

# Supporting Information

## **Controlled growth of silica-titania hybrid functional nanoparticles through a multistep microfluidics-based nucleation/growth separation method**

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## Chemicals

Tetraethoxysilane (TEOS: Tokyo Chemical Industry Co., Ltd.), Titanium tetraisopropoxide (TTIP: Tokyo Chemical Industry Co., Ltd.), isopropyl alcohol (IPA: Wako Pure Chemical Industries, Ltd.), 28 %-aqueous ammonia solution (NH<sub>3</sub>aq: Kanto Chemical Co., Inc.), octadecylamine (ODA: Aldrich, Inc.) and 3-aminopropyltriethoxysilane (APTES: Sigma, Inc.) were utilized in the present study. All the chemicals were used as received.

## Experimental procedures

For the STNPs synthesis, five starting solutions (Solutions A-E) were prepared. Detailed composition of each solution is summarized in Table S1. The Solutions A, B, C and D were individually flowed in perfluoroalkoxyalkane (PFA: 1.0 mm inner diameter, 1/16 inch outer diameter, product of YMC Co., Ltd.) tubes with a syringe pump (CXN1070, product of ISIS, Co., Ltd.) at 10 mL/min. Solutions A and B, and Solutions C and D were mixed respectively in a polytetrafluoroethylene (PTFE) fluidic channel with a Y shape junction (the channel cross section of ca. 1 mm<sup>2</sup>, KeyChem mixer, product of YMC Co., Ltd.). After that, resultant two reaction solutions, *i.e.* Solution A+B and Solution C+D, were mixed in the second fluidic channel placed just after the first two fluidic channels. The first and second fluidic channels were connected by 10 cm PFA tubes. Then, the mixture of the four Solutions A-D was flowed through a PFA tube with 70 cm in length and was added into the Solution E under magnetic stirring. After the addition, the final reaction solution was aged at room temperature for 24 h. Finally, a slightly turbid suspension was obtained (see Fig. 2 in the main text). In the case of the amino-STNPs synthesis, 1.481 mL of APTES was added to the Solution A instead of TEOS and the total volume was adjusted to 12.5 mL by reducing the amount of IPA.

To prepare a powder sample for nitrogen adsorption/desorption measurements, 20 mL of the suspension was taken out. Then, 1 mL of 1 mol/L-aqueous hydrochloric acid and 19 mL of pure water were added to the suspension. The acidic suspension was transferred to an oven and was aged at 333 K for 30 min. After that, 1mL of 1 mol/L-aqueous sodium hydroxide was added to the suspension to neutralize. Soon after precipitate was formed, the suspension was centrifuged (9000 rpm, 5 min). The precipitate was washed with pure water repeatedly and was dried at 333 K for a few hours.

Table S1. The amount of each chemical used for the STNPs synthesis.

Solution A		Solution B			Solution C		Solution D		Solution E		
TEOS (mL)	IPA (g)	NH <sub>3</sub> aq (g)	H <sub>2</sub> O (g)	IPA (g)	TTIP (mL)	IPA (g)	H <sub>2</sub> O (mL)	IPA (g)	ODA (g)	H <sub>2</sub> O (mL)	IPA (g)
1.418	8.7	0.758	2.84	6.98	0.458	9.44	0.078	9.74	0.1368	40	123.3

## Characterization

Scanning electron microscope (SEM) images were obtained using a Hitachi Ultra-high Resolution Scanning Electron Microscope SU8000 at an accelerating voltage of 10 kV. Prior to each measurement, samples were coated with a few nanometers of platinum. The average particle size ( $D$ ) and coefficient of variation ( $CV$ ) values were obtained from the SEM images by counting 100 particles.  $CV$  values can be calculated from the following equation.

$$CV = \frac{\sqrt{\sigma^2}}{D}$$

where  $\sigma$  is standard deviation.

Transmission electron microscope (TEM) images, scanning transmission electron microscope (STEM) image and elemental mapping images were recorded using a JEM-2100F and JED-2300 (JEOL Ltd.) at an accelerating voltage of 200 kV. The NPs suspension was dropped onto a Cu grid (High Resolution Carbon Substrate on STEM100Cu grids, and STEM Cu150P grids, Okenshoji Co., Ltd.) and the grid was dried under vacuum for a few days before measurements.

A particle size distribution was measured by a dynamic light scattering (DLS) technique using an ELSZ-2000 (Otsuka Electronics Co., Ltd.). The as-synthesized STNPs suspension was used for the measurement.

Nitrogen adsorption/desorption isotherms of the washed STNPs were measured at 77 K on a Belsorp Mini instrument (Bel Japan, Inc.). Prior to the measurements, the samples were dried at 393 K under nitrogen gas flow for 3 h.

Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a SII EXSTAR 6000 TG/DTA6300 at the heating rate of 10 K/min under air flowing.  $\alpha$ -alumina powder was used as a reference material to obtain DTA curves.

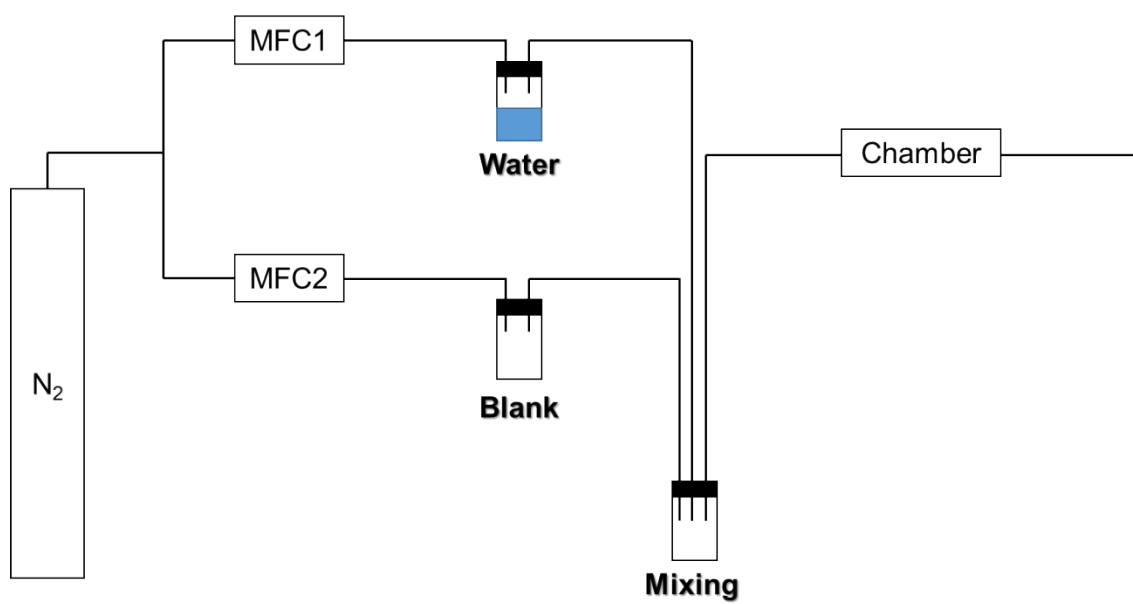
Fourier Transform-Infrared (FT-IR) spectra were measured using a Nicolet 4700 FT-IR spectrometer (Thermo Fisher Scientific Inc.) equipped with an ATR attachment. The measurement system was purged with nitrogen before measurements.

For quartz crystal microbalance (QCM) experiments, gold-plated QCM resonators (5 mm in diameter; 9 MHz resonance frequency) were coated with the amino-STNPs and PVP. The coating was done by drop-casting the NPs suspension (aqueous IPA) or PVP aqueous solution onto the QCM electrode and the electrode was dried in air. Then, the coated QCM was used to investigate mass changes caused by exposure to water vapour. An experimental setup for the QCM measurements is shown in Scheme S1. Briefly, the coated QCM was placed in a sealed chamber made of PTFE. Pure nitrogen was used as a carrier gas and its flow rate was controlled by a mass flow controller (FCST1005C-4F2-F100-N2, Fujikin Inc.). The mass flow controller was connected to a vial containing water with a PTFE tube (1.0 mm inner diameter, 1/16 inch outer diameter) and the vial was further connected to another empty vial where carrier nitrogen and water vapour were fully mixed. In

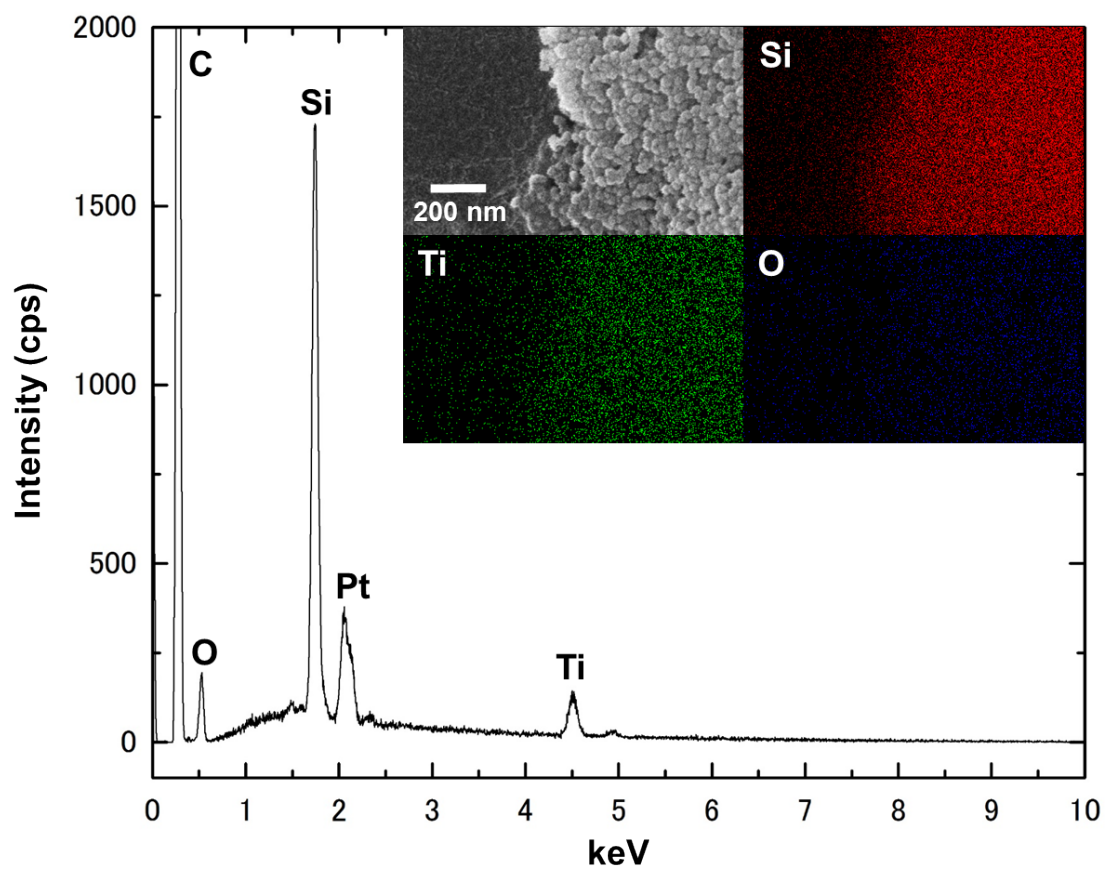
addition to the sample gas line, another line with a blank vial was connected to the mixing vial in the same way using another mass flow controller. Taking advantage of these two gas lines, we can switch the gas flow from the sample gas to pure carrier, allowing to wash out the surface of the coated QCM. After the mixing vial, the gas line was connected to the chamber. The introduced gas was released from an outlet of the chamber. Resonance frequency shifts before and after exposure to water vapour were recorded by a QCM922A (SEIKO EG&G Co., Ltd.).

### **Effect of HCl washing on the nanostructure of STNPs**

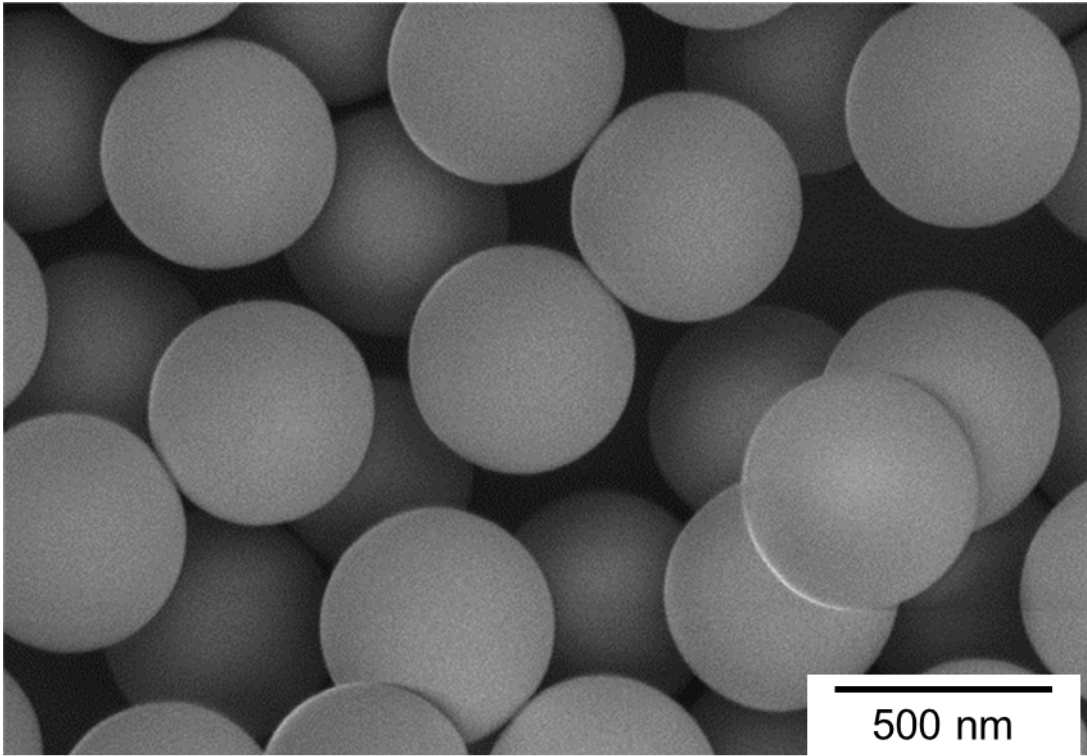
Since 7.8 wt% of ODA is incorporated inside the STNPs (confirmed by TG-DTA shown in Fig. 4(a) and Fig. S5) and might work as a structure directing agent, we washed the NPs with hydrochloric acid to remove ODA for possible formation of porous structure (see Experimental procedures for detail). We added 1 mol/L of aqueous hydrochloric acid to the STNPs suspension and the suspension was aged at 333 K for 30 min. The appearance of the suspension did not change after 30 min and no precipitate formation was observed. Then, the same amount of 1 mol/L-sodium hydroxide aqueous solution was added to neutralize the suspension. Soon after that, precipitate was formed. The precipitate was collected by centrifugation and washed repeatedly with water. An SEM image of the washed STNPs is shown in Fig. S5 (ESI). The size and shape of the washed NPs did not change, although the NP surface seemed to be relatively rough as compared to the as-synthesized NPs. We found that SiO<sub>2</sub>/TiO<sub>2</sub> weight ratio decreased to 2.7, suggesting slight dissolution of silica species during the sodium hydroxide addition. Indeed, a washing process using sodium hydroxide instead of hydrochloric acid resulted in a large decrease of SiO<sub>2</sub>/TiO<sub>2</sub> weight ratio up to 0.6 in 30 min. We confirmed that longer hydrochloric acid washing (20 h) did not cause any change in SiO<sub>2</sub>/TiO<sub>2</sub> weight ratio (still 2.7), indicating that outer part of the STNPs is mainly composed of silica. Taking into account that a few wt% of ODA was also removed by the washing process, the STNPs would become slightly porous, resulting in the larger specific surface area.



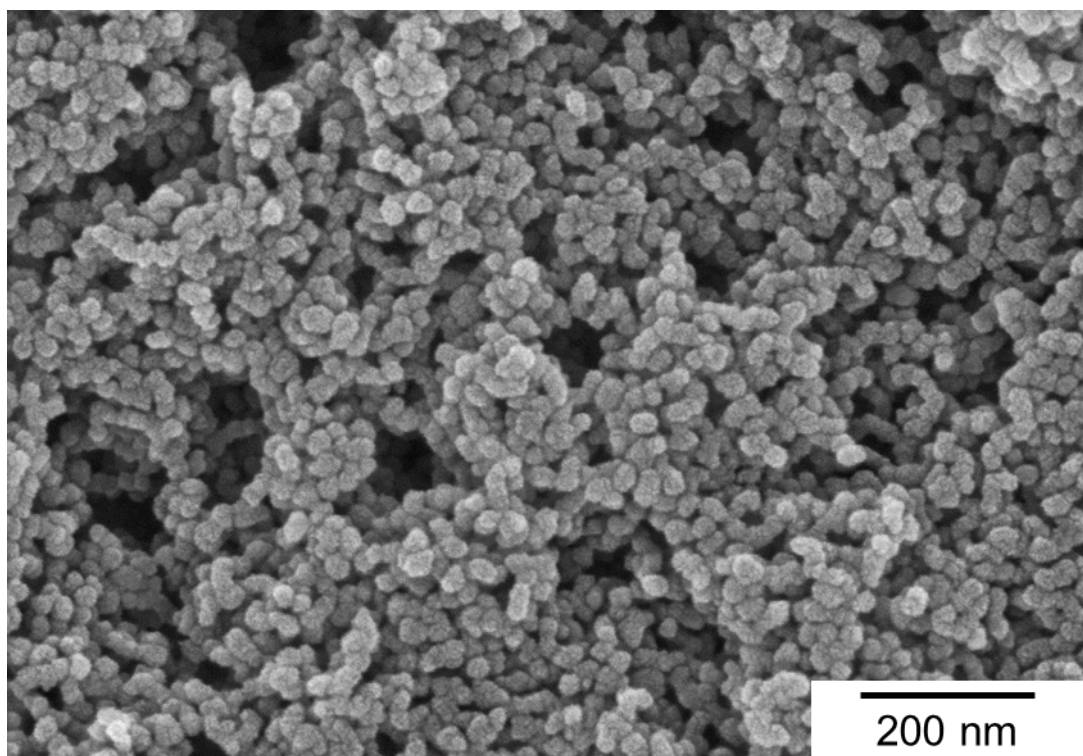
**Scheme S1** Experimental setup for the QCM measurements.



**Fig. S1** EDX result of the STNPs. The inset shows corresponding SEM and elemental mapping images of Si (red), Ti (green) and O (blue).

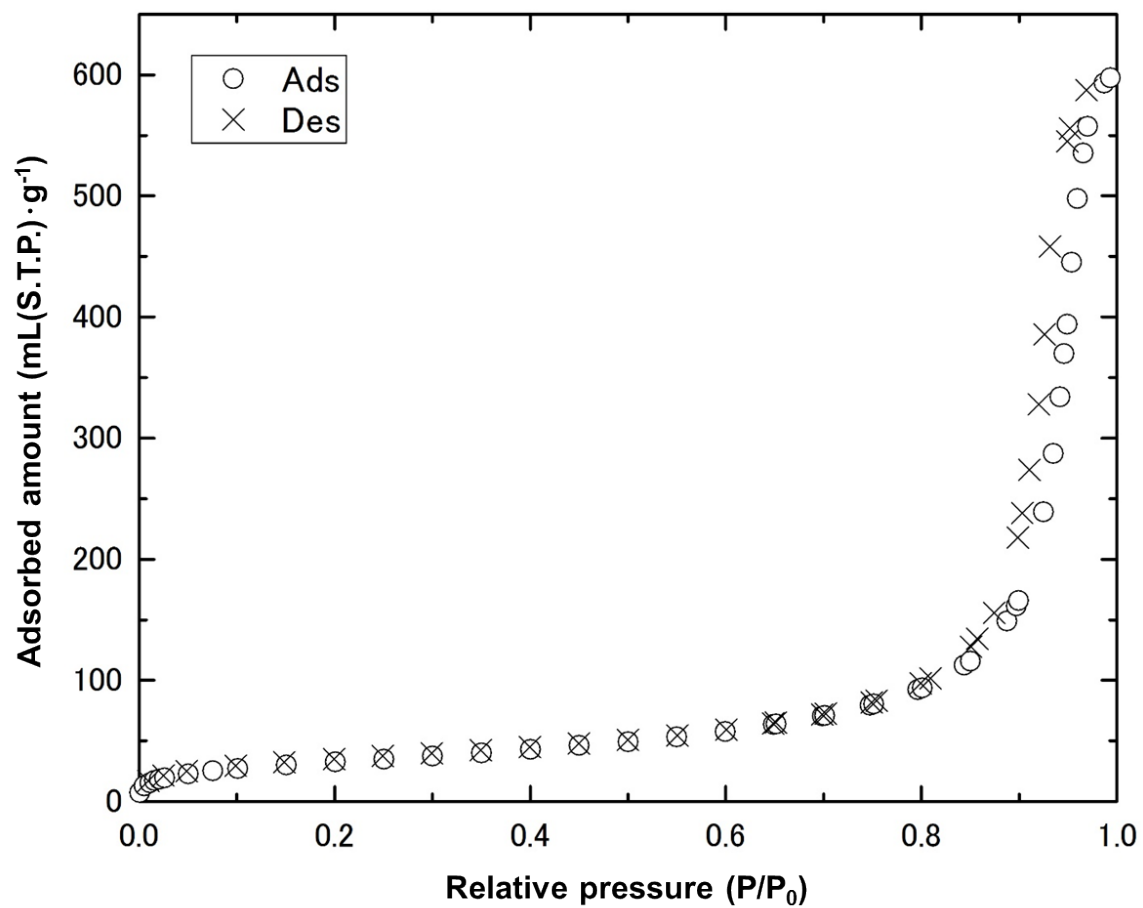


**Fig. S2** SEM image of monodispersed silica spherical particles synthesized using a single microfluidic channel.

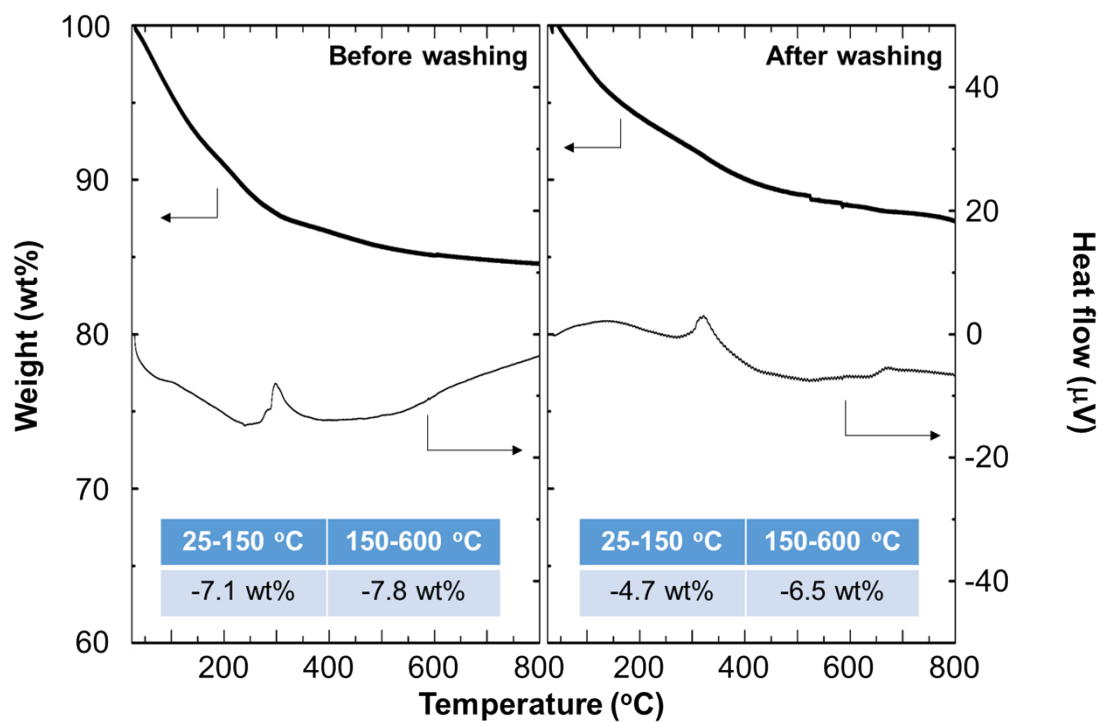


**Fig. S3** SEM image of the STNPs after washing with 1 mol/L-hydrochloric acid at 333 K for 30 min.

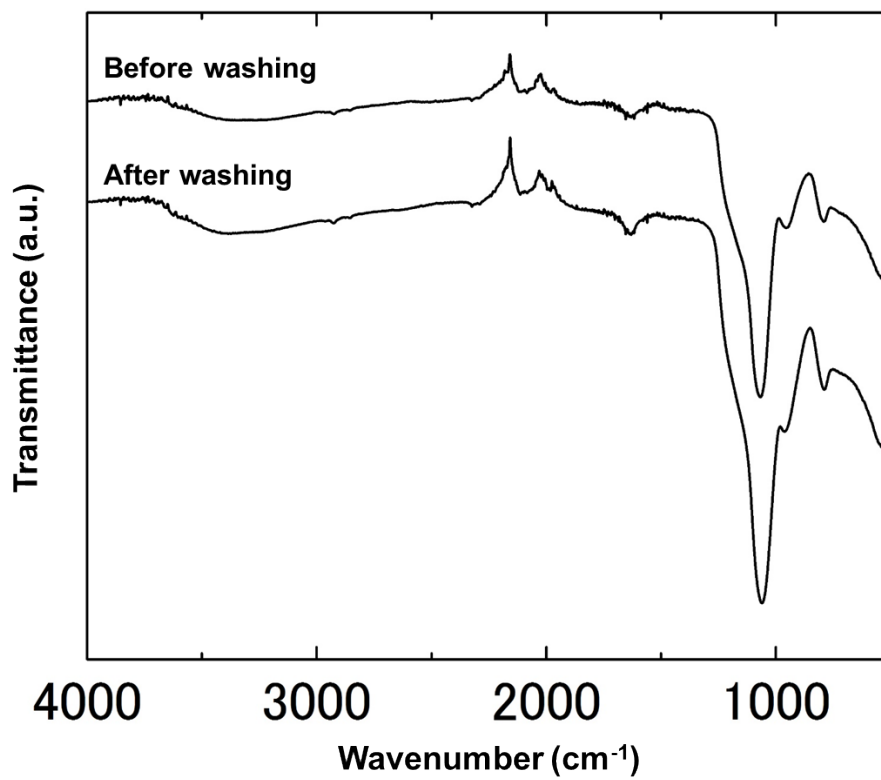




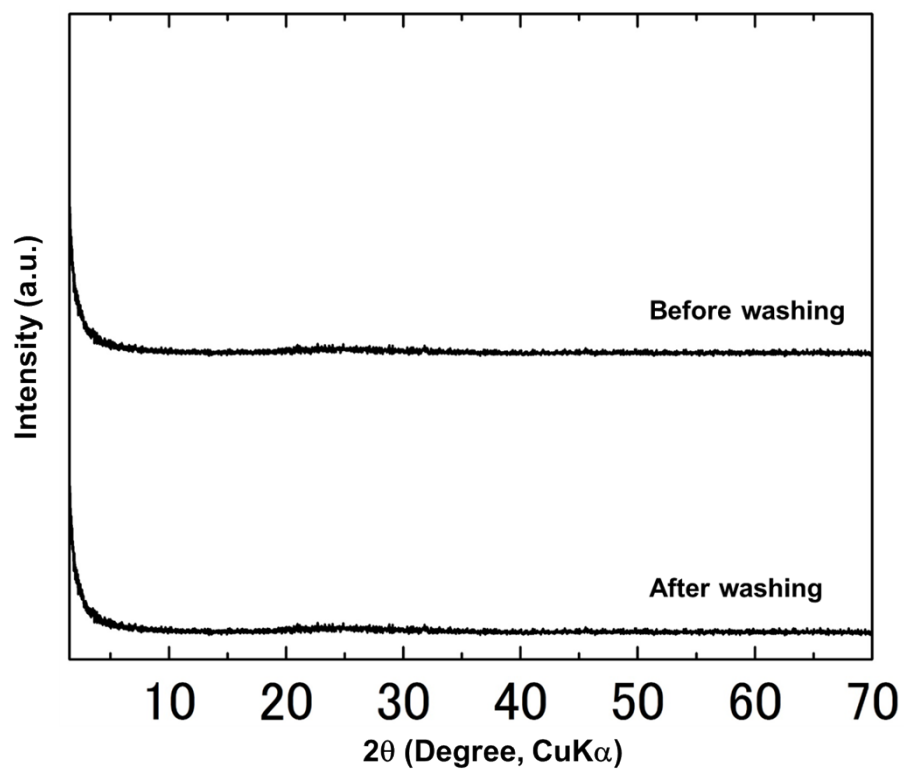
**Fig. S4** Nitrogen adsorption/desorption isotherms of the STNPs after washing with 1 mol/L-hydrochloric acid at 333 K for 30 min.



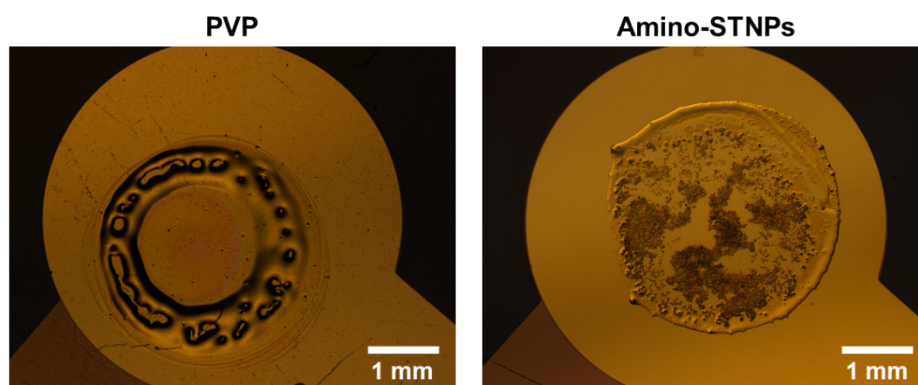
**Fig. S5** TG-DTA curves of the STNPs before and after washing with 1 mol/L-hydrochloric acid at 333 K for 30 min.



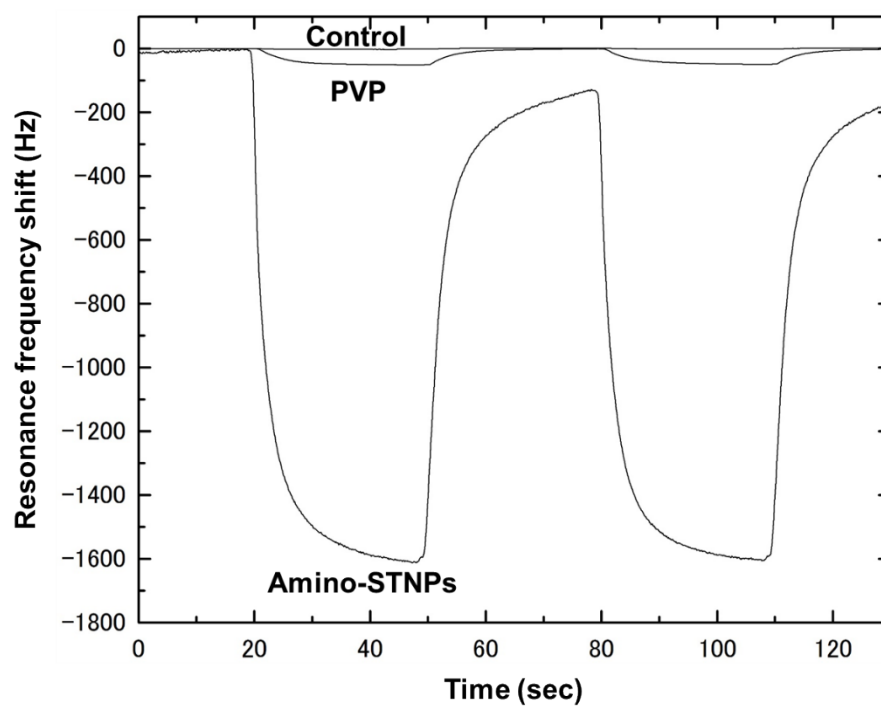
**Fig. S6** FT-IR spectra of the STNPs before and after washing with 1 mol/L-hydrochloric acid at 333 K for 30 min.



**Fig. S7** XRD patterns of the STNPs before and after washing with 1 mol/L-hydrochloric acid at 333 K for 30 min.



**Fig. S8** Optical microscope images of amino-STNPs-coated QCM and PVP-coated QCM.



**Fig. S9** Resonance frequency shift of amino-STNPs-coated QCM exposed to dry nitrogen gas containing water vapour. Resonance frequency shifts of PVP-coated and non-coated QCM are also shown. This data is the raw data of Fig. 4 in the main text (this data is not normalized by the coating weight).