An Easy Preparation of BaTiO₃/PAM organic/inorganic hybrid material Using Surface-Initiated Process

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Abstract—We developed an easy surface-initiated polymerization process to prepare BaTiO₃/PAM organic/inorganic hybrid hydrogel material, which would have potential applications in intelligent soft substances. As various organic–inorganic hybrid nanoparticles can be synthesized by this property, it has broad applications in fields such as nano hybrid material, nanocomposites and medicine.

1. Introduction
Comprehending and utilizing the unique functionalities of nanoparticles has attracted considerable research attention.[1,2] To realize the full advantages of these excellent properties on nanoscale,[3] the nanoparticles should be combined with other materials that possess the desirable properties, to form hybrid composites.[4,5] For example, in the field of polymer chemistry the development of organic/inorganic hybrid composites has opened up exciting new horizons, making the preparation of composite multifunctional materials possible.[6,7] In addition, the advent of organic/inorganic mixture composite materials has boosted significant advancements in fields such as biomaterials [8] and supramolecular chemistry.[9]

Here we imparted the initiation property to BaTiO₃ by peroxidizing it in a mixed solution of H₂O₂ and NaOH, and then the surface-modified BaTiO₃ nanoparticles were added in the mixture solution of reducing agent FeCl₂ and AM under N₂ conditions. After 30 min, the mixture changed into a brownish-yellow sticky gel, which confirmed the formation of the hybrid organic (PAM)/inorganic (BaTiO₃) composite (BaTiO₃@PAM). The chemical process associated with the formation of this composite is shown in Fig. 1.
2. Experimental

2.1. Materials
Acrylic acid (AA, from Beijing Xingjin Chemical Factory), Acrylamide (AM, Shantou Xilong Chemical Factory Guangdong), Potassium persulfate (KPS, Beijing Hengye Zhongyuan Chemical Co., Ltd), N, N'-Methylene bisacrylamide (NMBA, Tianjin Jinke Research Institute of Fine Chemical), NaOH and Sucrose were obtained from Beijing Chemical Factory. All of them were of analytical grade and used without further purification.

2.2. Characterization
The X-ray diffraction (XRD) patterns of the carbon materials were obtained with a Shimadzu 7000 diffractometer instrument using Cu Kα radiation (λ= 0.15406 nm). The surface morphology of the carbon materials were observed by using a scanning electron microscope (SEM: HITACHI S-4800, Japan). The Fourier Transform Infrared Spectrophotometry (FTIR, IFS113V, Bruker) was used to identify the functional groups.

2.3. Sample preparation
In a typical experiment, barium titanate was added to the mixed solution of sodium hydroxide and hydrogen peroxide. After 10 min of reaction, barium peroxide was prepared by washing and drying. Then, the compound nanoparticles were prepared in the redox system, which used barium peroxide as an initiator and ferrous sulfate as a reducing agent.

3. Results and discussion
To study the surface changes of the BaTiO₃ nano particles, the functional groups were tested. Fig. 2 shows the Fourier-transform infrared (FTIR) spectra of pure barium titanate (BT) along with the products obtained by the surface treatment of barium titanate with the hydrogen peroxide solution (BT-OH) and the sodium peroxide solution (BTO), respectively. The graph shows that the broad peaks of the two surface-modified products at 3445 cm⁻¹ are significantly enhanced, indicating that several hydroxyl groups[10] have been added to the surface of barium titanate. I
To confirm the reaction process, the valence of the Ba, O and Ti are tested. Fig. 3 shows the XPS results of pure barium titanate and barium peroxide. The valence states of titanium and barium did not change while a new peak of 528.5 eV is generated in the O1s X-ray photoelectron spectrum of barium peroxide, which is not attributed to pure barium titanate. Because the energy of the peroxide group itself is higher than that of the more stable oxygen atom in the lattice, it can be presumed that the peak corresponds to the peroxide group.

![XPS comparison diagram for O1s elements (a) and barium peroxide (b) BOT@PAM](image1)

Fig. 4 shows the DTA and TG curves obtained by the differential thermogravimetric analysis of the polymerization products. According to the TG curve, the polymerization product has four obvious weightlessness stages. The first stage occurs at 50−250 °C and the weight loss rate is about 13.18%.

![DTA and TG curves obtained by differential thermal - thermogravimetric scanning](image2)

Fig. 5 shows that the surface of pure barium titanate is smooth, while the surface of barium peroxide appears foggy because of the presence of some unevaporated solution after the oxidation treatment. The small black dots of barium titanate and several polymers growing around it can be clearly seen in the composite polymer.
Figure 5. TEM images of (a) pure barium titanate particles BT, (b) oxidized barium titanate BTO, (c) BTO/polyacrylamide composite BTO@PAM, (d) BTO/polyacrylamide composite BTO@PAM.

Fig. 6 shows the influence of different amounts of barium peroxide on the composite nanoparticles. The figure illustrates that the maximum weight loss rate is reached when the dosage of barium peroxodioxide is 0.08 g, and the value of GP (representing the average polymer coverage of particles) is the highest, reaching 5.55. This proves that more reaction sites can be activated and more polymers can be grafted at this time, and that the initiated polymer polymerization is relatively uniform.

Figure 6. The GPC of the BTO@PAM composites

4. Conclusions
In summary, we have developed a easy process to prepare BTO@PAM nano hybrid material, which will enable a new polymerization mechanism. We believe that the phenomenon proposed in this study holds great promise for the study of surface properties of nano materials.

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