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# Photo-driven synthesis of hollow platinum nanospheres

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**Abstract:** *Hollow platinum nanospheres with a porous and uniform shell are prepared by using templating polystyrene beads coated with a porphyrin photocatalyst under white light irradiation. The porphyrin molecules on the surface of the polystyrene beads localize the reduction of aqueous platinum solution onto the bead surface with the aid of ascorbic acid as the electron donor. The templating polystyrene spheres can be removed by etching with chloroform, resulting in hollow, porous, platinum nanospheres. The shell thickness of the spheres can be controlled by varying the concentration of platinum precursor.*

**Keywords:** Photocatalysis, Hollow Spheres, Platinum.

## 1. Introduction

Hollow nanospheres possess tunable structural features such as shell thickness, interior cavity size, and chemical composition, leading to relatively high surface area, low density, material economy, and reduced cost compared with their solid counterparts[1]. Metallic hollow nanospheres are of special interest and importance due to various applications in biomedical[2,3], catalytic[4], and optical sciences[5]. We now report a new method utilizing commercial polystyrene beads covered with a photocatalyst to grow uniform and porous platinum nanoshells, followed by core removal with an organic solvent resulting in hollow platinum nanospheres. Synthetic control over the nanoshells is realized by simply varying the concentration of platinum precursor.

## 2. Experimental

In a typical synthesis, 1 mL aqueous suspension of beads with an average diameter of 99-nm (10.2 wt% solid content) is mixed with 9 mL of ethanol containing 17.6 mg of tin-IV-octaethyl porphyrin (SnOEP) in a round-bottom flask. Subsequently, ethanol and water in the mixture are removed by rotary evaporation resulting in pink flakes peeled off the glass wall. The flakes, composed of polystyrene beads and SnOEP, are collected and further dried in a desiccator under vacuum. SnOEP molecules are hydrophobic; they are expected to reside on the hydrophobic surface of the beads. 1.76 mL of 20 mM aged $K_2PtCl_4$ aqueous solution and 0.24 mL Nanopure water are mixed with 2 mg of the dried beads coated with SnOEP. The mixture is sonicated for an hour in a water-bath cleaner to well suspend the beads. Next, 2 mL of 150 mM ascorbic acid aqueous solution is added to the above mixture. The reaction system is allowed to react under stirring and dual incandescent irradiation (800

nmol-cm$^{-2}$-s$^{-1}$) for 30 minutes. After discontinuation of the stirring, colourless transparent supernatant with black precipitates at the bottom is observed, suggestive of the completeness of the reduction reaction.

### 3. Results and discussion

Transmission electron microscope analysis on the black precipitate reveals that polystyrene core/platinum shell nanostructures are obtained. Based on the measurement of 100 individual shells in different areas, the platinum nanoshells are determined to be 12.4 ± 1.8 nm in thickness. The monodispersity of the nanoshells arises from the photocatalytic seeding process, which is capable of rapidly generating a large number of initial seeds on each bead according to the following simplified equations:

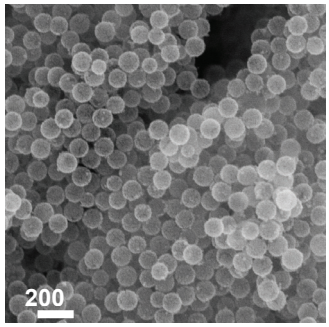
1)$SnOEP + h\nu = SnOEP^*$

2)$SnOEP^* + ED = SnOEP^{-\bullet} + ED_{ox}$

3)$2SnOEP^{-\bullet} + Pt^{2+} = 2SnOEP + Pt^0$

where ascorbic acid is used as the electron donor (ED). The central polystyrene core and SnOEP can be readily etched away by placing dried samples into chloroform for at least 5 minutes under ambient conditions. Most of the platinum nanoshells are intact after chloroform treatment as shown in Fig. 1, suggesting that the platinum shells are well formed even with nanopores embedded.

**Figure 1.** SEM images of hollow platinum nanospheres after chloroform etching.




## 4. Conclusions

In conclusion, a novel method for the preparation of hollow platinum nanospheres with a uniform and porous shell has been developed by photocatalytic seeding and autocatalytic growth of platinum on polystyrene beads. The polystyrene core/platinum shell and the hollow platinum nanospheres have potential applications in catalysis and electrocatalysis.

## References

1. Y.D. Yin, R.M. Rioux, C.K. Erdonmez, S. Hughes, G.A. Somorjai, A.P. Alivisatos, Science, 711 (2004) 304.
2. L.R. Hirsch, R.J. Stafford, J.A. Bankson, S.R. Sershen, B. Rivera, R.E. Price, J.D. Hazle, N.J. Halas, J. West, PNAS, 13549 (2003) 100.
3. L.R. Hirsch, J.B Jackson, A. Lee, N.J. Halas, J. West, Anal. Chem., 2377 (2003) 75.
4. S.W. Kim, M. Kim, W.Y. Lee, T. Hyeon, J. Am. Chem. Soc., 7642 (2002) 124.
5. Y.J. Xiong, B. Wiley, J.Y. Chen, Z.Y. Li, Y.D. Yin, Y.N. Xia, Angew. Chem. Int. Ed., 7913 (2005) 44.