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## COMMUNICATION

## Unique Surface-Initiated Property of Nanoparticles and Application for the Synthesis of Hybrid Organic/Inorganic Nanoparticles

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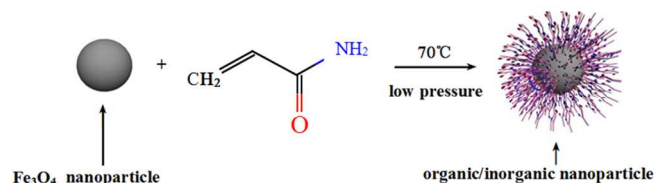
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We report a unique property of nanoparticles to initiate acrylic acid and acrylamide solution polymerization under low air pressure conditions. This property could be applied to synthesize a wide variety of hybrid organic/inorganic nanoparticles, which hold great promise for use in nanophotonics, catalysis, and medical applications.

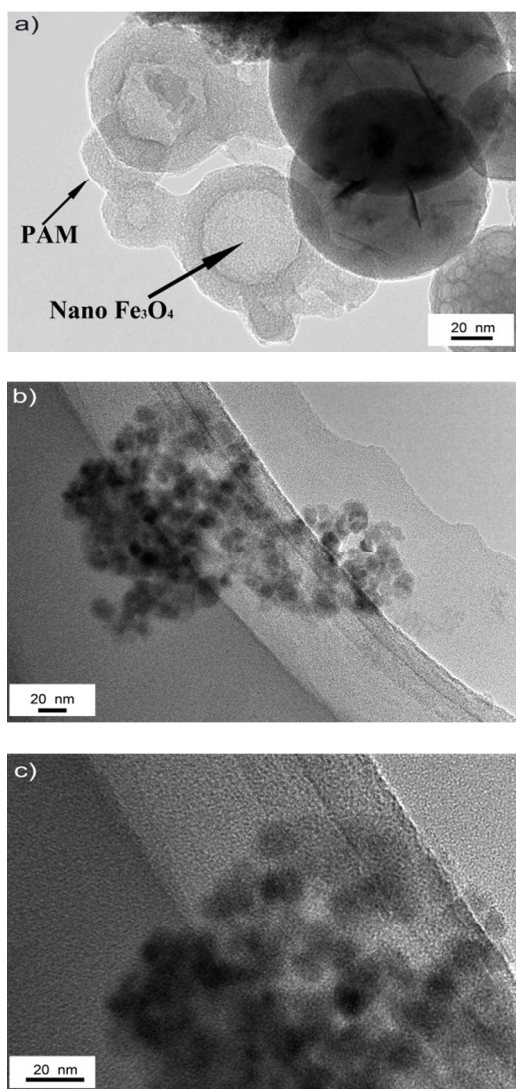
Understanding and utilizing the unique functionalities of nanoparticles has been an active area of research receiving significant attention.<sup>1-3</sup> To realize the complete advantages of these exceptional properties on the nanoscale,<sup>4,5</sup> the nanoparticles should be incorporated into other materials that possess desirable properties, to form hybrid composites.<sup>6,8</sup> For instance, the development of organic/inorganic hybrid composite materials has opened up new exciting opportunities in the field of polymer chemistry, enabling the preparation of complex and multifunctional materials.<sup>9-11</sup> In addition, the advent of organic/inorganic hybrid composite materials has facilitated significant advancements in the field of biomaterials,<sup>12</sup> supramolecular chemistry, and so on.<sup>13-16</sup> Herein, we establish that nanoparticles could initiate AM and AA polymerization directly, thus demonstrating a novel strategy for the synthesis of new organic/inorganic hybrid composite materials.<sup>17-19</sup> The mechanism underlying the protocol proposed in this study is different from the surface-initiated controlled polymerization, wherein the polymers are initiated on the surfaces of the nanoparticles by using other initiators.<sup>20-23</sup> Furthermore, we believe that the methodology proposed in this study will initiate a new polymerization mechanism, which will enable the design of polymeric materials with useful and tunable properties.

The unique property of nanoparticles was accidentally discovered when we added AM to an Fe<sub>3</sub>O<sub>4</sub> hydrosol at 70°C under low air pressure conditions. After 40 min, the mixture changed into a sticky gel, which confirmed the formation of the hybrid organic (PAM)/inorganic (Fe<sub>3</sub>O<sub>4</sub>) composite (Fe<sub>3</sub>O<sub>4</sub>@PAM). The chemical process associated with the formation of this composite is shown in Fig. 1.



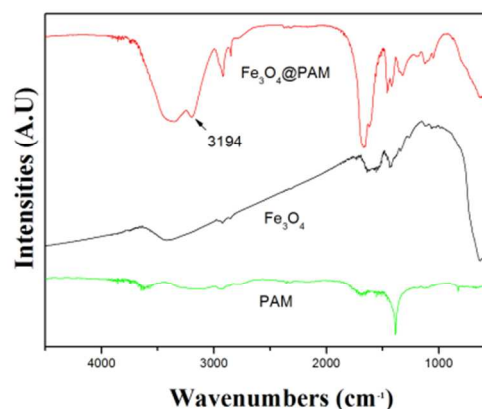
**Fig. 1** Chemical process underlying the formation of hybrid organic (PAM)/inorganic (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@PAM).

Fig. 2a shows the typical high-resolution transmission electron microscopy image (HRTEM) of Fe<sub>3</sub>O<sub>4</sub>@PAM dispersed in ethanol. It is observed that the relative amount of PAM coating increases with a decrease in the diameter of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles. In other terms, small Fe<sub>3</sub>O<sub>4</sub> nanoparticles are amply coated with PAM, while large Fe<sub>3</sub>O<sub>4</sub> nanoparticles are barely coated with PAM. This is consistent with the experimentally observed phenomenon that the diameter of the nanoparticles significantly influences the reaction rate. More specifically, smaller nanoparticles result in a higher reaction rate, whereas bigger nanoparticles (diameter >100 nm) barely initiate the AM polymerization. Fig. 2b and 2c show the HRTEM images of the Fe<sub>3</sub>O<sub>4</sub>@PAM dissolved in water. As evidenced from the HRTEM images, the organic PAM is coated onto the surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and most of them agglomerated because of the presence of PAM. Fig. 2d shows the typical thermogravimetry-differential scanning calorimetric (TG-DSC) curve of Fe<sub>3</sub>O<sub>4</sub>@PAM, indicating a grafting percentage (GP%, mass ratio of the organic and the inorganic components) of 400%. Thermal degradation of the grafted PAM occurred in the temperature range 410–460°C.



**Fig. 2** HRTEM and TG-DSC curve of  $\text{Fe}_3\text{O}_4@PAM$ . a) HRTEM image of  $\text{Fe}_3\text{O}_4@PAM$  dispersed in ethanol, the relative amount of PAM coating increases with a decrease in the diameter of the  $\text{Fe}_3\text{O}_4$  nanoparticles. b), c) HRTEM image of  $\text{Fe}_3\text{O}_4@PAM$  dissolved in water; as evidenced from the image, the organic PAM is coated onto the surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles. d) Typical TG-DSC curve of the  $\text{Fe}_3\text{O}_4@PAM$ .

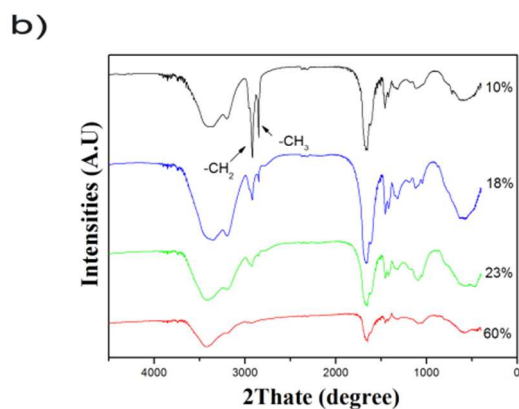
As mentioned earlier, the mechanism of the proposed reaction is different from that reported:<sup>24</sup> the reaction is initiated from the surface of the nanoparticles directly without other initiators, probably because of the strong chemical bonding between the AM solution and the  $\text{Fe}_3\text{O}_4$  nanoparticles under low air press condition. This postulate was further verified by Fourier-transform infrared spectroscopy (FTIR) analysis of  $\text{Fe}_3\text{O}_4@PAM$  (Fig.3). The FTIR spectrum of  $\text{Fe}_3\text{O}_4@PAM$  exhibits the characteristic absorption bands of both pure  $\text{Fe}_3\text{O}_4$  nanoparticles and pure PAM, in addition to a new absorption band at  $3194\text{cm}^{-1}$ . This indicates the possibility of a new chemical bond that binds PAM with the  $\text{Fe}_3\text{O}_4$  nanoparticles.



**Fig. 3** Fourier transform infrared (FTIR) spectra of  $\text{Fe}_3\text{O}_4@PAM$  hybrid,  $\text{Fe}_3\text{O}_4$  and PAM. The FTIR spectrum of  $\text{Fe}_3\text{O}_4@PAM$  exhibits a new absorption band at  $3194\text{cm}^{-1}$ , indicating a new chemical bond between PAM and the  $\text{Fe}_3\text{O}_4$  nanoparticles.

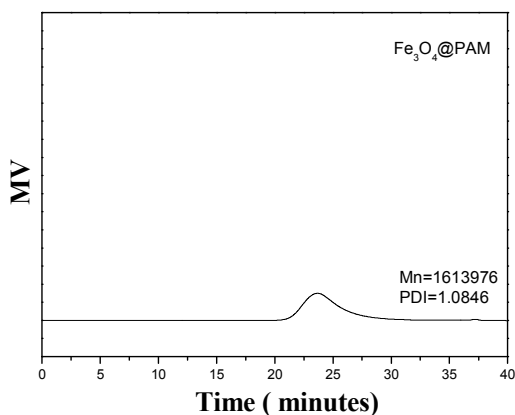
To gain further insight into the characteristics of the proposed chemical reaction, we prepared different  $\text{Fe}_3\text{O}_4@PAM$  hybrids by varying the experimental conditions. It could be realized that the air press is the most important factor influencing the chemical reaction. When the air press was in the above  $0.02\text{Mpa}$ , the reaction virtually is not initiated. Overall, the reaction rate increases with increasing the air press. In addition, with an increase in temperature, the reaction rate increases, and the optimum temperature is  $60\text{--}70^\circ\text{C}$ . It is worth noting that the preparation methodology plays an important role in the formation of the  $\text{Fe}_3\text{O}_4@PAM$  hybrid. The reaction solution needs to be heated to the optimum temperature initially, followed by a decrease in air press (experimental setup is shown in Fig. 4a). Notably, the AM content shows an intriguing trend: when the initial reaction solution has a high concentration of AM, the resulting  $\text{Fe}_3\text{O}_4@PAM$  hybrid has a lower PAM content, and vice versa. This is verified from the FTIR spectra of the hybrids (Fig. 4b), which indicate differences in the  $-\text{CH}_2$  and  $-\text{CH}_3$  stretching regions, demonstrating that the thickness of the organic coating by grafting on the surfaces of nanoparticles increases with a decrease in the initial concentration of AM in the reaction solution.





**Fig. 4** Experimental sets and FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>@PAM. a) Photograph of the experimental setup used in this study. b) FTIR spectra of the Fe<sub>3</sub>O<sub>4</sub>@PAM hybrids synthesized in the reaction solutions with different AM mass concentrations (10%, 18%, 23%, and 60%), demonstrating that the extent of organic coating by grafting on the surfaces of the nanoparticles increases with a decrease in the initial concentration of AM in the reaction solution.

Fig. 5 shows the GPC trace of the Fe<sub>3</sub>O<sub>4</sub>@PAM hybrid particles: Mn = 1613976 g/mol and PDI = 1.0846, showing that the hybrid system is monodisperse.



**Fig. 5** GPC trace of the Fe<sub>3</sub>O<sub>4</sub>@PAM hybrid particles

To demonstrate the universality of the unique property identified in this study, we used different initiators, namely, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe, Co, Ni, Au, Ag, and Pt nanoparticles. All the abovementioned materials could successfully initiate the polymerization of AM solution under appropriate conditions. The experimental findings also suggest that TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles could be used as initiators to initiate the polymerization of AA solution directly under the conditions of low air press. We also attempted to initiate the reactions of other vinyl monomers, namely, poly(methyl methacrylate) (MMA), polystyrene (PS), poly(4-vinylbenzocyclobutene) (PVA), and poly(acrylonitrile) (PAN), using the nanoparticles as initiators. The result indicated that the nanoparticles could only initiate the polymerization of AA and AM in water solution under low air press conditions, and not the

polymerization of other vinyl monomers. This indicated that carboxylic acid is necessary for the reaction.

In summary, we have made an exciting discovery that nanoparticles show a unique surface-initiated property under the low air press conditions, which will enable a new polymerization mechanism. This property facilitates a novel, simple, and facile technique for the synthesis of new hybrid organic/inorganic nanoparticles and supramolecular polymers. The results of systematic analysis revealed that the condition of low air press has a major influence on the surface properties of the nanoparticles. We believe that the phenomenon proposed in this study will hold great promise for the study of the surface properties of nanomaterials.

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## Method

In the typical experiment, nanoparticles were mixed with 50 ml of the reaction solution containing 10 g of AM. After 20 min of ultrasonication, the reaction solution was heated to 70°C, and then, the air press was decreased for about 1 h. Finally, the obtained product was washed with ethanol.

## Notes and references

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