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Systematic synthesis of polyimide@inorganics core-shell microspheres via ion-exchange and interfacial reaction



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ABSTRACT

Uniform and stable core-shell microspheres composed of a polyimide (PI) core and thin metal/oxide/sulphide shells were prepared by an interfacial reaction of metal-ion-doped polymeric cores in reduction or in the air or sodium sulphide solutions, respectively. The silver shells on polyimide microspheres were prepared by the introduction of silver ions into ion-exchangeable surface-modified polyimide, and subsequently an in situ reduction of the silver ions in solution. Oxides shells such as SnO₂, Co₃O₄, NiO, CuO or ZnO were prepared by thermally treating the ion-doped microspheres in air, while amorphous sulphides shells such as CuS, ZnS, CoS or Ag₂S were prepared by an interfacial reaction of metal-ion-doped microspheres in its corresponding sodium sulphide solutions. The adhesion properties between the copper sulphide and PI substrates are demonstrated superior. This simple strategy is promising in the fabrication of a whole range of inorganic shells on polyimide microspheres, which may offer tailor-designed multi-functionalities based on the distinctive species of these inorganic shells.

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1. Introduction

The syntheses of inorganic functional materials/structures, such as metal, metal oxide and metal sulphide coatings on the nanoscale arouse a great deal of interest from both the basic scientific and application standpoints. In recent years, new techniques have been developed to synthesize composite microspheres made by polymeric cores and inorganic shells by virtue of the combination of low density which is attributable to the organic cores, and the electrical conductivity, magnetic and even ferromagnetic behavior possessed by the inorganic shells [1–5].

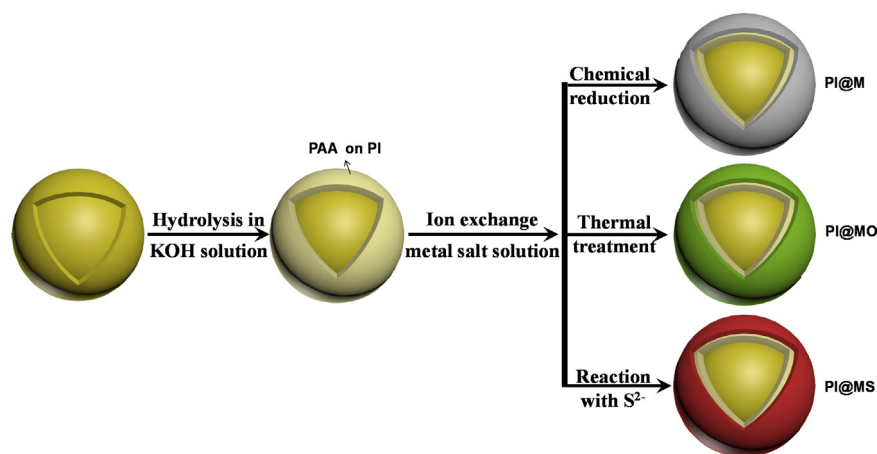
Key functionalities, such as high catalytic performance, high temperature and high chemical resistance are required in many demanding applications, however, traditional organic/polymeric-core based micro-/nano- particles/spheres have many shortcomings, for instance, low intrinsic thermal stability and chemical resistance. Hence, polyimide (PI) becomes a promising candidate as the core materials on the basis of its excellent thermal and mechanical properties [6–8], high chemical resistance [6–9], low dielectric constant [7–9], superior resistance to ultraviolet exposure and nuclear radiation [2], and good patterning capability [7].

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Previous works have been focused on the fabrication of noble metals, metal oxides and/or metal sulphides on polyimide microspheres that could be used in a wide range of applications including but not limited to biosensing, bioanalysis, imaging, light emitting devices and photovoltaic cells on the basis of their unique optical and electronic properties [5,10–11]. To the best of our knowledge, however, there is no work reported on the fabrication of inorganic functional materials on polyimide cores. Recently, relying on the reduction techniques, metals or metal oxides onto pre-formed polymeric cores have been successfully prepared at the laboratory scale. For instance, Goedel [1] reported that uniform and stable core-shell microspheres composed of a poly(methyl methacrylate) (PMMA) core and a thin metallic shell of nickel-phosphorus, cobalt-phosphorus, or mixed metal alloys were prepared by dispersion polymerization of methyl methacrylate, and then electroless plating. In another work, noble metal nanoparticles deposited on polystyrene spheres via ultrasound irradiation yielded nanocrystalline Ag, Au, Pd, and Pt particles on the surface of polystyrene as as-synthesized materials [12]. Although these from-exterior-to-surface processes are powerful methods to prepare metalized shells on polymeric cores, the poor adhesion between metal nanoparticles and matrix is one of the major drawbacks [13], hindering their potential applications. To this end, we have reported earlier the controllable growth of noble metals or sulphides nanoparticles onto the surfaces of PI films via solid-liquid interfacial reduction of ions-doped polymeric films in various solutions, which offers great inorganic-polymeric substrates



Scheme 1. Schematic of the preparation methods of PI microspheres coated with a variety of inorganic shells.

bonding and adhesion because of an intrinsic mechanical interlocking mechanism [10].

Herein, we report a new route to prepare core-shell nanoparticles relying on the ion-exchange forces to ensure surface segregation of a large variety of inorganic nanocrystal shells, including noble metals, metal oxides and metal sulphides, on the pre-formed polymeric core. The strategy is demonstrated through the synthesis of PI@Ag, PI@Cu, PI@ZnO, PI@CuO, PI@NiO, PI@Co₃O₄ and PI@SnO₂ using a cation-exchange coordination protocol. The preparation process is outlined in **Scheme 1**: (1) formation of ion-exchangeable sites, poly(amic acid) (PAA) layer, on polyimide microspheres via hydrolysis reaction; (2) followed by aim ions loading via ion-exchange reaction in metal salt solution at ambient temperature; (3) in situ reaction, such as reduction, oxidation, or complexing, occurring at the interfaces of the liquid-solid or air-solid during the synthesis.

We envision that the methods proposed here will serve as a benchmark for preparing other core-shell/organic-inorganic composite systems as well. The shells consist of a variety of nanocrystals (e.g., noble metals, metal oxides, metal sulphides) with different physical and chemical properties that are highly desirable in many potential applications [12,14–15].

2. Experiment section

The preparation process mainly involves three major steps: i) pristine polyimide microspheres (diameter of ca. 11 μm , Institute of Chemistry, Chinese Academy of Sciences, China) were firstly immersed into 4 M aqueous KOH solution at 40 $^{\circ}\text{C}$ for ten minutes and then rinsed thoroughly with deionized water; ii) the surface-modified PI microspheres were then immersed into an aqueous metal salt solution for several minutes to allow cation-exchange reactions, during which the selected metal ions were incorporated into the modified layers by replacing potassium ions; iii) next metal shells or metal sulphides shells were obtained via immersing the metal ions-doped polymeric microspheres into aqueous reducing solutions or sodium sulphide solutions, respectively. Finally, metal oxide shells on PI microspheres were fabricated via thermal treatment in air. X-ray Diffraction (XRD) of these resultant core/shell microspheres was performed using an X-ray Diffractometer (D/Max2500VB2+/PC, Rigaku, Japan). Transmission electron microscope (TEM) images were obtained using a H-800 type Hitachi instrument at an accelerating voltage of 200 kV. Samples were embedded into epoxy resin and then sectioned by an ultra-microtome.

3. Results and discussion

We firstly chose noble metals, e.g., silver, as an example to demonstrate the effectiveness of this method in yielding PI@Ag core-shell materials with high quality. Uniform PI@Ag core-shell microspheres can be obtained through the reduction of silver-ion-doped PI microsphere in aqueous dimethylamineborane (DMAB) solution at ambient temperature. In a typical synthesis, it involves of i) putting the PI microspheres into 0.1 M AgNO₃ for 30 min to conduct ion-exchange reaction and ii) carrying out reduction of the modified microspheres in 0.3 ml DMAB/50 ml H₂O for 10 min under agitation at ambient temperature.

During the ion-exchanging process, the preformed poly(amic acid) layers on PI microspheres were submerged into aqueous metal salt solutions for a certain time to proceed cation-exchange reactions, during which the potassium ions were replaced by another metal ions which were subsequently incorporated into the modified layers. Notably, not all metal ions are ion-exchangeable during the ion-exchanging process. Only those who have less than +2 cations can be incorporated into the modified layers. When the salts have more than +2 cations, such as Fe³⁺, the metal ions are very difficult to entrap into the modified layers because each +3 cation would combine with three carboxylic groups through complexation reaction, hindering the migration of the cations.

Fig. 1a shows the XRD patterns of both the pristine PI and PI@Ag core-shell microspheres. Clearly by comparison, face-centered cubic (FCC) structured Ag shells were successfully coated on PI cores using the aforementioned approach, and the appearances of the PI microspheres changed dramatically from the light yellow to black color (see **Supplementary Information**). **Fig. 1b** and **c** show the SEM images of PI and PI@Ag core-shell microspheres, respectively, indicating both the success in mass production and great uniformity. The thickness of the silver layers on PI cores is measured as ca. 100–200 nm (**Fig. 1d**). The PI@Ag core-shell microspheres also show certain flexibility and acceptable adhesion properties between the inorganic shells and PI cores. Great silver-polyimide adhesion is evident on the basis of no observable peel-off effect of the inorganic shell in the cutting process for preparing the samples by ultra-microtome, as shown from the TEM images in **Fig. 1d**.

Based on the similar synthetic processes, other metal ions can also be doped into the hydrolysis layers of PI microspheres. Through additional solid-liquid interfacial reactions, we obtained many functional metal oxides and sulphides on PI cores. Thermal treatment of ion-doped polymeric microspheres in air will result in its corresponding metal oxides through oxidation. For example, as shown in **Fig. 2** when the tin-doped PI microspheres were

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