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# Graphene-induced tiny flowers of organometallic polymers with ultrathin petals for hydrogen peroxide sensing

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A B S T R A C T

A facile and efficient approach for scalable synthesis of polymer flowers decorated with Prussian blue (PB) and graphene nanosheets is reported for the first time. This approach involved graphene-induced crystallization of polyethylene capped with a cyanoferrate complex (PE–Fe), followed by *in situ* coordination polymerization of cyanoferrate complex with $Fe^{3+}$ on the surface. The morphological and thermal analyses demonstrated that graphene nanosheets prompted the crystallization of PE–Fe, affording the formation of hybrid flowers of 3 μm. The tiny flowers were comprised of ultrathin petals of 10 nm in thickness, which consisted of a single polyethylene lamella sandwiched between two PB/graphene nanolayers. Hybrid flowers exhibited excellent electrocatalytic activity toward reduction of hydrogen peroxide. Maximum reduction current of hybrid flowers was two orders of magnitude higher compared with conventional PB particles. Moreover, the sensors based on hybrid flowers showed by far higher successive performance ability as contrast to conventional PB particles. Such graphene-induced flower-like nanoarchitectures offer a catalog of functional nanomaterials useful for biosensing and nanodevices.



## 1. Introduction

Flower-like nanomaterials have received numerous interests due to their overwhelming advantages such as resistance to aggregation, large surface area and low packing density. Synthesis of inorganic flowers including metals and metal oxides has been extensively explored through electrodeposition and wet chemistry approaches [1–9]. Recently, polymer flowers exhibiting superb hydrophobicity have also been generated by means of self-assembly of polymers [10,11]. In contrast, there are limited works on polymer/inorganic hybrid flowers. Hybrid flowers combine the advantages of both components including flexibility of polymers and catalytic performance of inorganic metal species, generating new and desirable functions. This enables them to meet the overall requirements for engineering applications such as superior catalytic performance together with acceptable mechanical strength and stability for biosensors [12–24]. Moreover, synthesis of hybrid flowers is crucial for fundamentally understanding the correlation among composition, structure and property of nanomaterials. However, synthesis of polymer/inorganic hybrid flowers is limited by the lack of proper approaches.

Graphene, as a unique two-dimensional carbonic nanostructure, has attracted tremendous attention due to its large surface area, superior conductivity, high strength and

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Young's modulus, as well as excellent stability. Intense efforts have been devoted to constructing graphene-based nanomaterials through ion beam lithography, chemical vapor deposition (CVD), wet-spinning, and so on. The incorporation of graphene endows the nanomaterials exceptional properties and functionalities for various applications including energy storage, chemical sensing, flame retardant, electrodes, field effect transistor, optoelectronic devices, biological engineering [25,26]. The key lies in controlling the morphology of nanomaterials and distribution of graphene at nanoscale, which dictates directly the performances of the ultimate nanomaterials.

Crystallization is recognized as one of naturally-occurring self-assembly process. Crystallization of polymers has attracted particular interests due to the formation of hierarchical and flexible nanostructures. Recently, crystallization is utilized as driving forces for the formation of polymeric nanostructures. Macromolecular chains fold back and forth during crystallization to form anisotropic nanostructures with varied morphologies including rods, lamellae, and so on, depending on the composition and self-assembly conditions [27–31]. A number of crystalline block copolymers and end-functionalized homopolymers have been used to fabricate nanostructures through crystallization-driven self-assembly. PFS based copolymers (PFS: poly(ferrocenyldime thylsilane)) self assembled into cylindrical micelles with PFS cores, driven by crystallization of PFS block [32–35]. Crystallization-driven cylindrical micelles were amendable to polyethylene (PE) and poly(ε-caprolactone) (PCL) based block copolymers [36–38]. Recently, fluorescent polymer nanosheets have been fabricated through crystallization of polymers [39]. Crystallizable polymers terminated with fluorescent group were allowed to crystallize. During crystallization of polymers, fluorescent groups were expelled out of lamellar crystals of polymers, and finally resided on the surface. This afforded the formation of polymer nanosheets with surface-enriched fluorescence groups, which showed sensitive response to explosives. More recently, Janus polymer nanosheets have been achieved by evaporation-induced crystallization of dicarboxyl capped PCL at a water/pentyl acetate interface [40]. The two surfaces of the nanosheets showed distinct water contact angle. Herein, we report a facile and efficient approach for scalable synthesis of polymer flowers decorated with Prussian blue (PB) and graphene nanosheets for the first time. This approach involved graphene-induced crystallization of polyethylene capped with a cyanoferrate complex (PE–Fe), followed by *in situ* coordination polymerization of cyanoferrate complex with $Fe^{3+}$ on the surface. We demonstrated that graphene was capable of inducing the crystallization of PE–Fe. During crystallization of polyethylene, both cyanoferrate complex and graphene were expelled out of PE crystals, and finally located on their surface. Such inorganic ferrate layers and graphene nanosheets having high free energy were inclined to absorb PE segments and initiate the crystallization of PE in turn. When the crystallization growth rate and nucleation rate are comparable, flower-like structures formed. After coordination polymerization of cyanoferrate with $Fe^{3+}$ on surface, polyethylene/Prussian blue/graphene (PE–PB/graphene) hybrid flowers were achieved, as illustrated in Fig. 1. The hybrid flowers showed significantly improved thermal stability, surface area and electrocatalytic activity toward reduction of hydrogen peroxide. Such graphene-induced flower-like nanoarchitectures offer a catalog of functional nanomaterials useful for biosensing, nanodevices, and so on.

## 2. Experimental section

### 2.1. Materials and chemicals

Graphene (reduced graphene oxide) nanoplatelets were purchased from Strem Chemicals Inc. An oxygen content and

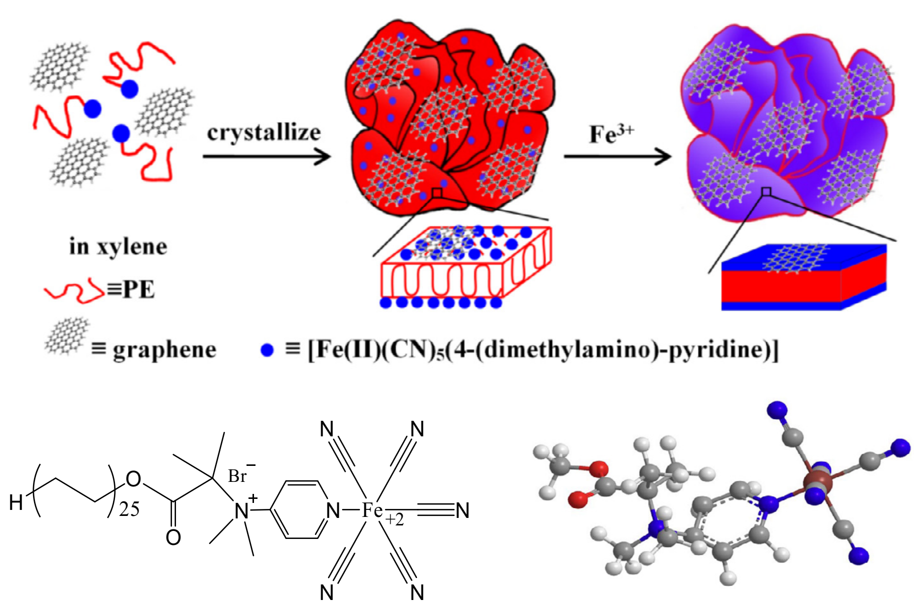


**Fig. 1 – Schematic illustration for synthesis of PE–PB/graphene hybrid flowers, chemical structure and ball-stick modeling of polyethylene terminated with [Fe(II)(CN)$_5$(4-(dimethylamino)-pyridine)] (PE–Fe). For clarity, a methyl group is used to stand for polyethylene in the ball-stick modeling. (A color version of this figure can be viewed online.)**