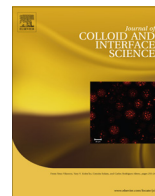




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Short Communication

Metal nanocrystal/metal–organic framework core/shell nanostructure from selective self-assembly induced by localization of metal ion precursors on nanocrystal surface

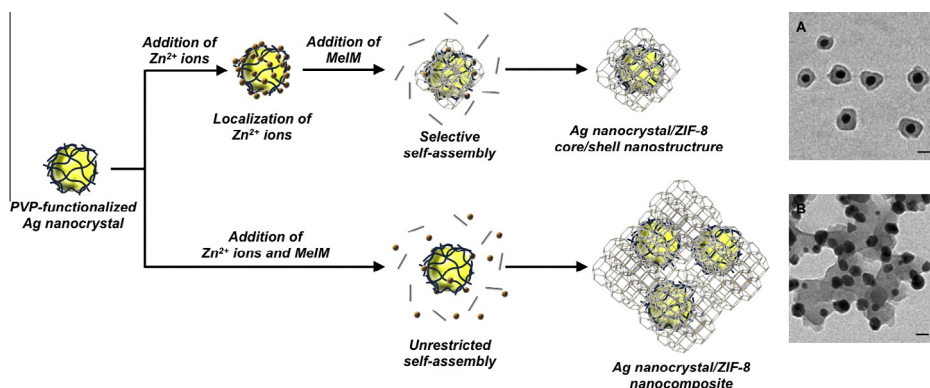


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GRAPHICAL ABSTRACT



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ABSTRACT

Metal nanocrystal/metal–organic framework core/shell nanostructures have been constructed using metal ion-trapped nanocrystals as scaffolds through a selective self-assembly of framework components on the nanocrystal surfaces. The resulting nanostructures exhibit unique catalytic activity toward nitrophenol analogs.

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Nanosized inorganic materials have exhibited new interesting physicochemical properties such as localized surface plasmon resonance, band gap engineering, and superparamagnetism [1–3].

Thus, an important challenge in nanomaterial chemistry is to improve and/or enhance the properties of nanomaterials. One approach of considerable interest is the fabrication of nanostructures that consist of inorganic nanomaterials and porous materials. These nanostructures exhibit novel properties based on the combination of nanocrystals and porous materials that are attractive for applications in sensors, catalysts, and drug delivery systems

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[4–6]. Porous materials, which typically consist of mesoporous silica [7] and zeolites [8], enable the accessibility of substances to inorganic nanomaterials to be controlled according to their storage/release properties. The properties of porous materials are dependent on the aperture size, shape, and dimensionality of pores, and are thus important for providing selectivity of substances for inorganic nanomaterials/porous materials hybrid systems.

Metal–organic frameworks (MOFs), a class of crystalline microporous materials constructed by self-assembly of metal ions and functional organic linkers [9–11], are good candidates for hybrid materials with inorganic nanocrystals. The pore structure in MOFs is highly designable in terms of uniform pore size and surface characteristics for realizing tunable framework–guest interaction. Therefore, inorganic nanocrystals/MOF composites have received much attention from a fundamental perspective and due to their potential applications [12–17]. Recently, numerous approaches have been developed to prepare inorganic nanocrystals/MOF composites [18–20], one of which involves the incorporation of nanocrystal precursors into as-prepared MOF crystals, followed by decomposition/reduction of the precursors. The resultant composites are potentially promising materials for applications in heterogeneous catalysis because small and naked inorganic nanocrystals can be formed in the MOF crystals [21,22]. However, it is difficult to control the size and shape of the inorganic nanocrystals in the range of tens of nanometers, which is necessary in order to control their properties. Thus, another approach to the fabrication of these composites has been developed based on the self-assembly of MOFs on the nanocrystal surfaces [23–25]. By utilizing this approach, inorganic nanocrystals with the desired size and shape can be dispersed within MOF crystals. However, the research to date has been mostly focused on the study of applications in catalysis, sensors, and gas sorption. Therefore, understanding the growth mechanisms for MOFs on nanocrystal surfaces, and control of the composite structure are still challenging research topics.

Herein, we report the preparation of a Ag nanocrystal/[Zn(MeIm)₂]_n (ZIF-8; MeIm = 2-methylimidazole) framework nanostructure based on selective self-assembly of the framework components on the nanocrystal surfaces. This can be achieved using Zn²⁺ ion-trapped Ag nanocrystals as scaffolds for MOF growth. This strategy offers opportunities to prepare nanocrystal/MOF core/shell nanostructures and control the MOF shell thickness in the composites. The growth mechanism for these core/shell nanostructures is also investigated. In addition, the catalytic activity of the resultant nanostructures for the reduction of organic molecules is evaluated.

Ag nanocrystals were prepared in the presence of polyvinylpyrrolidone (PVP) using the dimethyl formamide (DMF) reduction method [26]. After purification, a DMF solution of zinc nitrate was added to the DMF suspension of PVP-functionalized Ag nanocrystals and the mixture was stirred for 30 min at room temperature. A DMF solution of MeIm was then added to the mixture containing nanocrystals and Zn²⁺ ions, and the reaction solution was heated at 200 °C for 1.5 h via microwave radiation (final concentration: Ag nanocrystals, 3.8×10^{-9} mol L⁻¹; zinc nitrate, 1.4×10^{-3} mol L⁻¹; MeIm, 6.7×10^{-3} mol L⁻¹) (see [Supplementary Information for detailed descriptions](#)).

PVP molecules were used as a stabilizer for the nanocrystals to coordinate with the metal ions, so that PVP-functionalized Ag nanocrystals could be used as a platform for the localization of the MOF precursor metal ions (Fig. 1). This reaction was performed by the addition of the zinc nitrate solution to the Ag nanocrystal dispersion. To estimate the effect of the amount of Zn²⁺ ions trapped to PVP molecules on this reaction, inductively coupled plasma spectroscopy (ICP) measurements were conducted on the

supernatant from the mixed solution containing Ag nanocrystals and Zn²⁺ ions after centrifugation. The results revealed that almost all of the added Zn²⁺ ions (approximately 90%) were trapped on the surface of the nanocrystals (the supernatant contained 10% of initially added Zn²⁺ ions). The mixture of these nanocrystals and MeIm was heated by microwave radiation, which produced well-dispersed and isolated Ag nanocrystals/ZIF-8 core/shell nanostructures (Fig. 1A). The size of the Ag nanocrystals in the obtained nanostructures remained the same as that of the initial Ag nanocrystals, and the ZIF-8 shells had an average thickness of ca. 6.3 nm. ZIF-8 crystals without Ag nanocrystals were not observed, which suggests that the self-assembly of ZIF-8 components occurred selectively on the Ag nanocrystal surfaces. Powder X-ray diffraction (XRD) analysis of the obtained nanostructures was conducted to investigate the crystal structure. All XRD peaks for the nanostructures were consistent with those for Ag nanocrystals and ZIF-8 frameworks, which confirmed that the ZIF-8 shells on the nanocrystal surfaces had ordered frameworks (Fig. S1). Gas adsorption measurements were conducted to investigate the pore properties of the MOFs. Brunauer–Emmett–Teller (BET) measurements indicated that the obtained nanostructures had gas adsorption/desorption properties similar to those of the pure ZIF-8 framework (Fig. S2). In addition, a thermogravimetric analysis profile of the nanostructures was almost the same as that measured for pure ZIF-8 crystals (Fig. S3). From these characterization measurements, the obtained samples were identified as Ag nanocrystal/ZIF-8 core/shell nanostructures.

A time course analysis of the reaction was performed using transmission electron microscopy (TEM) to investigate the growth process (Fig. 2). It can be seen that Ag nanocrystals and ZIF-8 components were aggregated in the initial stage of reaction for 30 min (a large amount of unreacted components remained in the reaction solution). The unreacted components could form disordered aggregation during cooling process, leading to the formation of the aggregates consisting of nanocrystals and ZIF-8 components. The growth of ZIF-8 frameworks on the nanocrystal surfaces was first observed following reaction for 40 min, although a large number of aggregates were still present. After 50 min, aggregated core/shell nanostructures were clearly observed, which confirmed the selective self-assembly of ZIF-8 components. After reaction for 50 min, the shell thickness of the nanostructures was slightly increased with the reaction time. On the basis of these observations, we propose the core/shell nanostructure growth mechanism shown in Fig. 1. Zn²⁺ ions are initially trapped by PVP-functionalized Ag nanocrystals through coordination bonds to the nitrogen and/or oxygen atoms of the PVP molecules. The formation of Ag nanocrystal/ZIF-8 core/shell nanostructures then occurs through the selective self-assembly of ZIF-8 components on the nanocrystal surfaces; [27] the formation of core/shell nanostructures from ZIF-8 crystals was not observed without the participation of Ag nanocrystals. The localization of Zn²⁺ ions on the surfaces of the Ag nanocrystals is necessary for the formation of core/shell nanostructures, because the core/shell nanostructures were not formed without the initial functionalization process for the localization of Zn²⁺ ions (Fig. 1B).

The shell thickness was characterized for nanostructures formed with various concentrations of Ag nanocrystals and ZIF-8 components (Fig. 3). As the concentration of Ag nanocrystals was reduced from 7.6 to 3.8 nM, while the concentration of ZIF-8 components was fixed (the concentrations of zinc nitrate and MeIm were 1.4 and 6.7 mM, respectively), the MOF shell thickness increased from 2.7 ± 0.59 to 6.3 ± 0.92 nm. A further decrease in the concentration of Ag nanocrystals from 3.8 to 1.9 nM resulted in a further increase of the MOF shell thickness (7.3 ± 0.99 nm). For a Ag nanocrystal concentration of 0.95 nM, aggregated core/shell nanostructures were still observed, although the shell

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