

Postchemistry of Inorganic–Organic Hybrid Particles in Aqueous Solution: Metal–Cation Exchange

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The inorganic–organic hybrid micro/nanoparticles have emerged as an exciting new research area^[1–4] owing to their highly tailorable properties, as well as their potential applications in drug delivery,^[5,6] catalysis,^[7] biosensing,^[8] biomedical imaging,^[6a,9] gas storage,^[10] spin-crossover,^[11] and optics.^[12] Unlike inorganic particles, the inorganic–organic hybrid micro/nanostructures can be easily tuned by switching the different metal centers and linkers. So far, work in this area has predominately focused on size/shape control, property-tailoring, and nano-technological applications. The inherent chemistry of inorganic–organic hybrid particles remains largely unexplored.^[2b] The conversion of inorganic–organic hybrid particles into novel micro/nanostructures through the exchange of metal cations or organic ligands, could be technologically useful for creating novel inorganic–organic hybrid materials and achieving new physical phenomena.

Recently, our group has already demonstrated the possibility of chemical reactions among organic particles.^[13] As part of our ongoing efforts to explore the chemical reactivity of organic and organic–inorganic hybrid micro/nanomaterials, we are increasingly interested in developing inorganic–organic hybrid micro/nanostructures with more-tunable properties through a judicious choice of coordination force and environment. Such procedures would allow for an additional level of control over their morphology as well as the optical, magnetic, and electrical properties.

Herein, we report that the discovery of the sub-microspherical particles of polymerized Zn(SPh)₂ networks, formed by a reprecipitation method, can perform a metal–cation exchange in aqueous solution to produce crystalline nanoparticles and nanowires. In a typical experiment, the starting inorganic–organic hybrid material {Zn(SPh)₂}_n (**1**) was synthesized according to a previously reported procedure.^[14] The spherical particles of **1** formed spontaneously on slow addition of a solution of **1** in *N,N*-dimethylformamide into water in the presence of P123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)) nonionic surfactant. The Zn²⁺ cations in these spherical particles can be exchanged in aqueous solution by Pb²⁺, Cd²⁺, or Hg²⁺ ions to form different shapes, such as wires or pebble-like particles. The successful exchange of metal cations in the framework is due to the different bond energy of the M–S bonds and the solubility of the products, that is, the *K*_{sp} value.^[15]

To the best of our knowledge, the metal–cation exchange in the metal–chalcogenide framework together with the change of shape is unprecedented, although the exchange of free-metal cations (not in a framework) in crystalline metal–chalcogenide materials has been demonstrated to enlarge the pore volume or remove hazardous metals from aqueous solution.^[16] In most cases, this kind of exchange does not affect the spatial arrangement of frameworks.

Scanning electron microscopy (SEM) and optical microscopy images of the as-prepared hybrid particles are shown in Figure 1. The SEM image (Figure 1a) of Zn(SPh)₂ compositions shows spherical particles with an average diameter of 300 (±200) nm, which is consistent with that measured by dynamic light scattering (DLS). After exchanging Zn²⁺ ions with Pb²⁺, Cd²⁺, or Hg²⁺ ions in aqueous solution, the spherical particles became wire-shaped structures for Pb(SPh)₂ and Hg(SPh)₂, and pebble-like particles for Cd(SPh)₂. SEM images revealed that the diameter and length of Pb(SPh)₂ nanowires were in the range of 500 nm–1 μm and above 5 μm, respectively (Figure 1b), whilst Hg(SPh)₂ has a relatively narrow size distribution (200–500 nm) with

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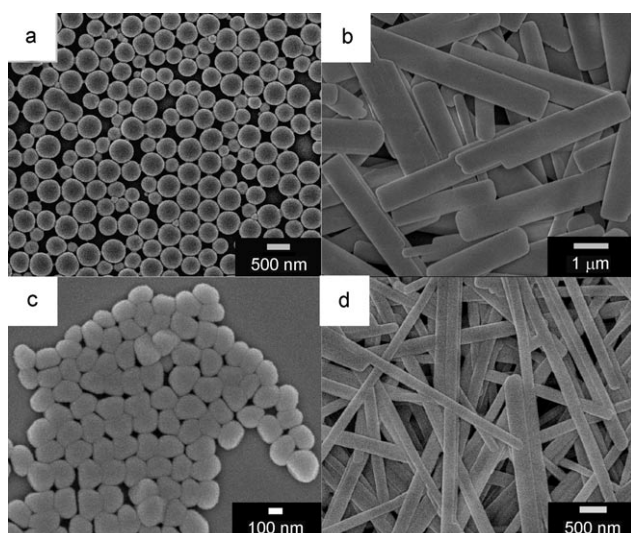


Figure 1. The SEM images of a) Zn(SPh)₂ spherical particles, b) Pb(SPh)₂ nanowires, c) Cd(SPh)₂ pebble-like nanoparticles, and d) Hg(SPh)₂ nanowires.

the length of up to 10 μm (Figure 1d). Interestingly, the shape of the Cd(SPh)₂ structures is pebble-like (Figure 1c), which is completely different to the structures of Pb(SPh)₂ and Hg(SPh)₂. The average size of Cd(SPh)₂ particles was 200 (±100) nm. All of the as-prepared particles were stable in water and the dried state. The polarized optical microscopy (POM) images of the resulting Pb(SPh)₂ and Hg(SPh)₂ nanowires further indicate that they are crystalline in nature (see the Supporting Information, Figure S1). The composition of all the structures were confirmed by energy dispersive X-ray spectroscopic (EDX) analysis (see the Supporting Information, Figure S2–S5).

Powder X-ray diffraction (XRD) revealed that the Zn(SPh)₂ spherical particles (Figure 2) were amorphous whilst Pb(SPh)₂, Cd(SPh)₂, and Hg(SPh)₂ were crystalline (Figure 3). Note that the starting {Zn(SPh)₂}_n polymer (Figure 2b) crystallizes in the orthorhombic space group *P*2₁2₁2₁ with the cell data (NBS ID: 504063, *P*2₁2₁2₁, *a* = 16.529(2) Å,

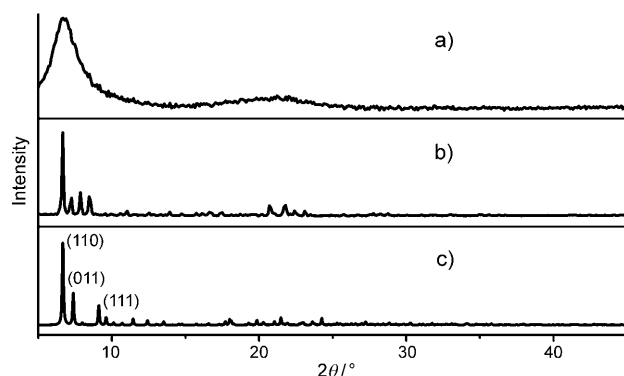


Figure 2. The powder X-ray diffraction (XRD) patterns of a) Zn(SPh)₂ spherical particles, b) starting material {Zn(SPh)₂}_n polymer, and c) the simulated one.

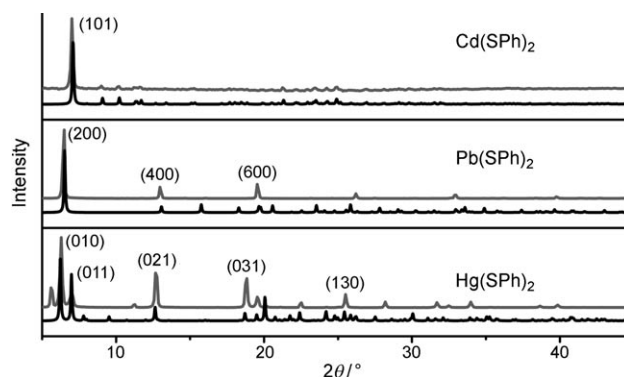


Figure 3. The powder X-ray diffraction (XRD) patterns of Cd(SPh)₂, Pb(SPh)₂, Hg(SPh)₂ (gray line), and the simulated ones (black line).

b = 22.129(3) Å, and *c* = 14.241(2) Å).^[14] The XRD pattern for the Pb(SPh)₂ nanowires was indexed in space group *P*2₁*ca*, as previously reported, with ‘standard’ lattice constants (*P*mcn, *a* = 27.1492 (11) Å, *b* = 6.0119 (2) Å, *c* = 7.2935 (3) Å, CCDC 670193; see the Supporting Information, Figure S6),^[17] whilst the Cd(SPh)₂ nanoparticles yielded a similar XRD pattern with the following published lattice parameters (NBS ID: 565704; see the Supporting Information, Figure S7): *P*2₁2₁2₁, *a* = 15.492 (3) Å, *b* = 15.626 (5) Å, and *c* = 20.805 (6) Å.^[18] XRD analysis of Hg(SPh)₂ nanowires showed that this material has a high crystallinity (cell data: *P*-1, *a* = 4.6711 (9) Å, *b* = 14.359 (3) Å, *c* = 22.266 (5) Å, and $\alpha = 82.99$ (3)°, $\beta = 89.04$ (3)°, $\gamma = 83.99$ (3)°), and adopts a unique structure (see the Supporting Information, Figure S8).^[19]

A possible exchanging mechanism was studied and proposed using the lead system as an example (see the Supporting Information, Figure S9). When Pb²⁺ salts were added into a solution of Zn(SPh)₂ nanospheres, the spherical particles started to decompose. Slowly, Pb(SPh)₂ nanorods began to form. This process might be ascribed to the different relative solubilities of Zn(SPh)₂ and Pb(SPh)₂. The same results were also observed in the Hg(SPh)₂ and Cd(SPh)₂ systems.

Figure 4a shows the UV/Vis absorption spectra of the spherical Zn(SPh)₂ particles, Pb(SPh)₂ nanowires, Cd(SPh)₂ pebble-like particles, and Hg(SPh)₂ nanowires in aqueous solution. The spherical Zn(SPh)₂ particles gave one absorption peak at 250 nm whilst Cd(SPh)₂ nanoparticles had two absorption peaks at 250 nm and 310 nm. All of these peaks

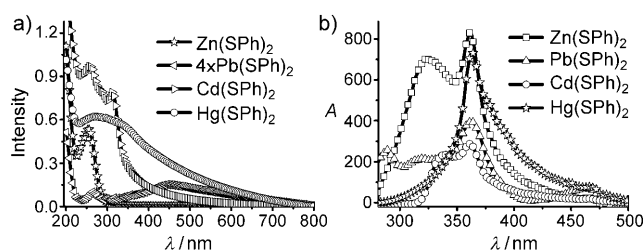


Figure 4. a) The UV/Vis absorption spectra of different particles in aqueous solution. b) Photoluminescence (PL) spectra of different particles.

were similar to the reported results.^[20] Interestingly, Hg-(SPh)₂ and Pb(SPh)₂ nanowires showed very broad absorption peaks at 300 nm and 450 nm, respectively, which might be explained by their broad size distribution. The photoluminescence spectra of Zn(SPh)₂ spherical particles, Pb(SPh)₂ microstructures, Cd(SPh)₂ nanoparticles, and Hg(SPh)₂ nanowires are shown in Figure 4b. When Pb(SPh)₂ particles were excited at 465 nm, no peak was observed at longer wavelength.

In conclusion, spherical Zn(SPh)₂ particles have been successfully prepared by a reprecipitation method. The Zn²⁺ cations in the as-prepared spherical particles were successfully exchanged with Pb²⁺, Cd²⁺, and Hg²⁺ ions in aqueous solution. The resulting structures were characterized by SEM, XRD, and EDX. This new method might have potential applications in waste-water treatment and separation. In addition, the conversion of inorganic–organic hybrid particles could offer a new route for preparing new hybrid micro-/nano-structures and tuning their physical properties through the exchange of metal cations or organic ligands. We believe that this concept can provide a more-powerful tool for designing and synthesizing inorganic–organic hybrid micro-/nano-materials for further applications.

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