

## 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 SnO<sub>2</sub> 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<sup>-3</sup> 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 SnO<sub>2</sub> 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 SnO<sub>2</sub> 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, WO<sub>3</sub>, MoS<sub>2</sub> as well as TiO<sub>2</sub>-based nanomaterials [10–16] and among them TiO<sub>2</sub> is the most popular photocatalyst [17]. However, its

photocatalytic activity is suppressed by the high compensation rate of electron-hole pairs. Meanwhile, tin oxide (SnO<sub>2</sub>) 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, SnO<sub>2</sub> QDs are prepared in aqueous solution with SnCl<sub>2</sub>·2H<sub>2</sub>O as the raw material and CH<sub>4</sub>N<sub>2</sub>S as the catalyst. The photocatalytic performance of SnO<sub>2</sub> 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.

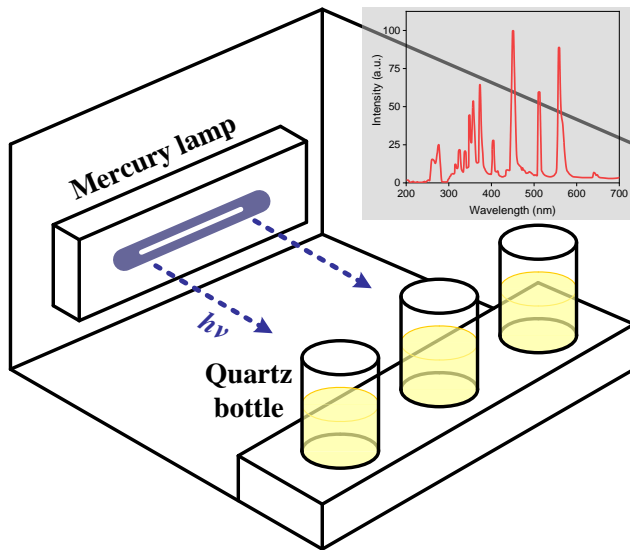
### 2. EXPERIMENTAL DETAILS

SnO<sub>2</sub> QDs were prepared from the analytical source reagents of SnCl<sub>2</sub>·2H<sub>2</sub>O and CH<sub>4</sub>N<sub>2</sub>S by a facile method, which had been described before [21, 22]. SnCl<sub>2</sub>·2H<sub>2</sub>O and CH<sub>4</sub>N<sub>2</sub>S 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<sup>-5</sup>–10<sup>-1</sup> mol/L for further operations.

The crystal structure of SnO<sub>2</sub> 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,

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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).



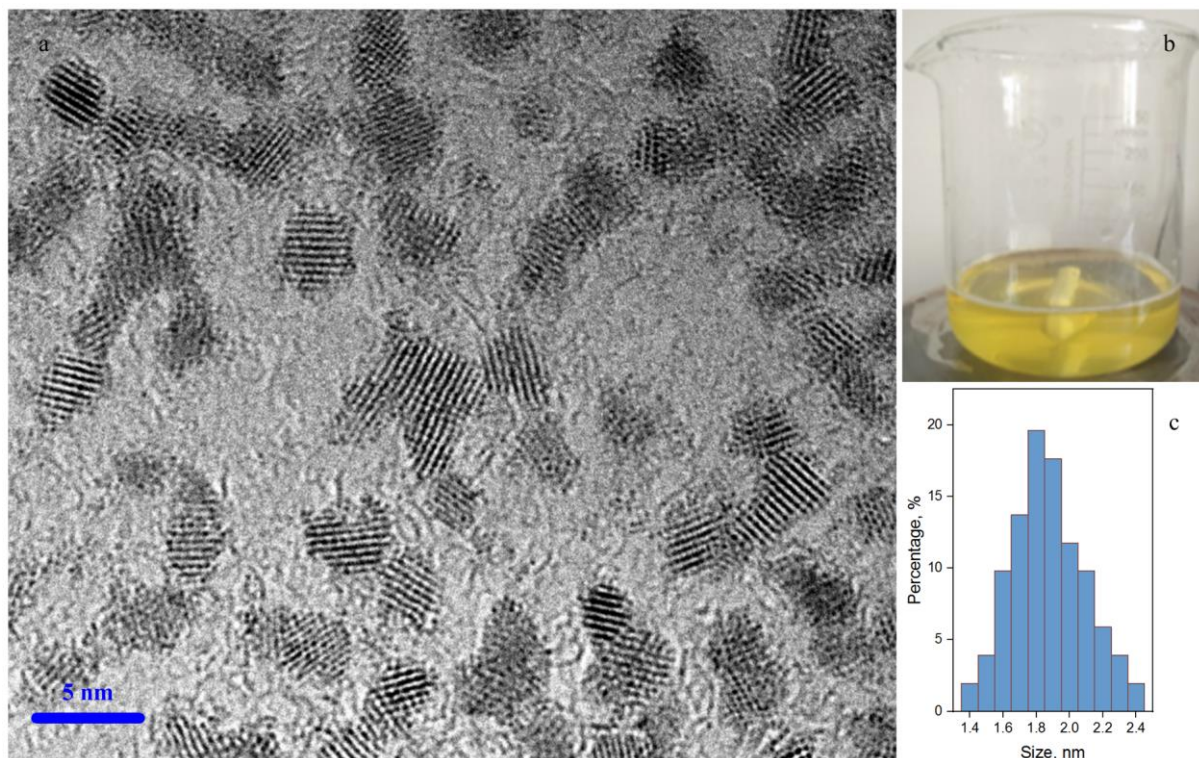
**Fig. 1.** Schematic drawing of facilities for octane degradation in quartz bottles under the irradiation from a high pressure mercury lamp

The photocatalytic performance of SnO<sub>2</sub> 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,

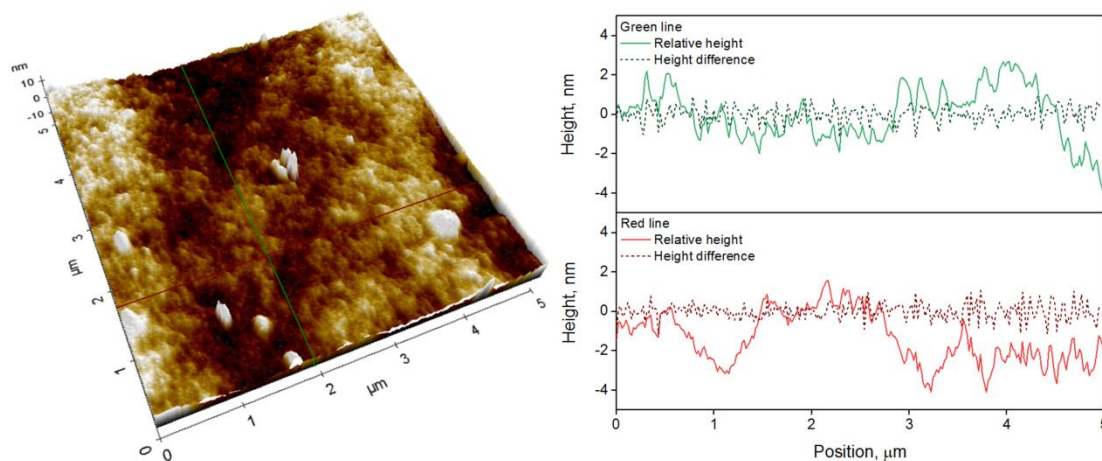
the spectrum of which was shown in 0 inset. Octane (C<sub>8</sub>H<sub>18</sub>), which was the main compound in fuel oil, was selected to be the representative of organic pollutants in contaminated water. Octane was weighed and commingled into 30 ml SnO<sub>2</sub> QD aqueous solution with a certain 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  $D = (1 - m/m_0) \times 100\%$ , where *m* and *m*<sub>0</sub> 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<sub>2</sub> 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<sub>2</sub> QDs. 0 shows the AFM morphology of the SnO<sub>2</sub> 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.

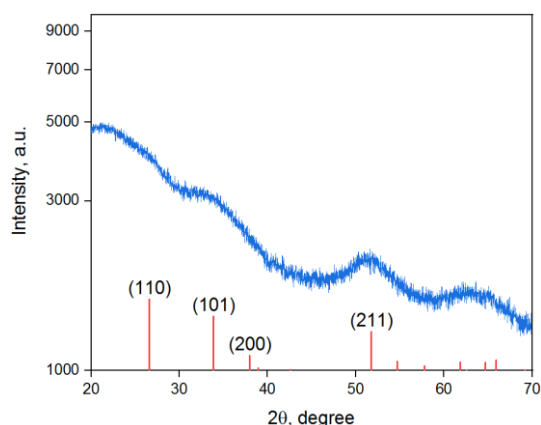


**Fig. 2.** Morphology of SnO<sub>2</sub> quantum dots: a – HRTEM; b – photo; c – size distribution



**Fig. 3.** AFM observation of SnO<sub>2</sub> quantum dots spin-coated on a substrate of polished silicon wafer

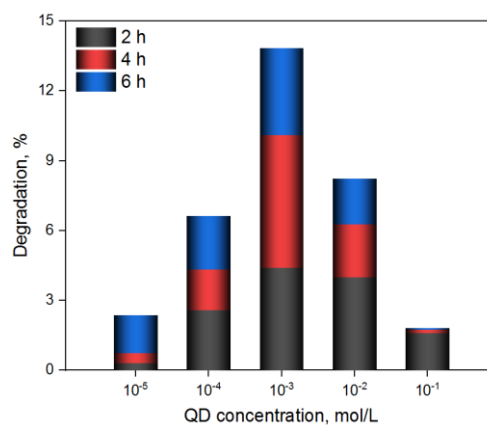
0 reveals the XRD pattern of SnO<sub>2</sub> QDs with standard diffraction peaks [23]. An obvious (211) peak is observed while the (110) and (101) peaks are inapparent. The crystallite size of QDs is calculated to be 2.0 nm from the (211) peak according to Scherrer's formula and this conclusion is consistent with the results from HRTEM and AFM observations.



**Fig. 4.** XRD pattern of SnO<sub>2</sub> quantum dots with standard diffraction peaks

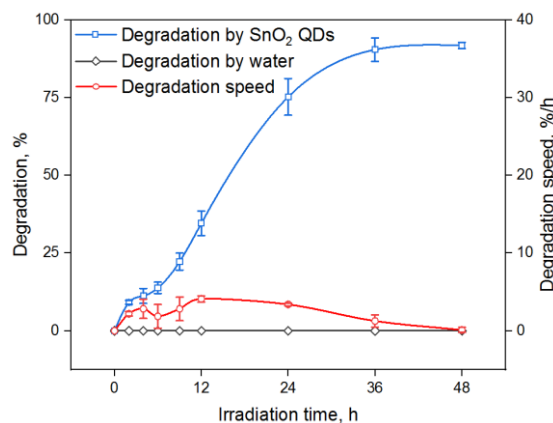
0 illustrates the influence of QD concentration on the degradation efficiency of octane. An optimized QD concentration is observed at 10<sup>-3</sup> mol/L, which removes 13.8 % of octane in 6 hours. The optimized concentration infers that there are two mechanisms that influence the degradation performance of SnO<sub>2</sub> QDs. One of them promotes the degradation under low QD concentration while the other one makes inhibition of octane elimination. In general, the degradation mechanism of QD photocatalyst can be ascribed to the oxidation of organic pollutants by the electrons, which are activated by light irradiation. When the QD concentration is low, the number of photogenerated electrons is so small that the degradation efficiency is quite limited. With the increase of QD concentration, the octane degradation is promoted by the increasing electrons activated from QDs. However, when the QD concentration reaches to a certain level, the possibility of collision between QDs becomes remarkable based on Brownian motions. In this case, there is a self-inhibition effect [24] that the photogenerated electrons on the QD surface are captured by a neighbor grain, which

prevents electrons from interacting with octane molecules. Therefore, the photocatalytic process is interrupted and a decreasing degradation efficiency is observed.



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

**Error! Reference source not found.** reveals the performance of SnO<sub>2</sub> QDs with concentration of 10<sup>-3</sup> mol/L on octane degradation in a period of 48 hours. The degradation speed reaches the maximum of 4.1 %/h at irradiation time of the 12 th hour. The speed slows down when further octane degradation takes place and approaches to zero at the 48 th hour.



**Fig. 6.** Octane degradation performance of SnO<sub>2</sub> quantum dots with concentration of 10<sup>-3</sup> mol/L and deionized water in a period of 48 hours



At this time, 91.9 % octane is removed by the SnO<sub>2</sub> QDs under irradiation. Compared to the photocatalytic activity of the popular TiO<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> QDs shows a bright prospect of the photocatalyst for practical application in water remediation.

#### 4. CONCLUSIONS

The SnO<sub>2</sub> 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<sup>-3</sup> mol/L shows the maximum degradation efficiency and the degradation speed reaches the peak at the 12 th 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<sub>2</sub> QDs.

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