

Photochemical Modification with CdS and Enhanced Visible-light Photocatalytic Activity of Mesoporous TiO₂ *

CdS 光化学修饰介孔 TiO₂ 及其增强的可见光催化活性

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Abstract: **【Objective】**To improve the photocatalytic activity of mesoporous TiO₂. **【Methods】**Mesoporous TiO₂ was prepared by the method of evaporation-induced self-assembly (EISA), while TiCl₄ and Ti(OC₄H₉)₄ as titanium sources, and block copolymer P123(EO₂₀PO₇₀EO₂₀) as the template. Using the photochemical modification technology, composite material was prepared with good response of visible light by doping CdS to its framework. The obtained samples were characterized by X-ray diffraction (XRD), transmission electronic micrograph (TEM), atomic absorption spectrophotometer(AAS)and photocatalytic. **【Results】**The results of XRD and TEM proved the synthesis of ordered hexagonal mesoporous materials. AAS determined the composite material content of 0.96 mg/g Cd. In 500 W xenon lamp, 2 × 10⁻⁵ mol/L methylene blue (MB) as model pollutant, the photocatalytic results showed that the photocatalytic activity of the mesoporous CdS/TiO₂ composite was further improved. **【Conclusion】**The mesoporous CdS/TiO₂ composite material with enhanced visible-light photocatalytic activity can be prepared by photochemical modification technique.

Key words: mesoporous CdS/TiO₂, photochemical, photocatalytic, visible light, EISA

摘要: **【目的】**提高介孔 TiO₂ 材料的光催化活性。 **【方法】**采用蒸发诱导自组合法(EISA),以四氯化钛和钛酸丁酯为钛源,嵌段共聚物 P123(EO₂₀PO₇₀EO₂₀)为模板剂,制备介孔 TiO₂。用光化学修饰法将 CdS 掺进介孔 TiO₂ 中,合成对可见光有较好响应的复合材料,并利用 X 射线衍射(XRD)、透射电镜(TEM)、原子吸收分光光度法(AAS)和光催化等手段对样品进行表征。 **【结果】**XRD 和 TEM 结果表明成功合成有序的六方介孔材料;AAS 确定复合材料中 Cd 的含量为 0.96 mg/g;光催化于 500 W 氙灯下以 2 × 10⁻⁵ mol/L 次甲基蓝(MB)为模型污染物,结果显示 CdS/TiO₂ 复合材料的可见光催化活性明显提高。 **【结论】**光化学修饰法制备的介孔 CdS/TiO₂ 复合材料可增强其可见光催化活性。

关键词:介孔 CdS/TiO₂ 光化学 光催化 可见光 EISA

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0 Introduction

【Research significance】 Mesoporous TiO_2 has better adsorption property and higher catalytic activity than non-mesoporous materials due to its high specific surface area. It is widely used for effective decomposition of organic pollutants in water or air under UV light irradiation. However, limited by titania's low quantum efficiency and high band gap (3.0 ~ 3.2 eV, located at the ultraviolet (UV) wavelength range), very few visible light is available. To depress the recombination of photogenerated electron-hole pairs in photocatalytic processes, ingredient or structure modification have thus become an appealing challenge for developing photocatalytic technologies. **【Previous research progress】** Accordingly, semiconductor^[1-5], transition metal^[6-9], noble metal^[10-12] or ion^[13-17] doped mesoporous TiO_2 and photosensitized^[18] mesoporous TiO_2 have been developed. The couple of TiO_2 with narrow band gap materials such as CdS, CdSe, PbS, etc., was found to be effective for enhancing its visible light activity due to the fact that the photogenerated electrons from CdS could be injected into the conduction bands of TiO_2 , resulting in the photocatalytic reaction^[19-23]. Meanwhile, CdS/ TiO_2 composites have been extensively investigated for their applications in solar energy cells, catalysis, water purification and electrochromic devices^[24]. CdS/ TiO_2 composite nano-materials were studied frequently in the sol-gel^[25-27], photoelectrochemical^[24, 28-30], coprecipitation^[31-35] system. A self-assembly method was also used to prepared macroporous CdS/ TiO_2 films materials^[36] or solar cells^[35]. **【Research breakthrough point】** To date, the studies of CdS doped mesoporous TiO_2 compounds synthesized by photochemical modification technology have not yet been established. Nevertheless, compared to the photochemical method^[37-40], hereinbefore synthesis methods often require a long time and multiple-step procedures with the problem of high costs. For instance, as the most widely used method of mesoporous TiO_2 modification, the sol-gel method has to take alkoxide type, water, temperature, gel formation time and catalyst into account^[8-9, 16, 41-42]. And the coprecipita-

tion method has to bath with a great deal of organic solvent to control its hydrolysis rate^[31-35]. **【Key issues to be resolved】** By changing the light intensity and illumination time at room temperature to control the intensity of reaction, photochemical modification of nano-materials is more feasible. In this present work, using P123 as a template agent, mesoporous TiO_2 was prepared using the EISA method. Applying a vacuum-aided photochemical reduction technique, CdS was incorporated into its framework. The mesoporous CdS/ TiO_2 composite was obtained with UV-light irradiation. And its physical and photochemical performances were studied. The preparation of mesoporous CdS/ TiO_2 is schematically shown in Fig. 1.

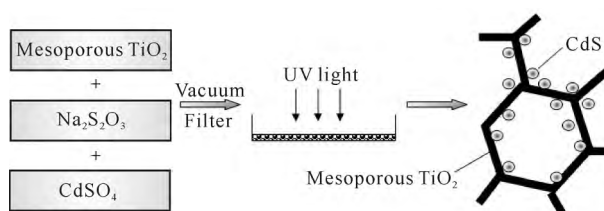


Fig. 1 A schematic procedure for preparation of mesoporous CdS/ TiO_2

1 Materials and methods

1.1 Synthesis of mesoporous TiO_2

A typical synthesis went as follows: First, 1 g block copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich) was dissolved into 20 mL ethanol, and then 1 mL TiCl_4 and 3 mL $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were dissolved into this solution, respectively. Here, Ti precursor particles were fully adsorbed on the surface of P123 micelle^[43]. Second, the resulting mixed solution was aged in an dish (with a lip made of paper) with a low humidity at 40°C for 12 h, to evaporate the solvent and form a mesostructured copolymer/Ti hybrid transparent gel. Third, the gel was baked at 100°C for 30 min. In this process, the micelle which adhesion metal ions inside the sol-film self-assembly arranged in the network structure^[44]. Last, sol-film was calcined in air with a ramp of $5^\circ\text{C}/\text{min}$ to 350°C and remained there for 70 min in non-air atmosphere, to remove the template and obtain crystallined mesoporous TiO_2 (sample S1).

1.2 Photochemical modification of Mesoporous TiO₂

An aqueous solution of 80 mL containing 0.15 mol/L CdSO₄ and 0.0168 mol Na₂S₂O₃ was prepared using deionized water, then vacuumed 5 min in order to eliminate the air from mesoporous and made the solution into the pores. Then, the sample was positioned so that radiation intensity received was 0.84 mW/cm² at $\lambda=254$ nm, and the diameter of the illumination region was approximately 15 mm. After 24 h, the excess CdSO₄ and Na₂S₂O₃ were washed away with 2% HNO₃, and various methods were used to determine the properties of mesoporous CdS/TiO₂ (sample S2).

1.3 Photocatalysis

A 500 W Xenon lamp was positioned inside a cylindrical quartzose vessel and surrounded by a circulating water jacket to cool the lamp. 0.05 g of photocatalyst was suspended in a 200 mL aqueous solution of 2×10^{-5} mol/L methylene blue (MB). Prior to irradiation, the suspensions were magnetically stirred for 30 min to ensure establishment of an adsorption/desorption equilibrium among the photocatalyst, MB and atmospheric oxygen. At room temperature and under normal pressure, 5 mL of the suspensions were collected every 20 min, and then centrifuged to separate the photocatalyst particles. The degradations of MB were analyzed by a UV-vis spectrophotometer (752, Shanghai Jinghua Technology Instrument Co., Ltd) and the absorption peak at 665 nm was monitored.

1.4 Characterization

Low-angle XRD measurement ($0.6 \sim 3^\circ$, 40 kV/20 mA, $0.25^\circ/\text{min}$) was made on a Rigaku D/MAX-2200 X-ray diffractometer with Cu K _{α} radiation, while wide-angle XRD measurement ($20 \sim 80^\circ$, 30 kV/20 mA, $3.6^\circ/\text{min}$) was made on a XRD-2000 X-ray diffractometer. Crystal size was measured from XRD peak broadening using the Scherrer equation. Direct TEM (JEM-2010HR, operated at 200 kV) photograph was also used to determine the structure of sample S1.

Sample S2 solution was prepared by melt in 10 mL concentrated H₂SO₄ (150°C, 1.5 h), then a TSA-986 flame atomic spectrophotometer ($\lambda=228.9$

nm) was used to determine its cadmium content.

2 Results and discussion

2.1 Characterized by XRD and TEM

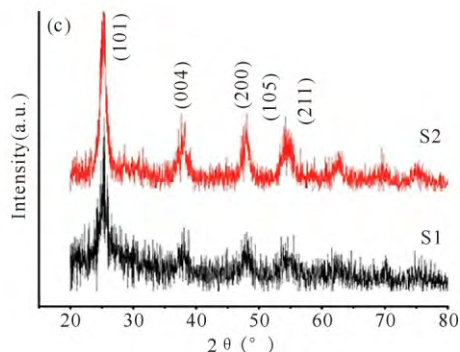
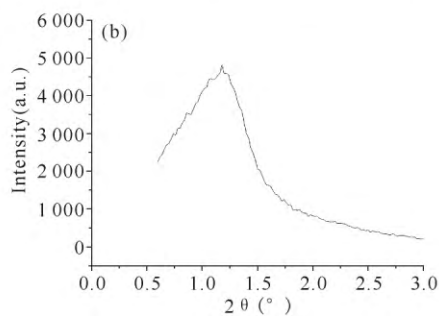
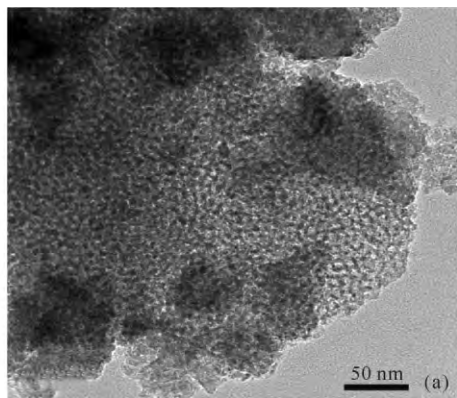
Low-angle X-ray diffraction (LXRD, Fig. 2b) shown that sample S1 obtained a peak at 1.18° , from Scherrer equation, its crystallite size is near by 9 nm, belonging to mesoporous materials; and the height and narrow diffraction peak sufficiently prove that the mesoporous TiO₂ sample's pore structure with good short-range order. The size measured by XRD was found to correspond closely with that measured by direct TEM imaging (Fig. 2a) for these powder. Observing reveals that the mesoporous TiO₂ is prepared with mesoporous ordered distribution, continuous pore, and hexagonal arrays. Wide-angle X-ray diffraction (WXR) patterns of the prepared sample were shown in Fig. 2c. The five Bragg diffraction peaks are found at $20 \sim 60^\circ$, corresponding to the anatase (101), (004), (200), (105) and (211) crystal planes, respectively. WXR result of mesoporous sample S2 is similarity to sample S1, but there are some miscellaneous weaker peaks at the range of $20 \sim 30^\circ$, which may be CdS diffraction peaks because of the small amount CdS doping. However, CdS diffraction peaks and TiO₂ strong diffraction peaks are adjacent or overlapping. Therefore, it is difficult to tell them apart.

2.2 Characterized by AAS

Measurement of cadmium content of sample S2, which has a dosage of 0.012 mol Cd, determines that the incorporation amount of Cd is 0.96 mg/g, that is, $n(\text{Ti}) : n(\text{Cd}) = 1.4 \times 10^{-4}$ ($R = 0.99696$).

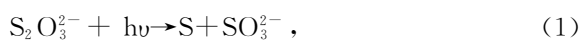
2.3 Formed mechanism

Mesoporous CdS/TiO₂ is expected to be formed by the following mechanism^[19,27,39]. An aqueous solution containing S₂O₃²⁻ ions and Cd²⁺ ions is introduced into the pores of mesoporous TiO₂ using a vacuum method. The vacuum can remove the air from its channels and drive the precursors into the pore networks, subsequently. And being irradiated under UV light, the S₂O₃²⁻ ions act as a reductant to release solvated electrons and sulfur atoms. The S₂O₃²⁻ ions are considered to adsorb photons and be dissociated under irradiation.

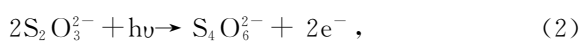


(a) TEM photography of sample S1; (b) low-angle XRD of sample S1; (c) Wide-angle XRD figure of the samples S1 and S2

Fig. 2 Characterizations of mesoporous TiO₂ (S1) and mesoporous CdS/TiO₂ (S2)



The $S_2O_3^{2-}$ ions also supply solvated electrons.



And then, CdS particles are formed in the pores.



2.4 Enhanced visible-light photocatalytic activity

On the preparation of a series of mesoporous CdS/TiO₂ composite materials that have different amount of CdS were characterized by photocatalysis. Among them, sample S2 has the best photocatalytic efficiency, whose dosage of Cd is 0.012 mol and $n(S_2O_3^{2-}) : n(Cd^{2+}) = 1.4$. As shown in Fig. 3, com-

paring with pure TiO₂, the photocatalytic activity of CdS/TiO₂ composite materials have been significantly improved with a good response to the visible light.

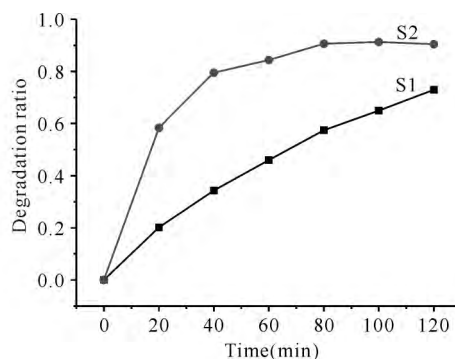


Fig. 3 Photocatalytic performance of mesoporous TiO₂ before and after doping CdS to its framework

2.5 Photocatalysis mechanism

As shown in Fig. 4, mesoporous TiO₂ can be coupled by interparticle electron transfer from irradiated CdS nanocrystals to its conduction band. Upon UV excitation, an electron of anatase TiO₂ (3.2 eV band gap) may be promoted from the valence band to the conduction band (E_{CB}) leaving behind a beneficial hole in the valence band (E_{VB})^[30]. When coupling CdS with TiO₂, photogenerated electrons (E_{CB}) flowed toward CdS and accumulated at CdS and formed Schottky barrier between CdS and TiO₂ (References[45-46]).

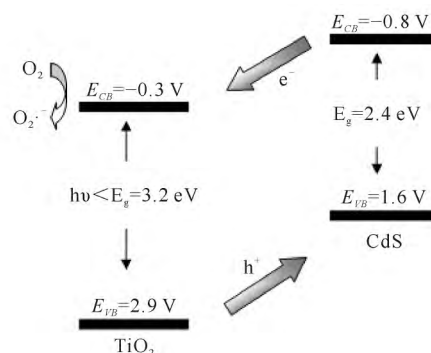
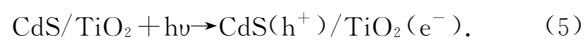


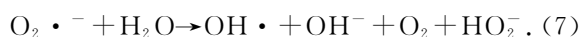
Fig. 4 Schematic diagram illustrating charge injection from excited CdS into TiO₂



The electrons are then scavenged by molecular oxygen O₂ to yield the superoxide radical anion O₂ •⁻ in oxygen-equilibrated media.



These new formed intermediates can interreact to produce hydroxyl radical OH •.



The $\text{OH} \cdot$ radical is a powerful oxidizing agent capable of degrading most pollutants.



3 Conclusion

The mesoporous CdS/TiO₂ composite material with enhanced visible-light photocatalytic activity can be prepared by photochemical modification technique. Due to its good chemical stability and non-toxic, we can foresee that it will not trigger unnecessary responses, in other words, it may be generate to low foreign objects. The reaction region and its strength can be controlled by light. It is obviously, with moderate price, the material is readily available with the best operability, strong coverage, and high refractive index^[40]. Therefore, the materials have good prospects in water or soil pollution, dust-proof paints and coatings, and life sciences field.

References:

[1] HE C X, TIAN B Z, ZHANG J L. Thermally stable SiO₂-doped mesoporous anatase TiO₂ with large surface area and excellent photocatalytic activity[J]. *Journal of Colloid and Interface Science*, 2010, 344(2): 382-389.

[2] JING D, GUO L. WS₂ sensitized mesoporous TiO₂ for efficient photocatalytic hydrogen production from water under visible light irradiation[J]. *Catalysis Communications*, 2007, 8(5): 795-799.

[3] LI L, LI Y J, MA Y, et al. Preparation and photocatalytic behaviors of nanoporous polyoxotungstate-anatase TiO₂ composites[J]. *Journal of Rare Earths*, 2007, 25(1): 68-73.

[4] BANERJEE A N. The design, fabrication, and photocatalytic utility of nanostructured semiconductors: Focus on TiO₂-based nanostructures[J]. *Nanotechnology, Science and Applications*, 2011, 4: 35-65.

[5] KIM H, KIM J, KIM W, et al. Enhanced photocatalytic and photoelectrochemical activity in the ternary hybrid of CdS/TiO₂/WO₃ through the cascaded electron transfer[J]. *The Journal of Physical Chemistry C*, 2011, 115(19): 9797-9805.

[6] MALWADKAR S S, GHOLAP R S, AWATE S V, et al. Physico-chemical, photo-catalytic and O₂-adsorption properties of TiO₂ nanotubes coated with gold nanoparticles[J]. *Journal of Photochemistry and Photobiology A Chemistry*, 2009, 203(1): 24-31.

[7] CHAN C C, CHANG C C, HSU W C, et al. Photocatalytic activities of Pd-loaded mesoporous TiO₂ thin films[J]. *Chemical Engineering Journal*, 2009, 152(2/3): 492-497.

[8] LEE A C, LIN R H, YANG C Y, et al. Preparations and characterization of novel photocatalysts with mesoporous titanium dioxide (TiO₂) via a sol-gel method[J]. *Materials Chemistry and Physics*, 2008, 109(2/3): 275-280.

[9] KORZHAK A V, ERMOKHINA N I, STROYUK A L, et al. Photocatalytic hydrogen evolution over mesoporous TiO₂/metal nanocomposites[J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2008, 198(2/3): 126-134.

[10] SONG C X, WANG D B, XU Y H, et al. Preparation of Ag-TiO₂ hollow structures with enhanced photocatalytic activity[J]. *Materials Letters*, 2011, 65(5): 908-910.

[11] TANAKA A, SAKAGUCHI S, HASHIMOTO K, et al. Preparation of Au/TiO₂ with metal cocatalysts exhibiting strong surface plasmon resonance effective for photoinduced hydrogen formation under irradiation of visible light[J]. *ACS Catalysis*, 2013, 3(1): 79-85.

[12] PRIMO A, CONCEPCION P, CORMA A. Synergy between the metal nanoparticles and the support for the hydrogenation of functionalized carboxylic acids to diols on Ru/TiO₂ [J]. *Chemical Communications*, 2011, 47(12): 3613-3615.

[13] HUANG S, YANG L Z, LI F Y. Effect of double elements Co-doping on nano-TiO₂ photocatalysis of rhodamine B solution[J]. *Advanced Materials Research*, 2013, 798: 25-29.

[14] KIM D, TSUCHIYA H, FUJIMOTO S, et al. Nitrogen-doped TiO₂ mesosponge layers formed by anodization of nitrogen-containing Ti alloys[J]. *Journal of Solid State Electrochemistry*, 2011, 16(1): 89-92.

[15] SHI Y D, GUO Q, XIE Y S. The preparation of C, N, S Tri-doped TiO₂ and visible-light photo-degradation of methylene blue and dyes[J]. *Advanced Materials Research*, 2011, 287: 1735-1743.

[16] SREETHAWONG T, LAEHSALEE S, CHAVADEJ S. Comparative investigation of mesoporous- and non-mesoporous-assembled TiO₂ nanocrystals for photocatalytic H₂ production over N-doped TiO₂ under visible light irradiation[J]. *International Journal of Hydrogen Energy*, 2008, 33(21): 5947-5957.

[17] HOU Y D, WANG X C, WU L, et al. N-doped SiO₂/TiO₂ mesoporous nanoparticles with enhanced photocatalytic activity under visible-light irradiation [J].

Chemosphere, 2008, 72(3): 414-421.

- [18] LUCARELLI L, NADTOCHENKO V, KIWI J. Environmental photochemistry: Quantitative adsorption and FTIR studies during the TiO₂-photocatalyzed degradation of orange II [J]. *Langmuir*, 2000, 16(3): 1102-1108.
- [19] WU L, YU J C, FU X Z. Characterization and photocatalytic mechanism of nanosized CdS coupled TiO₂ nanocrystals under visible light irradiation [J]. *Journal of Molecular Catalysis A: Chemical*, 2006, 224(1/2): 25-32.
- [20] SUN W T, YU Y, PAN H Y, et al. CdS quantum dots sensitized TiO₂ nanotube-array photoelectrodes [J]. *Journal of the American Chemical Society*, 2008, 130(4): 1124-1125.
- [21] ROBERT D. Photosensitization of TiO₂ by M_xO_y and M_xS_y nanoparticles for heterogeneous photocatalysis applications [J]. *Catalysis Today*, 2007, 122(1/2): 20-26.
- [22] ZHANG X W, LEI L C, ZHANG J L, et al. A novel CdS/S-TiO₂ nanotubes photocatalyst with high visible light activity [J]. *Separation and Purification Technology*, 2009, 66(2): 417-421.
- [23] JANG J S, KIM H G, BORSE P H, et al. Simultaneous hydrogen production and decomposition of H₂S dissolved in alkaline water over CdS-TiO₂ composite photocatalysts under visible light irradiation [J]. *International Journal of Hydrogen Energy*, 2007, 32(18): 4786-4791.
- [24] JIAH M, XU H, HU Y, et al. TiO₂@CdS core-shell nanorods films: Fabrication and dramatically enhanced photoelectrochemical properties [J]. *Electrochemistry Communications*, 2007, 9(3): 354-360.
- [25] SO W W, KIM K J, MOON S J. Photo-production of hydrogen over the CdS-TiO₂ nano-composite particulate films treated with TiCl₄ [J]. *International Journal of Hydrogen Energy*, 2004, 29(3): 229-234.
- [26] WANG C Y, SHANG H M, TAO Y, et al. Properties and morphology of CdS compounded TiO₂ visible-light photocatalytic nanofilms coated on glass surface [J]. *Separation and Purification Technology*, 2003, 32(1/2/3): 357-362.
- [27] KUMAR A, JAIN A K. Photophysics and photochemistry of colloidal CdS-TiO₂ coupled semiconductors-photocatalytic oxidation of indole [J]. *Journal of Molecular Catalysis A: Chemical*, 2001, 165(1/2): 265-273.
- [28] HAOE C, YANG B, REN H, et al. Fabrication of composite film comprising TiO₂/CdS and polyelectrolytes based on ionic attraction [J]. *Materials Science and Engineering C*, 1999, 10(1/2): 119-122.
- [29] QIAN X M, QIN D Q, SONG Q, et al. Surface photovoltage spectra and photoelectrochemical properties of semiconductor-sensitized nanostructured TiO₂ electrodes [J]. *Thin Solid Films*, 2001, 385: 152-161.
- [30] CHEN S G, PAULOSE M, RUAN C M, et al. Electrochemically synthesized CdS nanoparticle-modified TiO₂ nanotube-array photoelectrodes: Preparation, characterization and application to photoelectrochemical cells [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2006, 177(2/3): 177-184.
- [31] NIITSOO O, SARKAR S K, PEJOUX C, et al. Chemical bath deposited CdS/CdSe-sensitized porous TiO₂ solar cells [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2006, 181(2/3): 306-313.
- [32] HODOS M, HORVÁTH E, HASPEL H, et al. Photosensitization of ion-exchangeable titanate nanotubes by CdS nanoparticles [J]. *Chemical Physics Letters*, 2004, 399(4/5/6): 512-515.
- [33] MANE R S, YOON M Y, CHUNG H, et al. Co-deposition of TiO₂/CdS films electrode for photo-electrochemical cells [J]. *Solar Energy*, 2007, 81: 290-293.
- [34] KANG M G, HAN H E, KIM K J. Enhanced photodecomposition of 4-chlorophenol in aqueous solution by deposition of CdS on TiO₂ [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 1999, 125(1/2/3): 119-125.
- [35] WIJAYANTHA K G U, PETER L M, OTLEY L C. Fabrication of CdS quantum dot sensitized solar cells via a pressing route [J]. *Solar Energy Materials and Solar Cells*, 2004, 83(4): 363-369.
- [36] SINGH R S, RANGARI V K, SANAGAPALLI S, et al. Nano-structured CdTe, CdS and TiO₂ for thin film solar cell applications [J]. *Solar Energy Materials and Solar Cells*, 2004, 82(1/2): 315-330.
- [37] VIGIL E, FERNÁNDEZ-LIMA F A, AYLLÓN J A, et al. TiO₂-CuO three-dimensional heterostructure obtained using short time photochemical deposition of copper oxide inside a porous nanocrystalline TiO₂ layer [J]. *Microporous and Mesoporous Materials*, 2008, 109(1/2/3): 560-566.
- [38] SUN L, LAI Y K, WANG C L, et al. Ultrasound aided photochemical synthesis of Ag loaded TiO₂ nanotube arrays to enhance photocatalytic activity [J]. *Journal of Hazardous Materials*, 2009, 171: (1/2/3): 1045-1051.
- [39] PODDER J, KOBAYASHI R, ICHIMURA M. Photochemical deposition of CuS thin films from aqueous solutions [J]. *Thin Solid Films*, 2005, 472(1): 71-75.
- [40] SUNG-SUH H M, CHOI J R, HAH H J, et al. Com-

parison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO₂ under visible and UV light irradiation [J]. Journal of Photochemistry and Photobiology A: Chemistry, 2004, 163(1/2):37-44.

- [41] BESSEKHOUD Y, ROBERT D, WEBER J V. Synthesis of photocatalytic TiO₂ nanoparticles: Optimization of the preparation conditions [J]. Journal of Photochemistry and Photobiology A: Chemistry, 2003, 157(1):47-53.
- [42] YU J G, ZHAO X J. Effect of surface treatment on the photocatalytic activity and hydrophilic property of the sol-gel derived TiO₂ thin films [J]. Materials Research Bulletin, 2001, 36(1/2):97-107.
- [43] BECK J S, VAURTLI J C, ROTH W J, et al. A new family of mesoporous molecular sieves prepared with liquid crystal templates [J]. Journal of the American Chemical Society, 1992, 114(27):10834-10843.

- [44] YIN J B, ZHAO X P. Enhanced electrorheological activity of mesoporous Cr-doped TiO₂ from activated [J]. The Journal of Physical Chemistry B, 2006, 110(26):12916-12925.
- [45] ANANDAN S, SATHISH KUMAR P, PUGAZHENTHIRAN N, et al. Effect of loaded silver nanoparticles on TiO₂ for photocatalytic degradation of acid red 88 [J]. Solar Energy Materials and Solar Cells, 2008, 92(7):929-937.
- [46] SUBRAMANIAN V, WOLF E, KAMAT P V. Semiconductor-metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO₂ films? [J]. The Journal of Physical Chemistry B, 2001, 105(46):11439-11446.

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- [14] 蔡如钰. 基于人工神经网络的夜光藻密度预测模型 [J]. 中国环境监测, 2001, 17(6):52-55.
CHAI R Y. Artificial neural network predicting model of noctiluca scintillans density and physical and chemical parameters [J]. Environmental Monitoring in China, 2001, 17(6):52-55.
- [15] 高为炳. 变结构控制理论基础 [M]. 北京: 中国科学技术出版社, 1990.
GAO W B. The Theory of Variable Structure Control [M]. Beijing: Science and Technology of China Press, 1990.
- [16] 胡跃明. 变结构控制理论与应用 [M]. 北京: 科学出版社, 2003.
HU Y M. Variable Structure Control Theory and Application [M]. Beijing: Science Press, 2003.
- [17] 姚琼荃, 黄继起, 吴汉松. 变结构控制系统 [M]. 重庆: 重庆大学出版社, 1997.
YAO Q H, HUANG J Q, WU H S. The Variable Structure Control Systems [M]. Chongqing: Chongqing University Press, 1997.

- [18] 胡剑波, 庄开宇. 高级变结构控制理论及应用 [M]. 西安: 西北工业大学出版社, 2008.
HU J B, ZHUANG K Y. Advanced Variable Structure Control Theory and Application [M]. Xi'an: Northwestern Polytechnical University Press, 2008.
- [19] 高为炳. 非线性控制系统导论 [M]. 北京: 科学出版社, 1988.
GAO W B. Introduction on Linear Systems [M]. Beijing: Science Press, 1988.
- [20] ZIRILLI A, ROBERTS G N, TIANO A, et al. Adaptive steering of a containership based on neural networks [J]. Int Journal of Adaptive Control and Signal Processing, 2000, 14:849-873.
- [21] POWELL M J D. Radial Basis Functions for Multivariable Interpolation: A Review [M]. New York: Clarendon Press, 1987.

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