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Revealing 3D Information of Porous Catalytic Structures Prepared by Template Methods

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Nanostructures of diverse materials prepared by using monodispersed colloidal spheres as templates have found potential applications in many fields such as photonic crystals, sensors, and catalysts. Such nanostructured materials include polymers, oxides, metals, semiconductor compounds, as well as composites. Polystyrene (PS) beads are commonly used as the templates since the removal of the templates can be achieved by both calcination and dissolution [1,2]. Templates fabricated from a colloidal PS solution consist of many close-packed regions, where 26% void space can be used for filling up with functional materials [2]. After the removal of the PS spheres, the remaining nanostructures have high surface area and 74% spherical void volume, which allow efficient mass transport and further materials modification. These templated nanostructures incorporated with catalytic nanoparticles (NPs) attract a wide range of research interests, due to their potential in reducing and tuning the loading of precious catalytic metals, improving catalytic performance, as well as the scalability for mass production.

In this study, we demonstrate a generic fabrication procedure, previously established in our group, for the preparation of various nanostructured composite materials by using PS spheres as templates. This procedure provides efficient control in decorating surface of nanostructured materials with pre-synthesized NPs. The nanostructured composite materials, offering more options with various material combinations and controllable particle loadings, can be useful as catalytic media in the electrochemical or photochemical fields. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS) were used to characterize the structure and composition of as-prepared nanostructured composites. Focused ion beam (FIB) was also used to assist the characterization of the composite materials by milling and lifting out TEM samples, as well as sequential FIB milling and SEM imaging in order to gain the information on material and structure distribution within the composites.

In an example fabrication procedure for preparing Pt NPs loaded TiO_2 nanostructures, colloidal PS beads were first decorated with pre-synthesized Pt NPs at a desired loading [3]. After purification to remove unattached Pt NPs, the Pt decorated PS beads were then used to form self-assembled templates for TiO_2 nanostructures. The void volume of self-assembled templates was filled with TiO_2 produced by sol-gel method. The sacrificial PS beads were removed by high temperature air oxidation (300 ºC for >8 h), resulting in TiO_2 nanostructures with surface decorated with Pt NPs.

Figure 1A shows the high angle annular dark field (HAADF) STEM image of a PS bead decorated with Pt NPs of 3~4 nm with an average particle distance 6~7 nm. Figure 1B to D show HAADF STEM images of the nanostructured TiO_2 loaded with Pt NPs prepared by the template method. It can be seen in Figure 1D that the sizes and distribution of Pt NPs were not noticeably modified by the fabrication procedure. The filling of matrix material in the templates and the high temperature removal of the sacrificial templates did not lead to noticeable loss or aggregation of Pt NPs. Therefore, the described method can be used to obtain custom designed nanostructured composites that carry the NPs pre-decorated on the PS sphere templates.

More nanostructured composites were prepared by the described method, e.g., Pd or Pt loaded nanostructured Ni, up-converting NPs loaded TiO_2. In addition to the nanostructured composites with interconnected spherical voids, nanobowl composites were also prepared through this method by coating the surface of PS templates partially with physical vapour deposition. These nanobowl composites allow re-assemble the materials and voids, leading to new types of nanostructures. Figure 2 shows an example of the nanobowl composites containing Au/TiO_2 nanostructures decorated with Pt NPs.

References:

[1] OD Velev and EW Kaler, Adv. Mater. **12** (2000), p. 531.
[2] DS Raimundo, FJR Fernandez and WJ Salcedo, J. Integrated Circuits and Systems **1** (2006), p. 39.
[3] MTY Paul, B Kinkead, BD Gates, J. Electrochem. Soc. 161 (2014) p. B3103.
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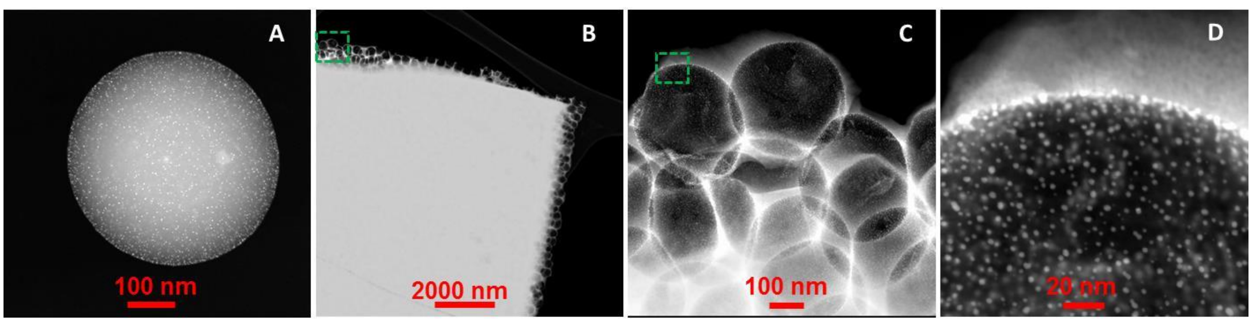

Figure 1. HAADF STEM images of (A) Pt NPs decorated PS bead, (B) Pt NPs loaded nanostructured TiO_2, (C) a thinner region highlighted by the dashed box in (B), (D) the region highlighted by the dashed box in (C) showing the uniform distribution of Pt NPs in nanostructured TiO_2.

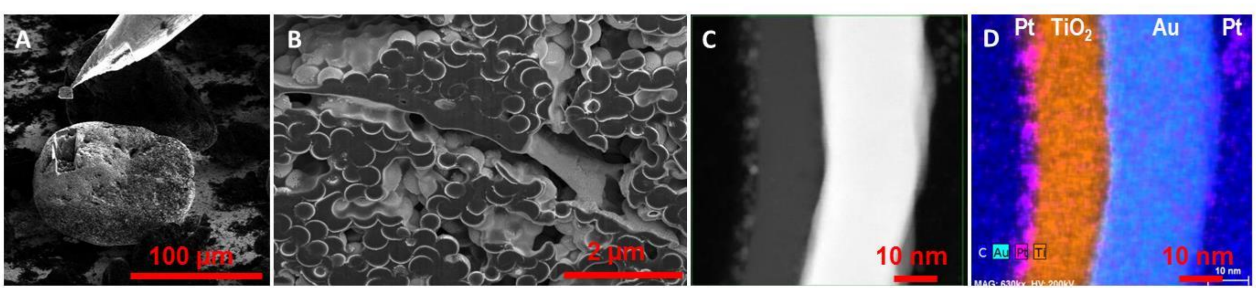

Figure 2. (A) SEM image showing the site for TEM sample lift-out, (B) SEM image showing a FIB milled and polished cross section, (C) HAADF STEM images of Pt NPs decoration, and (D) overlapped EDS maps from (C) on a tested structure of Au/TiO_2/Pt nanobowls.

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