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Synthesis of Hollow Polypyrrole–Platinum Complex Spheres and Their Successful Application as a Catalyst for Decomposition of Hydrogen Peroxide[1]

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Abstract—Hollow pyrrole–platinumpoly (PPy–Pt) complex spheres effectively catalyze the decomposition of hydrogen peroxide to form oxygen. The method used to synthesize the catalysts employs chemical polymerization of pyrrole with potassium hexachloroplatinate(IV) as oxidant and ZSM-5 molecular sieve as a hard template removable by dissolution. ZSM-5 molecular sieve used as template has the following merits: it can be easily removed, it is inexpensive and owing to micrometer size it shows a minimal aggregation. In addition, the use of the zeolite avoids the need for non-volatile surfactants which may be adsorbed onto the synthesized PPy–Pt complex spheres and interfere with their possible applications in catalysis. The new micronsized hollow PPy–Pt complex spheres are produced simply and cost-effectively, and they can be expected to play an important role in wastewater treatment technologies. The synthetic method may represent a novel route to prepare hollow conductive polymer spheres doped by various metals for specific applications.

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In recent decades, hollow spheres with nanometer to micrometer dimensions have been of great interest in many areas of science and technology. The wide variety of application includes the production of capsules suitable for controlled-release of various substances, catalysts, fillers, biomedical instrumentation and coatings. The use of hollow spheres in engineering, and the paint industry is also described. It is in particular their specific structure, surface permeability, large specific area and low density which have rendered them of such interest [1–3]. Polypyrrole (PPy) hollow spheres, particularly, have received a great deal of attention because they exhibit good environmental stability along with high and variable electric conductivity [4, 5]. Various methods have been developed to prepare hollow spheres including the template method in which polystyrene latex spheres [4], silica latex particles [5, 6], metals [7] and metal halides [8] are employed as templates removable by dissolution. The template method showed its feasibility, reproducibility, predictability and uniformity.

Compared to other template materials like polystyrene latex spheres [4, 9–12], silica latex spheres [5, 6, 13], metal [7] and metal halide [8], a template based on ZSM-5 molecular sieve has some advantages. They include quick removal, low cost and minimal aggregation owing to its micrometer size. In addition, the use of non-volatile surfactants can be avoided, which may be adsorbed onto the synthesized pyrrole–platinumpoly (PPy–Pt) complex spheres and interfere with their possible applications in catalysis. Very recently, we developed a new method for preparation of silver core–shell materials and hollow materials by using 5A and ZSM-5 molecular sieves as templates [14, 15]. To the best of our knowledge, there have been few reports on preparation of hollow conductive PPy spheres based on surface modified molecular sieves.

Catalytic decomposition of H_2O_2 is of great importance due to its vast applicability in water treatment technologies [16]. A variety of organic pollutants in wastewaters and soils can be successfully oxidized and degraded by hydrogen peroxide promoted by various catalysts such as pure metals (e.g. Ag, Cu, Fe, Mn, Ni, and Pt) and their oxides supported on silica, alumina and zeolites [16, 17]. Higher rates of decomposition of

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H_2O_2 are usually desired to increase the decomposition rates of the target pollutants [18]. The efficiency of supported catalysts has been found to be high in comparison to unsupported catalysts because in the unsupported state aggregation of catalyst reduces its efficiency [19].

In the present work, we report a facile method for synthesis of micron-sized hollow PPy–Pt complex spheres *via* chemical polymerization of pyrrole using potassium hexachloroplatinate(IV) as oxidant and ZSM-5 molecular sieve as a removable solid template. The catalytic activity of the hollow PPy–Pt complex spheres was investigated in the decomposition of hydrogen peroxide.

EXPERIMENTAL

Materials

Pyrrole monomer was purchased from Sinopharm Chemical Reagent Co., Ltd., dried with potassium hydroxide (2–3 g per 10 ml of pyrrole), then filtered and distilled at reduced pressure. Potassium hexachloroplatinate(IV) was purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. (3-Chloropropyl)triethoxysilane (CPTE) was obtained from Aldrich, and potassium hydroxide (> 82%) was acquired from Regent Chemical Co., Ltd., Tianjin, China. ZSM-5 molecular sieve, supplied by the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, was heated for 4 h at 600°C in a muffle furnace then cooled in a desiccator. Hydrofluoric acid (40%) was supplied by Tianjin Institute of Chemicals, China. Hydrogen peroxide (30%) and sodium hydroxide (> 96%) were purchased from Beihua Fine Chemicals Co., Ltd., Beijing, China. High purity water with resistance > 18.0 MΩ cm was used in all preparations.

Synthesis and Catalysis

ZSM-5 molecular sieve (1 g) was dispersed in a freshly prepared aqueous solution of CPTE (15 ml, 0.3 mol/l). To this mixture 2-propanol (80 ml) and ammonia solution (1 ml, 28.0–30.0 wt %) were added successively. The mixture was reacted for 3 h at 45°C under continuous stirring [20]. The deposits were collected and washed with ethanol and water several times to give CPTE-modified ZSM-5 particles.

The CPTE-modified ZSM-5 (0.2 g) was dispersed in ethanol (15 ml) by sonication for 10 min, then pyrrole monomer (0.4 ml, 5.6 mmol) was added to the dispersion. After sonication for 20 min, an aqueous solution (15 ml) containing K_2PtCl_6 (0.07 g, 0.14 mmol) was added to the suspension, and the mixture was stirred for 12 h to yield uniform ZSM-5 Py–Pt core/shell particles. The solid particles were separated from the reaction medium by centrifuging at 3000 rpm. After thorough washing with water and ethanol, the powdered product was dried at room temperature under vacuum for 4 h. The molecular sieve cores were dissolved by subsequent treatment with dilute hydrofluoric acid to obtain hollow PPy–Pt complex spheres. Specifically, the PPy–Pt-coated ZSM-5 molecular sieve (30 mg) was initially added to aqueous HF solution (50 ml, 7 wt %), and mixed by hand using a shaking motion at a frequency of 10 $\min^{-1}$. After storing for 1 h, the hollow PPy–Pt complex spheres were separated from the reaction medium by centrifuging at 3000 rpm. After thorough washing with water and ethanol, the product was dried at room temperature in vacuum for 4 h.

Decomposition of hydrogen peroxide was performed using a glass apparatus which was a modification of the apparatus described by Eyring and Daniels [21]. The apparatus was tested for gas leakage, then aqueous H_2O_2 solution (10 ml, 20 wt %) was poured carefully into an Erlenmeyer flask (25 ml) placed in the thermostat. After equilibration at 25°C, the hollow PPy–Pt complex spheres catalyst (3 mg) and NaOH (10 ml, 2 mol/l) were rapidly added successively to the flask, which was then closed with a stopper. The temperature of the reaction mixture was kept constant to within ±0.02°C, and the reaction mixture was continuously stirred at a constant rate to prevent the liberated oxygen from forming a supersaturated solution. Before reaching the gas burette the oxygen transferred through the glass wool was saturated with concentrated sulfuric acid to remove some impurities. The rate of decomposition of hydrogen peroxide was evaluated by measuring the volume of oxygen produced as a function of time. The experimental data reported herein are the average values recorded in five runs.

Characterization

Fourier transform infrared (FT-IR) spectra of the samples in KBr pellets were obtained with a NICOLET 5700 FT-IR spectrometer.

The Pt content in the hollow PPy–Pt complex spheres was measured using inductively coupled plasma mass spectrometry (ICP-MS, Nippon Jarrel Ash, ICAP575II) to analyze samples that had been dissolved in nitric acid.

Field emission scanning electron microscope (FESEM) images of ZSM-5/PPy–Pt core/shell particles and hollow PPy–Pt complex spheres were registered using a SUPRA35 FESEM instrument operated at 20.00 kV.

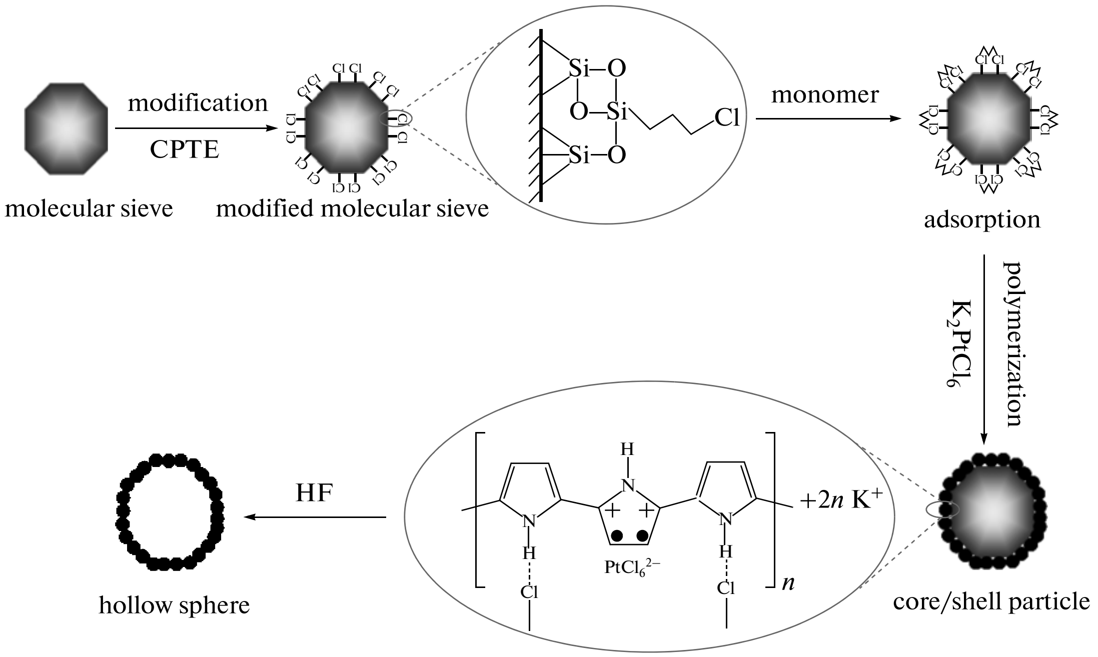

Fig. 1. Schematic representation of the synthesis of the hollow PPy–Pt complex spheres.

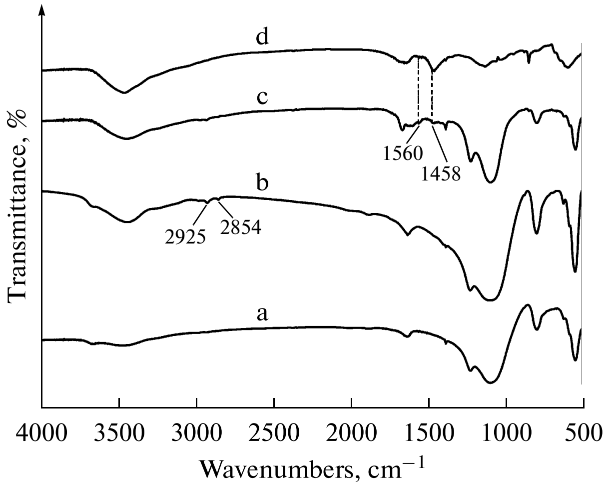

Fig. 2. FT-IR spectra for ZSM-5 molecular sieve (a), CPTE-modified ZSM-5 (b), ZSM-5/PPy–Pt core/shell particles (c), and hollow PPy–Pt complex spheres (d).

RESULTS AND DISCUSSION

The surface of ZSM-5 molecular sieve is hydrophilic and that of pyrrole is hydrophobic. Consequently, pyrrole is difficult to absorb on the surface of ZSM-5 and then polymerize to form a PPy shell. For that reason, prior to depositing pyrrole CPTE with bifunctional groups was assembled on the surface of the molecular sieve by forming Si–O–Si bonds under base-catalyzed hydrolysis. Due to the presence of the C–Cl groups of CPTE, PPy could be readily deposited on the CPTE-modified surface *via* hydrogen bonding interaction. A coating-like structure composed of PPy was then formed by chemical polymerization of the absorbed pyrrole in the presence of K_2PtCl_6 to cover the modified ZSM-5 core. The molecular sieve cores were dissolved by subsequent treatment with dilute hydrofluoric acid to obtain hollow PPy–Pt complex spheres. An outline of the synthesis is shown in Fig. 1.

Figure 2 shows FT-IR spectra of the ZSM-5 molecular sieve, CPTE-modified ZSM-5, the ZSM-5/PPy–Pt core/shell particles, and the hollow PPy–Pt complex spheres. The infrared spectra of samples were

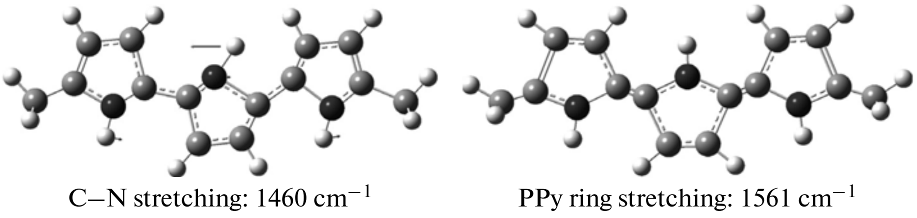

Fig. 3. The calculated normal modes for C–N stretching and PPy ring stretching.

recorded over the range 4000 to 500 cm^{-1} with 2 cm^{-1} resolution. Compared to the FT-IR spectrum of ZSM-5, the CPTE-modified ZSM-5 exhibited absorption peaks at 2925 and 2854 cm^{-1} which are attributed to methylene C–H stretching vibrations. This indicates that the surface of the ZSM-5 molecular sieve was modified by CPTE. The absorption bands around 1560 and 1458 cm^{-1} characteristic of PPy were observed in the spectra of both the ZSM-5/PPy–Pt core/shell particles and the hollow PPy–Pt complex spheres. Those absorptions are assigned to PPy ring stretching and conjugated C–N stretching [22–25], respectively, and show that PPy was successfully coated on the surface of the ZSM-5 particles.

To confirm the experimental result, a frequency analysis was done with Gaussian 03 software [26]. The ground state geometry of PPy with three monomer units was optimized with density functional theory [27], B3LYP functional [28] and 6-31G basis set, and the frequency analysis was performed at the same level of theory. To compare the calculation data with experimental results the scale factor of the frequencies was set to 0.987 [29]. Our theoretical calculations supported the experimental result that the surface of the ZSM-5 molecular sieves was coated by PPy: vibrations of these normal modes were labeled (Fig. 3).

Based on the ICP-MS analysis, the Pt content in the hollow PPy–Pt complex spheres was 890.0 μg/kg, demonstrating that PPy was successfully doped with Pt.

FESEM was used to analyze the extent of surface coverage, morphology, size distribution and thickness of the ZSM-5 particles, ZSM-5/PPy–Pt core/shell particles, and hollow PPy–Pt complex spheres. Examples of FESEM images are shown in Fig. 4. According to measurements made with FESEM, typical particles of ZSM-5 have nearly spherical shape with size in the range of 1 to 10 μm, and most of particles are about 1.5 μm in size (see Fig. 4f). An FESEM image of ZSM-5/PPy–Pt core/shell particles shown in Fig. 4a suggests that a relatively continuous PPy–Pt layer was formed. The coated particles were 2–8 μm in size, and their morphologies were significantly different from those of the ZSM-5 particles. As shown in Figs. 4b and 4c, the hollow PPy–Pt complex spheres obtained after dissolution of the cores were approximately spherical in shape and their morphologies were very rough, which should be of benefit for applications in catalysis. The PPy–Pt complex partial sphere shown in Figs. 4d and 4c was obtained by extensive sonication, and confirmed the hollow nature of the PPy–Pt complex spheres. Figs. 4d and 4c indicate that the outer surface of the sphere was very rough with a thick, compact wall 100 to 200 nm in thickness. The area (1 × 1.5 μm^2) of the dark region in the central part (in contrast to the light wall) agrees well with the size of the ZSM-5 particles. This excludes the possibility of formation of solid spheres and confirms the hollow structure of the PPy–Pt complex spheres. We have thus demonstrated that micron-sized hollow PPy–Pt complex spheres can be readily synthesized by using ZSM-5 molecular sieve as a template and K_2PtCl_6 as oxidant, followed by removal of the template. To the best of our knowledge, this is the first synthesis of hollow PPy–Pt complex spheres *via* chemical polymerization using a molecular sieve as a template.

The decomposition of hydrogen peroxide was carried out at 25 ± 0.02°C using the hollow PPy–Pt complex spheres as the catalyst. Because the decomposition of H_2O_2 yields oxygen, the rate of formation of oxygen reflects the rate of decomposition of hydrogen peroxide. An average rate of formation of oxygen for any time interval can be calculated by dividing the change in the volume of oxygen evolved by the time interval:

$$W = \Delta V_{\text{oxygen}}/\Delta t, \tag{1}$$

where W is the average rate of formation of oxygen, ΔV_{oxygen} denotes the change in the volume of oxygen, and Δt is the time interval. The results of a typical experiment are summarized in Fig. 5. It is apparent that a very small amount of the hollow PPy–Pt complex spheres (0.3% of the mass of H_2O_2) improves the efficiency of decomposition of hydrogen peroxide, because the slope of the curves is steeper in the presence of the catalyst. The average rate of the oxygen formation in the presence of the hollow PPy–Pt complex spheres increased to 4.7 ml/min in the period of 0.25–6 min, which is about 2.5 times that of the rate (1.9 ml/min) observed in the absence of the catalyst.

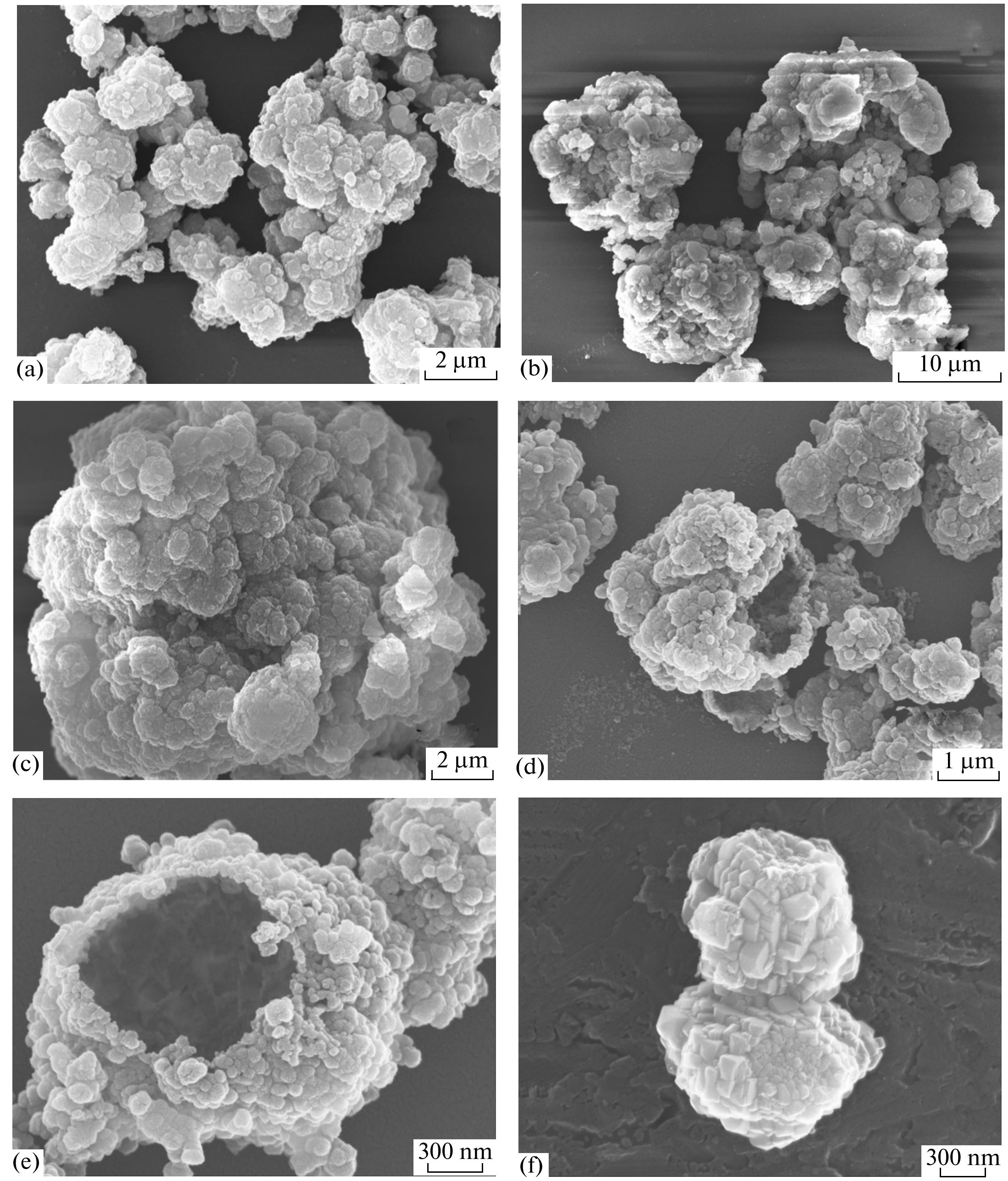

Fig. 4. FESEM images of ZSM-5/PPy–Pt core/shell particles (a), hollow PPy–Pt complex spheres (b), a hollow PPy–Pt complex sphere at higher magnification (c), broken hollow PPy–Pt complex spheres (d), a broken hollow PPy–Pt complex sphere at higher magnification (e), and ZSM-5 (f).

Experiments also showed that the average rate of oxygen formation markedly increased with NaOH added to the system. A blank test conducted in the absence of the catalyst and NaOH gave the average rate of oxygen formation of 2.7 ml/min for the period of 0.25–2 min. By contrast, the results with the hollow PPy–Pt complex spheres and NaOH show that the rate of the formation of oxygen can be increased to an average value of 39.9 ml/min during the same time interval, which is about 14.8 times higher than that of the average rate in the blank test. The experimental results indicate that the hollow PPy–Pt complex spheres are active for decomposition of hydrogen peroxide, and they are expected to play an important role in wastewater treatment technologies. The synthetic method reported here suggests a very promising way for the preparation

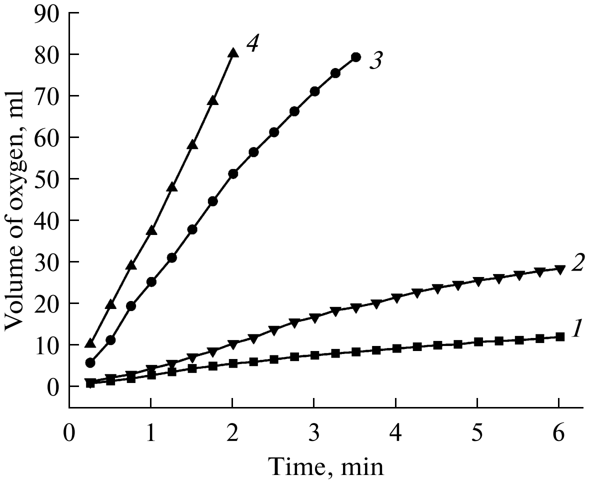

Fig. 5. Volume of oxygen formed by decomposition of hydrogen peroxide at 25°C: *1*—in the absence of catalyst and NaOH, *2*—in the presence of catalyst, *3*—in the presence of NaOH, *4*—in the presence of catalyst and NaOH.

of other hollow conductive polymer spheres doped by various metals.

To summarize, we were able to synthesize hollow PPy–Pt complex spheres using ZSM-5 molecular sieve as a removable template *via* chemical polymerization in which potassium hexachloroplatinate(IV) was used as oxidant. The formation of hollow PPy–Pt complex structures was confirmed by the FT-IR and FESEM analysis coupled with the ICP-MS characterization. The formation of hollow PPy–Pt complex spheres demonstrates that ZSM-5 molecular sieve is an effective template since it can be readily modified and removed, moreover it is inexpensive and shows a minimal aggregation. The hollow PPy–Pt complex spheres are catalytically active toward decomposition of hydrogen peroxide, and may weaken self-poisoning of the catalyst in water treatment due to a very small dosage used. The new hollow PPy–Pt complex spheres are produced simply and cost-effectively, and they are expected to play an important role in catalysis. The synthetic method reported here suggests a very promising way for the preparation of other hollow conductive polymer spheres doped by various metals.

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