

New approach to hybrid materials: Functional sub-micrometer core/shell particles coated with NiS clusters by γ -irradiation

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Abstract

Functional sub-micrometer core/shell hybrid particles coated with inorganic components have many promising applications as new materials based on their multiphase structures with unusual features. Herein we demonstrate a novel approach to produce such particles with potential applications in the fields of magnetic materials. PSt seed latex was prepared through emulsion polymerization. Core-shell P(St-co-Am) particles with polyacryamide (PAm)-rich shell were formed through interfacial-initiated seeded emulsion polymerization. Then spherical P(St-co-AM)/NiS sub-micrometer composites were successfully prepared by the reaction of nickelous sulfate (NiSO_4) and thioacetamide (CH_3CSNH_2) under ^{60}Co γ -irradiation at ambient temperature and pressure. P(St-co-AM)/NiS hybrid particles were confirmed with electron microscopy, X-ray diffraction and X-ray photo-electron spectroscopy. The properties of P(St-co-AM) hybrid particles were studied with UV-vis spectroscopy, photoluminescence spectroscopy and magnetic hysteresis loop analysis.

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1. Introduction

Much attention has been paid to the synthesis and characterization of core-shell sub-micrometer particles as functional building grafts in fabrication of materials with periodic structure and composition [1–5]. Such multi-layered polymers, having functional terminal groups, can be coated with various inorganic composites depending on the specific applications, such as epoxy-silica polymers hybrid materials [6–9]. These polymer-inorganic composites have the intriguing optical, electrical and mechanical properties [10–12] with quantum size effects [13,14], and are considered to have very promising applications in the field of chemical sensors, optical data storage devices, magnetic material [15], optical limiters, switches, drug delivery [16], non-linear optical materials and so on [17–20].

Many methods have been developed to synthesize the polymer particles coated with other composites [21–25].

Riedl B successfully synthesized organic-inorganic hybrid composites by controlled free radical polymerization [26]. Novel organic-inorganic hybrids were polymerized using sol-gel process and reactive processing without solvent [27–29]. Multi-disciplinary hybrid material with the core and double shells also has been successfully synthesized [30,31]. Substantial progress has been achieved in synthesis of core/shell polymers encapsulated with metal, metal-oxide, metal-sulfide [32] and the like.

Redox interfacial-initiated emulsion polymerization is a good way to produce polymer composite [33]. Hydrophobic core/hydrophilic shell amphiphilic composite lattices have been prepared by this method [33–35]. γ -Irradiation is one of the most simple and effective methods for the synthesis of hybrid materials. Our group has synthesized various inorganic/polymer nanocomposites and Yin et al. [36] have developed an γ -irradiation method to prepare polymer-metal hybrid nanocomposites. Firstly, monomer was polymerized in the solutions, with metal ions introduced before or after the polymerization. Secondly, metal ions in the polymer matrix were reduced by a reducing agent or by other means.

Here, we report a novel method for preparing hybrid sub-micrometer particles containing metal sulfide by

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γ -irradiation as shown in Scheme 1. This novel approach has two essential features: (1) The synthesis of core–shell sub-micrometer latex particles with hydrophilic surface by employing interfacial-initiated seeded emulsion polymerization; (2) in situ preparing NiS nano-clusters onto core–shell particles through the reduction reaction of NiSO_4 and thioacetamide under γ -irradiation, which offers a facile and mild synthetic route to hybrid sub-micrometer spheres of sulfide functional materials. However, such an approach remains to be extended to other metal composite and sulfide.

2. Experimental

2.1. Materials

Styrene (St) was distilled under vacuum and acrylamide (Am) was re-crystallized with chloroform. Both monomers were kept in a refrigerator before use. Cumyl hydroperoxide (CHPO), 2,2'-azobis(2-methylpropionamide) dihydrochloride (AMPA) are from Acros, nickelous sulfate (NiSO_4), ferrous sulfate hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), octylphenyl polyethyleneglycol ($n=10$) ether (OP-10), n -amyl alcohol, thioacetamide and isopropyl alcohol are all analytical reagents and used as received.

2.2. Preparation of PSt seed latex

Narrowly distributed PSt seed latex was synthesized via emulsion polymerization with non-ionic surfactant OP-10 as the emulsifier and n -amyl alcohol as co-emulsifier. OP-10 and n -amyl alcohol were dissolved in distilled water and St was added. Emulsion was obtained supersonically and the polymerization was carried out with AMPA as the initiator at 70°C while being purged for two hours with nitrogen. The reaction stood for 12 h to ensure the ultimate conversion.

The particle size and its distribution was determined on a

modified commercial laser light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- τ digital time correlator and a He–Ne laser (output power = 10 mW at 632 nm). Before DLS measurement, the latex was destabilized with ethanol, washed repeatedly with distilled water and ethanol and separated by centrifugation. The sub-micrometer particles were re-dispersed with distilled water and a filter was used to eliminate any dust ($0.80\ \mu\text{m}$). The intensity–intensity time correlation function $G^{(2)}(t, q)$ in the self-beating mode was measured. The Laplace inversion of $G^{(2)}(t, q)$ resulted in a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $\Gamma/q^2 = D$ at $q \rightarrow 0$ and $C \rightarrow 0$, so that $G(\Gamma)$ can be directly converted to the translational diffusion coefficient distribution $G(D)$ or the hydrodynamic radius distribution $f(R_h)$ by using the Stocks–Einstein equation: $R_h = k_B T / (6\pi\eta D)$ with k_B , T , and η being the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively [37]. Polydispersity index (PDI) of R_h was defined as Eq. (1).

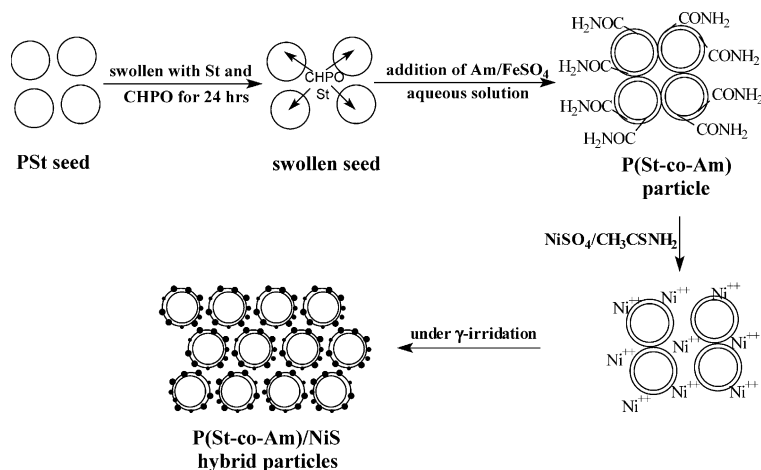
$$\text{PDI} = \frac{\mu_2}{\bar{r}^2} \text{ and } \mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma) d\Gamma \quad (1)$$

The morphology was observed under transmission electron microscopy (TEM, Hitachi H-800) with an accelerating voltage of 200 kV.

2.3. Preparation of P(St-co-AM) core–shell particles

P(St-co-AM) core/shell particles were synthesized by seeded emulsion polymerization. PSt seed latex was swollen with St containing CHPO for 24 h at room temperature. Then the latex was dropped continuously in monomer-staved state with an aqueous acrylamide solution containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and HCl at 30°C within 5 h. The polymerization stood for another 12 h.

The morphology of P(St-co-AM) core/shell particles was observed under TEM and their particle size was determined



Scheme 1. Schematic preparation of hybrid polymer-based material coated with NiS.

by DLS. The presence of PAM in P(St-co-AM) particles was confirmed on Fourier transform infrared spectroscopy (FTIR, Nicolet 759) with KBr pellets.

2.4. Preparation of P(St-co-AM)/NiS hybrid particles

CH₃CSNH₂, NiSO₄ and isopropyl alcohol in distilled water were introduced into P(St-co-AM) core/shell latex. After bubbling with N₂ for 40 min, the mixtures were irradiated in a field of 2.59×10^{15} Bq ⁶⁰Co γ -ray source at a dose rate of 80 Gy/min for an absorbed dose of 86 kGy. The whole reaction was performed at ambient temperature and pressure. After the reaction, the emulsion was destabilized with ethanol. The precipitate was separated by centrifugation and washed repeatedly with distilled water and ethanol. Then, P(St-co-AM)/NiS hybrid particles were dried under vacuum at room temperature for 2 days.

The morphology of P(St-co-AM)/NiS hybrid particles was observed under TEM as well as field-emission scanning electron microscopy (FESEM, JEOL JSM-6700) with the acceleration voltage of 10 kV. Their particle size was determined by DLS. Diffraction pattern of P(St-co-AM)/NiS hybrid particles was recorded on X-ray diffractometer (Rigaku D/max γ A) equipped with graphite monochromatic Cu K α radiation ($\lambda = 0.154178$ nm), at a scanning rate of 0.02°/s with 2θ in the range of 10–70°. X-ray photoelectron spectroscopy (XPS) was recorded on X-ray photoelectron spectrometer (ESCALAB MKII) using a non-monochromatic Al K α radiation (1486.6 eV) under high vacuum about 10^{-11} mbar.

2.5. Physical properties of P(St-co-AM)/NiS hybrid particles

UV–vis spectrum was obtained on Sahimadzu UV-2401 Spectrophotometer and photoluminescent spectrum was taken on Hitachi 850 fluorescence spectrometer with a Xe lamp ($\lambda_{\text{ex}} = 260$ nm) at room temperature.

Magnetic measurements for powder samples of several tens of mg were performed using a vibrating sample magnetometer (BHV-55, MODEL VSM VT-800, Riken Densh Co., LTD) at ambient temperature and at the fields ranging from 0 to 10 kOe. All the data were corrected for the contribution of the sample holder.

3. Results and discussion

3.1. Preparation of PSt seed particles

PSt seed latex was prepared through emulsion polymerization. The polymerization recipe and the particle size by DLS were summarized in Table 1. The data show the narrow distribution of PSt seed particles with hydrodynamic radius of 84 nm, which is in good consistence of TEM result as shown in Fig. 1(a). AMPA was used as the initiator to introduce some cations in the surface of seed particles, which facilitates the formation of core–shell morphology in the next polymerization.

3.2. Preparation of P(St-co-AM) core–shell particles

Scheme 2 presents an overview of redox interfacial-initiated seeded emulsion polymerization [35]. Oil-soluble St and CHPO were pre-swollen in the seed particles, while water-soluble AM and FeSO₄ were introduced slowly into the seed latex. CHPO and FeSO₄ make up a redox initiator pair, so the initiation mainly occurs at the interface between the seed particles and the medium, where those two components encounter each other. In this way, copolymerization of AM with St easily takes place at the interface to form core–shell structure. The polymerization recipe and the particle size were summarized in Table 1.

DLS data shows that P(St-co-AM) core–shell particles are larger than PSt seed particles while the size distribution hardly gets broader, indicating that secondary nucleation seldom happened during the seeded emulsion polymerization. After they were extracted with water for 3 days, their FTIR spectrum as well as that of PSt seed was recorded as shown in Fig. 2. The typical absorption band due to the carbonyl group of PAM is present at about 1700 cm^{-1} while the absorption bands due to PSt appear at 700, 757, 1029, 1452, 1493 and 1601 cm^{-1} . FTIR results demonstrate that PAM was incorporated onto the seed particles. The morphology of P(St-co-AM) core–shell particles was shown in Fig. 1(b), which demonstrates the core–shell structure with PSt (the black region) as the core and P(St-co-AM) (the pale region) as the shell.

Table 1
Preparation of PSt, P(St-co-AM) and P(St-co-AM)/NiS latex

Latex	Ingredients	Temperature and time	Particle size	
			R_h (nm)	PDI
PSt	<i>n</i> -Amyl alcohol: 1.0 ml; AMPA: 60 mg; St: 4 ml; OP-10: 1.012 g; H ₂ O: 50 ml	70 °C and 12 h	84	0.101
P(St-co-AM)	PSt latex: 40 ml; AM: 1.0 g; St: 0.3 ml; CHPO: 60 mg; FeSO ₄ ·7H ₂ O: 70 mg; H ₂ O: 10 ml;	35 °C and 15 h	98	0.112
P(St-co-AM)/NiS	P(St-co-AM) latex: 40 ml; NiSO ₄ : 0.4 g; thioacetamide: 0.3 g; γ -irradiation	Room temperature	103	0.126

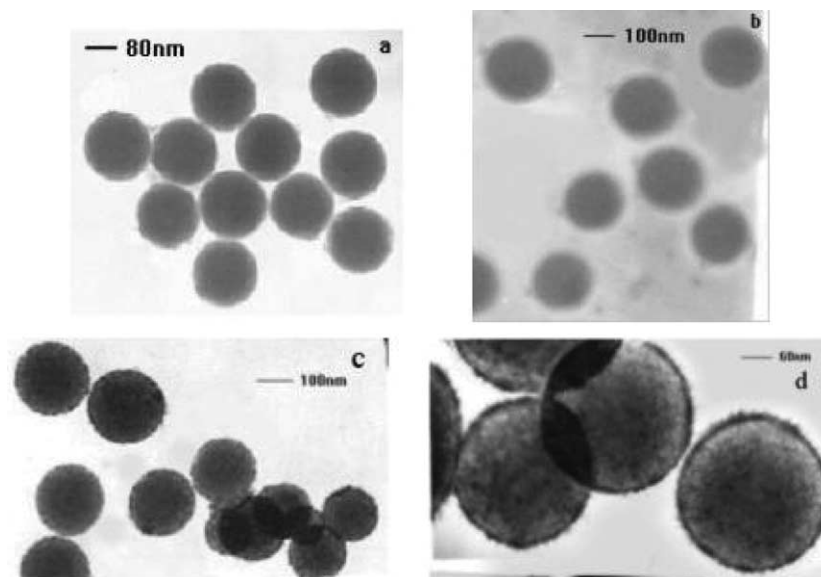
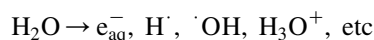


Fig. 1. TEM images of latex particles (a) PSt seed particles; (b) P(St-co-AM) core-shell particles stained with RuO₄; (c) P(St-co-AM)/NiS hybrid particles at lower magnification; (d) P(St-co-AM)/NiS hybrid particles at higher magnification.

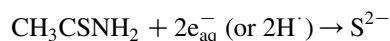
3.3. Preparation of P(St-co-AM)/NiS hybrid particles

NiS was introduced onto P(St-co-AM) particles by the reaction of thioacetamide with NiSO₄ under γ -ray irradiation. Isopropyl alcohol was used as a scavenger of oxidative radicals and chain-transfer reagent. The radiolysis of water produces many active species such as e_{aq}⁻, H \cdot and \cdot OH [38]. Then, the e_{aq}⁻ could reduce sulfur source to S²⁻, which reacted with Ni²⁺ to generate NiS. Meanwhile, isopropyl alcohol could eliminate the influence of oxidative radicals on the formation of S²⁻ anion. The possible reactions are described as follows.

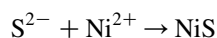
Radiolysis of water:



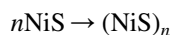
Reduction of thioacetamide:



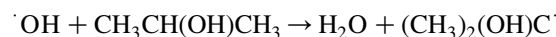
Combination:



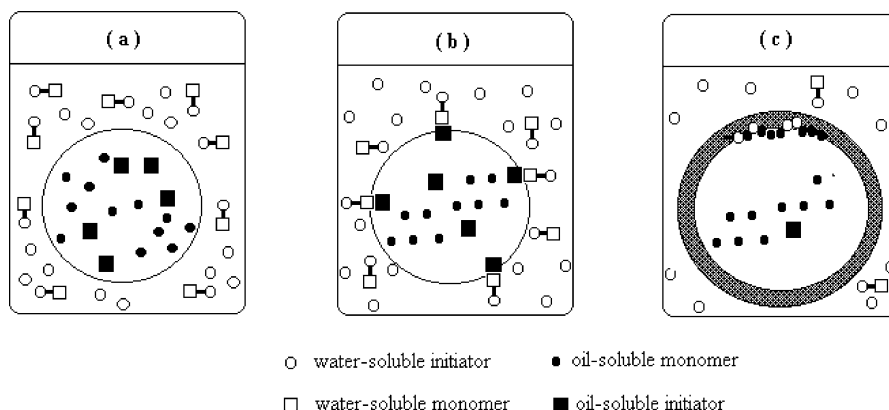
Aggregation:



Some oxidative radicals such as \cdot OH were scavenged by isopropyl alcohol.



DLS results shows that P(St-co-AM)/NiS hybrid particles have R_h of 103 nm and a broader size distribution compared with PSt seed particles. TEM image clearly indicates the presence of NiS clusters on the particles (the blackest dots) as shown in Fig. 1(c) and (d). FESEM images of P(St-co-AM) and P(St-co-AM)/NiS hybrid particles are shown in Fig. 3. Compare the surface of the two different pictures, which evidence the presence of NiS clusters on the surface.



Scheme 2. Outline of redox interfacial-initiated seeded emulsion polymerization.

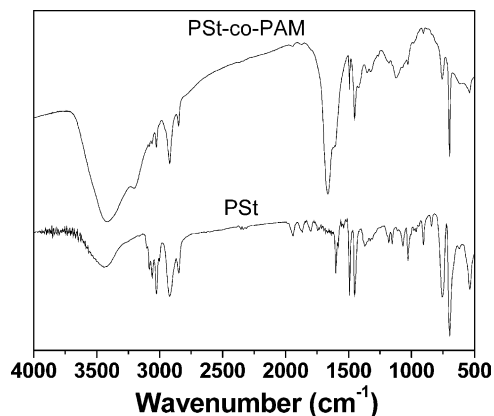


Fig. 2. FTIR spectra of PSt seed and P(St-co-AM) core-shell particles.

The XRD pattern of P(St-co-AM)/NiS hybrid particles was shown in Fig. 4. The four peaks at $2\theta = 30, 34.3, 46.6,$ and 53.7 are quite identical to the standard pattern of NiS (JCPDS card, File No: 2-1280). This result confirms the formation of NiS by using nickelous sulfate and thioacetamide under ^{60}Co γ -irradiation at ambient temperature and pressure.

The presence of NiS was also confirmed with XPS as shown in Fig. 5. XPS energy dispersion spectrum reveals the existence of the elements of N, H, O, C, Ni and S on the particle surface. The Ni_{2p} and S_{2p} electron binding energies were 854.00 and 162.20 eV, which indicates the valence states of Ni and S being +2 and -2, respectively. The calculated results of peak area showed that the molar ratio of Ni:S is 49.4:50.6, indicating the formation of NiS compound.

3.4. Physical properties of P(St-co-AM)/NiS hybrid particles

UV-vis absorption and photo-luminescent spectra of P(St-co-AM)/NiS sub-micrometer particles were in Figs. 6 and 7, respectively. UV-vis spectrum of the sample dispersed in ethanol by sonication shows a clear peak at 322 nm, which is assigned to the optical transition of the first excited state of the NiS nanoparticles. The absorption spectrum is shifted to much higher energy (~ 5.56 eV)

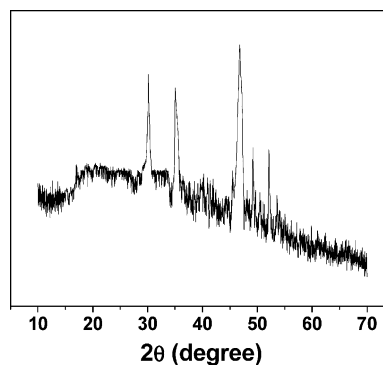


Fig. 4. XRD pattern of P(St-co-AM)/NiS hybrid particles.

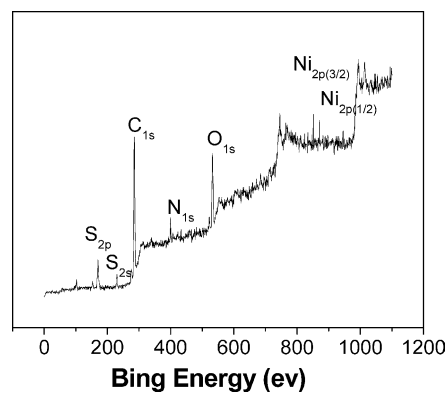


Fig. 5. XPS spectrum of P(St-co-AM)/NiS hybrid particles.

compared to that of bulk NiS (~ 2.1 eV) [39]. The explicit blue shift is due to the small size of the NiS quantum dots coated onto the P(St-co-AM) sub-micrometer spheres. Photoluminescent spectrum of P(St-co-AM)/NiS shows a peak at 316 nm. The blue shift with 54 nm is observed compared with the reported result of NiS layer-rolled structures, showing the maximum at 370 nm. These features indicate the quantum-confined effect of the nano-sized NiS.

Weight percent of NiS in P(St-co-AM)/NiS hybrid particles is 9.7 wt% based on the recipe of reactions. Magnetic hysteresis loop study was performed under VSM VT-800 at room temperature with magnetic fields up to 10 kOe and the results are shown in Fig. 8. The saturation

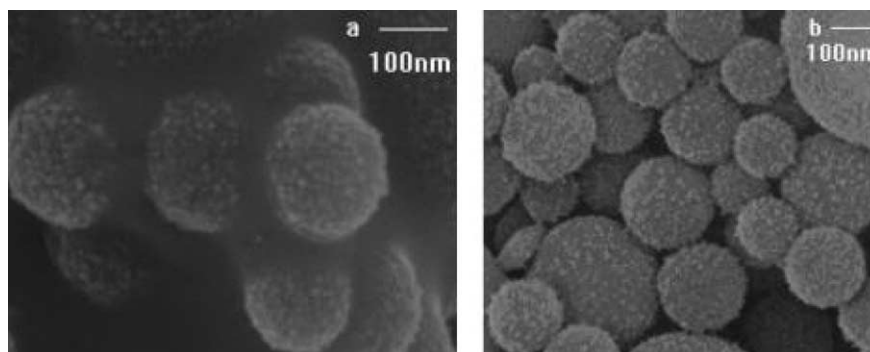


Fig. 3. FESEM images of composite particles (a) P(St-co-AM)/NiS hybrid particles; (b) P(St-co-AM) core-shell particles.

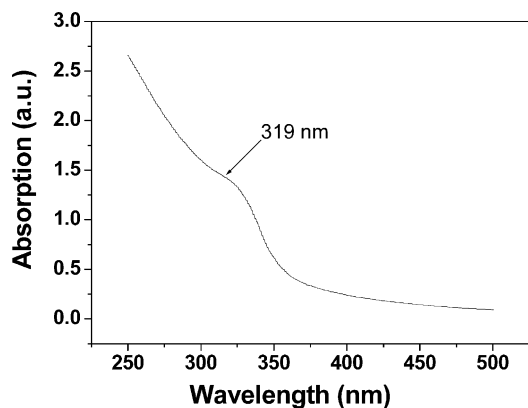


Fig. 6. UV-vis absorption spectrum of the P(St-co-AM)/NiS hybrid particles.

magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) of P(St-co-AM)/NiS hybrids is 0.26 emu/g, 680 Oe and 0.11 emu/g, respectively, indicating the soft ferromagnetic feature of P(St-co-AM)/NiS hybrids.

4. Conclusion

PSt seed latex was prepared through emulsion polymerization. Interfacial-initiated seeded emulsion polymerization of Am was carried out in the presence of CHPO/ST swollen PSt seed latex with Fe^{2+} as the reductive initiator. TEM observation, DLS analysis and FTIR characterization demonstrate the formation of P(St-co-AM) core-shell particles. Under γ -ray irradiation, NiS nano-clusters were deposited onto P(St-co-AM) core-shell particles through the reaction of NiSO_4 and thioacetamide, forming P(St-co-AM)/NiS hybrid particles. The nano-clusters of NiS were observed under TEM and FESEM, its chemical structure was confirmed with XRD and XPS. Both UV-vis and photoluminescence spectra show the blue shift, which is attributed to the nano-clusters of NiS. P(St-co-AM)/NiS hybrid particles show the soft ferromagnetic behaviour according to magnetic hysteresis loop study.

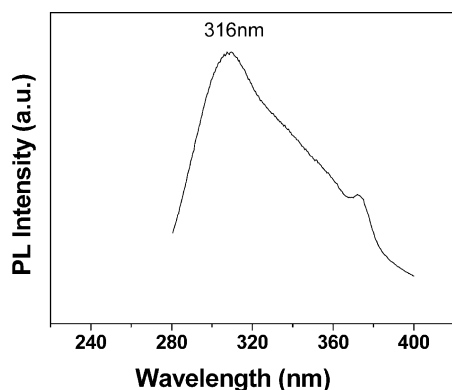


Fig. 7. Photoluminescent spectrum of P(St-co-AM)/NiS hybrid particles.

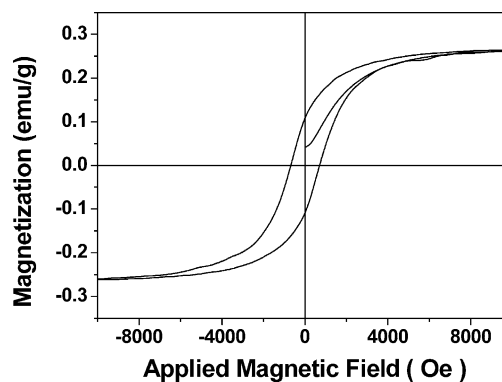


Fig. 8. Hysteresis loop of P(St-co-AM)/NiS hybrid particles.

Acknowledgements

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