Determination of Epoxy Groups on γ-Glycidoxypropyltrimethoxy-silane Doped Nanosilicas by Oscillo-polarographic

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In the present work, oscillo-polarographic was developed to determine epoxy groups on γ-glycidoxypropyltrimethoxysilane (GPTMS) doped nanosilicas (GPTMS/nano-SiO$_2$) quantitively. The method based on the quantitative reaction between dihydroxyl of hydrated epoxy groups and potassium periodate generating formaldehyde and the reaction between the formaldehyde and hydrazine sulfate generating a new compound (hydrazone) which could be adsorbed at the mercury electrode and yielded a sensitive polarographic wave. Optional conditions of sample treatment and ploargraphic determination were discussed in detail. This method involves simple operation and good accuracy for quantitive determination of epoxy groups on GPTMS/nano-SiO$_2$. It also has the potential to provide information of the amount of epoxy groups on other similar category products.

Key Words: Oscillo-polarographic, Glycidoxypropyltrimethoxy-silane, Epoxy, Nanosilica.

INTRODUCTION

As one of the most promising materials, γ-glycidoxypropyltrimethoxysilane doped nanosilica (GPTMS/nano-SiO$_2$) is feasible to be applied in the fields of analytical chemistry[1-3], life sciences[4,5], optics[6,7], industry[8-12] and catalysis[13,14]. It has been proved that the amount of epoxy groups on GPTMS/nano-SiO$_2$ is important to its properties and applications. However, at present, few efforts have been done for determining epoxy groups. This makes a lag of the preparation and applications of GPTMS/nano-SiO$_2$. Therefore, methods of quantitative determining epoxy groups on GPTMS/nano-SiO$_2$ are expecting and this work has become a necessary and attractive project. Characteristic and semiquantitative methods, such as X-ray photoelectron spectroscopy (XPS), Fourier transformation infrared spectrometry (FT-IR), time of flight-second ion mass spectrometry (ToF-SIMS), atomic force microscopy (AFM), scanning electron microscopy (SEM) and elemental analysis (EA) have been successfully employed to characterize the structure and the composition of the modified layer, elements' state on surface of various substrates and provide lots of the qualitative and the semi-quantitative informations[15-19], but these still could not meet the requirement[20].

Some studies have been carried out to determine GPTMS. For example, Maittala[21] and Dong[22] determined the GPTMS using gas chromatography (GC), but this method is difficult to determine epoxy groups on GPTMS/nano-SiO$_2$ because the inert silica is hardly vapourized or dissolved.

Titration method has been applied for measurement of epoxy groups on silicas. He *et al.*[23] have adapted a non-aqueous micro-titrimetric method for determining α-epoxide group on the bonded silica surface and we have also attempted the proposed method to determine epoxy group on GPTMS/nano-SiO$_2$'s surface. Radi *et al.*[24] determined amount of epoxy spacer grafted on silica based upon the property of epoxy group reacting with sodium sulfite generating free hydroxyl. However, these works seemed not very efficient because of the illegible end point. The strong adsorption exist between insoluble silicas and indicators. Our group have also conducted an UV-spectrometry for epoxy measurment[25] on GPTMS/nano-SiO$_2$, however, the incident light might be reflected or scattered by the nanoparticles that was not elimated, which lead to the adsorption increase and the results could not more really reflect the epoxy amount on GPTMS/nano-SiO$_2$.

So, an efficient method, which could overcome the influence of the nanoparticles, is necessary. In the present work, an oscillo-polarographic was tried to determine epoxy on GPTMS/nano-SiO$_2$. This could be feasible, because every determination were done on a new dropping mercury electrode, which avoid the interference of the nanoparticles. On the other hand, the active epoxy group on GPTMS/nano-SiO$_2$ could release formaldehyde after a series of chemical reactions and yielding formaldehyde, which on reacting with hydrazine forming hydrazone which could be adsorbed at the mercury eledtrode and yielded a sensitive adsorptive polarographic wave. Thus in our work, GPTMS/nano-SiO$_2$ were hydrolyzed with sulfuric acid, and then oxidized by potassium periodate to form formaldehyde. The yielding formaldehyde was reacted with hydrazine in CH$_3$COOH-CH$_3$COONa buffer to form hydrazone. The hydrazone could be adsorbed and yielded a sensitive polarographic wave at *ca.* -966 mV. The reaction processes for generating the hydrazone from GPTMS/nano-SiO$_2$ are schematically shown in Fig. 1.
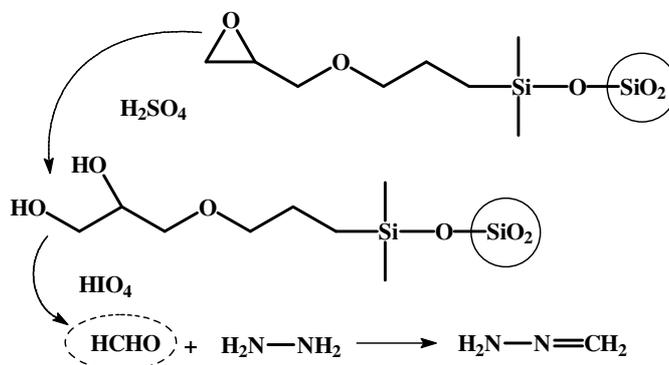
Fig. 1. Reaction processes for generating the hydrazone from GPTMS/nano-SiO$_2$

EXPERIMENTAL

The polargraphic measurements were conducted on a JP-303 polarograph, which comes from Chengdu Instrument Factor, China. The three-electrode was consisted of the static mercury dropping electrode (SMDE) as working electrode, an saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode.

γ-Glycidoxypropyltrimethoxysilane (GPTMS) doped nanosilicas (sample A and B), which were supplied by Henan Province Nanomaterial Engineering and Technological Research Centre, are industrial products. The reference GPTMS, analytical grade, was obtained from J.K. Chemical Ltd. All the other reagents were of analytical grade and water was of high purity.

Sample preparation: At 25 ± 1 ℃, 5-50 mg GPTMS/nano-SiO_2 were treated with 15 mL 0.025 mol L^{-1} H_2SO_4 by ultrasonic-assistant method for 40 min on an ultrasonic cleaner (KQ-100, Shanghai, China), then about 15 mL 0.05 mol L^{-1} NaOH were added to adjust pH to 5.2 ± 0.1 (measured with a pH 211 m, HANNA, Italy) and 4 mL 0.10 mol L^{-1} KIO_4 were added subsequently. After being kept for 30 min in dark, 0.1 mol L^{-1} $Na_2S_2O_3$ was added into the mixtures drop by drop until a primrose yellow (color of the generating iodine) disappearred. All the solutions were transferred into 100 volumetric flasks quantificationally.

Hydrazine sulfate solution: A stock solution of hydrazine sulfate was prepared by dissolving 2.0 g hydrazine sulfate in 80 mL H_2O and adjusted pH to 5.0 (measured with the pH meter mentioned above) with 5 mol L^{-1} KOH, then diluted to 100 mL with H_2O.

Procedure: 0.50-1.50 mL prepared samples solution, 2.0 mL CH_3COOH-CH_3COONa buffer solution and 0.8 mL hydrazine sulfate solution were added into 10 mL colorimetric tubes. 4 min later, the mixtures were diluted to 10 mL with H_2O and transferred to 25 mL electrolytic cell. Then polarograms were recorded by JP-303 polarograph under the following conditions: Derivative, 2-nd; Initial potential, -500 mV; Final potential, -1500 mV; Sweep rate, 100 mV/s; Pulse period, 5 s; Scan times, 3.

RESULTS AND DISCUSSION

Polarograms: According to the optional conditions, polarograms were recorded by a JP-303 polarograph. The hydrazone (formed from the yielding formaldehyde and hydrazine sulfate in the supporting electrolyte) is reduced on the mercury droplets and the peak potential is *ca.* -966 mV (Fig. 2). The polarograms of the supporting electrolyte and the formaldehyde in supporting electrolyte were also recorded, respectively, Fig. 2 showed that they were of no significant difference with each other and had no polarographic wave around -966 mV.

Optional conditions for sample preparation: To obtain a better prepared sample solution, there is a tremendous interst in investigating the treatment process of samples.
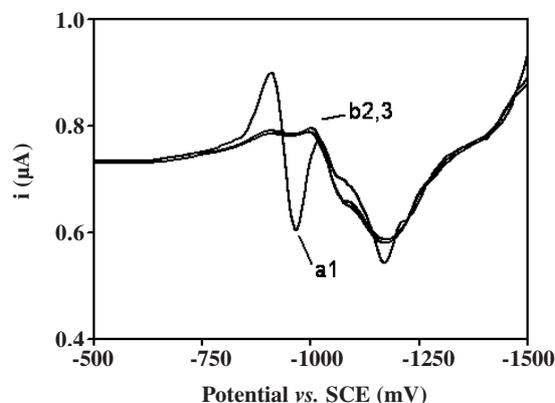
Fig. 2. Polargram for determining epoxy groups on GPTSM/nano-SiO$_2$. a1: Prepared sample A solution + CH$_3$COOH-CH$_3$COONa + hydrazine sulfate; b2: Prepared sample A solution + CH$_3$COOH-CH$_3$COONa; b3: Hydrazine sulfate + CH$_3$COOH-CH$_3$COONa

It has been reported that the epoxy groups could be hydrolyzed to dihydroxyl with diluent sulfuric acid on water bath at 60 ºC for more than 1 h. But we found that the results, obtained from prepared samples under the conditions above, were of poor reproducibility. It may be owing to that the epoxy groups on GPTMS/nano-SiO$_2$ have been hydrolyzed unevenly or incompletely. In fact, the soild GPTMS/nano-SiO$_2$ samples always were shown as precipitation on the bottom of the solution (when empoyled to reference GPTMS for the calibration curve, GPTMS appeared to be a oil-drop), which might lead to the epoxy groups can not be hydrolyzed completely. As ultrasonic wave can catalyze a chemical reaction, ultrasonic-assistant were attempted to treat the samples in this paper. It was suddenly proved to be an effective method. Results indicated that the samples can be dispersed uniformly and can be hydrolyzed completely (which was validated by the recovery tests of the reference GPTMS in sample A and B) under ultrasonic condition at 25 ± 1 ºC for 40 min.

pH was found to be important influencing factor for the oxidation of the hydro-lysis product by KIO$_4$. It was found that, over the pH range of 4.5-6.0, the content of epoxy groups obtained from GPTMS doped silica is tended to be stable and keeping maximum. Whether the pH is lower than 4.5 or higher than 6.0, the contents were always obtained on the low side. In this work, the solution's pH were adjusted to 5.2 ± 0.1 (measured with the pH 211 m) with 0.05 mol L^{-1} NaOH.

The iodate generating form the oxidation reaction and the surplus periodate reacts with hydrazine sulfate, so 0.1 mol L^{-1} sodium thiosulfate were employed to elimate them. More attention should be paid to because the excessive thiosulfate ion would cause interference into the polarographic determination. It is lucky that, there is a primrose yellow (which comes from the generating iodine) disappearance, during the process of the addition of sodium thiosulfate drop by drop. It was proved that this method is feasible and the deviation is less than ± 4 %.

Optional conditions for polarographic determination: For the recording of the best polarogram, polarographic conditions such as supporting electrolytes and its concentration and pH, concentration of hydrazine sulfate and reaction time were investigated.

Polarogram was recorded in CH_3COOH-CH_3COONa, KH_2PO_4-K_2HPO_4, $NaOH$ and $Na_2B_4O_7$ solution, respectively. Results were shown that, there is a higher sensitive polarographic wave in CH_3COOH-CH_3COONa solution than the others (in fact, those polarographic waves are always too lower to be observed). Based upon this results, change the concentration of CH_3COOH-CH_3COONa solution and find that the the peak current values reached the maximum and remained constant while the concentration of CH_3COOH-CH_3COONa solution is in the range of 0.0075-0.0400 mol L^{-1}. For the further study, changing the ratio of HAc-NaAc, influence of pH on peak current was investigated. Results indicated that the peak current increased with the pH increase when the pH was lower than 4.7, kept stable betwee 4.7 and 5.2 and then decreased when the pH was higher than 5.2. So in the present work, 0.020 mol L^{-1} CH_3COOH-CH_3COONa solution (pH = 5.0) was seclected as supporting electrolyte.

Concentration of hydrazine sulfate has an important impact on the peak current. Kept the volume constant, it was found that the peak current increased rapidly with the increasing concentration of hydrazine sulfate and met a maximum at 0.60 g L^{-1} hydrazine sulfate and then remained constant. In this work, 0.80 g L^{-1} was confirmed.

Reaction time between the generating formaldehyde and hydrazine sulfate has also influence on the peak current. Results indicated that the reaction could be completed after 3 min at room temperature. It was also found the peak current can remain more than 5 h.

Linearity: Under the optimum conditions, the reference GPTMS solutions were prepared and detected for the calibration curve. It was found the calibration was linear over the original GPTMS concentration range between 3.8×10^{-7}-2.6×10^{-5} mol L^{-1} with the regression equation following as $i_p = 0.8498 + 0.2105$ c and correlation coefficient value of 0.9998 (Fig. 3). Where i_p is the peak current in 10^{-6} A and c is the concentration of GPTMS in 10^{-6} mol L^{-1}. Because GPTMS has an epoxy group, the equation above is also suitable for the various epoxy groups concentrations and could be employed for quantitative measurement of epoxy groups on GPTMS/nano-SiO_2.

Mass dependence of i_p for the both GPTMS/nano-SiO_2: When the different weights of the both GPTMS/nano-SiO_2 were analyzed, the relationship between the i_p and the weights of GPTMS/nano-SiO_2 (A and B) were found to be linear with correlation coefficient value of 0.9939 and 0.9962 (Fig. 4), respectively. From the obtained results and the linearity gained above, epoxy groups on GPTMS/nano-SiO_2 were readily calculated. Content of epoxy groups on both GPTMS/nano-SiO_2 in mmol g^{-1} were listed in Table-1. At the same time, the recoveries of standard addition (reference GPTMS added in GPTMS/nano-SiO_2) were carried out and
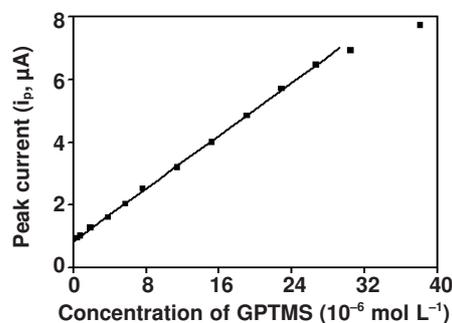
Fig. 3. Linear relationship between the peak curreents and concentrations of GPTMS
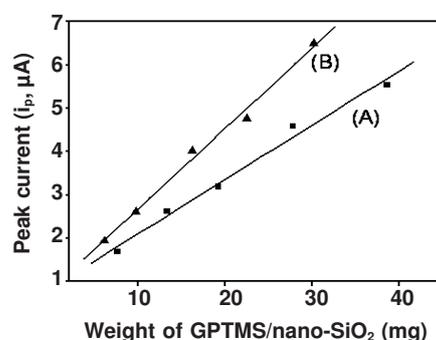
Fig. 4. Peak current vs. various weights of GPTSM/nano-SiO$_2$

results were aslo shown in Table-1. It shows that the relative standard deviation (RSD) of the five-cycle repeat measurements of sample A and B was calculated to be 2.8-3.5 %, showing acceptable reproducibility and the average recovery rate for reference GPTMS three-cycle in sample A and B is as high as 99.4-98.5 % with standard deviation (SD) of 1.5-2.1 %, respectively. This indicated that this method could be used for the quantitative analysis of epoxy groups on GPTMS/nano-SiO$_2$ with good accuracy and reliability.

TABLE-1
DETERMINATION OF EPOXY GROUPS ON GPTMS/NANO-SiO$_2$

Sample	Epoxy content (mmol g^{-1})	RSD (%, n = 5)	Recovery (% ± SD, n = 3)
A	0.5935	2.8	99.4 ± 1.5
B	0.8827	3.5	98.6 ± 2.1

Interference tests: Influences were examined in 2×10^{-6} mol L^{-1} reference GPTMS which is consist of various 1×10^{-3} mol L^{-1} disruptors. It was found that, taking ± 5 % deviation into account, the ions such as K$^+$, Na$^+$, Mg^{2+}, NH$_4^+$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and materials such as methanol, ethanol, acetone, acetic acid, silicas didn't disturb the determination. Acetaldehyde didn't interfere the determination when its concentration is less than 0.5×10^{-3} mol L^{-1}.

Conclusion

There are few reported methods that can be reliably employed for determining epoxy groups on GPTMS/nano-SiO$_2$. Measurements based on the addition reaction of the epoxy functionality (such as hydrochloric acid titration and perchloric acid titration) are both insensitive and unreliable because solid silica particles can adsorb indicator and catalyze the illegibility of the end-point. Some instrument analysis methods, such as GC, are efficient to determine volatile epoxide, but they still have many difficulties for determining epoxy groups on GPTMS/nano-SiO$_2$ because of the involatile and insoluble silica. In this paper, osciliopolarography has been developed to determine epoxy groups on GPTMS/nano-SiO$_2$. The accuracy and precision were validated by parallel determinations and recovery tests. It was found that this method is simple to determine amounts of epoxy groups on GPTMS/nano-SiO$_2$ with high sensibility. It was also hoped that it could provide some technical supports on analysis of other GPTMS doped products.

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