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ORIGINAL PAPER

# Preparation of poly(ethylene glycol)-grafted silica nanoparticles using a facile esterification condensation method

**Libang Feng · Yulong Wang · Na Wang · Yingxia Ma**

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**Abstract** Organic–inorganic hybrid nanoparticles have been prepared by the direct facile esterification condensation under extremely mild conditions as ambient temperature, moisture and atmospheric pressure, and the resulting composite particles are characterized by ESCA, FTIR, TEM, DLS, TGA, DSC, and XRD techniques. Results show that this facile graft method has high graft efficiency and the grafted poly(ethylene glycol) (PEG) accounts for about 55 wt% of the total silica composites. The resulting silica nanoparticles have core-shell structure with PEG on the outside and $SiO_2$ in the core. As a result, the dispersion behavior of nanoparticles and the thermal stability of the grafted PEG are improved by the formation of covalent ester bonds between PEG and the reactive silica nanoparticles. The PEG phase, however, is disturbed by the proximity of the oxide phase of $SiO_2$. Consequently, less crystal or faulty crystal of PEG is resulted when PEG is grafted onto the surfaces of silica nanoparticles.

**Keywords** Poly(ethylene glycol) · Grafting · Silicas · Nanoparticles · Esterification · Condensation

## Introduction

For the past decade, organic–inorganic hybrid materials have been considered as innovative advanced materials in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, mechanics, and electrochemistry [1, 2]. Thereupon, the

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design and synthesis of the hybrid materials becomes a fascinating area with numerous scientific and technological interests in the fields of optics, mechanics, ionoelectronics and biology [3, 4].These materials are diphasic media in which both inorganic and organic phases play major roles in the chemical and physical properties. Generally, these materials can be divided into two distinct classes with respect to the chemical nature of the organic–inorganic interface. In materials of class I, organic and inorganic components are mixed together and only ionic or weak bonds (hydrogen, Van der Waals…) govern the cohesion of the whole structure. In materials of class II, the two phases are linked together through strong chemical bonds (covalent or ionocovalent bonds) [5, 6].

Composite colloidal particle is one of hybrid materials which often have one material on the outside and the other in the center of the particle. This composite particle combines different material properties such as specific (bio)chemical, optical, electrical, magnetic and mechanical properties [7]. On the other hand, poly(ethylene glycol) (PEG) has been regarded as the most effective polymer for reducing protein adsorption and denaturation due to its low interfacial energy, non-adhesion property, and high dynamic motion [8, 9]. Because of fundamental importance and wide applications, lately, the modification of particle surface using PEG has been widely utilized in the field of drug delivery system for liposomes, emulsions, microspheres, and biosensing technology [10]. Nanocomposites obtained from silica ($SiO_2$) nanoparticles and PEG can be synthesized by two main routes: "grafting from'' and "grafting to" techniques [11–13]. For example, Joubert et al. [14] prepared PEG-grafted silica with the "grafting from" method in which the grafting polymer is grown from the surface of the particles. The method yielded high grafting density, however, the grafted polymers were of low molecular weight and had a broad molecular weight distribution. Bridger and Vincent [15] reported on the synthesis of PEG grafted silica particles via a triethoxysilane-terminated PEG reacted with bare silica. Xu et al. [16] prepared PEG-coated silica by adding hydroxyl terminated PEG at the start of the preparation procedure of silica particles by a synthesis according to Stöber in a methanol–ammonia mixture. Oh et al. [17] prepared PEG-grafted silica particles by adding end-functionalized PEG in the preparation process of silica in an emulsion. Here we present a new two-step method to prepare PEG-grafted silica nanoparticles by "grafting to" technique, and the hybrid nanoparticles are fabricated by the direct facile esterification condensation between alkyl–hydroxyl modified silica nanoparticles and carboxyl-terminated PEG under extremely mild conditions, such as ambient temperature, moisture and atmospheric pressure. Then the structure, surface composition, morphology, thermal and crystallization behavior of the resulting composite nanoparticles are investigated in detail.

## Experimental

### Materials

Silica nanoparticles with a mean size of 40 nm and a specific area of 200 $m^2/g$, were provided by Zhoushan Mingri Nano-material Co. Ltd. (Zhejiang, China) and dried in vacuum at 110 °C for 24 h before use. 3-Glycidoxypropyl trimethoxysilane (GPS) from Aldrich was used as received. *N*, *N*′-dicyclohexylcarbodiimide (DCC) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. and used as received. Toluene was dried with 3A molecular sieves before use. Tetrahydrofuram (THF), *N*, *N*′-dimethylformamide (DMF), ethanol (EtOH), acetone, etc., were from BASF Chemical Engineering Co. Ltd. (China) and used as received.

Carboxyl-terminated poly(ethylene glycol) (PEG–COOH) was synthesized by refluxing of poly(ethylene glycol) monomethyl ether ($M_n$: 5,000 g/mol, Fluka) with excessive succinyl anhydride in THF [18]. The resulting PEG–COOH was purified by multiple precipitations from THF solution in diethyl ether. 4-(Dimethylamino) pyridinium-p-toluenesulfonate (DPTS) was synthesized with 4-(dimethylamino) pyridine and p-toluenesulfonic acid [19].

## Preparation of epoxy groups modified silica nanoparticles

The epoxy groups modified silica nanoparticles, $SiO_2$–GPS, was prepared by grafting GPS onto the surface of silica nanoparticles. The method is similar to that of the epoxy groups was grafted onto the silicon substrate [18], and the detailed procedure is as follows: first, 3.0 g of silica nanoparticles was charged into a 250 mL of flask containing 150 mL of dry toluene, and then the suspension was dispersed with ultrasonication for 20 min. Secondly, the suspension was transferred into a 250 mL of three-necked flask equipped with an $N_2$ inlet, a thermometer with temperature controller, and a Graham condenser. Then 1.5 mL of GPS was added quickly and the suspension was refluxed at 110 °C for 8 h under $N_2$ atmosphere and magnetic stirring. After the reaction finished, the suspension was centrifuged at 4,500 rpm for 15 min and the precipitate was collected. Finally, the precipitate was redispersed into 50 mL of dry toluene with ultrasonication for 10 min and then centrifuged again. Next, the precipitate was dispersed into andydrous ethanol with ultrasonication and centrifuged once more. The operation of dispersion and centrifugation was repeated for two cycles, and the resulting precipitate, $SiO_2$–GPS, was dried under vacuum at 40 °C for 24 h.

## Introduction of alkyl–hydroxyl groups onto silica nanoparticle surface

The introduction of alkyl–hydroxyl groups onto the surface of silica nanoparticles was achieved by refluxing of $SiO_2$–GPS (1.0 g) in the 100 mL of EtOH solution of hydrochloric acid (1.6 M) at 100 °C for 2 h. In this case, the epoxy groups on the surface of nano-silica were converted into alkyl–hydroxyl units [20]. The resulting suspension was centrifuged and rinsed with the distilled water thoroughly until pH value of the eluent water approached 7. Finally, the precipitate was redispersed into EtOH with ultrasonication and then centrifuged again. The treated silica nanoparticle was abbreviated as $SiO_2$–$CH_2OH$.

## Synthesis of PEG-grafted silica nanoparticles

The PEG-grafted silica nanoparticle was prepared by grafting carboxyl-terminated PEG (PEG–COOH) onto silica surface via the direct esterification condensation. The reaction was conducted under extremely mild conditions, e.g., ambient temperature and atmospheric pressure by the use of DCC as an activating agent and DPTS as a catalyst.

The typical synthetic procedure was as follows: $SiO_2$–$CH_2OH$ (0.3 g), PEG–COOH (0.6 g), and DPTS (0.015 g) were charged into a 250 mL of round-bottom flask containing mixed solvents (20 mL of THF and 6 mL of DMF) and dispersed with ultrasonication for 10 min. Then 0.03 g of DCC dissolved in 10 mL of THF was added drop by drop under magnetic stirring. After the addition finished, the reaction was carried out at room temperature for 24 h. The resulting suspension was centrifuged, and the collected precipitate was redispersed with ultrasonication and extracted extensively in THF, acetone, and toluene, respectively, to remove the unreacted PEG–COOH, other residual substances and byproducts. Finally, the product was dried in vacuum at 40 °C to constant weight. The obtained product was white powder with a yield of over 77%.

The schematic processes for modification of the silica nanoparticles and the synthesis of the PEG-grafted silica are described in Scheme 1.

## Sample characterization

### FTIR analysis

The chemical structure of samples was measured by Fourier transform infrared spectroscopy (FTIR) with a VERTEX 70 FTIR spectrometer (Bruker, Germany) in the range of 400–4,000 $cm^{-1}$, and the KBr pellet technique was adopted.

### DLS analysis

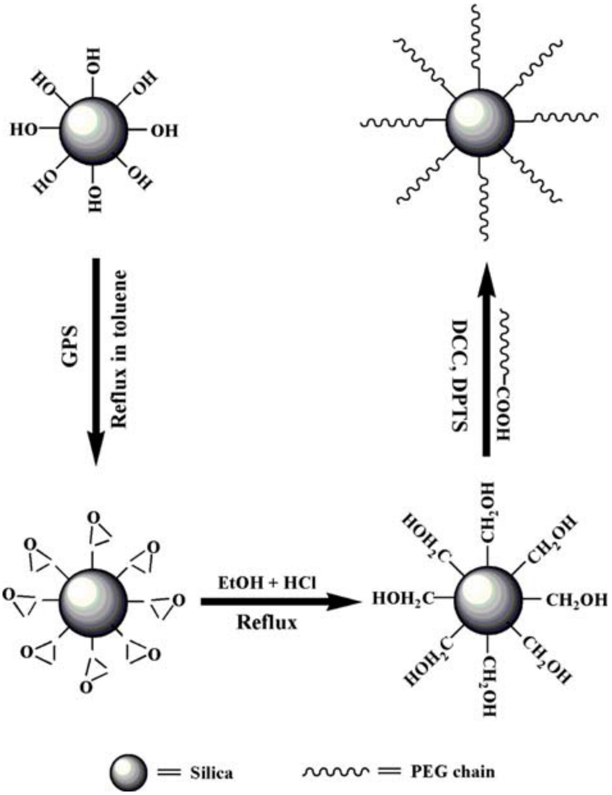
Dynamic light scattering (DLS) was used to monitor the change in hydrodynamic radius and aggregates. Measurements were carried out on a Beckman N4 Plus sub-micrometer particle size analyzer working at a fixed angle of 90° in the diluted toluene solution to obtain the intensity-average diameters of the particles. Each analysis was repeated three times to give the average particle size.

### ESCA measurements

The surface composition of the resulting samples was investigated by ESCA (electron spectroscopy for chemical analysis, also namely, X-ray photoelectron spectroscopy (XPS)) using a PHI-5702 multi-functional spectrometer with Al K$\alpha$ X-ray source under 14.0 kV, 2,500 W, and less than $10^{-6}$ Pa in the analyzer chamber pressure. Narrow scan spectrometer of C1s, O1s, and Si2p was collected at the pass energy of 29.35 eV and the peak analysis was performed using Multipak software. The binding energy of 285.0 eV for C1s was used as a reference.

### TEM measurements

The morphology of the samples was performed on HITACHI H-800 transmission electro microscopy (TEM) at an accelerator voltage of 200 kV. Samples for TEM



**Scheme 1** The procedure of grafting PEG chains onto the surface of silica nanoparticles

observation were prepared by dropping the particle suspension in toluene onto a carbon coated copper grid.

### *TGA analysis*

The thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermal gravimetric instrument (Germany). The temperature ranged from 30 to 1,000 °C with a heating rate of 20 °C/min under argon atmosphere.

### *DSC measurement*

Differential scanning calorimetry (DSC) measurements were conducted on a Shimadzu DSC-60 instrument calibrated with indium and *n*-octane. Samples with a weight of about 10 mg were performed from 25 to 150 °C with a heating rate of 10 °C/min and measurements were conducted in the second run.

### *X-ray diffraction*

Crystal structure identification was carried out using a Shimadzu XRD-7000L X-ray diffraction (XRD) meter with Cu K$\alpha$ irradiation ($\lambda = 1.5406$ Å) at a scanning rate of 0.02° per second in $2\theta$ ranging from 10° to 80°.

## Results and discussion

### Preparation of epoxy and alkyl–hydroxyl groups modified silica nanoparticles

To synthesize polymer-grafted silica nanoparticles by esterification condensation method, silica nanoparticles need to be prepared and modified first. In our synthetic procedure, the silica particles with mean size of 40 nm are used as model particles. Scheme 1 presents the procedure for the modification of silica particles and PEG grafting. First, the silica nanoparticles are modified with GPS under refluxing in toluene, introducing epoxy groups onto the particle surfaces, and the resulting particles are denoted as $SiO_2$–GPS. The unreacted GPS is washed away from the particles by repeat suspension, centrifugation and decanting of the supernatant. $SiO_2$–GPS is then refluxed in EtOH solution of hydrochloric acid to convert the epoxy groups into alkyl–hydroxyl units.

Under the selected modification conditions, it is possible to approach a reproducible preparation of covalently bonded thin layer of GPS at silica nanoparticle surface. The successful preparation of epoxy group-modified silica nanoparticles is confirmed by ESCA and FTIR measurements.

Figure 1a shows the survey scan spectrum of $SiO_2$–GPS. The major peak component at the binding energy (BE) of 532.8 eV is attributable to O1s, and the minor peak component at the BE of 285.0 eV is assigned to C1s. Meanwhile, peaks at the BE of 154.4 and 103.2 eV correspond to Si2s and Si2p, respectively. The peak of Si2p can be curve-fitted with two peak components with binding energy of 103.6 and 101.7 eV, and these two peaks are attributable to O–Si–O and O–Si–C species, respectively, as shown in Fig. 1b. The full-widths at half maximum of the curve-fitted peaks are 1.71 and 1.69, respectively, showing the rationality of the curve-fit. Thereupon, it can be proved that the GPS has been covalently bonded onto the silica nanoparticle surfaces successfully.

FTIR is also used to confirm the successful grafting. In the FTIR spectrum of bare $SiO_2$ (Fig. 2a), the absorption peak at 1,020–1,110 $cm^{-1}$ is assigned to the Si–O–Si asymmetric stretching vibration, and the peaks at 960 and 800 $cm^{-1}$ are ascribed to the asymmetric bending and stretching vibration of Si–OH, respectively. By contrast, FTIR spectrum of the $SiO_2$–GPS (Fig. 2b) shows –CH stretching vibration at 1,470 and 2,800–2,950 $cm^{-1}$, respectively, while both of these signals do not present in the spectrum of unmodified silica nanoparticles (Fig. 2a). Furthermore, the peak at 1,020–1,110 $cm^{-1}$ in the spectrum of $SiO_2$–GPS boosts up and a new absorption band at 1,730 $cm^{-1}$ ascribed to the carbonyl groups appears in the FTIR spectrum of $SiO_2$–GPS, indicating carbonyl compounds exist in the GPS-modified silica particles. The appearance of carbonyl compounds at the GPS/silica

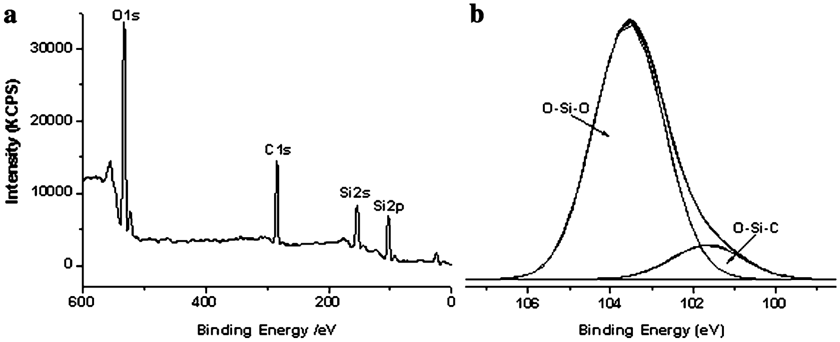
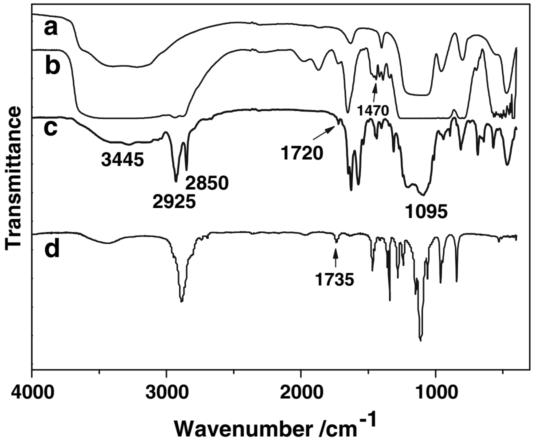


**Fig. 1** ESCA spectra of $SiO_2$–GPS: the survey scan spectrum (**a**) and the Si2p core-level spectrum (**b**)

**Fig. 2** FTIR spectra of $SiO_2$ (*a*), $SiO_2$–GPS (*b*), PEG-grafted silica (*c*), and PEG–COOH (*d*)



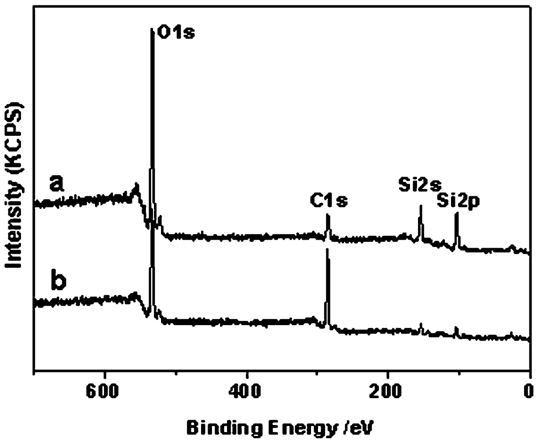
interface was also observed and proved in the literature [21]. In addition, there are absorption peaks around 1,640 and 3,000–3,600 cm$^{-1}$ for both spectra, which are assigned to the bending mode of physically absorbed water molecules. These results accord with that of ESCA analysis, showing the GPS-grafted silica nanoparticles are resulted indeed.

The epoxy groups at the surface of silica nanoparticles are converted into alkyl–hydroxyl groups through refluxing the $SiO_2$–GPS in EtOH solution of hydrochloric acid. The resulting nanoparticles, $SiO_2$–$CH_2OH$, are also characterized by ESCA and FTIR techniques, and the similar results are observed as those of $SiO_2$–GPS.

## Grafting PEG chains onto silica nanoparticle surfaces

The PEG chains are attached onto the surfaces of silica nanoparticles by esterification condensation between alkyl–hydroxyl units at the nanoparticle surface and PEG–COOH via the catalysis of DPTS and the activation of DCC under ambient temperature, moisture and atmospheric pressure. The resulting suspension is centrifuged, washed extensively with THF, acetone, and toluene, respectively, in

**Fig. 3** ESCA spectra of $SiO_2$–GPS (*a*) and PEG-grafted silica (*b*)



order to remove the unreacted PEG–COOH, DCC and the byproduct as urea (DCU). The obtained product, PEG-grafted silica, is characterized by FTIR and ESCA analyses, and results are shown in Figs. 2c and 3, respectively.

The FTIR spectrum of PEG-grafted silica (Fig. 2c) has much difference as compared with those of $SiO_2$–GPS (Fig. 2b) and PEG–COOH (Fig. 2d). For instance, peaks at 2,800–2,950 $cm^{-1}$ assigned to –CH stretching vibration become quite distinct, while the absorption for the stretching vibration of the ester carbonyl shifts from 1,735 $cm^{-1}$ (for PEG–COOH) to 1,720 $cm^{-1}$ (for PEG-grafted silica). The free PEG–COOH (namely, the unreacted PEG–COOH) has been removed by extracting with THF and toluene. Therefore, the absorption at 1,720 $cm^{-1}$ in FTIR spectrum of PEG-grafted silica must come from PEG chains fixed on the surface of silica nanoparticles, which indicating that PEG chains are fixed onto the silica surface covalently. Meanwhile, the absorption of C–O–C stretching vibration for PEG chains and Si–O–Si asymmetric stretching vibration overlaps, thereupon, the strong peak appears at 1,205–1,095 $cm^{-1}$. Likewise, the peak for bending mode of physically absorbed water molecules presents around 1,640 $cm^{-1}$ in Fig. 2c. These facts show that PEG chains have been successfully attached onto the surfaces of silica nanoparticles. In addition, there is no absorption around 1,600 $cm^{-1}$ for urea in the FTIR spectrum of PEG-grafted silica, indicating that byproduct-urea has been removed successfully as well.

The presence of the grafted PEG segments at the surfaces of silica nanoparticles is also verified by ESCA analysis. The typical ESCA survey scan spectrum for silica nanoparticles attached PEG chains is shown in Fig. 3b. Compared with the ESCA spectrum of $SiO_2$–GPS (Fig. 3a), it is very clear that the peak at BE of 532.8 eV corresponding to O1s becomes weak, and the peaks for Si2s at 154.4 eV and Si2p at 103.2 eV become very faint, while the peak for C1s at BE of 285.0 eV becomes quite strong, showing that the PEG layer around nanoparticles is thick enough to shield most of Si and O in the silica core from ESCA technique.

For the sake of verifying the grafted PEG chains at the silica nanoparticle surfaces quantitatively, the atomic quantification is determined using O1s, Si2p and C1s with the corresponding sensitive parameters of 0.733, 0.368 and 0.314,

**Table 1** Molar content of atoms and average particle size

| Sample | Molar content (%)[a] | | | Particle size (nm) | |
|---|---|---|---|---|---|
| | O1s | Si2p | C1s | DLS/PI | TEM |
| $SiO_2$ | – | – | – | 55/0.14 | 43 |
| $SiO_2$–GPS | 60.7 | 22.3 | 17.0 | 43/0.11 | 42 |
| PEG-grafted silica | 42.2 | 5.20 | 44.6 | 75/0.12 | 67 |

[a] Measured with ESCA

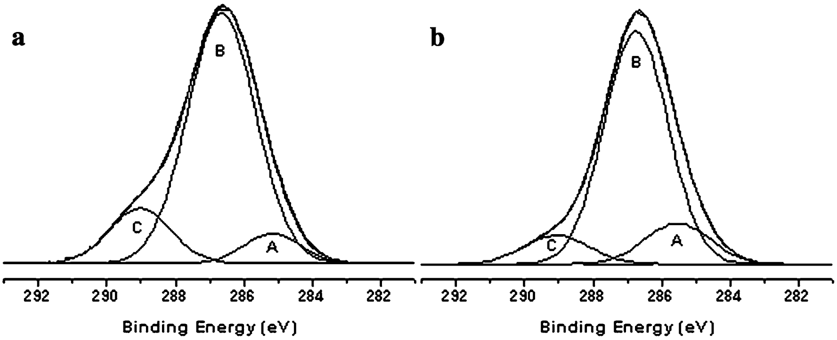


**Fig. 4** C1s core-level spectra of PEG–COOH (**a**) and PEG-grafted silica (**b**)

respectively. The areas from ESCA are interpreted as relative concentrations of the atoms involved, and the obtained results are showed in Table 1. As compared with the $SiO_2$–GPS, the molar contents of O1s and Si2p at the PEG-grafted silica surfaces decrease 30.5% and 76.7%, respectively, while C1s increases 61.9%, further indicating that PEG chains are grafted onto the silica nanoparticle surfaces successfully and part of Si and O atoms in center silica particles are shielded by the outside bonded PEG layer.

For the sake of verifying that PEG chains are grafted onto the surface of the silica nanoparticles with the ester bond furthermore, the C1s spectra of PEG-grafted silica together with PEG–COOH are decomposed into three component peaks using a Gaussian–Lorentzian fitting procedure. According to their binding energies, different carbon species can be distinguished as presented in Fig. 4 and Table 2. Figure 4 clearly shows that the high-resolution C1s spectra of PEG–COOH and PEG-grafted silica are consistent with three different carbon environments owning to binding energy, which are one by one attributable to the ester induced $\beta$-shifted carbon (peak A), C–O (peak B), and C=O (peak C). (The C–C/H can not be fitted because of the quite little amount). By comparing the C1s spectra (Fig. 4) and their fitting parameters (Table 2), it can be found that the atomic content of C=O (Peak C) decreases while that of the ester induced $\beta$-shifted carbon (Peak A) increases about 5.0 mol% for PEG-grafted silica as compared to those of PEG–COOH, indicating that PEG is covalently grafted onto silica surface successfully. The increase of the peak A indicates that more ester bonds exist after PEG chains grafting, while the

**Table 2** C1s core-level spectrum parameters for PEG–COOH (a) and PEG-grafted silica (b)

| Peak | Binding energy (eV) | | Full-width at half maximum | | Atomic % (peak area) | |
|---|---|---|---|---|---|---|
| | a | b | a | b | a | b |
| A (Ester induced $\beta$ shifted carbon) | 285.4 | 285.4 | 1.83 | 1.89 | 8.6 (385) | 13.6 (611) |
| B (C–O) | 286.6 | 286.7 | 1.88 | 1.87 | 80.4 (3615) | 77.6 (3487) |
| C (C = O) | 289.2 | 289.1 | 1.81 | 1.89 | 11.0 (493) | 8.8 (396) |

decrease of the peak C results from two reasons: the increase of the ester induced $\beta$-shifted carbon and the shielding by the outside bonded long PEG chains.

These facts together with results of FTIR measurements indicate that esterification reaction between alkyl–hydroxyl units at the silica surface and PEG–COOH takes place undoubtedly under the selected conditions, and PEG chains have been attached onto the surfaces of silica nanoparticles with covalent bond efficiently. Moreover, the grafting efficiency and the conversion of the PEG–COOH into the corresponding ester can be calculated with the experimental data quantitatively. For instance, the obtained amount of the product is over 0.693 g (=0.9 × 77%), and the unreacted PEG–COOH has been removed by extraction with THF and toluene. As a result, the amount of PEG–COOH that grafted onto the silica surface is not below 0.393 g (the amount of $SiO_2$–$CH_2OH$ almost keeps constant in the experiment, namely, 0.3 g). So the conversion of the PEG–COOH into the corresponding ester is over 65.5%. Meanwhile, the content of the grafted PEG–COOH in the PEG-grafted silica accounts for about 56.7% calculated with the experimental data, indicating the method has a high grafting efficiency.

## Morphology of PEG-grafted silica nanoparticles

The TEM micrographs of silica nanoparticles before and after PEG grafting are shown in Fig. 5. It can be found from Fig. 5a that most of the bare silica nanoparticles agglomerate in toluene while a fraction disperses with average particle size of 43 nm. Figure 5b shows $SiO_2$–GPS appears approximately spherical with an average diameter of about 41 nm while slight soft agglomeration presents. By contrast, TEM images of PEG-grafted silica (Fig. 5c, d) show gray zones of low contrast around the spherical particles that are not shown on the images of the pre-coated particles. The diameter of the composite particles increases to 65–70 nm, which is much larger than those of the initial bare silica and the $SiO_2$–GPS nanoparticles. The grey zones should be the grafted PEG domains, indicating that the resulting PEG-grafted silica composite particles are of core-shell morphologies with PEG on the surface and $SiO_2$ in the core. It is no doubt that our synthetic method for preparing the PEG-grafted silica nanoparticles is effective to form brush surfaces, which effectively decreases the interfacial tension of the inorganic nanoparticles in organic solvent, and thereby thoroughly broke up the soft agglomeration of particles and promotes their dispersion in organic solvent.

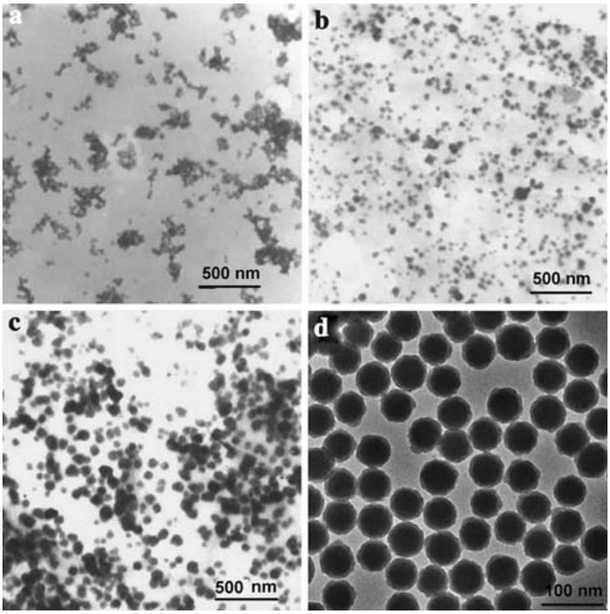


**Fig. 5** TEM photographs of $SiO_2$ (**a**), $SiO_2$–GPS (**b**), and PEG-grafted silica (**c**, **d**)

The average particle size of the silica particles in every step is investigated by DLS technique as well, and results together with those from TEM are listed in Table 1. Results from DLS analysis show that the bare $SiO_2$ has much large particle size and the polydispersity index (PI) as compared with those of $SiO_2$–GPS, indicating that there is serious agglomeration for bare silica particles. However, PI for both $SiO_2$–GPS and PEG-grafted particles decreases, manifesting that the dispersion behavior of nanoparticles is improved greatly by grafting organic molecules and polymer chains.

## Thermal behavior of PEG-grafted silica nanoparticles

The thermal behavior of PEG-grafted silica is evaluated by TGA and DSC measurements. The curves of the decomposition process for PEG-grafted silica together with bare $SiO_2$ and PEG–COOH are shown in Fig. 6. It can be found from the TGA measurement that the bare $SiO_2$ (Fig. 6a) has a weight loss of around 5% due to the loss of water molecules adsorbed onto the surface and the release of the structural water resulted from the bonded hydroxyl groups. The PEG–COOH (Fig. 6b) shows three areas of decreasing weight at temperature of about 0–150, 190–275 and 310–410 °C, respectively. The first range is due to the evaporation of the physically adsorbed water, and the second range with a weight loss of approximate 55% is associated with the decomposition of most of PEG domains while the third region is attributed by the thermal cracking of the residual organic molecules. Regardless of the weight loss percentage, the thermal gravimetric shape

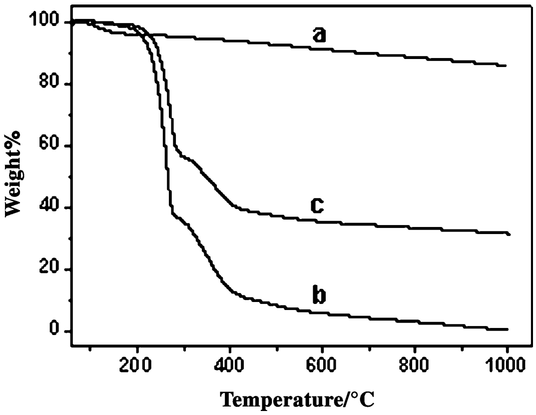


**Fig. 6** TGA curves of $SiO_2$ (*a*), PEG–COOH (*b*), and PEG-grafted silica (*c*)

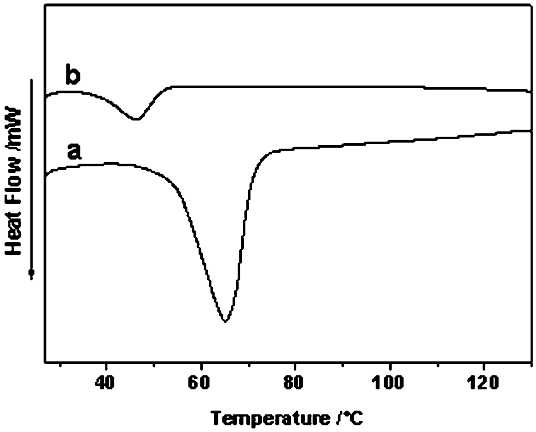
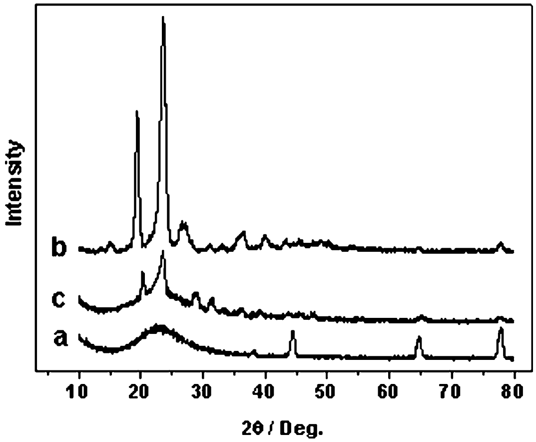


**Fig. 7** DSC traces of PEG–COOH (*a*) and PEG-grafted silica (*b*)

of PEG-grafted silica (Fig. 6c) is similar to that of PEG–COOH, while the two main ranges of decreasing weight locate at around 205–290 and 320–410 °C, respectively. Similarly, the first step corresponds to the release of the structural water and the decomposition of part of PEG molecules while the second one is caused by the decomposition of the residual polymers. In comparison with the original silica particles (Fig. 6a), the grafted content of PEG on the silica surface estimated by the weight loss is nearly 55% of the total amount of composite particles, indicating that the amount of the grafted polymer is fairly high. In addition, the temperature at which the weight drastically decreases is shifted to the high temperature by grafting of PEG chains, suggesting that the thermal stability of PEG is enhanced by the formation of covalent bonds to the reactive silica nanoparticles.

The thermal transitional temperature of PEG–COOH and PEG-grafted silica is also investigated by DSC analysis and the measurement traces are shown in Fig. 7. Both samples show melting peak of PEG domains. The melting point ($T_m$) of PEG attached on silica particles, however, locates at the low temperature (46.1 °C) as compared with that of the pure PEG–COOH (65.1 °C). On the other hand, the heat capacity of the PEG grafted on the silica nanoparticles is only 32.1 J/g, much lower

**Fig. 8** XRD traces of $SiO_2$ (*a*), PEG–COOH (*b*), and PEG-grafted silica (*c*)



than that of the PEG–COOH, 104.8 J/g. The result shows that the mobility of the grafted PEG chains is hindered by the proximity of oxide phase of $SiO_2$. As a result, PEG phase is strongly disturbed, which engenders the formation of less crystal or faulty crystal. Consequently, the resulting crystal of the grafted PEG melts at a low temperature with small quantity of heat enthalpy.

## Crystallization behavior of PEG-grafted silica nanoparticles

The crystallization behavior of the obtained composite nanoparticles together with bare $SiO_2$ and PEG–COOH is investigated by XRD, and the corresponding testing traces are shown in Fig. 8. The XRD trace of $SiO_2$ (Fig. 8a) indicates that the bare silica exists in an amorphous phase at the room temperature due to a broad peak centered at $2\Theta = 22.5°$, whereas the PEG–COOH (Fig. 8b) presents in a crystal phase since two distinct crystal peaks present at $2\Theta = 19.4°$ and 23.5°, respectively, which indicates that the PEG–COOH exists in monoclinic structure [22]. By contrast, both the amorphous peak of $SiO_2$ and the crystal peaks of PEG present in the XRD trace of the PEG-grafted silica (Fig. 8c). However, the position of the crystallization peak of PEG shifts a little and the intensity of the crystallization peaks reduce markedly as compared with that of the pure PEG–COOH, demonstrating that the PEG phase is disturbed by the proximity of oxide phase of $SiO_2$. Consequently, less crystal or faulty crystal of PEG is resulted. These results are absolutely consistent with the results from DSC measurements.

## Conclusions

This work presents a detailed study of silica–PEG hybrid materials. These nanocomposites are obtained by a new two-step grafting method. First, the surface of silica nanoparticles is activated by pre-coating with the silane coupling agent of GPS to introduce epoxy groups, and then alkyl–hydroxyl groups. Secondly, the activated particles react with the carboxyl-terminated poly(ethylene glycol) under extremely mild conditions, for instance, ambient temperature, moisture and atmospheric pressure, and then PEG-grafted silica nanoparticles are resulted. Results show that the resulting composite particles have core-shell structure, and the grafted PEG accounts for about 55 wt% of the total composite particles. For PEG-grafted silica particles, peaks for Si2 s and Si2p become quite faint while the peak for C1s becomes very strong from ESCA measurement as compared with the GPS modified silica nanoparticles. Meanwhile, the thermal stability of PEG is enhanced by the formation of covalent ester bonds with the reactive silica nanoparticles, while the PEG phase is disturbed and less crystal or faulty crystal of PEG is resulted after PEG grafting. Finally, this facile esterification condensation method can be extended to graft various functional polymers onto the surface of other inorganic particles.

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