve and recrystallize the insoluble materials at room temperature and pressure. The advantage of hydrothermal method is that it is easy to operate and does not cause pollution to the environment. The hydrothermal reaction is generally carried out in high pressure reactor, and the temperature is adjusted according to the experimental requirements. After heating up, the crystal nucleates and grows, and the required experimental samples can be obtained at the end of the reaction time. Because the hydrothermal method is carried out in a closed environment, the products with different morphologies can be obtained by controlling the reaction atmosphere and reaction time[11]. Cai successfully prepared spherical Zn2+ heterojunction by changing the dosage of Cu2O-ZnO by one-step hydrothermal method, which expanded its absorption range of visible light and increased the performance of photocatalytic hydrogen production by 10.3 times[12]. Gu prepared zero-dimensional ZnO quantum dots with size close to ZnO Bohr radius and good dispersion using ethanol as solvent. The obvious quantum effect and deep level luminescence enhancement were verified by experiments[13].

3.2. Sol-gel method

Sol-gel method means that the chemical reaction-prone compounds are evenly mixed in the liquid environment, and stable sol is formed by hydrolysis and condensation. The colloidal particles are slowly polymerized to form a gel with a certain spatial structure, and then dried, sintered and solidified to synthesize materials with a size of 1 nm or less. For example, Walied used the improved sol-gel method to synthesize ZnO quantum dots at a calcination temperature of 350 ℃ to 450 ℃[14]. Cabral synthesized 8 nm wurtzite ZnO quantum dots by Sol-gel method and used to explore the optimum conditions for the degradation of rhodamine B[15]. Sol-gel method has the advantages of low cost, simple operation, low requirements for experimental environment and easy surface modification. The common method is to change the types of reactants or experimental conditions to prepare ZnO quantum dots with different particle sizes[16]. The disadvantages are that the raw materials are expensive, the experimental process is long, the quantum yield is low, and there are a large number of micropores in the gel.

3.3. Sputtering method

The physical synthesis method is characterized by stable and controllable synthesis conditions, and can realize the preparation of special structure ZnO by adjusting the growth environment, controlling the morphology of ZnO and so on. Sputtering is one of the physical synthesis methods, and it is one of the main methods to synthesize ZnO at present. The basic principle of sputtering method is that ions bombarded the target material by the action of high voltage electric field or magnetic field, and the sputtered momentum and energy are transferred to the atoms on the surface of the cathode target[17]. Sputtering methods are mainly divided into three categories: DC sputtering, radio frequency sputtering, binary sputtering and reactive sputtering. The advantages of this method are simple operation, low temperature in the experimental process, high purity of the compound, high cost of experimental instruments and equipment, high requirements for the experimental environment, and so on. Niu deposited ZnO ETL by magnetron sputtering, which reduced the oxygen vacancy and hydroxyl number on the surface of ZnO, and the power conversion efficiency reached 13.04%[18].

3.4. Precipitation method

Precipitation method is a common method to get nanomaterials by mixing specific precipitant with soluble salt solution, then washing and drying the precipitated insoluble matter after heat treatment. The direct precipitation method is a method to precipitate quickly after mixing the raw materials which are prone to chemical reaction, while the homogeneous precipitation method requires a series of chemical reactions to precipitate precipitates at an average speed and slowly. The advantage of this method is that the operation method is simple, and the disadvantage is that the purity of the prepared catalyst is low, and the particle size is too large. Saleh synthesized vanadium-doped ZnO nanoparticles by coprecipitation method[19]; Gao synthesized Mn-doped ZnO nanoparticles by precipitation method, and studied the effect of dopants on the carrier concentration in ZnO[20].

4. Application of ZnO Quantum Dots

ZnO quantum dots have both polar and non-polar faces, and the different growth rates of each surface lead to the diversification of ZnO nanostructures, such as cubic rock salt structure, cubic zinc blende structure and hexagonal wurtzite structure[21]. There are many morphological characteristics of nano-ZnO, such as nanorods[22], nanowires[23], nanowires[24] and so on. Because the size of ZnO quantum dots is about 1 to 10 nm, the quantum size effect shows that QDs have more excellent properties, such as strong photosensitivity, high catalytic activity, adjustable morphology, good antibacterial[25] and so on.

ZnO quantum dots can be used as fluorescent probes in biological detection because of their non-toxic properties. For example, Tang prepared ZnO quantum dots with different fluorescent colors by adjusting the pH value of the precipitate and coated them with silica to form ZnO@SiO2 core-shell nanomaterials[26]. Because of its low cytotoxicity, it has a broad application prospect in cell labeling. In addition, because the size of ZnO quantum dots is less than 10 nm, the photoreaction is stable and almost does not cause light scattering, so scientists use it as a good photocatalyst. For example, Sujinnapram prepared yttrium-doped ZnO nanoparticles by precipitation method, which reduced the grain size and improved the photocatalytic activity[27]. Zheng prepared nano-ZnO by solvothermal method using zinc acetate as raw material, then graphene quantum dots (GQDs) were prepared by pyrolysis of glucose, and then mixed with them to prepare ZnO-GQDs composites with a particle size of 30 to 50 nm. The degradation rate of rhodamine B was up to 90.24% with mercury lamp as light source and illumination of 120 min[28]. Similarly, due to the small size of ZnO quantum dots, the surface of the material is easy to be modified, so some scientists focus on using it as light shielding materials. For example, Chen synthesized ZnO QDs by sol-gel method, then coated it with CdS, and prepared PVB-ZnO/CdS composite film with PVB resin as matrix by solution blending, which realized the controllable shielding of UV and blue light in the region of 360-420 nm[29]. Because ZnO quantum dots have good photoluminescence properties and excellent antibacterial properties, they are often used in biomedical fields. For example, Song synthesized and characterized ZnO quantum dots modified by polyvinylpyrrolidone, and verified its obvious inhibitory effect on SW480 tumor cells[30].

5. Study on Treatment of Uranium Waste Liquid with ZnO Quantum Dots

Uranium (U), with a nuclear charge of 92, is the heaviest radioactive element that can be found in nature. All isotopes of uranium are radioactive. There are four valence states of U (III), U (IV), U (V) and U (VI), but they exist mainly in the form of UO_2 and UO_2^{2+} [31]. Among them, UO_2^{2+} has relatively large ion radius, good affinity to water, easy to cause environmental pollution, and difficult to deal with, but the solubility of UO_2 is low, so solid-liquid separation can be realized by precipitation. The photocatalytic treatment of waste liquid containing uranium is also to convert UO_2^{2+} into UO_2 through the strong reducibility of photogenerated electrons.

Ren synthesized rodlike and flaky nanostructured zinc oxide by hydrothermal method. The maximum adsorption capacity for 50 mg/L uranium solution is 75.1 mg/g, and the saturated adsorption capacity for 500 mg/L uranium solution is 920.75 mg/g[32]. Liu synthesized flower ball nano-ZnO in pH=5, T=298 K by hydrothermal method, and the reaction time was 180 min. The adsorption effect of 700 mg/L uranyl ion solution was the best, and the maximum adsorption capacity was 2439 mg/g[33]. Using graphene and zinc nitrate hexahydrate as raw materials, Wang prepared rod-like ZnO-GO composites by wet chemical method. Under the condition of pH=4.5, the maximum adsorption capacity of simulated uranium waste liquid was 179.8 mg/g[34]. By using glucose instead of ethylene glycol, Yang prepared spherical ZnO particles with a yield of 99%. The single adsorption capacity of 500 mg/L uranyl ion was 1004 mg/g at pH=4 and room temperature (25 ℃). The cyclic adsorption-desorption performance of ZnO for uranyl ion was excellent, and the removal rate of simulated radioactive waste liquid could reach 92% after five times treatment[35]. Yu deposited $Cu_{80}Co_5Ni_5Cd_5In_5$ nanocrystals on the surface of ZnO, which was used to reduce soluble U (VI) to U (IV). The enrichment amount was 2405.3 mg/g in 60 min, and the stability was good[36]. Kaynar studied the adsorption properties of nano-porous ZnO for uranyl ion in aqueous solution under different conditions, and the single molecule adsorption capacity of U (VI) was 1111mg/g at 303 K[37].

6. Conclusion and Prospect

Although ZnO quantum dots are in the stage of vigorous development, there are few studies on their application in the treatment of radioactive nuclear waste liquid. The reason is that there is a big gap between the actual situation of radioactive waste liquid and laboratory simulated nuclear waste liquid, which contains a large number of radionuclides such as Zr (IV), Mo (VI), organic waste liquid and so on[31, 38]. Taking ZnO quantum dots as the center, this paper introduces several preparation methods and their applications in biological detection, catalysis, light shielding, biomedicine and so on. By changing the raw materials, temperature and other conditions, it is expected that ZnO quantum dots with better properties can be prepared and put into commercial production for the treatment of radioactive uranium-containing waste liquid.

References

[1] Jihua Z. Treatment of phosphating wastewater by chemical precipitation [J]. Industrial Water treatment, 2000 (05): 43-44.

[2] Qing Y, Lian H, Youjun W. Research progress on treatment technology of medium and low-level radioactive wastewater [J]. Environmental Science and Management, 2007 (09): 103-106+117.

[3] Yaoyao H, Hanfang H, Runping S. Research progress of radioactive wastewater treatment technology [J]. Applied Chemical Industry, 2018, 47 (01): 185-189.

[4] Ruomeng H, Ying J. Research progress of radioactive wastewater treatment technology [J]. Environmental Engineering, 2014, 32 (S1): 57-60+84.

[5] P. M Y, C. D E C, Euzébio S et al. TiO_2/SiO_2 dopant-free nanophotocatalysts for highly efficient photocatalytic water splitting: Challenging traditional TiO_2-based systems[J]. Journal of Molecular Structure, 2022, 1269.

[6] Zhehan Y, Lihua Z, Seiichi W. Facile modification of TiO_2 nanoparticles with H_2O_2 + NH_4F for enhanced visible light photodegradation of rhodamine B and methylene blue[J]. Materials Today Communications, 2022, 33.

[7] Shaopeng Wang. Paper-based photochemical biosensor based on ZnO/quantum dot nanomaterials [D]. Jinan University, 2020.

[8] Jia Z, Meng L, Hanbin L. MAA modified ZnO quantum dots and their luminescent properties [J]. Chinese Science: chemistry, 2010, 40 (04): 322-330.

[9] Chaomin G, Haihan Y, Yuehan Z, etc. Controllable construction and photocatalytic activity of $ZnO@SnO_2$ heterojunction composite nanotubes [J]. Journal of Composite Materials, 2021: 1-10.

[10] Han L, Kaiyi L, Wenyu H, etc. Simple synthesis and photocatalytic activity of core-shell $ZnO/g\text{-}C_3N_4$ nanocomposite photocatalyst [J]. Journal of Photonics, 2021, 50 (11): 388-402.

[11] Shenghui T, Peifan W, Hui W, etc. Preparation and optical properties of nano-ZnO arrays with different morphologies by hydrothermal method [J]. Functional Materials, 2012, 43 (24): 3417-3419+3424.

[12] Xiaoli C. Preparation and properties of semiconductor metal oxide (Cu_2O, ZnO) composites [D]. Zhengzhou University of Light Technology, 2019.

[13] Baoxiang G, Pei M, Mingxiao Q, etc. Hydrothermal synthesis and quantum effect characterization of zero-dimensional ZnO nano-quantum dots [J]. Material Guide, 2013, 27 (S1): 14-16.

[14] Walied M, Abd E H, Hala H et al. Remarkable Recycling Process of ZnO Quantum Dots for Photodegradation of Reactive Yellow Dye and Solar Photocatalytic Treatment Process of Industrial Wastewater[J]. Nanomaterials, 2022, 12(15).

[15] Bezerra C R L, Fontes G F M, Oliveira S S K K et al. Surface modification of ZnO quantum dots coated polylactic acid knitted fabric for photocatalytic application[J]. Journal of Applied Polymer Science, 2022, 139(25).

[16] Xiao C, Tao X, Chengjun X, etc. Progress in synthesis of ZnO quantum dots by sol-gel method [J]. Guangdong Chemical Industry, 2017, 44 (18): 96-97+109.

[17] Yangyang Q, Mingxue L, Qiongxi L, etc. Application and research progress of magnetron sputtering technology in textile field [J]. Modern Textile Technology, 2022: 1-14.

[18] Haihong N, Cunlong F, Xiantao W et al. Magnetron sputtered ZnO electron transporting layers for high performance perovskite solar cells[J]. Dalton transactions (Cambridge, England: 2003), 2021, 50(19).

[19] F D N, A T, R S. Synthesized vanadium doped ZnO through the co-precipitation method[J]. Journal of Physics: Conference Series, 2020, 1442.

[20] Qianqian G, Yuqiang D, Xianchang L et al. Effects of Mn dopant on tuning carrier concentration in Mn doped ZnO nanoparticles synthesized by co-precipitation technique[J]. Journal of Materials Science: Materials in Electronics, 2018, 29(5).

[21] Xiunie Z, Xiaoyan W. Research progress of nanocomposites based on ZnO quantum dots [J]. Plastic auxiliaries, 2017 (01): 6-12+44.

[22] Xiaochen S, Xin Z, Hongdong L et al. Nanodiamond driven structure evolution of ZnO nanorods[J]. Applied Surface Science, 2022, 573.

[23] Tianchen J, Xin L, Jianbo S. UV-enhanced NO_2 sensor using ZnO quantum dots sensitized SnO_2 porous nanowires[J]. Nanotechnology, 2022, 33(18).

[24] Peng H. Preparation and luminescence properties of ZnO nanocrystals by hydrothermal method [D]. Lanzhou University, 2010.

[25] Yunchun L, Songtao X, Dan X et al. Antibacterial activity of ZnO quantum dots and its protective effects of chicks infected with Salmonella pullorum[J]. Nanotechnology, 2021, 32(50).

[26] Tang X, Choo E, Ling L et al. Synthesis of ZnO Nanoparticles with Tunable Emission Colors and Their Cell Labeling Applications[J]. Chemistry of Materials: A Publication of the American Chemistry Society, 2010, 22(11): 3383-3388.

[27] Supphadate S, Sutthipoj W. Synergistic effects of structural, crystalline, and chemical defects on the photocatalytic performance of Y-doped ZnO for carbaryl degradation[J]. Journal of Environmental Sciences, 2023, 124.

[28] Bo Z, Leiming L. Preparation and photocatalytic properties of nano-ZnO-graphene quantum dot composites [J]. New Chemical Materials, 2015, 43 (11): 92-94.

[29] Xin C, Canyao W, Jie S, etc. Study on UV and blue light shielding and photoaging of PVB-ZnO/CdS composite film [J]. Plastics Industry, 2018, 46 (08): 35-38.

[30] Tianming S, Yawei Q, Zhe R et al. Synthesis and Characterization of Polyvinylpyrrolidone-Modified ZnO Quantum Dots and Their In Vitro Photodynamic Tumor Suppressive Action[J]. International Journal of Molecular Sciences, 2021, 22(15).

[31] Jinqiu R, Mingqiang S, Lingjie Z, etc. Research progress of photocatalysis and its treatment of uranium wastewater [J]. Modern Chemical Industry, 2020, 40 (02): 62-66.

[32] Jiaojiao R. Preparation of ZnO nanocrystals and the crystal plane effect of U (VI) adsorption [D]. Nanhua University, 2019.

[33] Biao L, Yubao Z, Bin O, etc. Adsorption properties of uranium (VI) by zinc oxide with different morphologies [J]. Shandong Chemical Industry, 2017, 46 (07): 28-30.

[34] Huanning W. Preparation of carbon-based nanocomposites and their adsorption properties for uranium ions [D]. Donghua University of Technology, 2019.

[35] Kaiyuan Y. Preparation and uranium adsorption properties of MgO and ZnO multistage structures [D]. Harbin University of Engineering, 2017.

[36] Kaifu Y, Pengyan J, Haibo Y et al. Cu-based nanocrystals on ZnO for uranium photoreduction: Plasmon-assisted activity and entropy-driven stability[J]. Applied Catalysis B: Environmental, 2021, 288.

[37] Kaynar Ü H, Ayvacıklı M, Kaynar S Ç et al. Removal of uranium (VI) from aqueous solutions using nanoporous ZnO prepared with microwave-assisted combustion synthesis[J]. Journal of Radioanalytical and Nuclear Chemistry, 2014, 299(3).

[38] Abdel-Galil E A, Tourky A S, Kasem A E. Sorption of some radionuclides from nuclear waste effluents by polyaniline/SiO_2 composite: Characterization, thermal stability, and gamma irradiation studies. [J]. Applied Radiation and Isotopes, 2020, 156(C).