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One-step hydrothermal synthesis of hollow ZnO microspheres with enhanced performance for polyacrylate

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ABSTRACT

In this study, hollow ZnO microspheres were successfully synthesized by a one-step template-free hydrothermal synthetic route straightforwardly just for 30 min at 90 °C. More importantly, hexamethylenetetramine and trisodium citrate played a significant role in the fabrication of hollow ZnO microspheres, and distilled water served as the main solvent without adding any organic solvent and surfactants. The architecture and morphology of as-obtained ZnO microstrutures were estimateded by field-emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (PXRD) and Brunauer-Emmett-Teller (BET). With the morphological evolution apperceived in the time-dependent growth of hollow ZnO microspheres, a possible formation mechanism based on Ostward ripening inside-out was proposed. Then, polyacrylate/hollow ZnO composite latex was obtained by physical blending of hollow ZnO microspheres and polyacrylate emulsion. As expected, hollow ZnO microspheres has a significant impact on water vapor permeability, water resistance and mechanical porperties. Among them, the water vapor permeability and water resistance was relatively increased by 71.18% and 38.42%, respectively.

1. Introduction

Polyacrylate is an excellent film-forming material with superior cohesiveness, flexibility, low-cost, transparent, brightness and many potential outstanding performances, that is widely used in leather finishing, coating fabrics, textile adhesive and so on [1–5]. However, the poor hygienic properties of dense polyacrylate coating affect significantly the wearing comfort, which often reduces its usability and restricts its further applications. Hygienic behavior constitutes such as air permeability and water vapor permeability. Thereinto, poor water vapor permeability can be caused by blocking the water vapor molecular diffusion channels to the outside. Therefore, a large number of efforts based on designing and modifying of polyacrylate film to fabricate the high-performance polymeric film have been investigated, including modification of epoxy resin, polyurethane, organic silicone/fluorine, and inorganic nano-materials principally et al. [6–11]. Recently, organic-inorganic composite systems have attracted considerable attention due to their unique functional performances arising out of the cooperativity between polymeric and inorganic phase as well as their interactivities promising extensive potential applications in various fields of material science [12–15]. There are numerous researches reporting on the synthesis of polymer/inorganic composites with different inorganic materials, such as SiO_2, TiO_2, and ZnO [16–18]. Among all inorganic materials, ZnO exhibits abundant morphologies, considerable chemical and physical properties, favorable stability, excellent antibacterial and environmental friendliness behavior due to large exaction binding energy of 60 meV at room temperature and its direct wide band gap of 3.37 eV [19–22]. Hollow ZnO nanostructures, which have low density, large specific surface area, good permeability and abundent hydroxyl groups on the ZnO surface, are satisfactory inorganic fillers in improving the comprehensive performances of polyacrylate film [23–25]. Also, particular hollow structure provides the cavity structure and two surfaces (external shell and internal shell), which can enhance the free volume, surface activities, give high surface-to-volume ratio, and so on. Therefore, in order to improve the water vapor permeability of polyacrylate film, hollow ZnO microspheres can be used as inorganic fillers to increase the size and number of free volume (the pores between ZnO nanoparticles and their interface with polymer matrix). Furthermore, its intrinsic hollow structure could furnish water vapor molecular diffusion channels to the outside, improving the water vapor permeability of polyacrylate film.

In recent years, fabrication of well-defined hollow ZnO architectures

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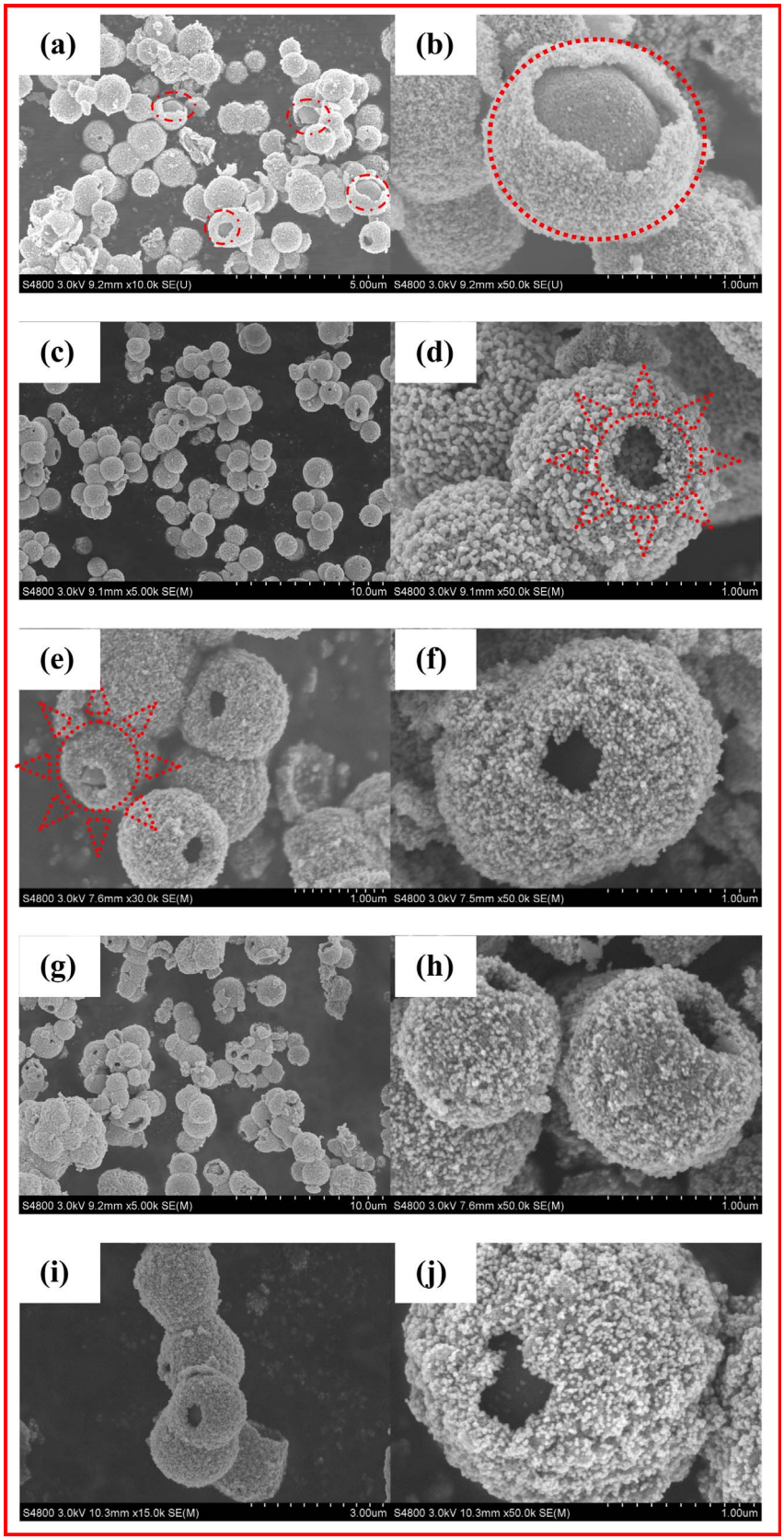

Fig. 1. Time-dependent hollow ZnO microspheres: low (left) and high (right) magnification FESEM images of the samples synthesized at 90 °C for different reaction time: (a, b) 5 min; (c, d) 10 min; (e, f) 20 min; (g, h) 30 min; (i, j) 40 min.

with micrometer-sized has attracted enormous interest [26,27]. Until now, a general hydrothermal approach to fabricate well-defined hollow ZnO architectures accompanies the use of removable or sacrificial templates, involving either the hard ones such as polystyrene spheres and carbon spheres, or the soft ones such as surfactants and gas bubbles [28–31]. However, the use of a template results in high experiment cost, complex removal process of templates, a time-consuming synthesis process and so on, posing a significant impurities pollution and collapse