Research Advances in Photocatalysis of Inorganic Hollow Spheres

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Received 29 August 2014; revised 30 September 2014; accepted 30 October 2014

Abstract

Inorganic hollow spheres have shown their superiority in photocatalytic area due to the large specific surface area, controllable structure and their own special optical, electrical, magnetic properties. According to the classification of inorganic hollow spheres as photocatalysts, recent research progress and application status have been summarized in this paper. At last, the future developments of inorganic hollow spheres in photocatalytic field have been discussed.

Keywords

Inorganic Hollow Spheres, Photocatalysis, Application, Progress

1. Introduction

Hollow spheres, also known as 0D nanomaterial, were spheroidal aggregates with hollow structure assembled by their 1D nanomaterial. Due to their characteristics of controlled morphology, uniform size, large specific surface area and low density, extensive attention has been paid so far in material area [1]-[5]. Particularly, inorganic hollow spheres with special optical, electrical, magnetic, mechanical and catalytic properties have been widely used in bio-pharmaceutical, catalyst, carrier, controlled release, photonic crystal, electrochemistry and environmental protection [6]-[11]. Under the urgent situation of environmental pollution, inorganic hollow spheres as photocatalyst turned into a way to solve environmental problems. Inorganic hollow spheres have peculiar hierarchical porous structure, which makes reactant molecules easily transfer to the active sites of porous wall to improve their photocatalytic efficiency. Moreover, the hollow structure allows multiple reflections of ul-

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traviolet and visible light in inner hole to enhance utilization of light [12]. In this paper, according to the classification of photocatalytic inorganic hollow spheres, recent research progress has been introduced and application status has been concluded. The future developments of inorganic hollow spheres in photocatalytic field have been discussed.

2. Metal Oxide Hollow Spheres

2.1. Titanium Dioxide (TiO_2)

The valence and conduction band of TiO_2 is composed of the filled 2p orbitals of oxygen and 3d, 4s and 4p orbitals of titanium, respectively. Its energy gap is about 3.2 eV, which makes TiO_2 being the most promising photocatalyst. The specific band potential gives its strong oxidizing property, high chemical durability and photoelectric conversion efficiency, as well as price superiority. Furthermore, the large specific surface area and low density of hollow structure can effectively enhance photocatalytic activity of TiO_2 [13]. The TiO_2 hollow spheres obtained by Li and co-workers can completely remove azo-dye Rhodamine B (Rh B) under visible light irradiation in 240 min, which is only 50% for DeGussa P25 under the same experimental conditions [14]. However, TiO_2 can be excited only under ultraviolet light (less than 5% of the full solar spectrum). Besides, easily recombination of photogenerated electrons and holes and low interfacial charge transfer rate into TiO_2 lead to reduction of photocatalytic efficiency. Therefore, three principal methods have been used to enhance photocatalytic activity of TiO_2: ameliorate crystal composition, enlarge specific surface area and modify surface of TiO_2 hollow sphere. In the process of crystal growth, the more exposed of {001} and {110} facets which have high interface energy means higher photocatalytic activity [15]-[17]. Wang et al. [18] prepared TiO_2 hollow sphere with sixty percent exposure of {001} facets, which has higher photocatalytic activity than that of commercial photocatalyst P25. Figure 1 shows XRD pattern, SEM images and TEM images of anatase TiO_2 hollow microspheres with exposed {001} facets. Jiao et al. [19] discovered that the interface energy of {116} facets was similar to that of {110} facets through X-ray diffraction analysis. The photocatalytic property of TiO_2 hollow sphere consisting of highly active {116} plane-oriented crystallites exceed that of common TiO_2 hollow sphere, because curved {116} facets can multi-reflect incident light to enhance capture rate. The TiO_2 hollow spheres with special morphology were obtained to add specific surface area thus improve photocatalytic performance such as multi-shell structure [20] [21]. Tao et al. [22] prepared flower-like TiO_2 hollow spheres assembled by nanosheet, which has a higher surface area (65 m²/g) than that value of commercial TiO_2 (7 m²/g). Therefore, Degradation performance of methyl orange (MO) by the flower-like TiO_2 hollow sphere is better than that of commercial TiO_2.

![Figure 1](image-url)
In recent years, surface modification of TiO₂ hollow spheres has been widely researched to improve their photocatalytic efficiency. 1) Doping metal ion into TiO₂ lattice to create defect position can capture electron from conduction band, reduce recombination of photogenerated electrons and holes in photocatalytic process and accelerate interface charge-transfer to raise photocatalytic activity. Transition metal, noble metal and rare-earth metal can be incorporate elements, such as vanadium, platinum, cerium, neodymium, etc. Vanadium-doped TiO₂ hollow spheres prepared by Liu et al. [23] can quickly degrade methylene blue under visible-light irradiation to show their excellent photocatalytic activity and renewability. Feng and coworkers [24] prepared platinum doped TiO₂ hollow spheres using carbon spheres as templates through hydrothermal precipitation method and adding hydrazine hydrate to reduce chloromplatinic acid. When platinum-doped content is 2.0%, the decolorization rate of obtained TiO₂ hollow spheres can achieve 100% under 2 hour ultraviolet light irradiation. Wang and coworkers [25] [26] use carbon spheres to prepare cerium and neodymium doped TiO₂ hollow spheres with dope concentration of 4% and 3.9% and apply them to dye decomposition. Results show that the apparent rate constant of doped TiO₂ hollow spheres in degrading dye is 31 and 9 times as that of P25. 2) Non-metal elements also can be doped, such as boron [27], nitrogen [28] [29], carbon [30] [31], fluorine [32], etc. Non-metal ion possess relatively high energy orbit. Once doped it can replace some part of oxygen in the TiO₂ lattice, thus bring in new level to lower energy gap and extend absorption wavelength. Yu et al. [33] prepared trifluoroacetic acid modified TiO₂ hollow spheres by one-pot hydrothermal treatment using titanium sulfate as titanium source, the photocatalytic activity of which manifested 2 times higher than that of P25. In order to further improve photocatalytic activity of TiO₂ hollow spheres, two or more kinds of ion can be doped to simultaneously provide electrons and holes trap to effectively suppress the recombination. Wang et al. [34] prepared cerium and nitrogen co-doped TiO₂ hollow spheres owning enhanced visible light photocatalytic performance in dye X-3B decolorization because nitrogen decreased the energy gap and photogenerated electron of TiO₂ valence band can transfer to the 4f orbit of cerium to inhibiting recombination. 3) Noble metal particles deposited onto the surface of TiO₂ hollow spheres can take advantage of their surface plasmon resonance to extend absorption wavelength to visible light region, therefore enhance photocatalytic performance [35] [36]. Xiang et al. [37] combine microwave and hydrothermal treatment to prepare TiO₂ hollow spheres with silver (Ag) nanoparticles deposited onto the surface, which have obvious absorption in the wavelength region from 400 to 600 nm and show better photocatalytic activity than pure TiO₂ and commercial Degussa P25 powders. The single-crystalline anatase TiO₂ hollow nano-hemispheres with bimetallic Ag/Pt nanoparticles uniformly loaded on both interior and exterior of the nano-hemispheres prepared by Jiang and co-workers exhibited excellent photocatalytic ability in the degradation of Rh B/ciprofloxacin (RhB/CIP) and hydrogen generation [38]. Figure 2 shows H₂ production rates of TiO₂, Ag@TiO₂, Pt@TiO₂ and Ag/Pt@TiO₂ photocatalysts with CH₃OH as sacrificial reagent.

2.2. Other Metal Oxide

Oxide of d region elements also own good photocatalytic activity, such as vanadium pentoxide [39], manganese dioxide [40], nickel oxide [41], tantalum oxide [42], ferric oxide (Fe₂O₃) [43], copper (I) oxide (Cu₂O) [44], tungsten oxide (WO₃) [45] [46], zinc oxide (ZnO) [47] [48], etc. Patrinoiu et al. [49] impregnated carbonaceous...
spheres templates with hydrated zinc acetate and then removed templates by thermal treatment to obtain zinc oxide hollow spheres. Under ultraviolet light irradiation, the phenol mineralization rate by zinc oxide hollow spheres can exceed 80%, which notably superior to commercial zinc oxide (Merck). Figure 3 shows effects of ZnO hollow sphere (HS) and commercial product (Merck) nature on degradation of phenol under same irradiation conditions. Cao and co-workers [50] prepared hexagonal \( \alpha \)-Fe\(_2\)O\(_3\) hollow spheres assembled by nanosheets through a microwave-assisted solvothermal route using ferric trichloride hexahydrate, sodium hydroxide and sodium dodecyl benzene sulfonate as raw materials and ethylene glycol as solvent. Degradation percentage of salicylic acid by the obtained hollow spheres under ultraviolet light in one hour can reach 60% and overtop 40% after using 2 times. Li et al. [51] prepared Nb\(_2\)O\(_5\) hollow nanospheres with high surface energy (001) planes via oswald ripening process, which owned high thermal stability, strong intensity of blue emission and efficiently split water under visible light irradiation.

Moreover, oxide of some p region elements also have photocatalytic activity, such as tin oxide (SnO\(_2\)), indium oxide (In\(_2\)O\(_3\)), etc. Manjula et al. [52] utilize glucose as structure-directing agent to prepare porous tin oxide hollow spheres, which not only can photodegrade dye but also can be reused. The indium oxide hollow spheres gained by Li et al. [53] using emulsion vesicles as templates can photodecompose Rh B under ultraviolet light irradiation.

Surface modification still can be employed to enhance photocatalytic property of the aforementioned metal oxide hollow spheres. Ma et al. [54] doped tungsten oxide hollow spheres with silver-silver chloride to further improve their photocatalytic activity. Rahimi et al. [55] successfully prepared Ba-Cd-Sr-Ti doped ferroferric oxide (Fe\(_3\)O\(_4\)) nanohollow spheres via a simple solvothermal method without any templates. The photocatalytic degradation rate of congo red solution by this nanohollow spheres under visible light irradiation can reach to 99.5% when pH is 6.

**2.3. Composite Metal Oxide**

When two or more kinds of semiconductor form a compound system with fixed microstructure, it can restrain the recombination of photogenerated electrons and holes to significantly improve the photocatalytic performance. Hence, composite metal oxide hollow spheres owned a more excellent photocatalytic activity than that of single metal oxide spheres. Composite metal oxide can be divided into metal oxide modification and non-metal oxide modification. 1) Two kinds of metal oxide can be mutually compounded, such as ZnO [56], Fe\(_3\)O\(_4\) [57], zirconium oxide (ZrO\(_2\)) [58] composited with TiO\(_2\); In\(_2\)O\(_3\) [59], SnO\(_2\) [60], CuO [61], GeO\(_2\) [62] composited with ZnO; Fe\(_2\)O\(_3\) composited with MnO [63]; bismuth oxide (Bi\(_2\)O\(_3\)) composited with WO\(_3\) [64], V\(_2\)O\(_5\) [65] [66], etc. When WO\(_3\) which has a low band gap combined with TiO\(_2\), it suppresses recombin-
tion of photogenerated electrons and holes on hollow spheres surface as well as broadens photo-responsive scope to enhance utilization rate for optical energy. Tian et al. [67] prepared hierarchical flower-like Bi$_2$MoO$_6$ hollow spheres via a solvothermal process in the presence of ethylene glycol, which can remove over 95% Rh B within 2 h under visible-light irradiation. Li et al. [68] prepared bismuth tungstate (Bi$_2$WO$_6$) hollow spheres using polystyrene particles as the template, with Bi$_2$O$_3$ deposited on their surface and sequentially calcination to obtain double-shell Bi$_2$O$_3$-Bi$_2$WO$_6$ hollow spheres. The internal electric field of p-n junction formed by close contact between p-type Bi$_2$O$_3$ and n-type Bi$_2$WO$_6$ can speed up separation of photogenerated charge to boost photocatalytic performance, which makes this composite hollow spheres can completely decompose Rh B in 3 hours under visible light irradiation. An Ag$_2$ZnGeO$_4$ photocatalyst was obtained by Zhang and co-workers [69] via an ion-exchange reaction between amorphous Zn$_2$GeO$_4$ suspension and Ag ions solutions. The Ag$_2$ZnGeO$_4$ hollow sphere obtained through ostwald ripening process shows superior photocatalytic activity. 2) Few research has been focused on non-metal oxide modification. The composite between TiO$_2$ and silicon oxide (SiO$_2$) is the relatively familiar one. Li et al. [70] prepared composite SiO$_2$-TiO$_2$ hollow spheres by coating colloid carbon microspheres template with Si-doped TiO$_2$ layer in a one-pot hydrothermal approach and sequentially calcination. The photodegradation rate of methylene blue solution under ultraviolet irradiation in 2 hours by the composite SiO$_2$-TiO$_2$ hollow spheres (80%) exceeds that of TiO$_2$ hollow spheres (54%). In order to further improve photocatalytic activity of the above composite hollow spheres, measures such as surface noble metal deposition and element doping can be taken. Zhao et al. [71] prepared Ag modified hollow SiO$_2$/TiO$_2$ hybrid spheres through successively coating polystyrene spheres (PS) with SiO$_2$ and TiO$_2$ layer, evenly loading Ag nanoparticles by reducing silver nitrate onto surface of TiO$_2$ layer, and then carrying out a calcination process to eliminate the template. The modified hollow spheres can efficiently degrade Rh B under both ultraviolet and visible light irradiation. Figure 4 shows UV-vis spectra of Rh B with Ag modified hollow SiO$_2$/TiO$_2$ hybrid

![Figure 4](image-url)
spheres after 1 h dark absorption, photocatalytic degradation of Rh B under UV irradiation, UV-vis spectra of the aqueous solutions of Rh B dye, photodegradation plot of the Rh B dye and the corresponding pseudo-first-order kinetic rate plot. Zhang et al. [72] prepared hollow cobalt, nitrogen co-doped TiO$_2$/SiO$_2$ microspheres using PS microspheres as templates, tetraethylorthosilicate and tetrabutyltitanate as precursors. The compound hollow spheres have a wide absorption wavelength to 600 nm and their photodegradation rate for Rh B under visible light irradiation in 40 minute can reach to 98%.

3. Metal Sulfide Hollow Spheres

3.1. Single Metal Sulfide

Metal sulfide as photocatalysts have attracted researchers’ general attention in recent years. Cadmium sulfide (CdS), a typical semiconductor of II-VI group with the band gap at 2.42 eV, owns outstanding photocatalytic property. Li et al. [73] prepared hollow CdS nanospheres with a diameter of about 130 nm and controllable shell thickness through 1-butyl-3-methylimidazolium-bis(trifluoro-methylsulfonyl)-imide ionic liquids as the templates, polyvinylpyrrolidone adjusting the formation of spheres and hexamethylenetetramine regulating the size and shell thickness. The photodegradation rate for methylene blue by the hollow CdS spheres can achieve 81% under ultraviolet irradiation in 80 minutes. Elements doping can effectively overcome its instability for light. Luo and co-workers [74] prepared nickel ion (Ni$^{2+}$) doped CdS hollow spheres via a template-free one-pot method. The obtained 1.2 mol% Ni-doped CdS hollow spheres can completely decompose Rh B under visible light ($\lambda > 420$ nm) in 35 minutes and the degradation rate keeps over 98% after using 4 times. Figure 5 shows the photoggradation plot for Rh B under visible light of Ni-doped CdS hollow spheres.

Besides, zinc sulfide (ZnS), indium sulfide (In$_2$S$_3$) and copper sulfide (CuS) also have a certain degree of photocatalytic property. Yu and co-workers [75] prepared hexagonal wurtzite ZnS hollow spheres via one-pot template-free hydrothermal route using zinc acetate dehydrate and thiourea as raw materials. The ZnS hollow sphere shows strong absorption less than 365 nm. Zhang et al. [76] successfully synthesized Bi-doped ZnS hollow spheres (BZ) with enhanced ultraviolet and visible-light photocatalytic activity because of the formation of an isolated state originating from Bi 6s above the top of the valence band of ZnS and the electron excitation from Bi 6s state to the conduction band occurred under visible light irradiation. Under the optimal content of Bi dopant ($R = 0.3$, which is defined as the nominal atomic ratio of Bi to Zn), that is 0.3 at%, the hydrogen production rate is 1030 and 134 $\mu$mol·h$^{-1}$·g$^{-1}$ under UV and visible-light irradiation, respectively.

Rengaraj et al. [77] obtained tetragonal porous In$_2$S$_3$ hollow spheres composed of two-dimensional nanosheets and nanorods via a one-step solvothermal method using thiosemicarbazine as both sulfur source and capping ligand. The above-mentioned hollow spheres can photodegrade 30% percentage of methyl blue solution.
Meng et al. [78] prepared hierarchical flower-like CuS hollow nanospheres via a solvothermal approach. The CuS hollow nanospheres obtained can photodegrade Rh B and 2,4-dichlorophenol aqueous solution because of the synergistic effect of surface hierarchical structure with large surface area, porous hollow sphere structure and high visible light utilization.

### 3.2. Composite Metal Sulfide

Compared to single metal sulfide, composite metal sulfide has more superior photocatalytic activity and broaden light responsive scope. However, until now few studies of composite metal sulfide hollow spheres concentrated on photocatalytic realm. The way to get composite metal sulfide hollow spheres is mainly by simple coupling and doping. Zhu et al. [79] prepared composite (Ag, Cu)₂S hollow spheres with cation exchange method using spherical aggregates of CuS nanoparticles as templates. The composite (Ag, Cu)₂S hollow spheres have strong absorption at ultraviolet light scope from 200 nm to 500 nm and infrared light scope from 1000 nm to 2500 nm, but weak absorption at visible light scope from 500 nm to 800 nm, which makes selective light absorption come true. Yu et al. [80] prepared composite CuS-ZnS hollow nanospheres by an ion-exchange method using ZnS solid spheres as a precursor and copper nitrate as raw materials. The photodegradation rate for Rh B by the composite hollow nanospheres is obviously higher than that of CuS and ZnS solid spheres. Bhirud et al. [81] prepared CdIn₂S₄ hollow spheres assembled by nanoparticles with a flower like morphology using cadmium nitrate tetrahydrate, indium nitrate trihydrate, thiourea and cetyl trimethyl ammonium bromide as raw materials. The rate of hydrogen production from H₂S photodecomposition for CdIn₂S₄ hollow spheres is 3171 μmol·h⁻¹, which is almost three fold enhancement than the highest rate of hydrogen production from normal bulk CdS (847 μmol·h⁻¹). Xing and co-workers [82] prepared a type of ternary Ag/Ag₂S/CuS₂ hollow microspheres with Cu₇S₄ hollow submicrospheres as the template, the photocatalytic activity of which was higher than those of Ag/Ag₂S, Cu₂O, Cu₇S₄ and P25 for the photodegradation of MO under visible light irradiation. Superoxide radicals and holes were confirmed to be the main reactive species for MO degradation through radical scavenger experiments. Figure 6 shows photoggradation plot for MO under visible light of the as-obtained Ag/Ag₂S/CuS₂ hollow microspheres.

### 4. Application

#### 4.1. Sewage Treatment

Organic pollutants durably presented in sewage often have reducibility. Consequently, inorganic hollow sphere photocatalysts can randomly oxidize organic pollutants by photo-generated holes and hydroxyl to carbon dioxide (CO₂), water and other nontoxic inorganic substances to purify water, as well as avoiding secondary water pollution. At present, photocatalytic technology can effectively degrade halogenated aliphatic hydrocarbon, dye, nitroaromatic compounds, polycyclic aromatic hydrocarbon, heterocyclic compounds, hydrocarbon, phenols, surfactants, pesticides and so on. For example, nitrogen doped TiO₂ hollow spheres can decompose bisphenol A [83], carbon, nitrogen co-doped TiO₂ hollow spheres can remove dye X-3B [84], copper ion doped TiO₂ hollow spheres can degrade chlorotetracycline [85], zirconium oxide doped TiO₂ hollow spheres can decompose Rh B [58], bismuth molybdate hollow spheres can decompose phenol [86] and Zn₂GeO₄ hollow spheres can degrade antibiotic metronidazole [87]. While inorganic hollow spheres as water purification material have achieved great progress, it also exists limitations such as unable to efficiently resolve high concentration wastewater and difficult to recycle for powder catalyst.

#### 4.2. Air Purification

Due to the vast application of organic materials and continuous off-gas emissions from automobile, there is a large amount of poisonous organic gas and nitrogen oxides suspending in our breathing air. Air purification by photocatalysts can operate at normal temperature and pressure, do no harm to environmental and human body, costs little, completely decompose organics. Dong et al. [88] prepared hierarchical (BiO)₂CO₃ hollow microspheres which can be reused as NO removal material in indoor air. The indium vanadate hollow spheres prepared by Ai et al. [89] can oxidize NO to nitric acid under visible light and maintain their photocatalytic ratio after reused. Ikeda et al. [90] encapsulates TiO₂ into a hollow SiO₂ shell to attain a type of composite material, which can decompose gas-phase acetone and isopropanol into CO₂. Nevertheless, absence of applied research on
Figure 6. (a) UV-visible absorption spectra of degradation of MO by Ag/Ag$_2$S/Ag$_3$CuS$_2$ under visible light ($\lambda > 420$ nm); (b) photocatalytic degradation of MO over different photocatalysts; (c) Linear transformation $\ln(C_0/C) = K_{app}$ of the kinetic curves of MO degradation over different photocatalysts. The inset shows the $K_{app}$ for MO degradation over different photocatalysts [82].

Air-handling equipment gives rise to the unrealizable industrialization of air purification by nanosize photocatalysts.

4.3. Hydrogen Production

Hydrogen gas is a kind of clean energy sources with a high combustion value, superior efficiency and environmental friendly. The hydrogen production chiefly depends on coal and natural gas so far, which could aggravate
consumption of nonrenewable resources and environmental pollution. The most ideal way to settle down the problem is to transfer solar energy into hydrogen energy with photocatalyst using renewable substance as raw materials such as water and biomass. The hierarchical Sn\(_2\)Nb\(_2\)O\(_7\) hollow spheres synthesized by Zhou et al. shows a superior visible-light-driven photocatalytic \(H_2\) production activity (3 \(\mu\)mol h\(^{-1}\)), which is about 4 times higher than that of the bulk Sn\(_2\)Nb\(_2\)O\(_7\) sample prepared by a conventional high temperature solid state reaction method [91]. Zhang [92] and co-workers prepared composite CdS-TiO\(_2\) hollow sphere by coupling TiO\(_2\) to CdS which had a conduction band potential more negative than that of H\(^+\)/H\(_2\) via a hydrothermal process, second step impregnation method and sol-gel method in sequence. The hydrogen production rate by the composite hollow spheres from water under ultraviolet light irradiation in one hour is 0.81 ml/g. After that, they prepared NiO-CdS hollow spheres with p-n junction, the hydrogen production rate by which under ultraviolet light irradiation in one hour (1.81 ml/g) precede the common composite CdS-TiO\(_2\) hollow spheres [93]. The reason is that interior electric field of p-n junction boosting transport rate of photo-production electronics. While great progresses have been achieved in hydrogen production by photocatalysts until now, it fails to meet practical applications for the low efficiency of directly water splitting.

### 4.4. CO\(_2\) Reduction

Greenhouse gas CO\(_2\) is a major cause to global warming. It is also a kind of potential carbon resources. Hence, effective control and utilization of CO\(_2\) becomes research focus. Present emission reduction technology requires numerous energy and exists potential safety problems in application. In the process of constant exploring emission reduction technology, it has been found that photogenerated electronics can change CO\(_2\) to organic compounds with high application value such as methane and methanol. Tu et al. [94] prepared hollow spheres consisting of alternating Ti\(_{0.91}\)O\(_2\) nanosheets and graphene nanosheets with polymer beads as sacrificial templates and via a microwave irradiation technique. The ultrathin Ti\(_{0.91}\)O\(_2\) nanosheets allow charge carriers to move rapidly onto the surface to take part in the photoreduction reaction and the alternating compact stacking structure allow the photogenerated electron to transfer fast from Ti\(_{0.91}\)O\(_2\) nanosheets to graphene nanosheets to extend lifetime of the charge carriers. The photocatalytic activity of the hollow spheres is 9 times higher than P25. It can reduce CO\(_2\) to carbonic oxide and methane. Photocatalytic reduction for CO\(_2\) operates at normal temperature and pressure, directly ultilizes solar light with no energy consumption, does no harm to environment, is the most promising conversion method.

### 4.5. Other Application

Photogenerated holes and electronics can directly react with compounds which deactive cytoderm, cytomembrane and cell leading to the death of bacterium. So, photocatalysts can be used as a new type of antibacterial materials. Feng et al. [95] prepared Ag-doped TiO\(_2\) hollow spheres by hydrothermal precipitation method using carbon spheres as the templates. TiO\(_2\) hollow sphere doping 9.4 mol% Ag has excellent antibacterial activities against scherichia coli, staphylococcus aurels and candida albicans at room temperature. Furthermore, hollow spheres with photocatalytic properties can be photoelectric detector [96].

### 5. Outlook

Inorganic hollow spheres show their excellent performance in photocatalytic area, which belongs to their large specific surface area, controllable structure and their own special optical, electrical, magnetic properties. They can be widely applied in sewage treatment, hydrogen production, air purification and other field. Metal oxide, metal sulfide and composite hollow spheres formed by metal oxide or sulfide have successfully prepared and primarily improve their photocatalytic property by controlling surface morphology and doping various other semiconductors. However, owing to the limitations of synthetic method, there exist some drawbacks including poor structure controllability, uneven shell thickness and broad particle size distribution, which are adverse to photocatalytic activity. Therefore, inorganic hollow spheres with well structure and property controllability remain to be one of the principal development trends in photocatalytic field. On the other hand, various types of inorganic hollow spheres own photocatalytic property, but the photodegradation efficiency is low. Rare earth elements possess unique f electronic configuration and abundant storage. So, hollow spheres composed of rare earth elements will be one of the research focuses in photocatalytic area.
Acknowledgements

The support from National Natural Science Foundation of China (No. 21106084), Shanghai Science and Research Innovation Foundation (No. 14zz164) and Shanghai Rising-Star Program (14QA143300) was appreciated.

References

http://dx.doi.org/10.1016/j.apsusc.2012.02.117

http://dx.doi.org/10.1021/jp204941u

http://dx.doi.org/10.1039/c3nr04043g

http://dx.doi.org/10.1039/c0cc00706d

http://dx.doi.org/10.1016/j.mseb.2012.08.010

http://dx.doi.org/10.1016/j.mseb.2010.04.037


http://dx.doi.org/10.1016/j.jhazmat.2010.01.111

http://dx.doi.org/10.1016/j.apsusc.2010.06.071

http://dx.doi.org/10.1016/j.matlet.2009.08.031

http://dx.doi.org/10.1016/j.jhazmat.2008.12.139

http://dx.doi.org/10.1016/j.apsusc.2009.11.023

http://dx.doi.org/10.1039/c2jm16924j

http://dx.doi.org/10.1016/j.cej.2012.04.095

http://dx.doi.org/10.1021/jp709615x

http://dx.doi.org/10.1016/j.molcata.2010.04.016

http://dx.doi.org/10.1016/j.powtec.2011.03.015

http://dx.doi.org/10.1039/c2ra22713d

http://dx.doi.org/10.1039/c2dt32040a


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