Materials Letters 139 (2015) 93–97

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Convenient one-pot approach for the preparation of novel atomically thin two-dimensional polymeric nanosheets, and its evolution in aqueous solution

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ARTICLE INFO

Article history:
Received 13 April 2014
Accepted 10 October 2014
Available online 22 October 2014

Keywords:
Hydrogen bond
Multilayer structure
Nanostructure
Polymers
Thin films

ABSTRACT

Atomically thin two-dimensional polymeric nanosheets were facilely synthesized via the polymerization between hexachlorocyclotriphosphazene and melamine. After the synthetic process, the polymeric nanosheets are of microspherical morphlogy, with the nanosheets being in the form of folded and crumpled structure. The folded and crumpled nanosheets could disintegrate to form outstretched nanosheet in aqueous solution, with the help of hydrogen bonds formed between the polymeric nanosheets and water molecules. A scanning probe microscope showed that the thickness of the hydrous polymeric nanosheets is about 0.91 nm. Transmission electron microscopy was used to study the disintegration process.

1. Introduction

Staudinger had opened up the area of polymers, which are assumed to be macromolecules composed of linear repeat units that are linked together via covalent bonds [1], and after that, synthetic chemistry has realized the expansion from zero-dimensionality to one-dimensionality. In recent years, researchers are making their effort to achieve the expansion of synthetic chemistry from one-dimensionality to two-dimensionality, not only for the curiosity to a whole new area, but also for the promising candidates of two-dimensional polymers for a vast range of applications involving membrane separation, sensors, catalysis and photoelectricity [2–5]. However, further expanding of synthetic chemistry to two-dimensionality aspects still faces many difficulties.

Up to now, the strategies that have been applied to create atomically thin 2D polymeric nanosheets (APNS) are mainly divided into two categories: interfacial/spatially-confined approaches, and "flask type" approaches [6]. Interfacial/spatially-confined approaches lead to APNSs with lateral size as high as several micrometers; however, the synthesis approaches are circumscribed, and the relevant APNSs have just been applied in some limited theoretical aspects [2,3]. "Flask type" approaches have been used to create APNSs; however, there are only oligomers with limited lateral size have been created up to now [7]. Facile approach leading to free-standing APNSs is still a challenge.

Hexachlorocyclotriphosphazene (HCCP), with each phosphorus atom bearing two chlorine atoms, is a versatile monomer and various nano/microfunctional materials based on it had been successfully prepared. Here, organic–inorganic hybrid APNSs, poly (cyclotriphosphazene-co-melamine) (PPM), were conveniently constructed via the polycondensation between HCCP and melamine (MA), and the evolution of PPM nanosheets was also investigated (Fig. 1). The thickness of the PPM nanosheetss is about 0.91 nm. To our knowledge, there is little report about synthesis of such APNSs via a so facile approach.

2. Experimental

Synthesis of PPM nanosheets: In a typical procedure, HCCP (149 mg) and MA (108 mg) were added to a three-neck flask containing 30 ml of DMF. Then 2 ml of triethylamine was added to the solution. The polycondensation was conducted in an ultrasonic bath for 48 h under the protection of nitrogen. Finally, the product was collected by centrifugation and washed several

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http://dx.doi.org/10.1016/j.matlet.2014.10.050
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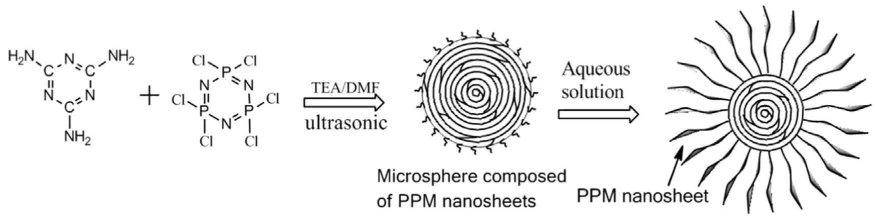

Fig. 1. Scheme for the synthesis of PPM nanosheets and the evolution of PPM nanosheets from crumpled morphology (microspheres) to outstretched morphology (outstretched nanosheets).

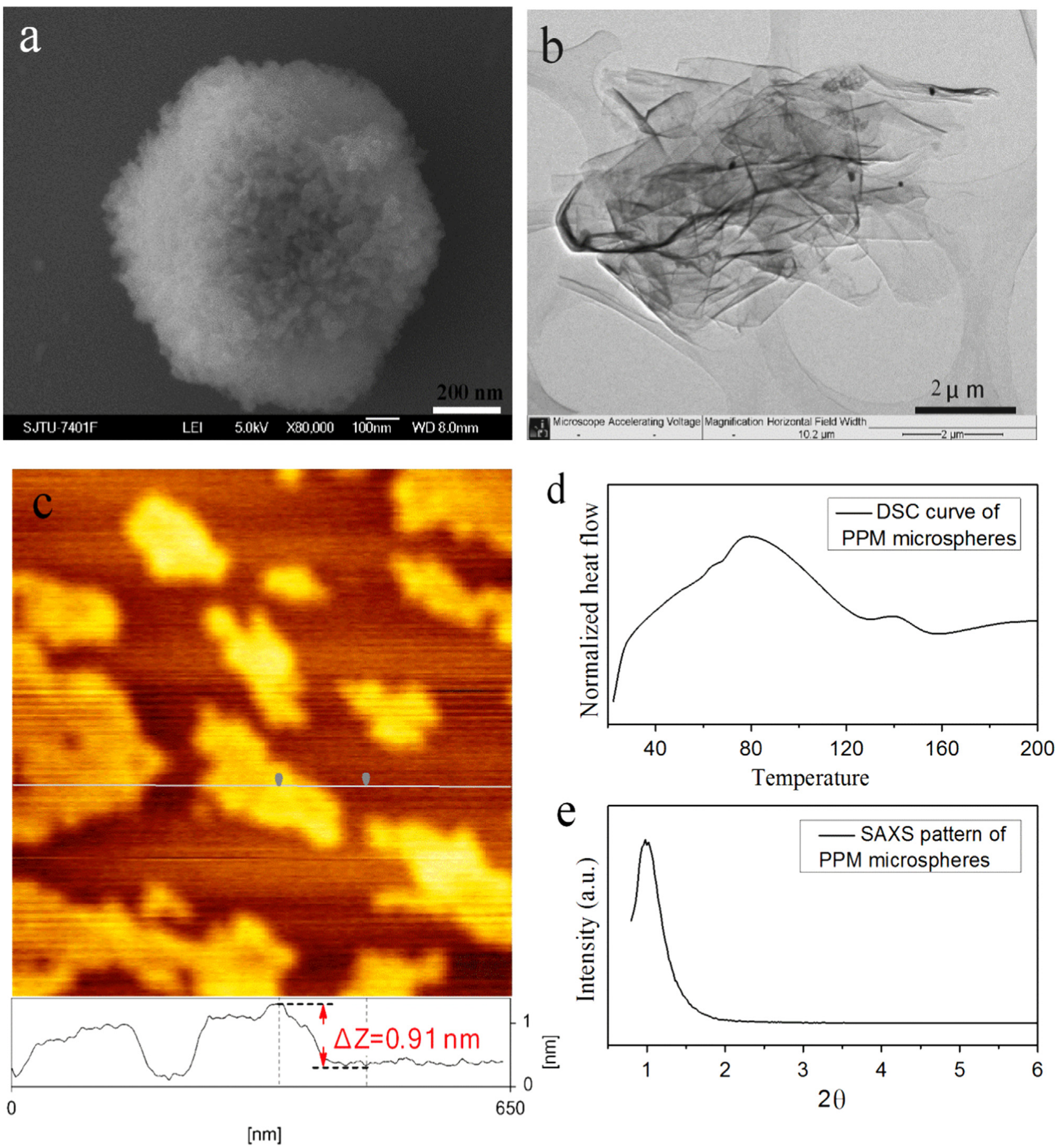

Fig. 2. (a) SEM image of microspherical PPM. The average diameter of microspherical PPM is about 1–2 μm. (b) TEM image of PPM APNSs, which are formed via dispersion of microspherical PPM in aqueous solution for 48 h at 30 °C. (c) SPM image of PPM nanosheets. (d) DSC curve of microspherical PPM. (e) SAXS curve of microspherical PPM.