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ORIGINAL CONTRIBUTION

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Synthesis and characterization of magnetic polymer microspheres with photoconductivity

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Abstract Novel magnetic polymer microspheres bonded with copper phthalocyanine were synthesized by esterfication between copper phthalocyanine and polystyrene microspheres with hydroxyl groups. The structure and properties of the magnetic polymer microspheres were identified by IR spectroscopy, elemental analysis and scanning electron microscopy, etc. The average diameter and diameter distributions were determined by laser diffraction size analysis. The results of property measurements show these novel microspheres have the advantages of good photoconductivity and good magnetic responsiveness.

Keywords Magnetic polymer microsphere · Copper phthalocyanine · Photoconductivity · Magnetic responsiveness

Introduction

In the past 20 years, magnetic polymer microspheres have been widely used in biomedical and bioengineering applications, such as cell separation, enzyme immunoassay, magnetic drug targeting, magnetic-field-assisted radionuclide therapy, etc., because of their relatively rapid and easy magnetic separation and specific surface [1, 2, 3, 4]. Recently such microspheres have been used to remove heavy-metal ions from industrial wastewater by adsorption/desorption [5] and have been attracting much interest owing to their optical and optoelectrical functions [6].

Obviously, further functionalized microspheres and some potential uses of microspheres are attracting much more attention. It is well known that phthlocyanine (Pc) is a cheap and good photoconductive material, which has also been widely used as a catalyst and a dye [7, 8]. In this study, microspheres which combine the merits of magnetic separation with photoconductivity were designed and prepared. The microspheres could have considerable uses, for example, if a bioreactive molecule, for instance, an antigen or antibody, was linked with a Pc molecule, it could be used as a novel diagnosis/detection reagent because of its changeable photoconductivity signal. In addition, as a catalyst support used in fine chemical synthesis, it also has the potential to assist in the cleaning of wastewater, etc.

Experimental

Materials

Styrene was treated with a 5% sodium hydrate solution to remove inhibitor. CuCl, urea, trimellitic anhydide, allyl alcohol, divinylbenzene (DVB) and other reagents were commercially available and of analytical grade. $SOCl_2$ was purified by redistillation. Water was double-distilled.

Synthesis

Preparation of copper 4,4′,4″,4‴-tetracarboxchloride Pc

The synthesis of copper 4,4′,4″,4‴-tetracarboxchloride PC [CuPc $(COCl)_4$] was according to the method described in Ref. [9].

Synthesis of magnetic polymer microspheres with hydroxyl groups

Magnetic polystyrene (PS) microspheres with hydroxyl groups (PSA) were prepared by dispersion polymerization of styrene (15.0 g) with allyl alcohol (2.0 g) using potassium persulfate (0.45 g) as an initiator in an ethanol/water (66 ml/39 ml) medium and in the presence of Fe_3O_4 magnetic fluid (10.0 g). Fe_3O_4 magnetic fluid with an average particle size of 50 nm was prepared by a precipitation–oxidation method as mentioned in our previous work [10]. PEG-4000 (6.0 g) was used as a stabilizer in the polymerization. DVB (0.1 g) was added to form a cross-linking shell; the molar ratio of styrene to allyl alcohol to DVB was 80:19:1. The required amounts of ingredients were added in a 250-ml round-bottomed flask equipped with a reflux condenser, and the reaction was carried out at 70 °C for 10–12 h under a N_2 atmosphere. The resulting microspheres were purified by repeated magnetic separation, and this purification procedure was repeated after the microspheres had been immersed in 1 M HCl solution for 24 h to remove the Fe_3O_4 powder not encapsulated by the polymer, then the product PSA was dried for 24 h at 60 °C in a vacuum.

Synthesis of magnetic polymer microspheres with photoconductivity

Magnetic polymer microspheres with photoconductivity (PSCuPc) were prepared as follows. PSA (2.0 g), $CuPc(COCl)_4$ (0.1 g), dimethylformamide (DMF) (30 ml) and several drops of pyridine were mixed in a 50-ml single-necked round-bottomed flask with a magnetic bar and equipped with a reflux condenser. The reaction mixture was heated to 80 °C for 6 h, after which a blue-green solid was obtained. The solid was collected by magnetic separation, then washed with DMF several times and dried for 24 h at 80 °C in a vacuum. The synthesis process is shown in Scheme 1.

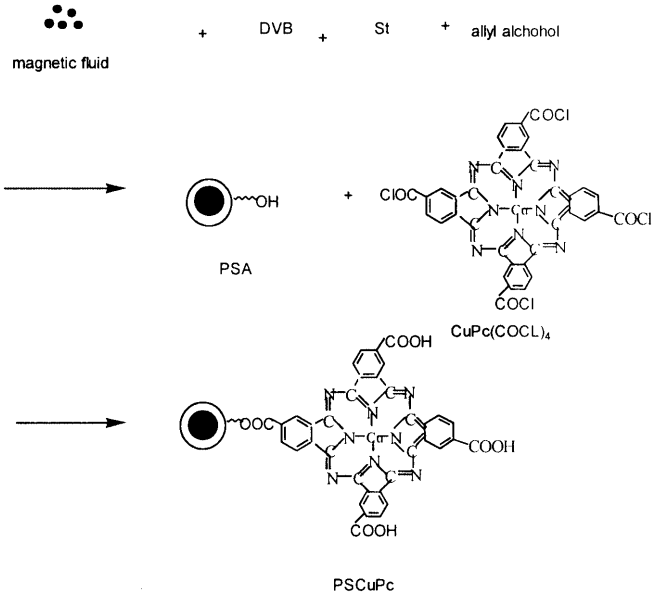
Characterization

The structure of the microspheres was confirmed by IR spectroscopy (Nicolet 200SXV FT-IR) with KBr pellets. The content of nitrogen in the microspheres was determined with a EA1108 elemental analyser; the content of CuPc was calculated from the nitrogen data. The content of magnetite entrapped in the microspheres was obtained by determining the iron content in PSCuPc using an ICA9000(N + M) plasma spectrograph. The morphology, the size and the size distribution of the microspheres were obtained using scanning electron microscopy (SEM, AMRAY-1000) and a laser diffraction size analysis (SALD-2001, Shimadzu, Japan) respectively.

The magnetic responsiveness of PSCuPc was determined as follows. PSCuPc (0.5 g) was suspended in 20 ml H_2O, then the supernatant transmittance of the suspension solution was determined with a spectrometer (721) at 580 nm after the mixture had been separated by an additional magnetic field (0.42 T) or sedimented for a certain time. By comparing the time for magnetic separation and sedimentation when the transmittance reached 95%, the magnetic responsiveness was tested. The whole process is shown in Scheme 2.

The photoconductivity of PSCuPc and $CuPc(COOH)_4$ was determined as follows. A double-layered photoreceptor device was made by coating the interface layer (IFL), the charge-generation layer (CGL) and the charge-transportation layer (CTL) successively onto an aluminium substrate. The IFL was polyamide. The CGL was formed by stirring 15 g glass beads, 0.1 g PSCuPc and 0.025 g poly(vinyl butyral) in 10 ml tetrahydrofuran for 6 h. The CTL contained α-naphthalic hydrazone, polycarbonate and poly(vinyl carbazole) (4:4:1 by weight).

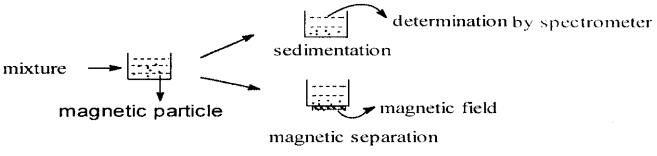
A GDT-I model photoconductivity measuring device was used with a 5 W, 24 V visible lamp as a light source to acquire photoconductivity data: charge acceptance, V_c, residual potential, V_r, dark decay (DD) and the time from the original potential to half that value on exposure, $t_{1/2}$. $t_{1/2}^{-1}$ can indicate photosensitivity; the bigger $t_{1/2}^{-1}$, the greater the photosensitivity.



Scheme 1. The synthesis process of magnetic polymer microspheres bonded with copper phthalocyanine (*PSCuPc*)

Results and discussion

The average diameter, the diameter distribution and the surface morphology of the microspheres were obtained by laser diffraction size analysis and SEM, respectively. The results are shown in Fig. 1 and 2. The average diameters of PSA and PSCuPc shown in Fig. 1a and b are 28.7 and 44.28 μm, respectively. The size distributions are multidistributional. The SEM photographs of PSA and PSCuPc are shown in Fig. 2. The PSA microspheres are smooth, as shown in Fig. 2a, but after reacting with $CuPc(COCl)_4$, the surfaces of the microspheres became blurred to some extent, as shown in Fig. 2b. It can be explained that in the synthesis of PSCuPc, DMF corroded the surface of PSA slightly although the PS shell was cross-linked by adding DVB. In addition, from Fig. 2b we found that some microspheres aggregated probably owing to the four COCl groups of CuPc $(COCl)_4$ reacting with no more than one microsphere at a time, and so the average size of PSCuPc was bigger



Scheme 2. Method for determining the magnetic responsiveness

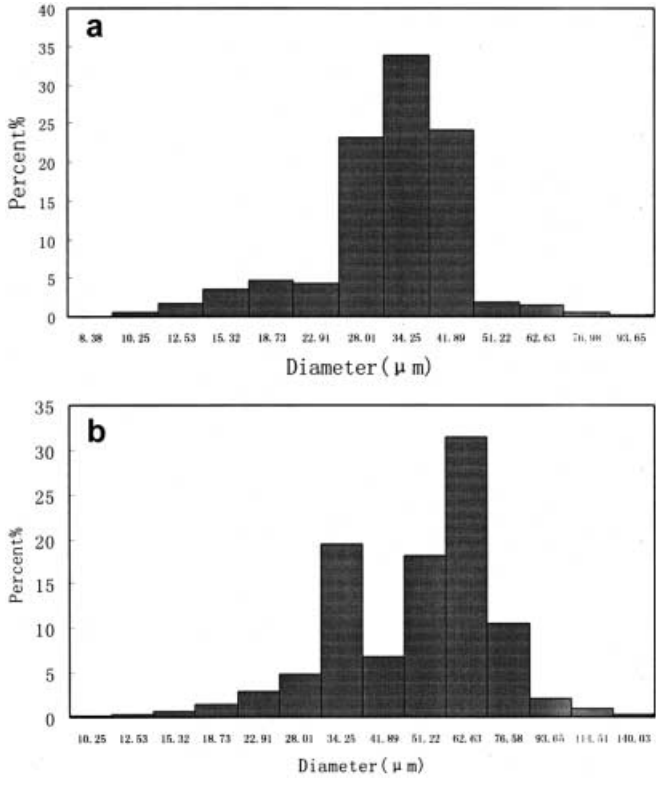


Fig. 1. Histogram of **a** polystyrene microspheres with hydroxyl groups (*PSA*) and **b** magnetic polystyrene microspheres bonded with copper phthalocyanine (*PSCuPc*)

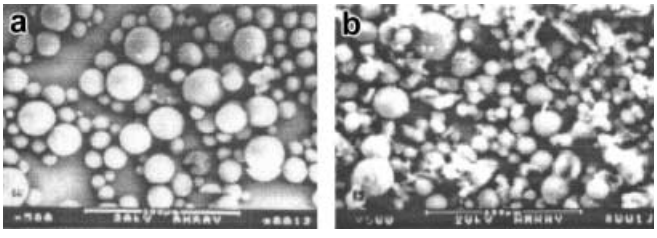


Fig. 2. Scanning electron microscopy photos of **a** PSA and **b** PSCuPc

than that of PSA. The mechanism will be investigated in detail in future work.

The IR spectra of $CuPc(COOH)_4$, PSA and PSCuPc are shown in Fig. 3. In the IR spectra of $CuPc(COOH)_4$ there is an absorption band at 1,697.20 cm^{-1} and a big, round absorption at 3,200 cm^{-1} due to carboxyl stretching and hydroxyl stretching, respectively. The spectra of PSA and PSCuPc show the typical spectrum of PS due to the adsorption bands in the region 2,000–1,750 cm^{-1} and the peaks at 755 and 698 cm^{-1}, but there is an absorption band at 1,725 cm^{-1} in the PSCuPc spectrum, which is attributed to ester carboxyl stretching, proving that $CuPc(COCl)_4$ had been successfully bonded on the PSA microsphere.

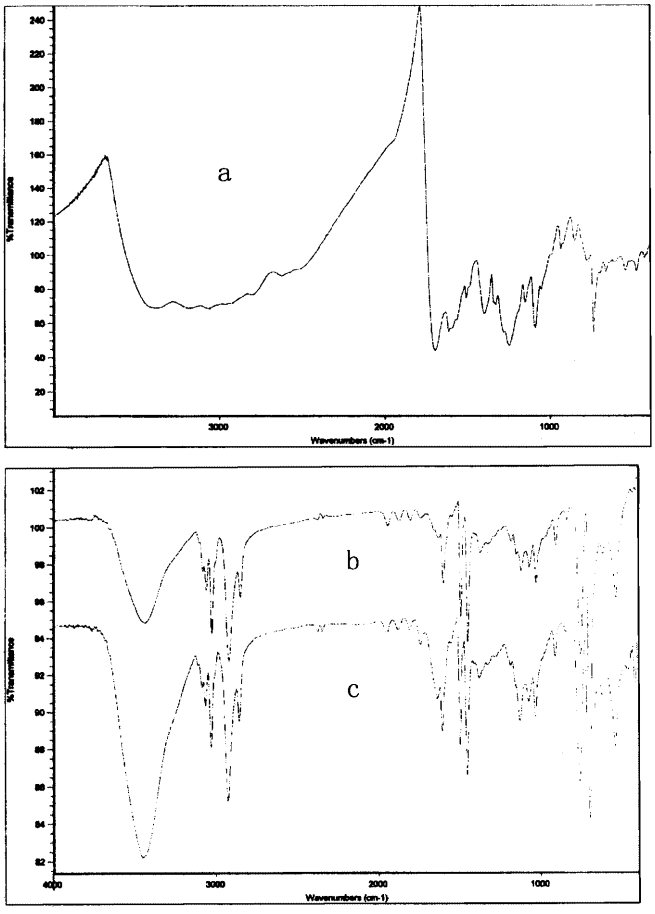


Fig. 3. IR spectra of **a** CuPc(COOH), **b** PSA and **c** PSCuPc

In order to confirm the result of the IR investigation, elemental analysis was performed. The results are shown in Table 1. In PSA there is no elemental N and Cu, but in PSCuPc both elemental Cu and N are present; the content of elemental Cu (0.15%) and N (0.29%) in PSCuPc is actually consonant with the ratio of Cu to N in $CuPc(COOH)_4$, which indicated that CuPc had been successfully bonded on the PSA microspheres. The Fe

Table 1. Elemental analysis of polystyrene microspheres with hydroxyl groups (*PSA*) and magnetic polystyrene microspheres bonded with copper phthalocyanine (*PSCuPc*)

Sample	N (%)	Fe (%)	Cu (%)
PSA	–	1.45	–
PSCuPc	0.29	1.48	0.15

Table 2. Photoconductivity of data of PSCuPc

Sample	V_c (V)	V_r (V)	DD (V/s)	$t_{1/2}$	$t_{1/2}^{-1}$
PSCuPc	821	23	68	0.90	1.11
$CuPc(COOH)_4$	630	125	184	3.53	0.28

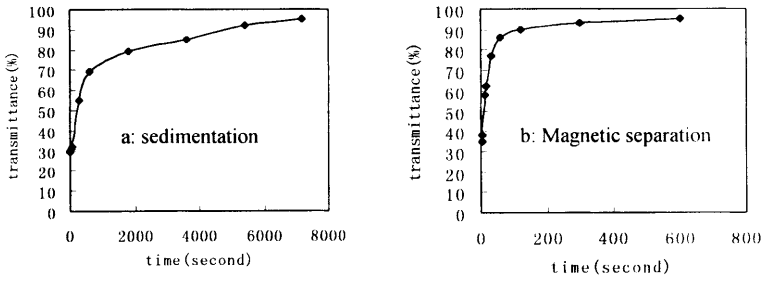


Fig. 4. Transmittance–time curves of a solution containing PSCuPc

content in PSA and in PSCuPc remained at almost the same level, which indicated that magnetite was not lost in the reaction. From the content of Fe in the microspheres, the content of magnetite in PSA and PSCuPc could be calculated; it was 2.00% in PSA and 2.04% in PSCuPc. Furthermore, it obviously confirmed the result of the IR measurements.

From the Cu or N content in $CuPc(COOH)_4$, the content of $CuPc(COOH)_4$ in PSCuPc could be calculated; it is about 1.76%, that is to say, the mean coverage of $CuPc(COOH)_4$ on PSCuPc is 0.23 $mmolg^{-1}$.

The photoconductivity of the magnetic polymer microspheres was measured using a double-layered photoreceptor device. The results in Table 2 show the photoconductivity data of PSCuPc and $CuPc(COOH)_4$. The exposure is 30 lux. From the results we can see there was a higher charge acceptance ($V_c = 821$ V) and a lower residual potential ($V_r = 23$ V) for PSCuPc than for $CuPc(COOH)_4$. The rate of dark discharge of PSCuPc is smaller (DD = 68 Vs^{-1}) than that of $CuPc(COOH)_4$ (DD = 184 Vs^{-1}), which indicates that the charge retention of PSCuPc is better than that of $CuPc(COOH)_4$. Furthermore, the time of half discharge of PSCuPc is 0.9 s, which is a much lower value than that of $CuPc(COOH)_4$ (3.53 s) and indicates much better photoconductivity and photosensitivity than for $CuPc(COOH)_4$. Chen et al. [11] investigated the photoconductivity of PS-*co*-$CuPc(NO_2)_2$. They think that there is interaction between the PS main chain and $CuPc(NO_2)_2$; this is beneficial for charge occurring by light transfer and hence is beneficial for promoting the photoconductivity property of this kind of polymer. In the PSCuPc microspheres there is also interaction between PS and $CuPc(COOH)_4$, so PSCuPc showed better photoconductivity than $CuPc(COOH)_4$.

Magnetic responsiveness is an important property of magnetic particles. Using this property we can realize fast separation and purification. We determined the magnetic responsiveness of PSCuPc by comparing the time for the supernatant transmittance to reach 95% under sedimentation and magnetic separation. The results are shown in Fig. 4. It was found that it took about 2 h for the transmittance to reach 95% under sedimentation, but only about 10 min under a magnetic field of 0.42 T. So PSCuPc showed good magnetic responsiveness.

Conclusions

Novel magnetic polymer microspheres with photoconductivity were synthesized. The photoconductivity and magnetic responsiveness were tested. The results showed that PSCuPc microspheres have good photoconductivity, photosensitivity and magnetic responsiveness. They may be used as a detection or cell-separation reagent.

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