Asian Journal of Chemistry Vol. 21, No. 8 (2009), 6073-6084

Determination of γ-Aminopropyltriethoxysilane and Amino Group on Nanosilica-Doped γ-Aminopropyltriethoxysilane Composites Using Perchloric Acid

DELIANG LI*†, JIANYING QU†, ZHIXIAN CHANG† and ZHIJUN ZHANG
Key Laboratory of Ministry of Education for Special Functional Materials,
Henan University, Kaifeng 475004, P.R. China
E-mail: lideliang@henu.edu.cn

The prepared nanosilica-doped γ-aminopropyltriethoxysilane (APS) composites (APS-SiO_2) were characterized by means of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). Then a method to determine content of APS and amino in APS-SiO_2 through titration with the perchloric acid-glacial acetic acid standard solution in non-aqueous solution was established. Influence of solvent, amount of acetic anhydride, the dispersant and its amount on results were discussed in detail and the end point was indicated by a potentiometric titration method. For the titration of APS-SiO_2, the influence of nanoparticles' concentration on results was also discussed. Because of the addition of 2-ethylhexanol, the dispersibility of sample was improved, at the same time, the freezing point of the titration system was decreased. Therefore, the stability of the system was improved and the applied field of this method was developed. It was found that this method is simple in terms of operation and can be readily used to determine the purity of APS and amino on APS-SiO_2 with good accuracy and reproducibility.

Key Words: γ-Aminopropyltriethoxysilane, Nanosilica, Determination, Perchloric acid.

INTRODUCTION

As one of the most promising materials, nanosilica is focused on in many fields, *i.e.* resin and rubber[1,2]. But its application is limited in some aspects because of its poor compatibility with organic materials. Surface modification is an effective way to resolve surface defects. At present, many scientists have modified nanosilca with γ-aminopropyltriethoxysilane (APS) successfully[3,4] to improve its performance and gained a series of encouraging results. These compounds are widely used in the fields of analytical chemistry[5], biochemistry[6], catalyst technology[7], *etc*. It proved that the amount of APS (or amino groups) on APS-SiO_2 is of great importance to its properties and applications. But, it has not systemic studies for accurate determination of the amount and distribution of modifiers (such as silane coupling agents (SCA)) and

---

†College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China.

surface functional groups of nanomaterials. The methods for surface analysis of nanoparticles, such as spectroscopic analysis, thermoanalysis and scanning probe microscopy (SPM) can give right surface information of functional groups of nanoparticles, but quantitative results with more errors. So, accurate analysis of modifier and surface functional groups of nanomaterials is very significant.

Only chromatography is reported to determine APS up to now. Liu[8] and Jukka[9] analyzed APS with the capillary chromatograph, confirming the position of gas chromatography peak using gas chromatography (GC) technique and linear range and detection limit were also investigated. Fu[10] and his co-workers analyzed APS by gas chromatography-mass spectrometry (GC/MS) and separated the components in samples and determined corresponding optimum separation condition. Then molecular structures of each component were identified by GC/MS technique and the MS decomposition rule. All these methods for determination of APS are based on capillary gas chromatography. However, because of higher reactivity, silane coupling agents can cause the big destructive effect on the fluid of capillary at higher temperature, resulting in lower separation ability and shorter lifetime of capillary column and worse reproducibility. In addition, the produced SiO_2 can jam the nozzle of hydrogen flame detector, which makes the sensitivity reduce obviously[11].

For APS-SiO_2, researches are focused on its characterization using X-ray photoelectron spectroscope (XPS)[12,13], nuclear magnetic resonance (NMR)[13,14], infrared spectra[13,15-17] and element analyzer (EA)[17,18]. Among these methods, methods of XPS, NMR and IR can give qualitative and semi-quantitative information of APS on SiO_2, which can not give accurate amount of functional groups on the surface of nanoparticles. Element analyzer can quantitate the nitrogen, but this method needs high-purified samples with great difficulty. To our knowledge, studies on quantitative analysis of amino on the surface of SiO_2 with simple and economy methods are much less reported. It was reported that Van[18] and Gang[19] determined surface amino on APS-SiO_2 by back titration method, which needed longer operation time and was not suitable for controlling analysis for adsorption between nanoparticles and indicator and bad reproducibility. Our group[20] analyzed the amount of amino on APS-SiO_2 through potentiometric titration using an all-solid pH sensor as indicator electrode with satisfied results, but the stability of electrode and reproducibility need further improvement. So, exploring a convenient and economic method to quantitate surface amino is very important for quality control of products and exploitation of new composite functional materials.

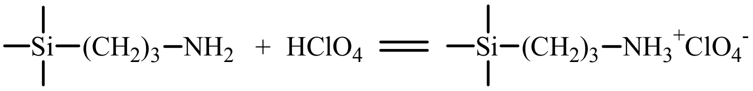
In this paper, the prepared APS-SiO_2 were characterized in detail. Then, based on the determination of organic amines by titration in non-aqueous condition[21], a method for quantitative analysis of APS, using perchloric acid-glacial acetic acid as the titrant, was described and developed to determine amino on APS-SiO_2. The optimum conditions for titration were discussed in detail. Satisfactory results were obtained for analyzing practical samples of APS (Nanjing Shuguang Co., China) and self-prepared APS-SiO_2.

EXPERIMENTAL

γ-Aminopropyltriethoxysilane (APS) was purchased from J&K's Capability of Chemical Development (Beijing, China) with content of 98.7 %. Sample A, a commercial APS, is obtained from Nanjing Shuguang Co. Sample B/C, APS-SiO_2 composites, are pilot product produced by Research Center for Nanomaterial Engineering and Technology of Henan Province. All the other reagent were of analytical grade.

Characterization of APS-SiO_2 composites: A JEM 100CX-II transmission electron microscope (TEM, Jeol Company, Japan) was performed to observe the morphology of the APS-SiO_2 composite and the sample for TEM analysis was prepared by transferring a small amount of the composite dispersed in toluene onto a copper stub. Infrared spectra were obtained using an AVATAR 360 Fourier transform infrared spectrophotometer (Nicolet). The thermal stability of the composite was examined using thermogravimetric analysis in ambient atmosphere on an Exstar-6000 thermoanalysis system (TGA) at the heating rate of 10 ºC/min from room temperature to 800 ºC. Besides, Axis Ultra X-ray photoelectron spectroscope (XPS, Al-Kα radiation) was used to analyze the chemical state of Si in the composite, using contaminated carbon (C1s: 284.6 eV) as the reference.

Principles: γ-Aminopropyltriethoxysilane (APS) and APS-SiO_2 exhibit the active amino, which can be titrated by strong acid. But the alkalinity of amino group is too weak to meet requirement of general titration analysis. In view of the fact that APS can hydrolyze easily, we take the perchloric acid in acetic acid as standard solution and crystal purple as indicator to titrate APS in non-aqueous solution. The chemical reaction is followed as:



$$-\overset{|}{\underset{|}{Si}}-(CH_2)_3-NH_2 + HClO_4 = -\overset{|}{\underset{|}{Si}}-(CH_2)_3-NH_3^+ClO_4^-$$

Amino content of APS and APS-SiO_2 were described with percentage of APS and ammonia neutralization number and calculated from eqns. 1 and 2, respectively.

$$x\% = \frac{M(V - V_0)(1 - \frac{t - t_s}{1000})c}{1000m} \times 100 \tag{1}$$

$$w_{NH_2} = \frac{(V - V_0)(1 - \frac{t - t_s}{1000})c}{m} \tag{2}$$

where m represents quality of a sample (g); x % represents percentage of APS; w_{NH2} represents ammonia neutralization number; V represents volumes of consumed perchloric acid solution for a sample (mL); V_0 represents volumes of consumed perchloric acid solution for a blank solution (mL); t is temperature of perchloric acid solution for titration (ºC); t_s is temperature of perchloric acid solution for calibration (ºC); c is concentration of perchloric acid solution (mol L^{-1}); M is the molarity of APS (g mol^{-1}).

Solution preparation: Crystal purple was prepared as 0.2 % acetic acid solution. Perchloric acid standard solution was prepared to 0.1 mol L^{-1} and calibrated as following method: 5.00 mL perchloric acid and 11.00 mL acetic anhydride were diluted into 50 mL acetic acid; after being placed in to a 500 mL flask dilute to volume with acetic acid; (3) owing to exothermicity, the solution volume was fixed after 24 h (4) the solution was calibrated using potassium hydrogen phthalate in acetic acid with crystal purple as indicator.

Methods: Standard APS was weighed and put into a dry conical flask, then 5 mL 2-ethylhexanol as dispersant and 20 mL acetic acid was added. After being stirred evenly, 3-4 drops crystal purple indicator was dropped into the solution and titrated with the perchloric acid standard solution. The colour of the system obviously transforms from purple blue to blue and keeps 0.5 min and does not vanish is the end point. During the titration of sample A, if the quantity of sample is more, more precipitates is produced, here the supersonic is needed for 2-3 min. During the titration of sample B/C, when blue colour appears, the supersonic is needed for 2-3 min to observe blue colour will be disappear or not. If blue colour disappears, the titration will be gone on; if precipitates or samples are too more, supersonic is needed for 3-4 times with each time of 2-3 min, until blue colour not disappear during supersonic process. Take down the volume of perchloric acid standard (V) and temperature (t). The blank experiment was carried out under the same condition.

Notably, precipitate can be produced sometimes in experiments, which creates adsorption phenomenon easily. So, the solution must be shaken for one minutes after the colour changes. It is alright when the colour does not return to purple. In order to avoid change temperature of the titrate system, the supersonic time cannot excessively long; doing the blank tests of sample B/C, the blank samples are unmodified nano-SiO_2.

RESULTS AND DISCUSSION

Characterization of APS-SiO_2 (Sample B/C): As the results of TEM, FT-IR, TGA and XPS obtained from sample B and C are similar, so we take sample B as example following to discuss.

Fig. 1 shows the TEM photograph of the APS-SiO_2 composite. The APS-SiO_2 was found to have spherical shape, with the diameter ranged within 20~30 nm.

Fig. 2 displays IR spectra of unmodified nano-SiO_2 and APS-SiO_2. The significiant IR absorption in unmodified nano-SiO_2 and APS-SiO_2 at 1250-1000, 800 and 458 cm^{-1} are attributed to asymmetric stretching, symmetric stretching and bending vibration modes of Si-O-Si groups, respectively. Compared to unmodified nano-SiO_2, the new peaks in APS-SiO_2 at 1487 cm^{-1} which is assigned to the symmetric deformation mode of NH_3^+ in the $SiO^{-}\cdots H\cdots NH_2^{+}$ group[22], 1573 cm^{-1} which may be arise from the NH_2 groups which participate in the hydrogen bonding system of the

SiOH···NH$_2$ group[22], implied that APS have been modified on the surface of nano-SiO$_2$. The appearances of stretching of -CH$_2$- (2934, 2889 cm^{-1}) and -NH$_2$ (3356, 3278 cm^{-1}) also confirmed the above result.

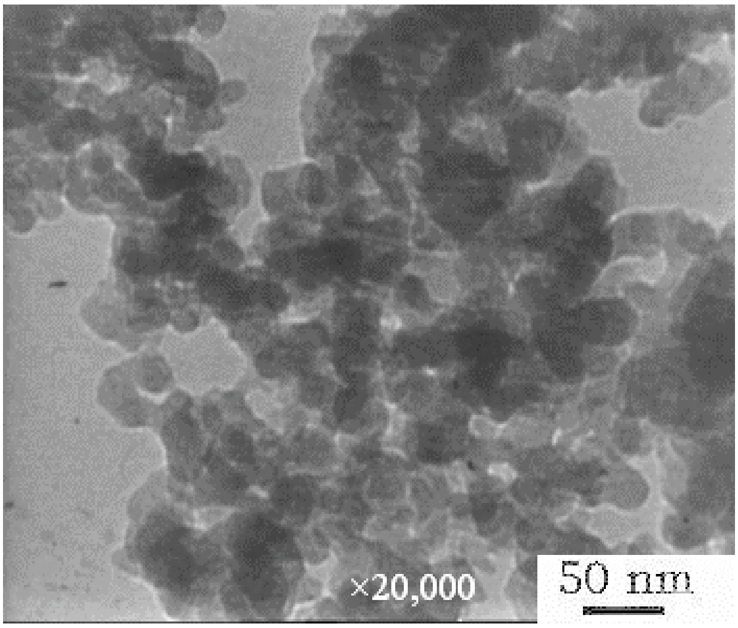


Fig. 1. TEM photograph of the APS-SiO$_2$

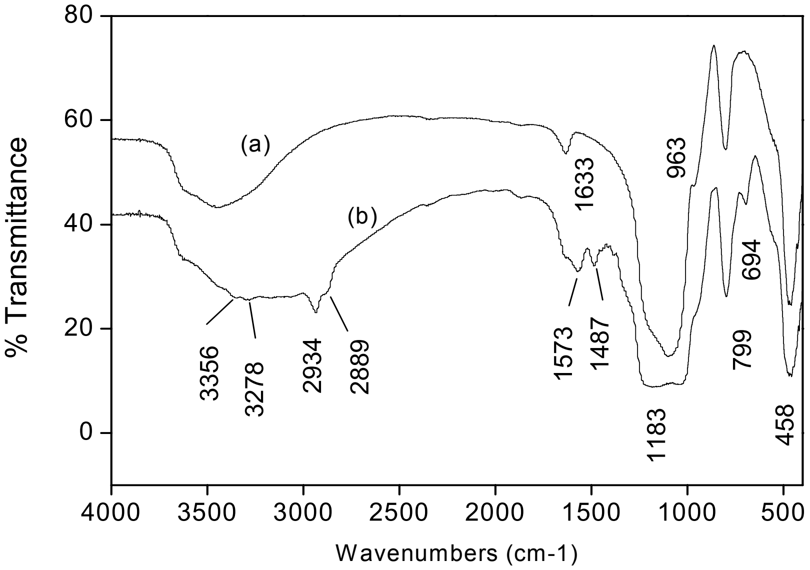


Fig. 2. IR spectra of (a) unmodified nano-SiO$_2$ and (b) APS-SiO$_2$

Fig. 3 shows the TGA curves of unmodified nano-SiO_2 and APS-SiO_2 composite in air. In the temperature range of 25-110 ºC, unmodified nano-SiO_2 and APS-SiO_2 composite showed a rapid weight loss about 2.0 and 4.8 %, respectively, which is attributed to the loss of adsorbed water on the surface of the materials. In the temperature range of 110-270 ºC, both have a slow weight loss about 1.5 and 3.4 %, respectively, which may be the loss of water in the network of the SiO_2. In the temperature range of 270-800 ºC, the unmodified SiO_2 had a weight loss of about 6.6 %, owing to the dehydration of silanol, while the APS-SiO_2 showed a weight loss of about 15.3 %, corresponding to the elimination of the organics on the surface of the composite.

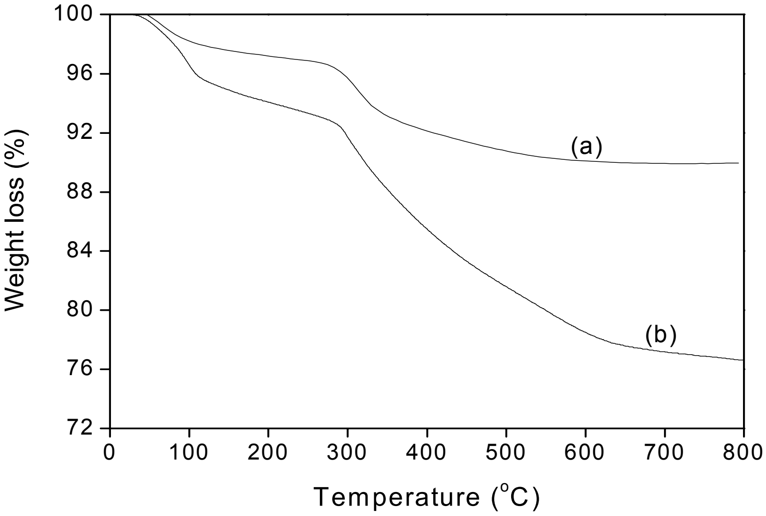


Fig. 3. TGA curves of (a) unmodified nano-SiO_2 and (b) APS-SiO_2

Fig. 4 displays the Si2p XPS spectra of the unmodified nano-SiO_2 and APS-SiO_2 composite. It showed that the characteristic Si2p peak of SiO_2 appears at about 103.6 eV. Compared to that of SiO_2, Si2p peak of APS-SiO_2 shifted to the lower energy about 103.0 eV with a larger full wave at half maximum, which can be curved-fitted to be two peaks at 103.6 and 102.8 eV(data not shown), corresponding to Si2p peak of SiO_2 and Si-alkyl[23,24], respectively. In addition, we can infer that the peak area at 102.8 eV is much larger than that at 103.6 eV, implying that the inorganic nano-silica core had been well capped by the organic modifying layer which can also be said that the nanoparticles have a SiO_2 core and an organic surface layer.

Selection of titrants: Since APS belongs to weak alkali, acidic solvent must be selected in non-aqueous titration in order to improve its alkalinity. Acetic acid is applied widely due to its stability in air. In addition, species with weak alkali in water would capture protons easily in acetic acid, it is an ideal solvent to titrate weak alkali.

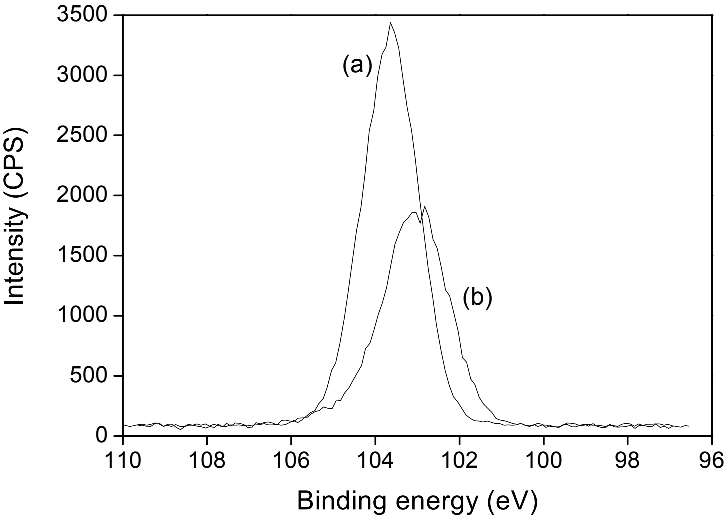


Fig. 4. Si2p XPS spectra of (a) unmodified nano-SiO_2 and (b) APS-SiO_2

Glacial acetic acid is a sparse proton solvent, so the titrant must be strong acid. The strength of sulfuric acid, hydrochloric acid and perchloric acid which are used commonly are same in water, but are different in many non-aqueous solvents. Perchloric acid is the strongest acid in glacial acetic acid and strength of other inorganic acids decreases progressively in the following order: perchloric acid > hydrobromic acid > sulfuric acid > hydrochloric acid > nitric acid. On the other hand, perchloric acid can dissolve into many non-aqueous solvents with stability and salts resulted by perchloric acid and organic/inorganic alkalis have greater solubility in non-aqueous solvents generally. So, the perchloric acid solution in glacial acetic acid was chose as the titrant.

In order to confirm the correctness of perchloric acid - glacial acetic acid solution system, we prepared the perchloric acid with alcohol, glacial acetic acid, chloroform, acetone and propionic acid systems and titrated standard APS according to the experimental method, respectively. Experiments showed that alcohol can dissolve perchloric acid well and have no deposit nearly in the titrate process, which is suitable for the titrate, but the colour of indicator changes unobviously and the end-point is difficult to find. Chloroform and propionic acid can not dissolve perchloric acid and taking acetone as the solvent, the system shows yellowish brown after keeping aside for 0.5 h, which may result from the redox reaction between perchloric acid and acetone. Glacial acetic acid can dissolved perchloric acid with good results. So perchloric acid-glacial acetic acid solution is selected as the titration system.

Influences of acetic anhydride: Titrate APS with the perchloric acid in non-aqueous condition, so the water can affect the titration. In general, the commercial perchloric acid contains 28-30 % water (for example perchloric acid contains 29.36 % water), at the same time the solvent of perchloric acid is glacial acetic acid, so we select the acetic anhydride as the absorbent for water. Water in perchloric acid can be taken out because the acetic anhydride can produce glacial acetic acid when it mixed with water. To determine the quantity of acetic anhydride used, we have determined the influence of volume ratio of perchloric acid and acetic anhydride on the result, shown in Table-1.

TABLE-1
INFLUENCES OF ACETIC ANHYDRIDE

Volume ratio of perchloric acid and acetic anhydride	1:0	1:1.5	1:2.2	1:3
APS (%)	98.11	98.34	98.72	98.31
Relative error (%)	-0.60	-0.36	0.02	-0.40

It is observed that the determination result have no error when the volume ratio of perchloric acid and acetic anhydride is 1:2.2, which is also the quantity of the acetic anhydride for the water in the perchloric acid theoretically. If the volume ratio of perchloric acid *vs.* acetic anhydride deviates 1:2.2, it led the result to be low. And the volume ratio of the perchloric acid and acetic anhydride deviates 1:2.2 far away and the negative error is more. The possible reason is that, when the added acetic anhydride is not enough, the system contains water, so the end-point of titration is not clear, which causes the result to be low, while acetic anhydride is added excessively, it can react with APS (primary amine) to produce imine, but alkaline nature of imine is weaker than the corresponding amine.

Influence of dispersant: Smoke can be given off when glacial acetic acid is added to the amino silane coupling agents directly with exothermally, which can cause the sample losses. In order to promote dispersal of the sample, right amount dispersant should be added. Therefore, we take 5mL toluene, chloroform, ethyl alcohol and 2-ethylhexanol as the dispersant to experiment, respectively. Results showed that exothermicity and smoke phenomenon vanish after adding toluene, but in the titrate process, the precipitation appears early and create problem to the titrate, also its toxicity is strong. The smoke and the exothermic phenomenon also vanish after adding chloroform, in titrate process, precipitation quantity of chloroform is slightly less than toluene, but the titrate result is still somewhat lower. Less smoke can emit exothermally after adding the ethyl alcohol, in the titrate process, no precipitation is produced nearly, but the end point is not clear and often lag which resulted in the determination result to be higher; after adding the 2-ethyl hexanol, in the titrate process, although still have a few precipitation, the smoke phenomenon vanished, its toxicity is also weak and does not influence on the analytical result. Therefore 2-ethylhexanol is selected as the dispersant. The experiments show that if the amount of 2-ethylhexanol is less which will result in the smoke phenomenon cannot vanish completely, if the amount of 2-ethylhexanol is excessive which will result in salt produced by the titration process is easy to separate out. When 0.2-0.8 g sample dissolve in the 20-30 mL glacial acetic acid, 5 mL 2-ethyl hexanol should be added in the solution. At the same time, because the freezing point of the glacial acetic acid is 16.6 ºC, the solution can crystallizes in the low density of perchloric acid dissolve the anhydrous acetate at about 15 ºC, it is unable frequently to be used in winter. Addition of the 2-ethylhexanol can improve the mutual solubility for the system, which reduces the freezing point to enhance its stability for uses in many fields.

Confirmation of the end-point through potentiometric titration: In the titrate process, the colour of the crystal violet indicator changes from purple-purple blue-blue-bluish green-to green. In order to determine the end-point accurately, we records the potential and the corresponding colour change of the titrate process, as shown in Fig. 5 (the E-potential, V-volume of consumed perchloric acid). According to second derivative method, when $\Delta^2E/\Delta V^2$ (Δ - change quantity) appears the opposite mark, corresponding two volumes of the titrant, between them must have cause to $\Delta^2E/\Delta V^2 = 0$, which can be calculated. Based on this, the volume of perchloric acid at end-point means the end-point of titration. And the further calculation showed the content of APS sample was 98.70 %. At that time, the crystal violet indicator changes from purple blue to blue. From Fig. 5, it is observed that the titration jump is in a big range with 120 mV, which indicated that this method was feasible.

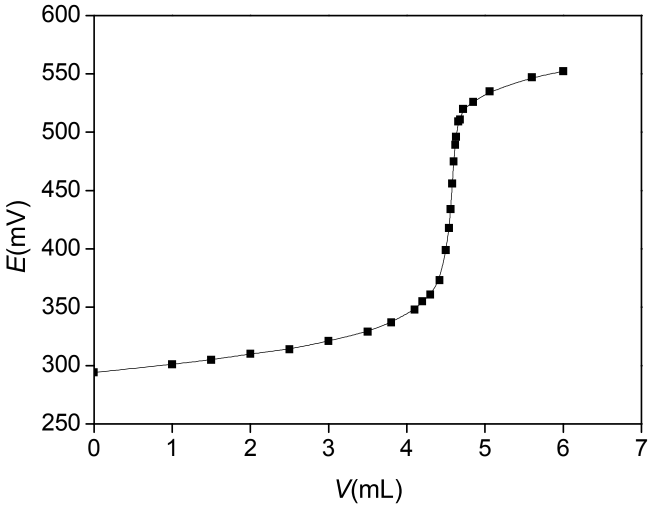


Fig. 5. E-V curve

Effect of concentration of APS-SiO₂ on the titrate results: APS-SiO_2 can not dissolve but disperse in glacial acetic acid - 2-ethylhexanol solution. In order to investigate whether the concentration of APS-SiO_2 (mass of APS-SiO_2 in 25 mL system) can influence the titrate results or not, two systems of sample B + 5 mL of 2-ethyl hexanol + 20 mL glacial acetic acid and sample B + 10 mL of 2-ethylhexanol + 15 mL of glacial acetic acid were selected to test. The results were shown in Fig. 6. It indicated that the results are of further accuracy when the concentration of APS-SiO_2 was in a certain range. For the system of sample B + 5 mL of 2-ethylhexanol

+ 20 mL of glacial acetic acid, the quantity of sample B is ≤ 0.8 g with better result. For the system of sample B + 10 mL of 2-ethylhexanol + 15 mL of glacial acetic acid, the quantity of sample B is ≤ 1.0 g with better result. When the concentration of APS-SiO_2 is too higher, the value of amino neutralization will reduced, it may because that wrap or adsorption during APS-SiO_2 nanoparticles enhanced with increasing of concentration of APS-SiO_2, so it is difficult for nanoparticles to disperse with the result that the end-point will appear in advance. Comparing these two systems, it can be seen that increase the quantity of dispersant of 2-ethylhexanol will enhance the concentration of APS-SiO_2. High amount of 2-ethylhexanol will reduce the solubility of salts produced by reaction of perchloric acid and APS-SiO_2 and make salts separate out. At the same time, it will influence the changing colour of indicator. In addition, with the increasing of the concentration of APS-SiO_2, more supersonic times will be needed during the titration. For sample B of 0.5-0.8 g, supersonic of 2-4 times with each time of 2-3 min can appear end point. But when concentration is higher, supersonic for 2-3 min can not disperse the system uniformly. If supersonic time is too long, it will make the system temperature increase or indicator degradation.

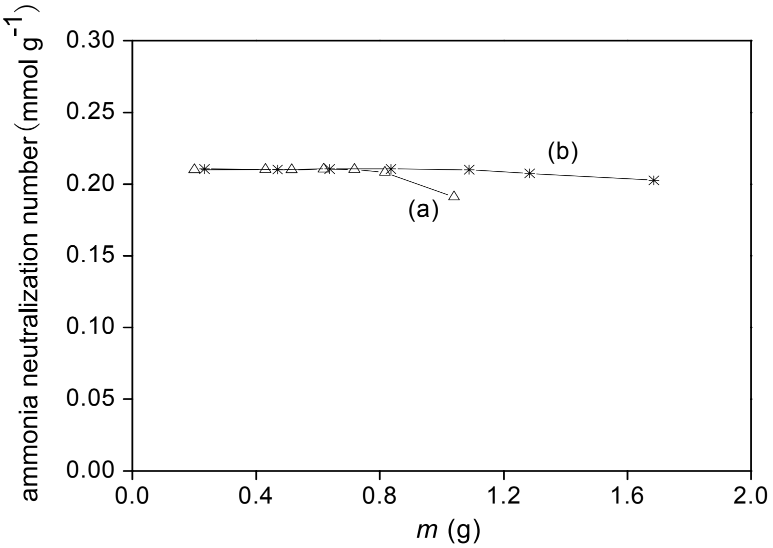


Fig. 6. Effect of concentration of APS-SiO_2 on results. (a) Sample B + 5 mL of 2-ethylhexanol + 20 of CH_3COOH; (b) Sample B + 10 mL of 2-ethylhexanol + 15 mL of CH_3COOH

Samples analysis and determination of recovery: Based on the method, sample A or B/C was titrated with the standard perchloric acid (sample B/C was titrated with ≈ 0.02 mol L^{-1} perchloric acid). On the basis of the titration results, the amino content of sample A and B/C were calculated. The analytical data were showed in Table-2, which demonstrated the precision of this method was satisfying.

Further, using dimethyloctylamine (97.33 %, determined by GC method) as standard substance, recovery experiment for sample A and B were done, respectively. The results are shown in Table-3 and one could observed that the recovery ratios of the sample A and B are 99.59-101.0 and 99.61-102.0 %, SD are 0.62 and 0.86 %, respectively, which indicated this method is accurate.

TABLE-2
DETERMINATION RESULTS OF SAMPLE

Samples	A (n=5)	B (n=5)	C (n=5)
Content	98.88 %	0.2104 mmol g^{-1}	2.285 mmol g^{-1}
RSD	0.24 %	0.58 %	0.47 %

TABLE-3
RECOVERY OF STANDARD APS IN SAMPLE A AND B

Samples	Recovery (%)	Ave. (%)	SD (%)
APS in A	101.0, 99.66, 100.5, 100.6, 99.59	100.3	0.62
APS in B	102.0, 100.8, 101.1, 99.61, 100.7	100.8	0.86

Conclusion

The prepared APS-SiO_2 were characterized by means of TEM, XPS, TGA and FT-IR. A direct titration method has been developed to determine the content of the APS and the amino on surface of the APS-SiO_2 in non-aqueous, taking the standard perchloric acid - glacial acetic acid as the titrant, the acetic anhydride as absorbent, 2-ethylhexanol as the dispersant and the crystal violet as the indicator. This method is volumetric analysis, which does not need the precise instruments with high accuracy and precision and the recovery ratios of the sample A and B are 99.59-101.0 and 99.61-102.0 %, RSD are 0.62 and 0.86 %, respectively. 2-Ethylhexanol as the dispersant was taken into the titrate system. It not only promoted the sample diffusion to improve the system mutual solubility, but also reduced the freezing point to enhance its stability. It is hoped that this method could be used for the convenient and fast quantitative analysis of APS and the amino groups on APS-SiO_2 or other similar category products. It is also hoped that the method would help to provide technical support to the development and application of novel high-performance multifunctional composites.

REFERENCES

1. J.Z. Ma, J. Hu, Z.J. Zhang and L.Y. Liu, *J. Compos. Mater.*, **40**, 2189 (2006).
2. N. Rattanasom, T. Saowapark and C. Deeprasertkul, *Polym. Test.*, **26**, 369 (2007).
3. A. Krysztafkiewicz, T. Jesionowski and S. Binkowski, *J. Colloid. Surface. A*, **173**, 73 (2000).
4. A. Simon, T.C. Bouhacina, M.C. Porté, J.P. Aimé and C. Baquey, *J. Colloid. Interf. Sci.*, **251**, 278 (2002).
5. N. Tokman, S. Akman and M. Ozcan, *Talanta*, **59**, 201 (2003).

6. J. Kim, H. Jia, C. Lee, S. Chung, J.H. Kwak, Y. Shin, A. Dohnalkova, B. Kim, P. Wang and J.W. Grate, *Enzyme Microb. Tech.*, **39**, 474 (2006).
7. Y. Wan, F. Zhang, Y.F. Lu and H.X. Li, *J. Mol. Catal. A-Chem.*, **67**, 165 (2007).
8. X.M. Liu, B.Y. Wu and J.L. Yan, *Silicone Mater. (China)*, **17**, 18 (2003).
9. M. Jukka, P. Sirpa and L. Jyrki, *Analyst*, **124**, 665 (1999).
10. Q. Fu, Z.Y. Qian and M. Zhao, *Modern Scientific Instruments (China)*, **2**, 13 (2000).
11. J. Wang, M. Zhao and H.L. Gao, *Zhejiang Chemical Industry (China)*, **5**, 11 (2003)
12. C. Perrochot, M.M. Chehimi, M. Delamar and F. Fievet, *Surf. Interface Anal.*, **26**, 689 (1998).
13. F. Garbassi, L. Balducci, P. Chiurlo and L. Deiana, *Appl. Surf. Sci.*, **84**, 145 (1995).
14. E. Satu, I.I. Eero, N. Lauri, V. Jari, T.P. Tuula and R. Andrew, *J. Phys. Chem. B*, **108**, 11454 (2004).
15. E. Satu, I.I. Eero and N. Lauri, *Langmuir*, **19**, 3461 (2003).
16. I. Shimizu, H. Okabayashi, K. Taga, E. Nishio and J. Charmian, *Vib. Spectrosc.*, **14**, 113 (1997).
17. A. Walcarius, M. Etienne and J. Bessilere, *Chem. Mater.*, **14**, 2757 (2002).
18. B.A. Van and A. Vrij, *J. Colloid Interf. Sci.*, **156**, 1 (1993).
19. S. Gang, H. Adrian and L. Rastislav, *Colloid. Surface. B*, **35**, 59 (2004).
20. Y. Zhang, X.H. Li, Z.J. Zhang and K.Z. Liu, *Anal. Lett.*, **38**, 1249 (2005).
21. A.X. Zhang, S.L. Yuan and H.F. Ruan, *Silicone Material and Applications (China)*, **5**, 23 (1995).
22. C.H. Chiang, H. Ishida and J.L. Koenig, *J. Colloid Interf. Sci.*, **74**, 396 (1980).
23. J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics Division, Perkin-Elmer Corporation, USA (1992).
24. L.S. Kasten, V.N. Balbyshev and M.S. Donley, *Prog. Org. Coat.*, **47**, 214 (2003).

(*Received*: 23 September 2008; *Accepted*: 23 May 2009) AJC-7581