



Photochemical synthesis of iridium submicroparticles and their application in catalytic reduction of methylene blue

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ABSTRACT

Iridium submicroparticles (SMPs) were prepared at room temperature via a photochemical reduction route in aqueous solution with polyvinylpyrrolidone (PVP) as capping agent. We found that the incident wavelength has a great effect on the growth rate of Ir SMPs. The shorter the wavelength is, the faster the generation of Ir SMPs is. The Ir SMPs were composed of the Ir nanoparticles (NPs), showing discus-like hierarchical structure. The presence of PVP during photochemical synthesis is crucial for the discus-like morphology and the hierarchical structure. The as-prepared Ir SMPs exhibit high catalytic activity, good recyclability and stability for the reduction of methylene blue (MB). Moreover, the hierarchical structure allows the presence of large amounts of Ir NPs as a group, which significantly improves the separation efficiency of the catalyst from reaction media by centrifugation.

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1. Introduction

Platinum group metals have attracted extensive attention due to their potential applications in various fields including detecting and sensing [1,2], fuel cells [3,4], and catalysis [5,6]. Among the platinum group metals, iridium is well-known for its catalytic activity for organic dye degradation [7], hydrogenation reaction [8], and oxygen reduction reaction [9]. However, the low terrestrial abundance of Ir results in its high cost, and greatly restricts its large-scale applications in industry. Therefore, the recovery of Ir catalysts is extremely important for its application. It is highly desirable to improve both the catalytic activity and the recovery efficiency of the Ir catalysts. The activity of Ir catalysts can be improved through the following two ways: (1) controlling the morphology of Ir catalysts to expose more active crystalline facets, and (2) enlarging the specific surface area of Ir catalysts by simply decreasing the particle size. However, decreasing the size of Ir catalysts makes it difficult to recover the catalyst for recycling, because small catalyst particles are more difficult to be separated from the reaction system via the simple separation process such as centrifugation and chemical precipitation.

From the perspective of improving the catalytic activity and the recycling efficiency of Ir catalysts, the hierarchical porous Ir submicroparticles (SMPs) composed of small Ir nanoparticles (NPs) are particularly attracting, as the small Ir NPs ensure large specific area of the catalyst, while the submicrometer dimension of SMPs provides great convenience for the separation and recovery of the Ir catalysts. As a consequence, it is highly desirable to prepare Ir NPs and assemble them into submicro-sized structures. In a previous work, we prepared Rh NPs and in the meantime successfully assembled the Rh NPs into spherical hierarchical SMPs with the help of capping agent of polyvinylpyrrolidone (PVP) [10], confirming the feasibility of one-step synthesis of SMPs that are composed of noble metal NPs.

Metal NPs and SMPs are typically synthesized by chemical [11,12], electrochemical [13,14], or photochemical reduction [15–17] of the corresponding precursors. Photochemical synthesis is an important tool for the preparation of metal NPs at room temperature due to the following two reasons. (1) Light irradiation can provide driving force for the reduction of the precursors, thus accelerating the growth of metal NPs [18]. (2) Synthesis reactions driven by light irradiation can be easily started or terminated at any time by simply turning on or off the light [19]. Furthermore, it is possible to modulate the growth rate, size and morphology of metal NPs via tuning the irradiation parameters, such as incident wavelength [20,21], light power density [22], and irradiation

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time. Thus photochemical routes have been widely employed in the synthesis of metal and metal oxide NPs, such as Ag [15,23], Au [24,25], Pd [26], Pt [17], TiO₂ [27], ZnO [28], and MoO_{3-x} [29]. In our previous work, IrO_x NPs were successfully prepared via photoinduced hydrolysis of IrCl₃ [30]. However, the photo-assisted growth of Ir SMPs or NPs is rarely reported. Kundu and Liang reported the morphology-controlled synthesis of Ir NPs and demonstrated that Ir NPs were promising catalysts for organic dye degradation [7]. For all noble-metal-based catalysts, the recyclability and the recovery yield are extremely important issues for their practical application. However, no work concerning the recyclability and the recovery yield of Ir catalysts has been reported.

In a previous work [31], we demonstrated that Ir SMPs with well-defined morphology and uniform size could be prepared via a NaBH₄ reduction approach at elevated temperature. Based on this work, we present here a facile photochemical route to synthesize Ir SMPs at room temperature, in which heating was replaced by UV irradiation to promote the reduction process. The influence of incident wavelength on the growth rate of Ir SMPs was investigated. Morphological characterization results indicate the obtained Ir SMPs are disc-like with high-roughness surface, and are composed of large numbers of small Ir NPs. In addition, we demonstrate that the obtained Ir SMPs show high catalytic activity, good recyclability and high recovery yield for the reduction of methylene blue (MB).

2. Experimental

2.1. Materials

Iridium chloride trihydrate (IrCl₃·3H₂O) and polyvinylpyrrolidone (PVP, MW: 58000) were purchased from Alfa Aesar company. Sodium borohydride (NaBH₄) was obtained from Tianjin Fuchen Chemical Reagents Factory. Sodium hydroxide (NaOH) and absolute ethanol were purchased from Beijing Chemical Reagents Co. Methylene blue was obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with ultrapure water (18 MΩ cm).

2.2. Photochemical synthesis of Ir SMPs

In a typical synthetic procedure, 14 mg IrCl₃·3H₂O and 133 mg PVP were dissolved in 12 mL of water in a beaker, giving a clear yellow solution. Then 8 mL of 25 mM NaBH₄, which was freshly prepared in ice bath, was quickly injected into the above yellow solution. The mixed solution was then placed under the ultraviolet (UV) or monochromatic light irradiation with continuous stirring, and kept at room temperature by a water bath. The UV light was generated from a PLS-SXE300UV xenon lamp equipped with a UV filter (Beijing PerfectLight Science & Technology Co., Ltd., output wavelength: 260–410 nm). Different bandpass filters with the wavelengths required were equipped to output monochromatic light. The distance from the lamp to the reaction solution was 15 cm for polychromatic UV irradiation and the power density of polychromatic UV on the solution was 12 mW/cm². While for monochromatic light irradiation, the distance was adjusted to ensure a power density of 5 mW/cm² for all the wavelengths. To monitor the reaction progress, parts of the solution were taken out and diluted at fixed time intervals for the UV–vis characterization.

After 3 h of UV irradiation, the solution turned dark brown, indicating the generation of Ir SMPs. The obtained Ir SMPs were separated from the solution via centrifugation at 12000 rpm for 15 min. The collected Ir SMPs were rinsed with copious water until pH 7 was attained, followed by drying in vacuum at 50 °C. The as-

prepared Ir SMP powder was stored in a nitrogen-protected vial. Before the catalytic experiment, 3.6 mg of Ir SMPs was re-dispersed in 0.8 mL of water, giving a colloid solution of Ir SMPs with the concentration of 23.4 mM. Herein the concentration of Ir SMPs is used to reflect the concentration of zero-valent Ir(0) in colloid solution. The colloid solution was stable for several weeks without precipitation. To prepare Ir SMP samples for SEM and TEM characterization, Ir SMPs were re-dispersed in ethanol because ethanol evaporates much more quickly than water.

2.3. Characterization

The UV–vis absorption spectra were obtained from a UV2600 spectrophotometer (Tianmei Co., China). The as-prepared Ir SMPs were characterized by field emission scanning electron microscopy (FE-SEM, Supra-55, Zeiss, Germany, accelerating voltage: 10 kV), transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan, accelerating voltage: 200 kV), and X-ray diffraction (XRD, Rigaku X-ray diffractometer, Japan, Cu Kα source, 40 kV, 40 mA). The as-prepared Ir SMPs were dispersed in ethanol under sonication, and the resulting colloid solution was dropped onto Si substrate or copper grid supported carbon film for SEM or TEM characterizations, respectively. The specific surface area of Ir SMPs was determined by Brunauer–Emmett–Teller method (BET, ASAP 2020, Micromeritics, USA) with nitrogen as adsorption gas. The catalysts powder were placed in a test tube and degassed for 10 h at 100 °C under vacuum ($p < 10^{-4}$ Pa). The specific surface areas of the catalysts were calculated based on BET interpretation of the adsorption curves at $p/p_0 = 0.06–0.30$, where p and p_0 are the equilibrium vapor pressure and the saturation vapor pressure of N₂ at 77.35 K respectively. A cross sectional area of 0.162 nm² was assumed for the N₂ molecule.

2.4. Catalytic reduction of MB

The activity of the as-prepared Ir SMPs was evaluated through the catalytic reduction of MB by NaBH₄, and the reaction was carried out in a quartz container at room temperature with magnetic stirring. Firstly, the aqueous colloid solution of as-prepared Ir SMPs (170 μL, 23.4 mM) and 1 mL of 10 mM MB solution were mixed with 38 mL of water in the container under stirring. Then 1 mL of 0.4 M NaBH₄ which was freshly prepared in ice bath, was quickly injected into the mixed solution. The final concentrations of catalyst, MB and NaBH₄ in the solution were 0.1 mM, 0.25 mM and 10 mM, respectively, and the pH value of the mixed solution was 8.0. The reaction completed within 4 s, which was too fast to record the change of UV–vis spectrum with reaction time. Therefore, we only recorded the spectra for the solution before and 4 s after NaBH₄ injection. Before recording the spectra, the Ir SMP catalyst was separated from the solution by centrifugation, and the supernatant was diluted 25 times. In addition, we intentionally slowed down the reaction by lowering the concentrations of the Ir SMP catalyst in the mixed solution by 50 times. The final concentrations of catalyst, MB and NaBH₄ in the solution were 2.0 μM, 10 μM and 10 mM, respectively, and the pH value of the mixed solution was 7.5. And then UV–vis spectra of the reaction solution were recorded at fixed time intervals without diluting the solution.

3. Results and discussion

3.1. Photochemical generation of Ir SMPs

In this work, UV light was introduced to power the reduction of IrCl₃ by NaBH₄ to produce Ir SMPs, and the reaction process was monitored by UV–vis spectroscopy. Fig. 1 presents the UV–vis spectra of the reaction solution as a function of time in the dark

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