In Situ Monitoring of the Generation of Monodisperse Silica Particles during the Hydrolysis of Tetraethyl Orthosilicate with Piezoelectric Quartz Crystal Impedance Analyzer

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The piezoelectric quartz crystal (PQC) impedance analyzer was used to monitor *in situ* the generation of monodisperse silica particles during the hydrolysis of tetraethyl orthosilicate (TEOS) and their adsorption onto an Au electrode in alcohol solutions containing water (6—15 mol/L) and ammonia (0.2—2.0 mol/L). The equivalent circuit parameters, the resonance frequencies and the half-peak width values of the conductance spectra of the PQC resonance were obtained. The resonant frequency decreased notably while the motional resistance changed very slightly (within 1 Ω) during the hydrolysis reaction, suggesting that the mass effect dominated the adsorption of generated monodisperse silica particles on the gold electrode in this system. Changes in f_0 indicated that the ammonia concentration affected the hydrolytic reaction obviously, and the influence of water concentration on the reaction was small while the water was significantly excessive. Kinetics of monodisperse silica particle adsorption occurring at the electrode | solution interface was analyzed using a first-order reaction scheme. In addition, the electrolyte-induced precipitation of the monodisperse silica particles was monitored and discussed. The mean size, the number of adsorbed particles per area and the converge of monodisperse silica particles were obtained from scanning electron microscope (SEM) observations.

Keywords piezoelectric quartz crystal impedance, monodisperse silica particle, tetraethyl orthosilicate hydrolysis, gold electrode, surface adsorption

Introduction

Minute SiO_2 particles have been widely used in many fields, *e.g.* nano-sized SiO_2 particles were used as immunofluorescent substitute for fluorescent immunological labeling.[1,2] Kolbe[3] observed the formation of silica particles via tetraethyl silicate hydrolysis in alcohol solution in the presence of certain bases for the first time. Stöber *et al.*[4] reported that the silica particles of uniform size could be obtained from hydrolysis of alkylsilicates with ammonia as a morphological catalyst. Nuclear magnetic resonance (NMR),[5] gas chromatography (GC)[6] and transmission electron microscope (TEM)[4] have been used to study the process of alkylsilicates hydrolysis and generation and growth of silica particles. These methods are *ex situ* method for the study on this reaction. Piezoelectric quartz crystal impedance (PQCI) analysis technique has been widely used as a powerful tool for the studies of some physical and/or chemical properties of many tested systems.[7-19] But no successful attempt has been reported to monitor *in situ* the generation of suspended monodisperse of particles yet. In this work, the PQCI technique and SEM observation were applied to monitor the generation of monodisperse silica particles from the TEOS hydrolysis reaction, and to determine the particle number per unit area and the coverage of monodisperse silica particles on the electrode surface.

Experimental

Materials

Tetraethyl orthosilicate, ammonium hydroxide and ethanol of analytical grade quality were purchased from Shanghai Reagent Factory.

AT-cut silver-plated 9 MHz piezoelectric quartz crystals (PQC) of 12.5-mm diameter were commercially obtained from the National 707 Factory (Beijing, China). The silver electrode on one side of the PQC was dissolved using several drops of concentrated nitric acid, and a gold electrode was then vacuum-evaporated from a highly pure gold foil with an Eiko IB ion coater (Hitachi Inc.). The geometric area of the gold electrode was 0.30 cm^2. To remove possible surface contamination, the gold electrode surfaces were treated with $H_2SO_4 + H_2O_2$ (3:1, *V/V*) for 5 min, then rinsed thoroughly with doubly distilled water. A conventional glass reaction cell of a volume of *ca.* 50 mL was used. The test solution (40 mL) was stirred at a constant rate with a magnetic

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stirring bar.

Instruments

The experimental setup used in this work is shown in Fig. 1. It included an HP 4395A network/spectrum/impedance analyzer and an IBM-compatible personal computer (PC), and was described in detail in literature.[13] The conductance (G) and susceptance (B) of the PQC resonance were measured synchronously on the HP 4395A equipped with an HP 43961A impedance test adapter and an HP 16092A test fixture. The equivalent circuit parameters were obtained at a time interval of *ca*. 1.6 s and displayed continuously on the VB form during experiments.

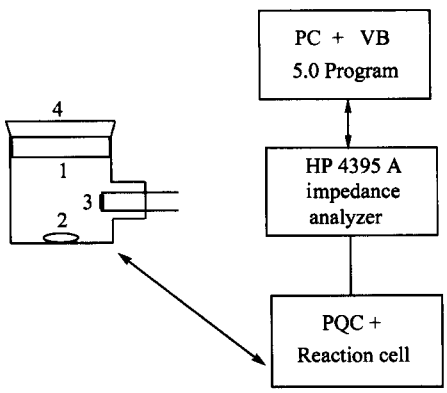

Fig. 1 Schematic diagram of the QCI test assembly. 1: Reaction cell; 2: magnetic stirring bar; 3: PQC sealed on one terminal of glass tube using 702 silicon rubber adhesive; 4: stopper.

a Hitachi S-570 scanning electronic microscope (SEM) was used to observe the surface morphology of the Au electrode.

Procedures

The gold-coated quartz crystal was sealed on one terminal of a glass tube with 704-silicon rubber adhesive to allow one side of the quartz crystal in contact with electrolyte solution. The gold electrode was connected to the ground terminal of the HP 16092A. The silver electrode on the other side of the PQC was placed in air and connected to the non-ground terminal of the HP 16092A. Admittance measurements were performed under conditions of 101 points, a frequency span of 40 kHz covering the resonant frequency of the PQC, an IF BW value of 10 kHz and a source power value of 0.5 dBm.

Throughout the measurement, ammonia was used as a catalyst for generating spherical silicon particles. At the beginning of each test, pure alcohol, water and ammoniac solution in a determined molar ratio were mixed in the reaction cell equipped with a stopper. The PQC was immersed in this mixed solution and connected to the HP 4395A for the PQCI measurements. After the PQCI responses had become stable, TEOS was added while the equivalent circuit parameters were monitored simultaneously. The tested solution was agitated with a magnetic stirrer. The reaction conditions for the hydrolysis of TEOS employed in this work were the same as Stöber's work.[4] The size of the generated silica particles was of monodispers feature, which was confirmed with TEM observation.

Calculation method

The Butterworth-Van Dyke (BVD) equivalent electrical circuit mode[10,12,14,17] was widely applied to analyze the PQC resonance. The BVD equivalent circuit parameters, motional resistance (R_1), motional inductance (L_1), motional capacitance (C_1) and static capacitance (C_0) can be obtained by the simultaneous nonlinear fitting of experimental data of the conductance (G) and susceptance (B) of the PQC resonance to the BVD model. Four independent parameters are obviously required as the estimation parameters during the fitting, *e.g.* R_1, C_0 and two parameters among L_1, $1/C_1$ and f_0. The G and B equations of the BVD model used for the fitting are given as follows[10-13]

$$Y = G + jB = \frac{R_1}{R_1^2 + U^2} + j(\omega C_0 - \frac{U}{R_1^2 + U^2}) \quad (1)$$

where $\omega = 2\pi f$, $U = \omega L_1 - 1/(\omega C_1) = (1/C_1)(\omega_0^2 - 1/\omega)$, $\omega_0 = 2\pi f_0$, and Y is the admittance of the PQC resonance.

Besides the four independent equivalent circuit parameters, three characteristic frequencies and the half peak width of the electroacoustic conductance spectrum ($\delta f_{G1/2}$) can also be obtained as follows[17-19]

$$f_0 = \frac{1}{2\pi\sqrt{L_1 C_1}} \quad (2)$$

$$\omega_s^2 = (2\pi f_s)^2 = \frac{L_1 - C_0 R_1^2 + \frac{2L_1 C_0}{C_1} - \sqrt{C_0^2 R_1^4 + L_1^2 - 2L_1 C_0 R_1^2 - \frac{4L_1 C_0^2 R_1^2}{C_1}}}{2C_0 L_1^2} \quad (3)$$

$$\omega_p^2 = (2\pi f_p)^2 = \frac{L_1 - C_0 R_1^2 + \frac{2L_1 C_0}{C_1} + \sqrt{C_0^2 R_1^4 + L_1^2 - 2L_1 C_0 R_1^2 - \frac{4L_1 C_0^2 R_1^2}{C_1}}}{2C_0 L_1^2} \quad (4)$$

$$\delta f_{G1/2} = f_{HG1/2} - f_{LG1/2} = f_{B\min} - f_{B\max} = R_1/(2\pi L_1) \quad (5)$$

where f_0 is the resonant frequency at which the reactance (X) and susceptance (B) of the motional arm vanish; f_s and f_p are the series resonant frequency and the parallel resonant frequency where X and B of BVD equivalent circuit vanish, respectively. $f_{HG1/2}$ and $f_{LG1/2}$ are the higher and lower frequencies at half peak height in the G spectrum, and $f_{B\min}$ and $f_{B\max}$ are the frequencies at minimum and maximum B values, respectively, and all symbols are in their international units.

The mass change was calculated from the Sauerbrey equation[20] and then the mass coverage was calculated from following equation

$$\Delta m/A = -\Delta f_0/(2.26 f_{0g} \times 10^{-6}) \quad (6)$$

where Δf_0 and f_{0g} are the frequency shift and the fundamental frequency of the quartz crystal in Hz, respectively, Δm is the mass loaded on the electrode surface in g, and A is the geometric area of the electrode in cm^2.

Results and discussion

PQCI *responses during the generation of monodisperse silica particles*

Fig. 2 shows the simultaneous responses of Δf_s, Δf_0, Δf_p, ΔR_1, ΔC_0, SiO_2 coverage and $\Delta f_{G1/2}$ during the generation of the monodisperse silica particles from the TEOS hydrolysis, with ammonia as a catalyst. Adding TEOS into 40 mL of 0.3 mol/L $NH_3 \cdot H_2O$ + 6 mol/L H_2O alcohol solution caused a notable decrease in the resonant frequency together with slight increases in the motional resistance (R_1) and in the half peak width ($\delta f_{G1/2}$). This fact reflects the adsorption of silica particles on surface of the Au electrode. But the static capacitance (C_0) remained almost unchanged in the experiment, suggesting that the dielectric properties of the medium between the two PQC electrodes and the conductivity of the text solution changed very slightly. R_1 represents the energy dissipation of the quartz crystal resonance into the surrounding environment. Martin *et al.*[7] reported a series of equations of equivalent circuit parameters reflecting the solution density-viscosity effect. From these equations the relationship between ΔR_1 and Δf_0 due to net changes in the solution density and viscosity has been obtained, expressed as follows and validated experimentally[11,15]

$$\Delta R_1 = \frac{4\pi L_q \Delta f_0 \sqrt{f \mu_q}}{\sqrt{\overline{C}_{66} f_{0g}}} \approx -4\pi L_q \Delta f_0 \quad (7)$$

where Δf_0 and ΔR_1 are changes in the resonant frequency and motional resistance of the PQC due to variations of solution density and viscosity, respectively; f_{0g} and f_0 are resonant frequencies of the PQC in air and liquid, respectively; L_q is the motional inductance in air; μ_q is the shear modulus for AT-cut quartz (2.947×1010 N/m^2); $\overline{C}_{66}$ is the lossy piezoelectric stiffened elastic constant (2.957×10^{10} N/m^2); and f_0 can be approximately used in the calculation instead of f with an error below *ca.* 0.3%.[7,15] In our experiment, a 9 MHz crystal was used. The ratio of Δf_0 vs. ΔR_1 calculated from Eq. (7) is 10.4 Hz/Ω, indicating that a change in the liquid density/viscosity equivalent to a 1-Ω ΔR_1 is able to cause a frequency shift of some 10 Hz. As is well known, a viscous loading (liquid and foreign viscous film loading) can result in a large increase in R_1. In our experiment, the change in the motional resistance was very small (within 1 Ω), suggesting that the hydrolytic product (SiO_2) of TEOS is rigid particles, and their adsorption on the Au electrode surface resulted in a rigid loading. So the Sauerbrey's rigid approximation was reasonably valid to estimate the mass of SiO_2 adsorbed onto the electrode surface. According to the Sauerbrey equation,[20] the mass change can be calculated out from the frequency shift (Δf_0) for a rigid and thin film loading. In fact, values of the dry mass of the SiO_2 adsorption found experimentally were generally below the wet mass by some 10%. Therefore, dynamic SiO_2 coverage value was calculated via Eq. (6).

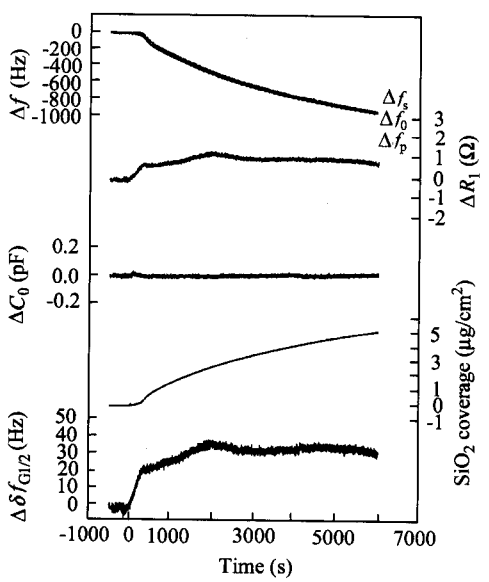

Fig. 2 Simultaneous responses of Δf_s, Δf_0, Δf_p, ΔR_1, ΔC_0, $\Delta\delta f_{G1/2}$ and SiO_2 coverage during the hydrolysis reaction of TEOS in 40 mL of alcohol solution containing $NH_3 \cdot H_2O$ (0.3 mol/L) + H_2O (6 mol/L). TEOS was added at time zero to a final concentration of 0.22 mol/L.

Besides the motional resistance, the half peak width of the G spectrum is often mentioned as a gauge of the viscoelastic property of a foreign film.[8] In our previous work, the value of the half peak width ($\delta f_{G1/2}$) was calculated using the experimental data,[17,18] and it has also been used to estimate the viscoelastic property of a foreign film in Hz. In this work, the

$\delta f_{G1/2}$ values were calculated from Eq. (5). The value of the $\delta f_{G1/2}$ change was only 32 Hz during the TEOS hydrolysis in 6 mol/L H_2O + 0.3 mol/L $NH_3 \cdot H_2O$ alcohol solution, indicating that the viscoelastic change after the SiO_2 adsorption on the Au electrode is small. It should be noted that the differences among Δf_s, Δf_0 and Δf_p were very small (Fig. 2) during the TEOS hydrolysis, obviously owing to small changes in R_1, C_1 and C_0 here.

We found that a first-order kinetic equation is suitable to analyze the process of the adsorption of the SiO_2 particles on a gold electrode surface during the investigated hydrolysis reaction (frequency responses in Fig. 2),

$$\Delta f = \Delta f_{max}(1 - e^{-kt}) \quad (8)$$

where Δf_{max} is the frequency changes at $t \to \infty$, and k is the first-order apparent rate constant (s^{-1}). We fitted Δf data using the nonlinear least-squares fitting program embedded in the Sigmaplot Scientific Graphing Software, Version 2.0, and the relative sum of the residual squares (q_r) was defined as

$$q_r = \frac{\sum_1^N (f_{fit} - f_{exp})^2}{\sum_1^N f_{exp}^2} \quad (9)$$

where Δf_{fit} and Δf_{exp} are the frequency-change values fitted and experimentally obtained, respectively, and N is the number of the response signal points. By fitting the experimental data (Δf vs. time in Fig. 2) to Eq. (8), best fits of Δf_0, Δf_s and Δf_p vs. time data are $k = 4.56 \times 10^{-4}$ s^{-1}, $\Delta f = -725.1$ Hz, $q_r = 1.57 \times 10^{-4}$ for Δf_0; $k = 4.52 \times 10^{-4}$ s^{-1}, $\Delta f = -708.9$ Hz, $q_r = 9.12 \times 10^{-5}$ for Δf_s; $k = 4.99 \times 10^{-4}$ s^{-1}, $\Delta f = -734.3$ Hz, $q_r = 1.08 \times 10^{-4}$ for Δf_p, respectively. The small q_r values suggest that the fitting is quite satisfactory.

In order to further prove the adsorption of the SiO_2 particles on the Au electrode, we performed cyclic voltammetric tests before and after the adsorption of SiO_2 particles on the Au electrode in 2 mmol/L $K_4Fe(CN)_6$ + 0.2 mol/L $NaClO_4$ solution. Fig. 3 shows the cyclic voltamogram obtained before and after the experiment (shown in Fig. 2). It is clear that the redox couple of $Fe(CN)_6^{3-}/Fe(CN)_6^{2-}$ exhibits a more irreversible behavior after the adsorption of SiO_2 particles on the gold electrode, suggesting that the gold electrode surface is occupied by SiO_2 particles to a significant extent and the electron exchange ability on the electrode surface covered with SiO_2 particles has become weaker.

Influence of the concentration of water and ammonia on the hydrolysis reaction of TEOS

Prior to investigating the water-concentration effect on the hydrolysis reaction of TEOS, it is necessary to examine the water-concentration effect on the PQC responses under our experimental condition. Fig. 4A shows the relationship of

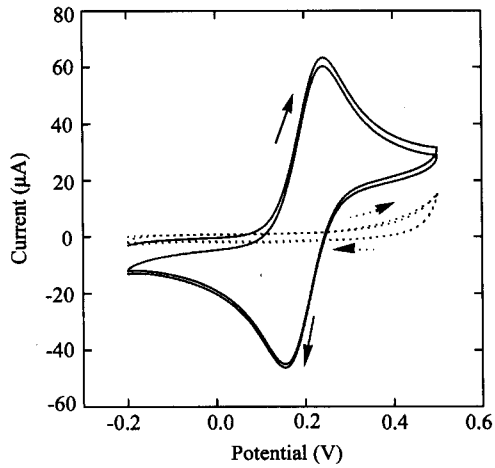

Fig. 3 Cyclic voltammograms for a bare Au electrode (solid line) and a silica-particles-modified Au electrode (dashed line) in $K_4Fe(CN)_6$ (2 mmol/L) + $NaClO_4$ (0.2 mol/L) solution.

Δf_0 vs. ΔR_1 at the water concentration from 1.52 mol/L to 15.87 mol/L. The regression equation can be expressed as follows

$$\Delta f_0 = -11.02\Delta R_1 - 13.67 \quad (r = -0.9995) \quad (10)$$

The experimental slope value deviated only by 5.76% from the theoretical value that characterizes a net liquid loading effect, 10.4 Hz/Ω, indicating that the resonant frequency shift is caused by the changes of the solution density and viscosity when the water concentration changes, and the electrode-mass change due to water adsorption on Au can be overlooked.

Fig. 4B shows the frequency shift responses and the calculated SiO_2 coverage at four water concentrations during the hydrolytic reaction. The fitted results according to Eq. (8) are given in Table 1. We found that the resonant frequency $\Delta f_{0,max}$ and k are positively related to water concentration, but the effect of water concentration on the frequency response was not very significant while the water was greatly excessive in all of our experiments.

In order to investigate the effect of ammonia concentration on the hydrolysis reaction, the PQC responses were also monitored at various ammonia concentrations (0.08 mol/L to 3.71 mol/L). The results are shown in Fig. 5A. The relationship between the frequency shift and the motional resistance could be expressed as

$$\Delta f_0 = -10.12\Delta R_1 - 6.57 \quad (r = -0.9912) \quad (11)$$

Similarly, the slope of Δf_0 vs. ΔR_1 is −10.1 Hz/Ω here, which is very close to the characteristic slope value in the net liquid loading case.[1] This result suggests that the frequency shift resulted from the solution viscosity-density effect. In other words, ammonia was rarely adsorbed on the gold electrode surface, and it only acted as a catalyst in the hydrolytic reaction.

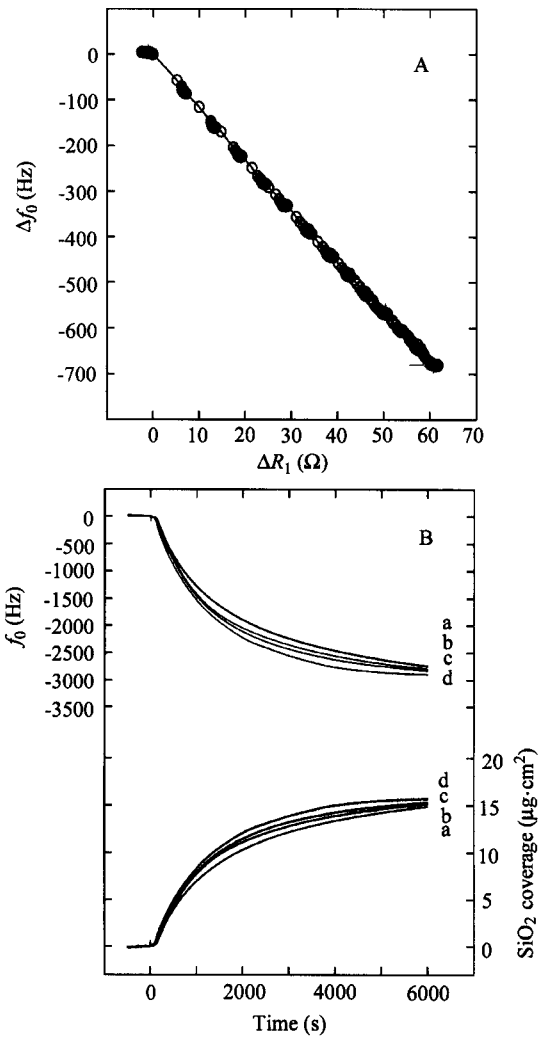

Fig. 4 (A) Relationship between Δf_0 and ΔR_1. Each point corresponds to one addition of 1 mL of water to 35 mL alcohol solution containing 0.5 mol/L $NH_3 \cdot H_2O$ and 1.52 mol/L H_2O, and then the water concentration was increased from 1.52 mol/L to 15.87 mol/L. (B) Time courses of simultaneous responses of Δf_0 and SiO_2 coverage during hydrolysis reaction of the TEOS in 40 mL of alcohol solution containg 0.5 mol/L ammonia and water of varying concentration. TEOS was added at time zero to a final concentration of 0.22 mol/L. Water concentrations (mol/L) were 6 (curve a), 9 (curve b), 12 (curve c) and 15 (curve d), respectively.

Fig. 5B shows the time courses of simultaneous responses of the frequency shift and the SiO_2 coverage at various ammonia concentrations. By fitting Δf_0 vs. time in Fig. 5B to Eq. (8), the values of $\Delta f_{0,max}$ and k were obtained and are listed in Table 1. From Fig. 5 and Table 1, it can be seen that the ammonia concentration influenced largely the response of PQC resonance, and an increase of the amount of the generated SiO_2 led to a decrease of the frequency. At the initial stage of the reaction, the frequency decreased rapidly in a solution with high ammonia concentration while the concentrations of water and TEOS were kept unchanged. This fact suggests that the ammonia concentration has a large effect on the hydrolysis rate. The responses of Δf_{max} were very different when the concentration of ammonia was changed, indicating possibly that the hydrolysis rate and the size of the SiO_2 particles affected the responses of Δf_{max} in this system. In other words, the adsorption of the SiO_2 particle of greater size led to a greater change of the frequency responses of PQC resonance.

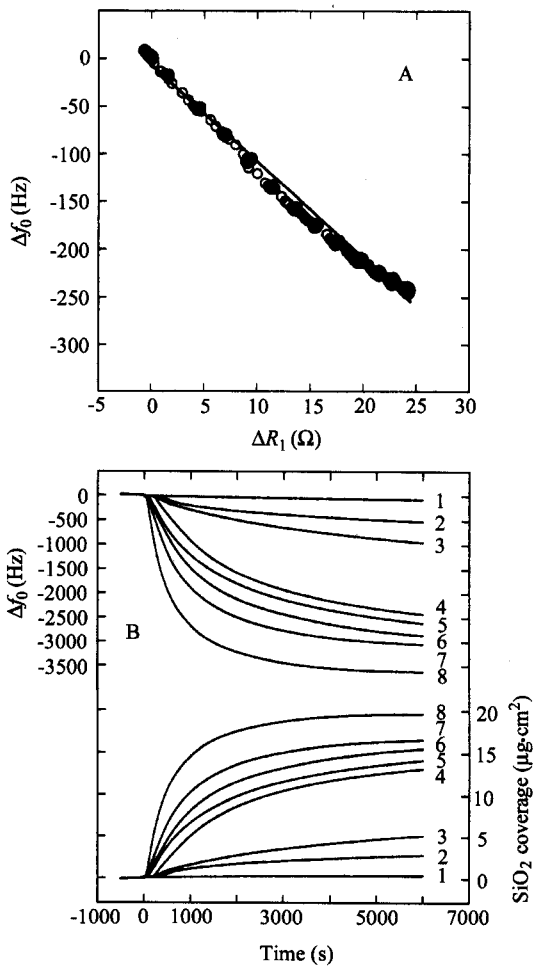

Fig. 5 (A) Relationship between Δf_0 and ΔR_1. Each point corresponds to one addition of 1 mL of 25% ammonia to 35 mL of alcohol solution containing 0.08 mol/L $NH_3 \cdot H_2O$ and 1.6 mol/L H_2O, and then the ammonia concentration was increased from 0.08 mol/L to 3.71 mol/L. (B) Time courses of simultaneous responses of Δf_0 and SiO_2 coverage during the hydrolysis reaction of TEOS in 40 mL of alcohol solution containing 9 mol/L water and ammonia of varying concentration. TEOS was added at time zero to a final concentration of 0.22 mol/L. Ammonia concentrations (mol/L) were 0 (curve 1), 0.2 (curve 2), 0.3 (curve 3), 0.4 (curve 4), 0.5 (curve 5), 1.0 (curve 6), 1.5 (curve 7) and 2.0 (curve 8), respectively.

In order to further confirm the effect of the SiO_2 particles size on the frequency of PQC resonance, we examined the surface morphology of the three Au electrodes used in the experiments corresponding to curves 2, 5 and 8 in Fig. 5B using an Hitachi S-570 SEM. The results are shown in Fig. 6.

Table 1 Parameters obtained by fitting frequency responses given in Fig. 4 to Eq. (8)

Water/Ammonia concentration (mol/L)		Δf_{max} (Hz)	k (s^{-1})	q_r	Surface coverage ($\mu g/cm^2$)
Water[a]	6	-2757	5.9×10^{-4}	7.5×10^{-5}	14.95
	9	-2778	6.7×10^{-4}	2.2×10^{-4}	15.09
	12	-2820	6.9×10^{-4}	5.2×10^{-4}	15.32
	15	-2922	7.2×10^{-4}	2.5×10^{-5}	15.87
Ammonia[b]	0	-73	3.8×10^{-4}	3.9×10^{-4}	0.40
	0.2	-551	4.1×10^{-4}	4.2×10^{-4}	3.00
	0.3	-1152	4.8×10^{-4}	2.7×10^{-4}	6.26
	0.4	-2597	5.4×10^{-4}	5.5×10^{-5}	14.10
	0.5	-2778	6.7×10^{-4}	2.2×10^{-4}	15.09
	1.0	-2840	7.4×10^{-4}	7.4×10^{-5}	15.43
	1.5	-2998	9.4×10^{-4}	1.5×10^{-4}	16.29
	2.0	-3544	1.4×10^{-3}	2.6×10^{-4}	19.25

[a] In the 0.22 mol/L TEOS + 0.5 mol/L ammonia alcohol solution. [b] In the 0.22 mol/L TEOS + 9 mol/L water alcohol solution.

Some small particles could be observed on the surfaces of these electrodes, though their precise microstructure can not be clearly identified by the present SEM. The significant difference in the size of the SiO_2 particles can be seen on the electrode surface. The size of particle generated in the test solution containing 2.0 mol/L ammonia (Fig. 6C) was larger than those in the test solution contained 0.2 mol/L and 0.5 mol/L ammonia (Fig. 6A). Therefore, the SEM observations supported the result of PQCI measurement mentioned above, namely, the size of the silica particle adsorbed on the electrode has influenced the frequency responses of the PQC.

Stöber *et al.*[4] reported that the silica particles were spherical. In our experiments, monodisperse spherical silica particles with 0.25-μm mean diameter were also obtained from the TEOS hydrolysis, as shown in Fig. 6C. The mean diameter and the number of SiO_2 particle per area of the electrode were obtained directly from SEM observation. Then the mass loading on the electrode surface was calculated from the frequency shift measured by PQC impedance, and the number of SiO_2 particles per unit area of electrode surface was calculated as well. The numbers of the particle per unit area obtained from SEM (Fig. 6C) and from the frequency shift are 9.8×10^8 and 1.07×10^9 per square centimeters, respectively. The mass coverages of the electrode surface obtained from SEM (Fig. 6C) and from frequency shift are 17.7 $\mu g/cm^2$ and 19.3 $\mu g/cm^2$, respectively. The results obtained from SEM deviated by -8.1% in number per area and -8.3% in SiO_2 mass coverage from piezoelectric quartz crystal impedance measurement. Similarly, according to the mass loaded on the electrode surface estimated from the PQC frequency responses and the size of the particles obtained from SEM observation, the average mass and density of a single spherical particle can be calculated. The methods depicted here may be used for smaller SiO_2 particles, such as described in Figs. 6A and 6B, if an SEM with higher resolution is available.

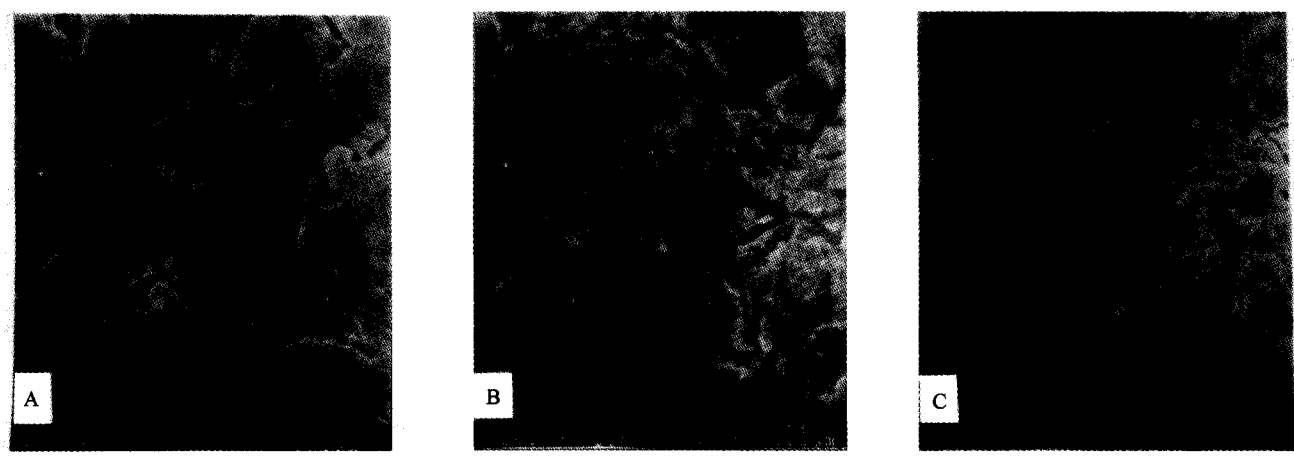

Fig. 6 SEM images of Au electrode surfaces with silica particles adsorbed. Electrodes used in the experiments corresponding to curve 3 (A), curve 5 (B) and curve 8 (C) in Fig. 5.

Electrolyte-induced precipitation of SiO_2 *particles*

Some monodisperse particles in the colloidal size range can be suspended in solution in a relatively stable state.[4] The presence of a relatively concentrated electrolyte can induce its precipitation. Fig. 7 shows the responses of Δf_s, Δf_0, Δf_p, ΔR_1, ΔC_0 and $\Delta\delta f_{G1/2}$ during adding 1.0 mol/L $NaClO_4$ alcohol solution into the suspended solution of monodisperse SiO_2 particle system which was obtained from the experiment shown in Fig. 5B (curve 5). There were almost no changes in f_s, f_0, f_p, R_1, C_0 and $\delta f_{G1/2}$ after adding $NaClO_4$ solution to a final concentration of 1.25×10^{-3} mol/L. Decreases in f_s, f_0 and f_p and increases in R_1, C_0 and $\delta f_{G1/2}$ started after an addition of $NaClO_4$ solution to a final concentration of 2.5×10^{-3} mol/L, but they were small. Sharp decrease in f_s, f_0, f_p and increase in R_1, C_0 and $\delta f_{G1/2}$ were observed while the added $NaClO_4$ solution reached to a final concentration of 5×10^{-3} mol/L, and simultaneously, large amounts of deposits were obtained in test solution. The response curves of PQC resonance appeared as a pseudo-plateau when the added $NaClO_4$ was over 7.5×10^{-3} mol/L. Unlike the SiO_2 particles adsorbed on the electrode (shown in Fig. 2), the three frequency responses have different sensitivity to electrolyte addition. The parallel resonance frequency has the highest sensitivity. The above facts suggest that the large changes in R_1, C_1 and C_0 result in the different sensitivities of the three frequency responses. The precipitate gravitated towards the bottom of the reaction cell when the solution stirring stopped, but the simultaneous PQCI responses observed during gravitation were very small.

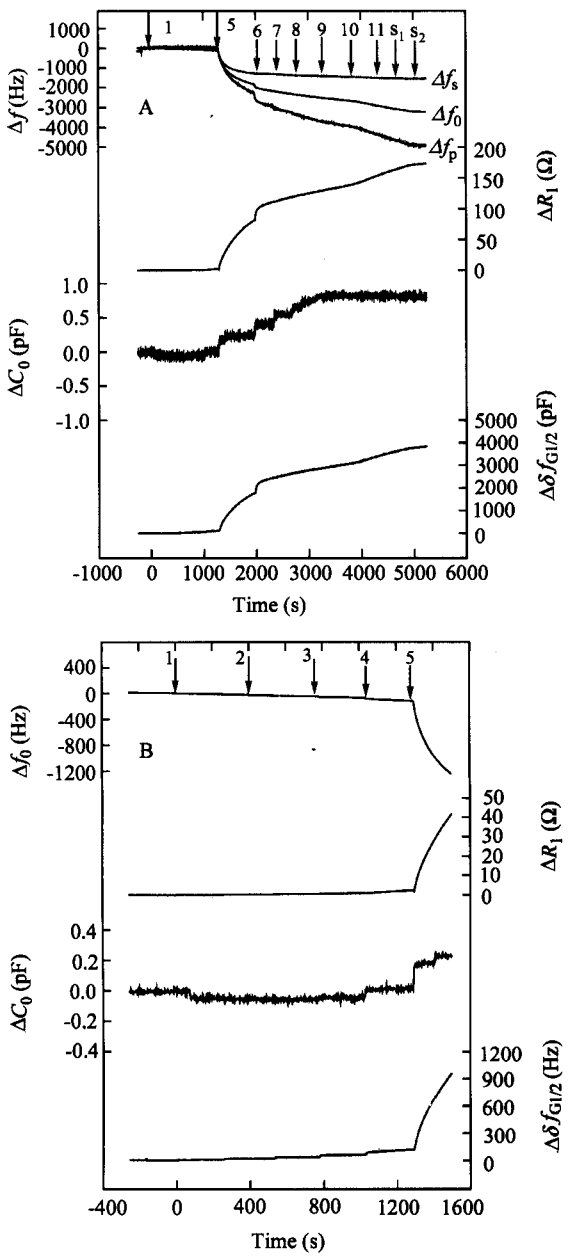

Fig. 7 Time courses of simultaneous responses of Δf_0, ΔR_1, ΔC_0 and $\Delta\delta f_{G1/2}$ during the monodisperse silica particle precipitation induced by the addition of 1 mol/L $NaClO_4$ alcohol solution. Arrows 1—11 indicate the additions of 1 mol/L $NaClO_4$ solutions to a final concentration of 5×10^{-5}(1), 3.75×10^{-4}(2), 7.5×10^{-4}(3), 1.25×10^{-3}(4), 2.5×10^{-3}(5), 5.0×10^{-3}(6), 7.5×10^{-3}(7), 1.0×10^{-2}(8), 1.25×10^{-2}(9), 1.5×10^{-2}(10) and 1.75×10^{-2} mol/L (11), respectively. Arrows s_1 and s_2 indicate the moment when the solution stirring was stopped and restarted, respectively.

Fig. 8 shows the relationship between $\Delta f_{0,\infty}$ and $NaClO_4$ concentration, where $\Delta f_{0,\infty}$ is the value of Δf_{max} in Eq. (8) and obtained by fitting Δf_0 responses for each $NaClO_4$ concentration to the equation. The response of Δf_0 was not linearly related to the concentration of $NaClO_4$. As $NaClO_4$ concentration increased, the values of $\Delta f_{0,\infty}$ initially increased, and then reached a quasi-steady value when the $NaClO_4$ concentration was over 7.5×10^{-3} mol/L.

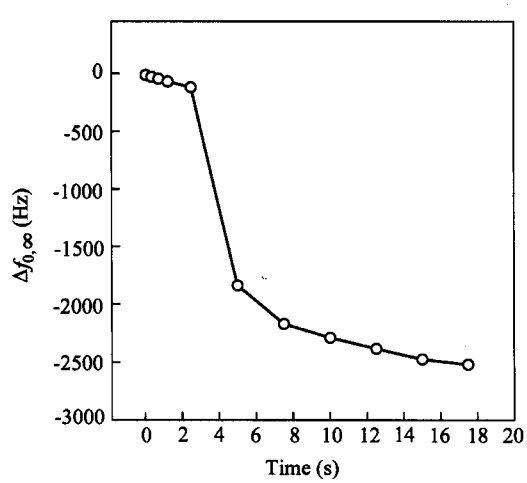

Fig. 8 $\Delta f_{0,\infty}$ vs. the concentration of added $NaClO_4$.

Conclusion

By using the piezoelectric quartz crystal impedance (QCI) analysis technique, generation and adsorption of

monodisperse SiO_2 particles during the hydrolysis reaction of TEOS with ammonia as a catalyst were monitored *in situ*. The influence of water and ammonia concentration, from 6 mol/L to 15 mol/L and 0.2 mol/L to 2 mol/L, respectively, were investigated versus the hydrolysis rate. It was found that the change of water concentration leads to a small change in frequency of PQC responses, and the ammonia concentration causes a significant variation of Δf_0. In all of our experiments, the frequency shift (Δf_0) change was great while the change in ΔR_1 was small, suggesting that SiO_2 particle generated and adsorbed onto Au electrode is principally a rigid loading in our test system. A first-order reaction model was used to analyze the adsorption kinetics of SiO_2 particles onto the Au electrode. In addition, the electrolyte-induced precipitation of the monodisperse particles suspended in solution was monitored and discussed. The scanning electron microscope observation supported the conclusion that the size of silica particles is related to the hydrolysis rate and the adsorbed SiO_2 particle of greater size leads to a greater frequency response of PQC resonance. The particle number per unit area, the coverage of monodisperse silica particles, average mass and density of a single spherical SiO_2 particle generated from the hydrolysis of TEOS have been calculated according to the SEM observation and the piezoelectric quartz crystal impedance measurement.

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