Polymer Langmuir–Blodgett film of organic–inorganic (Fe₂O₃) composite microgel*

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Abstract

Methylacrylic acid was used as a surfactant to prepare Fe_2O_3 organosol by the microemulsion method in a system of water–toluene. Then divinylbenzene was added into the organosol as cross-linking agent together with azo-iso-butyl nitrile as the initiator. An organic–inorganic composite microgel was obtained after reacting under supersonic stirring. This composite microgel showed very good amphiphilic properties. It could be transferred onto Si, CaF_2 and quartz substrates from a pure water interface using the Langmuir–Blodgett (LB) technique. IR and UV–visible spectra of the composite microgel have shown the presence of some residual vinyl groups; this means that the microgel could be further polymerized. The stability of these polymer LB films can be improved by further polymerization. Transmission electron microscopy (TEM) was used to detect the quality of the monolayer fabricated with this composite microgel. Using TEM together with the small-angle X-ray scattering method we obtained a particle size in the range 19–27 Å. The structure of the ferric oxide in the composite microgel was identified to be α-Fe_2O_3 from X-ray photoelectron spectroscopy and electron diffraction data.

1. Introduction

Because of the special chemical and physical properties of the nanosize particulate, the study of it has become more and more attractive [1–7]. One of the most challenging problems is to arrange these nanoparticulates in a defined and functional way while maintaining their mesoscopic physical properties [6]. Recently some authors have recognized that a Langmuir–Blodgett (LB) matrix can provide the necessary geometrical arrangement to control the organization of the nanoparticulate [8–13]. Two different methods have been generally adopted. The first consists in forming the nanoparticulate at the surface of the monolayer [8, 9] or within the multilayer [12, 13]. The second method consists of adsorbing the ionic particulate to the negatively charged monolayer or multilayer film [10, 11].

In this paper we present the synthesis of a new organic–inorganic composite microgel which was used to prepare LB films containing ferric oxide ultrafine particles by a different method.

It has been reported that Fe_2O_3 ultrafine particles have a strong third-order optical non-linear response and that a surfactant coating the ultrafine particles can greatly improve their third-order optical susceptibility

[7]. In our experiments, we used methylacrylic acid (MA) as a surfactant to prepare Fe_2O_3 ultrafine particle organosol. Divinylbenzene (DVB) was added into the organosol as cross-linking agent together with azo-iso-butyl nitrile (AIBN) as the initiator. After reacting under supersonic stirring, a composite microgel with an organic layer of MA–DVB copolymer tightly bound on the surface of the Fe_2O_3 ultrafine particles was obtained. By controlling the conversion of the polymerization reaction, we got a composite microgel on a nanosize scale showing very good amphiphilic properties. In this paper, it is proved that the LB films fabricated by this method have a good monolayer and multilayer structure. This provides a great prospect for developing new kinds of special material.

2. Experimental details

The $FeCl_3$, NaOH, hydrochloric acid (HCl), methanol and toluene used were all AR reagents bought from the Shenyang Reagents Company. MA was distilled at a pressure of 5 mm Hg, and DVB at a pressure of 10^{-4} mm Hg. The Fe_2O_3 composite particulate was prepared in a system of deionized water–toluene. The procedure was carried out in two steps as follows.

(1) 475 ml of water, 25 ml of 0.2 M aqueous $FeCl_3$ and 120 ml of toluene were poured into a beaker. This

solution was stirred and 0.4 M sodium methylacrylate (NaMA) was added dropwise. The PH of the solution was maintained at a value of 4 during the addition of NaMA. The final solution was further stirred for 20 min. The organic phase became gradually red. The iron-containing toluene solution was refluxed for 2 h in order to improve the crystallization of the colloid particulate. After this procedure an organosol of ferric oxide ultrafine particulate covered with MA was obtained.

(2) The ultrafine particulate organosol was mixed with DVB in different ratios. The solution was bubbled with N_2 for 5 min prior to the addition of AIBN. The solution was then heated to 70 °C and maintained at this temperature for 7 h. This solution was then poured into methanol which resulted in the precipitation of the composite microgel. This microgel showed a very good solubility in several organic solvents (toluene, chloroform, ethyl acetate and styrene).

By controlling the conversion of the monomer to the polymer, a composite microgel showing good amphiphilic properties was obtained. LB films of this microgel were prepared at 19 °C. The surface pressure of the deposition was 20 mN m^{-1} and the speed of deposition was 0.4 cm min^{-1}. UV–visible absorption spectra and X-ray photoelectron spectra of the microgel LB films were measured by using respectively CaF$_2$ substrates and Si or glass substrates. LB films for transmission electron microscopy (TEM) were prepared using copper grids attached to glass slides. The copper grids were covered with thin organic hydrophilic film prior to LB film deposition. For the X-ray photoelectron spectroscopy (XPS) measurements, the toluene solution containing the composite microgel was poured on a film of collodion.

IR spectra and UV–visible spectra were recorded with a Nicolet 5DX-FT spectrometer and Hitachi 557 spectrometer respectively. A photograph from TEM and a photograph of the electron diffraction image were obtained with a Hitachi H 500 transmission electron microscope. X-ray photoelectron spectra were recorded with a VG Scientific Escalab MKII spectrometer. Small-angle scattering spectra were recorded with a Rigaku D/max rA X-ray scattering instrument.

3. Results and discussion

3.1. Composite microgel

Figure 1, Fig. 2 and Fig. 3 present the IR spectra of MA, Fe$_2$O$_3$ ultrafine particles coated with MA and the composite microgel respectively. When comparing the spectra of Figs 1 and 2, it can be seen that the C=O stretching vibration band of MA located at 1692 cm^{-1} in Fig. 1 disappears completely in Fig. 2 and that the
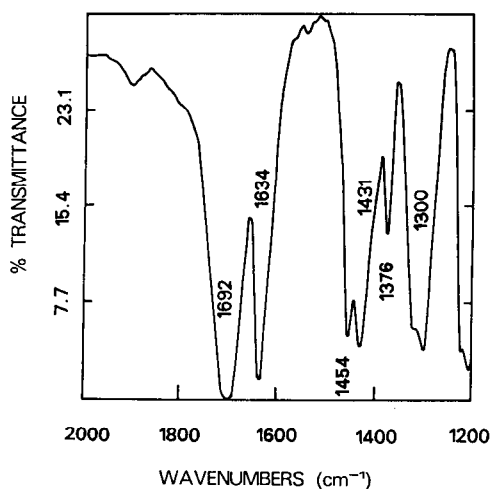
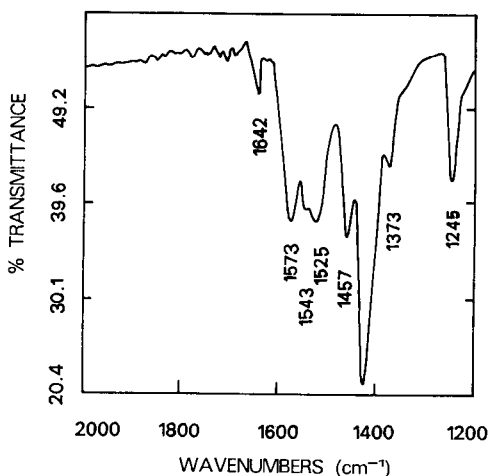Fig. 1. IR spectrum of pure MA on the surface of a KBr wafer.

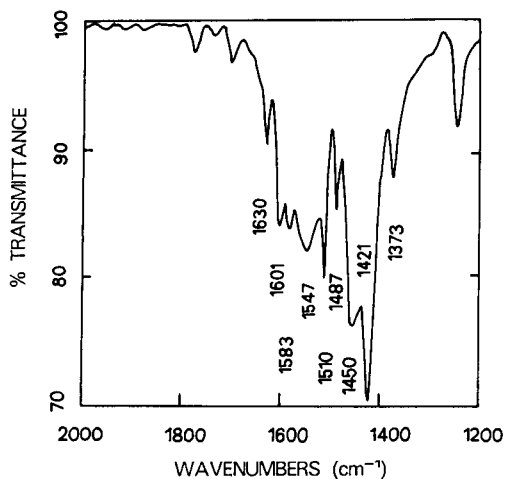Fig. 2. IR spectrum of the powder sample of Fe$_2$O$_3$ ultrafine particles coated with MA.

Fig. 3. IR spectrum of the composite microgel powder sample.

TABLE 1. The data for the ferric oxide interplanar distance d from the diffraction image of the composite microgel powder sample and reference

Number of diffraction rings	d (nm)	
	Calculated	α-Fe_2O_3 reference data
1	2.31	2.292
2	1.334	1.3115
3	1.149	1.1411

COO^- asymmetric stretching vibration band located between 1525 and 1573 cm^{-1} which was absent in Fig. 1 appears in Fig. 2. The O–H stretching vibration band located at 1300 cm^{-1} in Fig. 1 also disappears in Fig. 2 after the combination of the COO^- with Fe^{3+}. These changes imply that the MA is all chemically bonded on the surface of the Fe_2O_3 ultrafine particles. When comparing Figs. 2 and 3, it can be seen that the C–C vibration bands of the phenyl group located at 1601, 1510 and 1487 cm^{-1} appear in Fig. 3 after the copolymerization. This proves that DVB has been copolymerized with the MA bonded on the surface of ferric oxide ultrafine particles. The stretching vibration band of vinyl from DVB located at 1630 cm^{-1} also appears in Fig. 3 which suggests that the composite microgel can be further polymerized.

The interplanar distance d of the ferric oxide in the composite particulate can be calculated from the electron diffraction image of the composite microgel powder sample. These data together with those for α-Fe_2O_3 are listed in Table 1. A comparison between these two columns of data indicates that the ferric oxide in the composite microgel is α-Fe_2O_3. Further support for this conclusion is given below (see Section 3.3).

3.2. Composite LB film

Figure 4 shows the pressure–area isotherm of the composite microgel monolayer on a pure water surface at 19 °C. LB films were prepared at a constant surface pressure of 20 dyn cm^{-1}.
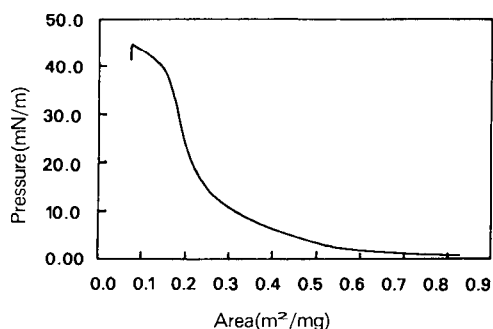
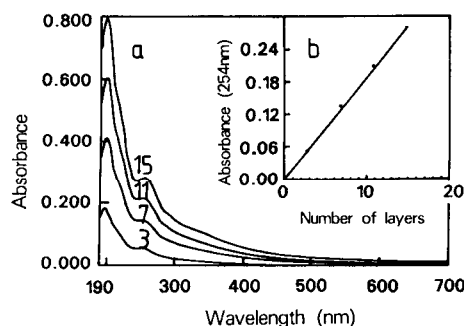Fig. 4. Pressure–area isotherm on a pure water surface at 19 °C; the pH value is 5.9.

Fig. 5. (a) UV–visible spectra of these seven, 11 and 15 layers deposited on CaF_2 substrates at 20 mN m^{-1}. (b) Absorbance vs. number of layers at 254 nm.

The absorption spectra of different layers of the composite microgel LB films deposited on CaF_2 substrates are shown in Fig. 5(a). Figure 5(b) presents the plot of the absorbance at 254 nm as a function of the number of layers of the composite microgel LB film. It can be seen that the absorbance increases linearly with the number of layers which strongly suggests that the microgel is very well transferred onto the CaF_2 substrate.

3.3. The structure of Fe_2O_3 in LB films

The XPS method was used to identify the structure of ferric oxide in the composite LB films. The data were obtained with seven-layer composite microgel LB film deposited on a glass substrate. Fe 2p (711 eV), Fe 3p (55.7 eV) and Fe 3s (93.7 eV) were identified as coming from α-Fe_2O_3 as reported in ref. 14.

3.4. Particle size and boundary effect

The TEM photograph of the composite microgel monolayer is illustrated in Fig. 6. We can see that the composite microgel particles peak close to each other to

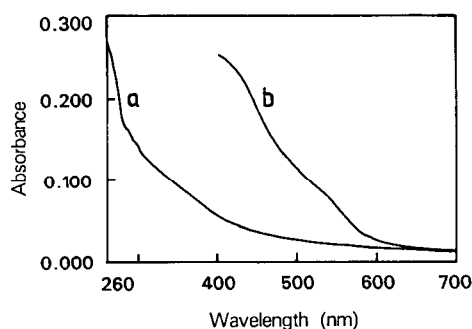Fig. 6. TEM photograph of one monolayer of the composite microgel (magnification, × 400 000).

Fig. 7. UV–visible spectra of Fe_2O_3: curve a, 15-layer composite LB film (particle size, 2.1 nm); curve b, Fe_2O_3 hydrosol (particle size, 65 nm). The details of sample preparation are being published elsewhere by Peng et al. [15].

form a very fine monolayer. Moreover the boundary between neighbouring particles can clearly be seen. This is presumably due to the existence of the MA–DVB copolymer layer at the surface of the ferric oxide ultrafine particulate. This clear boundary is the structural basis for the quantum confinement of the ferric oxide ultrafine particles. From this photograph it is possible to determine the particle size. It is in the range 19–27 Å with an average value of 21 Å. This value is smaller than the data (28 Å) obtained with the small-angle scattering method because the organic part cannot be seen with TEM. The statistical coverage of the substrate from the photograph is about 70%. Because each composite microgel can react with the neighbouring one, the film shows a very good stability. Indeed once the film is formed no organic solvent can wash it off the substrate.

If we compare the UV–visible spectrum of the 2.1 nm particle in a 15-layer composite LB film with that of the 65 nm particle in hydrosol (the preparation details of it are being published elsewhere by Peng et al. [15]), the onset of absorption shifts to short wavelengths as shown in Fig. 7. This result reveals that there

exists quantum confinement of nanoparticulate in the composite LB film.

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