Semiconductor Photocatalyst of Tin Oxide Quantum Dots Prepared in Aqueous Solution for Degradation of Organic Pollutants in Contaminated Water

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Stannous chloride and thiourea are used as source materials to prepare SnO2 quantum dots in the aqueous solution by a facile hydrolysis-oxidation process. The quantum dots have an average size of 1.9 nm with good dispersibility as well as long-term stability, and are validated to be an effective photocatalyst for the degradation of organic oil pollutants in contaminated water. The pollutant is removed by the quantum dots exposed to ultraviolet-visible irradiation at room temperature. The optimized condition is concluded to be a solution with quantum dot concentration of 10⁻³ mol/L and the degradation speed reaches the maximum at the 12 th hour after irradiation. After 48 hours, 91.9 % of octane is removed, concluding a high degradation efficiency. The prepared SnO2 quantum dots are potentially applicable in the remediation of marine environment as they hold the advantages of high efficiency, low cost and being environmental-friendly. The promotion and inhibition mechanisms of the photocatalytic SnO2 QDs at low and high concentrations are discussed.

Keywords: tin oxide, quantum dot, photocatalyst, pollution remediation, water environment.

1. INTRODUCTION

Recent statistics reported that there were about 3 oil spill incidents beyond 50 tons in China and 1049 tons of oil were lost to seawater annually [1]. The oil content of the seawater in the most of coastal areas had exceeded the water quality criteria (WQC) by 10 – 100 times [2]. Several conventional methods had been developed to remove the oil waste in the contaminated water but they were slow in processing, difficult in operation, low in removal efficiency and expensive in price [3 – 5]. Therefore, it is of great practical significance to degrade marine organic oil pollution by developing a novel method, which is of low cost, high degradation efficiency, safety and being environment-friendly.

The quantum dot (QD) is a kind of semiconductor with dimensions of several nanometers. It is highly chemical-active due to the large specific surface area and insufficient coordination atoms on surface, which has a large percentage of suspended bonds. When excited by external irradiation with sufficient energy, the valence electrons are provided possibility to transit to conduction band, forming electron-hole pairs. The excited electrons are able to interact with the adsorbates on the surface of QDs. When the adsorbates are organic pollutants, such as fuel oil, diesel or other petrochemical products, they will be oxidized to carbon dioxide and water by the electrons in the conduction band. In this process, the degradation of organic pollutants is completed with the assistance of QD photocatalysts [6 – 9]. There are a dozen types of semiconductor QD, such as ZnS, CdS, WO3, MoS2 as well as TiO2-based nanomaterials [10–16] and among them TiO2 is the most popular photocatalyst [17]. However, its photocatalytic activity is suppressed by the high compensation rate of electron-hole pairs. Meanwhile, tin oxide (SnO2) is another semiconductor photocatalyst candidate that has the characteristics of good stability, low-cost and simple preparation [18 – 20]. Furthermore, it is free of toxic elements and has good compatibility with the natural environment. Thus, it has the unique advantage to be applicable in oil pollution degradation and environment remediation.

In the present work, SnO2 QDs are prepared in aqueous solution with SnCl2·2H2O as the raw material and CH3N2S as the catalyst. The photocatalytic performance of SnO2 QDs is investigated by the degradation of octane in the contaminated water. An effective method is obtained to remove organic pollutants for environment remediation. The influences of QD concentration and irradiation time on photocatalytic properties are concluded. The mechanism of semiconductor QD photocatalyst is also discussed.

2. EXPERIMENTAL DETAILS

SnO2 QDs were prepared from the analytical source reagents of SnCl2·2H2O and CH3N2S by a facile method, which had been described before [21, 22]. SnCl2·2H2O and CH3N2S were mixed with mole ratio of 10:1 by dissolving into deionized water. The mixture was stirred in a magnetic stirring apparatus for 24 hours at room temperature. The QD concentration in aqueous solution was indicated by the concentration of Sn atoms. The initial QD concentration was kept to be 0.2 mol/L and the samples were diluted to 10⁻⁵ – 10⁻⁴ mol/L for further operations.

The crystal structure of SnO2 QDs was analyzed by X-ray diffraction (XRD, D/MAX-Ultima, Rigaku, Tokyo, Japan). The morphology was observed by high resolution transmission electron microscopy (HRTEM, JEM-3200FS, Japan). The morphology was observed by high resolution transmission electron microscopy (HRTEM, JEM-3200FS, Japan).
JEOL, Tokyo, Japan) and atomic force microscopy (AFM, Bruker Dimension Icon, Bruker, Karlsruhe, Germany). The Zeta potential was obtained by Malvern Zetasizer Nano ZS 90 (Malvern Panalytical Ltd., Malvern).

Mercury lamp

Quartz bottle

Fig. 1. Schematic drawing of facilities for octane degradation in quartz bottles under the irradiation from a high pressure mercury lamp

The photocatalytic performance of SnO\textsubscript{2} QDs was evaluated by the degradation of octane under the irradiation of ultraviolet-visible (UV-Vis) light at room temperature. The schematic drawing of the facilities for octane degradation is illustrated in 0. A high pressure mercury lamp (LT250, Lantian Development, Hebei, China) was employed to produce the emission of 150 W, the spectrum of which was shown in 0 inset. Octane (C\textsubscript{8}H\textsubscript{18}), which was the main compound in fuel oil, was selected to be the representative of organic pollutants in contaminated water. Octane was weighed and commingled into 30 ml SnO\textsubscript{2} QD aqueous solution with a certain QD concentration and the suspension solution was stirred in high-purity quartz bottles for 30 min. Then, the solution was exposed to irradiation for 2–48 hours. After degradation under irradiation, the remaining octane was separated and weighed. The degradation efficiency ($D$) was defined to be $D = \left(1 - \frac{m}{m_0}\right) \times 100\%$, where $m$ and $m_0$ were the mass of octane before and after the degradation, respectively.

3. RESULTS AND DISCUSSION

0 shows the HRTEM morphology and macroscopical observation of SnO\textsubscript{2} QDs in the aqueous solution. The aqueous solution appears to be transparent in yellow and can be maintained stable for month because of the Zeta potential of 17 mV. The QDs have an average grain size of 1.9 nm with good dispersibility and uniformity, as shown by the size distribution in 0 c. Some clear diffraction patterns of crystallite facets can also be observed, showing a good crystallinity of SnO\textsubscript{2} QDs. 0 shows the AFM morphology of the SnO\textsubscript{2} QD thin film, which is spin-coated on a substrate of polished silicon wafer. The morphology of thin film appears to be uniform and most positions have a relative height between –2 to 2 nm. Most of the height differences among neighboring positions are within ±1 nm, illustrating the grain size of 2 nm.

Fig. 2. Morphology of SnO\textsubscript{2} quantum dots: a – HRTEM; b – photo; c – size distribution
Fig. 3. AFM observation of SnO₂ quantum dots spin-coated on a substrate of polished silicon wafer reveals the XRD pattern of SnO₂ QDs with standard diffraction peaks [23]. An obvious (211) peak is observed while the (110) and (101) peaks are inapparent. The crystallite size of QDs is calculated to be 2.0 nm from the (211) peak according to Scherrer’s formula and this conclusion is consistent with the results from HRTEM and AFM observations.

Fig. 4. XRD pattern of SnO₂ quantum dots with standard diffraction peaks

Fig. 5. The influence of QD concentration on degradation of the octane pollutant

Fig. 6. Octane degradation performance of SnO₂ quantum dots with concentration of 10⁻³ mol/L and deionized water in a period of 48 hours

At this time, 91.9 % octane is removed by the SnO₂
QDs under irradiation. Compared to the photocatalytic activity of the popular TiO$_2$-based nanostructures, which degradation efficiency are 87.5 % to quinalphos [25], 91.7 % to 2-chlorophenol [25] as well as 90 % [26] and 97.6 % [15] to Rhodamin B, the present SnO$_2$ QDs show a degradation performance in the high level. However, the degradation efficiency is not only decided by the characteristics of photocatalysts, but also influenced by the properties of target organics. Moreover, the environmental conditions of pH value, oxygen supply and irradiation power are the key parameters that decide the photocatalytic activity. Nevertheless, the present degradation efficiency of SnO$_2$ QDs shows a bright prospect of the photocatalyst for practical application in water remediation.

4. CONCLUSIONS

The SnO$_2$ QDs are prepared in the aqueous solution via a facile hydrolysis-oxidation process. The average size of QDs is concluded to be 1.9 nm and a Zeta potential of 17 mV guarantees a good dispersibility as well as long-term stability in the aqueous solution. The photocatalytic performance of QDs is validated by the degradation of octane in water under irradiation at room temperature. A high degradation efficiency of 91.9 % is obtained after 48 hour irradiation. The QDs with concentration of 10$^{-3}$ mol/L shows the maximum degradation efficiency and the degradation speed reaches the peak at the 12th hour. Two mechanisms are discussed in the removal of octane pollutant. One of them promotes the degradation at low QD concentration and the other one leads to inhibition of photocatalytic performance at high QD concentration because of the self-inhibition between SnO$_2$ QDs.

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REFERENCES


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