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Alkali Metal Ion Sensing Using Absorbance Changes Based on Aggregation of Silica Nanoparticles Modified Chemically with Crown Ethers

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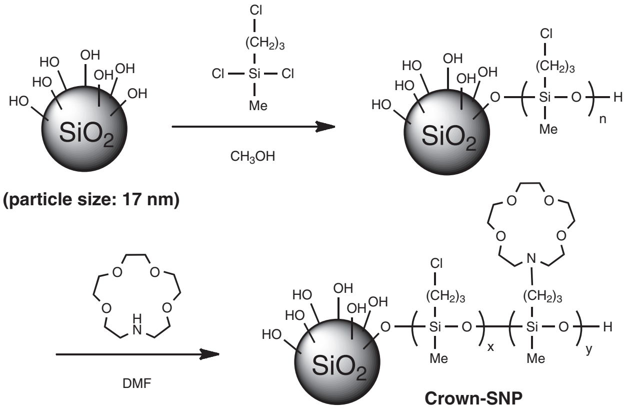
Crown-ether-modified silica nanoparticles (Crown–SNPs) were successfully prepared by simple chemical modifications of silica nanoparticles. The organic moiety introduced into silica nanoparticles was characterized by solid-state ^{13}C NMR and elemental analysis. No morphological damage of silica nanoparticles was recognized according to SEM observation. When an alkali metal salt was added to a solution containing Crown–SNPs, the absorbance changes, whose extent was dependent on the kind and the concentration of a metal ion, were observed.

Recently, functional nanoparticles (NPs) modified chemically with ionophores have received much attention in ion/molecule sensing.[1] In such fields, NPs play important roles as both a supporting material of ionophores and a signal transducer based on the phase transition from monodispersion to aggregation. Until now, it has been reported that some kinds of metal NPs emerge as important signal transducers because of their high sensitivity.[2] For example, in the cases of Au NPs,[3] their absorption spectra change upon aggregation due to the coupling of the surface plasmon resonance, and in the cases of CdSe/ZnS quantum dots,[4] their fluorescence spectra change upon aggregation due to the Förster energy transfer. However, these metal NPs can be functionalized only by alkanethiols,[5] whose synthesis is comparatively laborious. If NPs can be functionalized by simple chemical modifications, the study on NPs functionalized with ionophores will open new opportunities for ultrasensitive sensing.

Silica nanoparticles (SNPs) can be organically modified by silane coupling reagents[6] and purified via centrifugation with ease due to the high density of silica.[7] In addition, SNPs have several attractive versatile colloidal properties such as narrow size distribution, optical transparency, and excellent solvent dispersibility among numerous NPs. Also, there is no swelling or shrinkage with changes of pH and ionic strength, unlike organic polymer particles. Therefore, the application of SNPs to sensing materials is strongly persued today. In this study, crown ethers as an ionophore were introduced onto the surface of SNP, which we call Crown–SNP, and the classical host–guest interaction between a crown ether and an alkali metal ion was utilized as driving force of aggregation of Crown–SNPs. When a metal ion is added to a solution containing Crown–SNPs, it is expected that the dispersed state of SNPs will change from monodispersion to aggregation, which enables us to detect a metal ion.

Generally, crown-ether-modified silica materials have been prepared by chemical modifications using silane compounds bearing a crown-ether moiety.[8] However, these silane compounds are not commercial, and they need to be synthesized via hydrosilylation, which requires expensive Pt catalysis and strict control of water content.[9] Here, we devised an alternative method without using hydrosilylation, aiming at easy functionalization. The synthesis of Crown–SNPs is summarized in Scheme 1.



Scheme 1. Synthesis of Crown–SNP.

As a starting material, monodisperse SNPs (average primary particle size: 17 nm), which were donated by Fuso Chemical Co., LTD. (Japan), were utilized. First, 3-chloropropylmethyldichlorosilane was added to a methanol solution containing original SNPs, and the resulting mixture was stirred at room temperature for 24 h. After the reaction was completed, the product was collected via centrifugation followed by washing with water. After DMF was added to the residue, chloro-modified SNPs were dispersed by ultrasound sonication. Next, monoaza-15-crown-5 was added into the DMF solution, and the resulting mixture was stirred at 60 °C for 24 h. After the reaction was completed, the product was collected via centrifugation, followed by washing with toluene. Finally, Crown–SNPs were dispersed in CH_3CN by ultrasound sonication. For comparison, SNPs modified chemically with noncyclic secondary amine, bis(2-methoxyethyl)amine, (Ref-SNPs) were also prepared with a similar method. The CH_3CN solutions containing Crown–SNPs or Ref-SNPs were optically transparent, which means that both SNPs finely disperse in CH_3CN. A portion of the SNP solutions was completely dried, and the obtained solids were characterized by solid-state ^{13}C NMR and elemental analysis.

Figure 1 shows the solid-state ^{13}C NMR spectrum of Crown–SNP. The large "*a*" peak and small "*b*" peak around 70 ppm are assigned to the carbons next to the oxygen atom and the nitrogen atom, respectively. The "*c*," "*d*," and "*e*" peaks at 47, 26, and 14 ppm are assigned to the alkyl chain. The "*f*" peak is assigned to the methyl groups next to the silicon atom. Thus, all peaks originating from the organic moiety were recognized. This demonstrates that crown ethers were certainly introduced

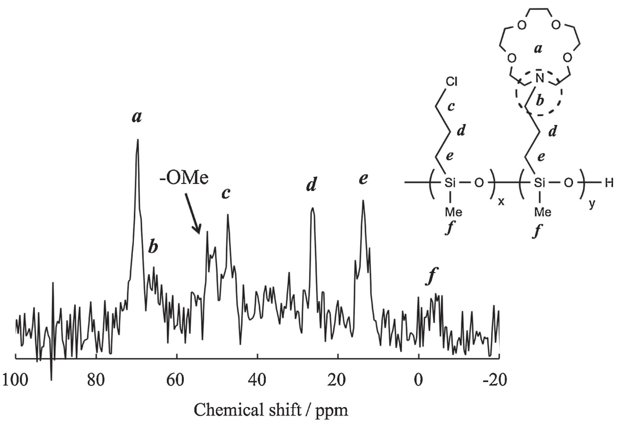


Figure 1. Solid-state ^{13}C NMR spectrum of Crown–SNP.

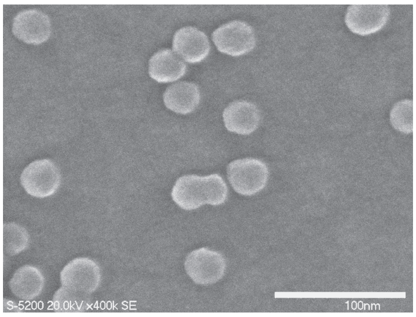


Figure 2. SEM image of Crown–SNP.

into the surface of SNP. The residual peak around 50 ppm is assigned to the methoxy groups existing inside SNP.[10] Also, the modification amount of monoaza-15-crown-5 to SNP and the substitution percent of chloro groups were determined to 0.186 mmol g^{-1} and 55%, respectively, by elemental analysis. In the case of Ref-SNP, those were determined to 0.321 mmol g^{-1} and 94%, respectively. Figure 2 presents a SEM image of Crown–SNP. Although silica materials might be dissolved by the basic chemical reactions,[11] fortunately we did not observe any signs of morphological damage in the resulting SNPs. Therefore, it was shown here that the treatment with secondary amine at 60 °C was mild enough to not transform and fuse SNPs.

The sensing ability toward an alkali metal ion of Crown–SNP was investigated and compared with those of Ref-SNP and unmodified SNP. Expectedly, when $NaClO_4$ was added to a CH_3CN solution containing Crown–SNP, the solution became partly clouded. Figure 3 shows the absorbance changes (Δ absorbance) at 400 nm for each CH_3CN solution containing Crown–SNPs, Ref-SNPs, or unmodified SNPs upon the addition of Na^+ at 25 °C. Here Δ absorbance is defined as $A_m - A_0$, where A_0 is the initial absorbance, and A_m is the absorbance at the given concentration of Na^+. In this approach, the concentration of SNP was fixed at 4.00 mg mL^{-1} [the concentration of monoaza-15-crown-5 was 0.744 mM ($M = mol\,dm^{-3}$)], and the measurement was performed while stirring. As the aggregation of Crown–SNPs reached equilibrium in a few minutes, the absorbance after 5 min on the addition of Na^+ was plotted. Only in the case of Crown–SNP, the absorbance gradually increased with the increase of Na^+. On the other hand, in the cases of Ref-SNP and unmodified SNP, only negligible changes in the absorption spectra were observed during the Na^+ titration. These results show that the complexation ability of the crown ring is necessary for the detection of Na^+. To clarify the mechanism of the absorbance increase by the addition of Na^+, the average particle diameter of Crown–SNPs in CH_3CN upon the addition of Na^+ was measured by dynamic light scattering (DLS) (Figure 4). The average particle diameter increased correspondingly with the increase of Na^+, and the profile was very similar to the absorbance changes upon the addition of Na^+. In addition, the ζ potentials of Crown–SNPs in the absence and presence of Na^+ (1 mM) were -76.9 and -19.3 mV, respectively. In consideration of these results, we conclude that Crown–SNPs aggregated because of the lowering of ζ potentials based on the complexation of the crown ring with Na^+ and thereby that the absorbance increased with the increase of turbidity.

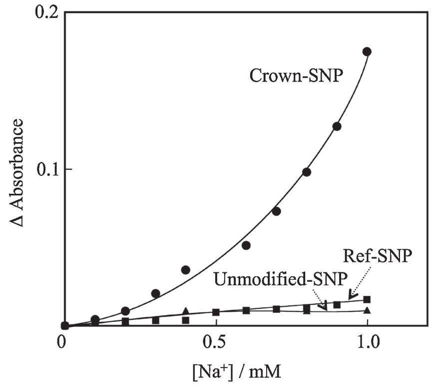


Figure 3. Absorbance changes at 400 nm for each CH_3CN solution containing Crown–SNPs, Ref-SNPs, or unmodified SNPs with different concentrations of $NaClO_4$ at 25 °C.

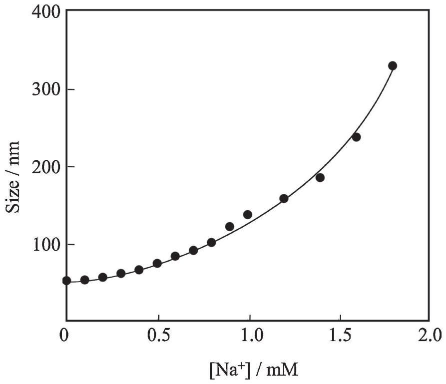


Figure 4. DLS curve of Crown–SNPs in CH_3CN with different concentrations of $NaClO_4$ at 25 °C.

Next, the selectivity of Crown–SNP was investigated. Figure 5 shows the absorbance changes at 400 nm for each CH_3CN solution containing Crown–SNP by adding $LiClO_4$, $NaClO_4$, or $KClO_4$. Among three alkali metal ions, the addition of Li^+ induced the largest absorbance change. As SNPs are negatively charged, the decrease of the surface charge resulting from the complexation of the crown ring with Li^+, which has the highest positive charge density, may lower the solvent dispersibility of SNPs most significantly.

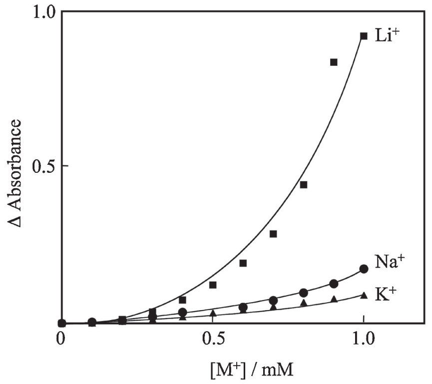


Figure 5. Absorbance changes at 400 nm for each CH_3CN solution containing Crown–SNPs with different concentrations of $LiClO_4$, $NaClO_4$, or $KClO_4$ at 25 °C.

In summary, we have showed a synthetic protocol of SNPs functionalized chemically with crown ethers by simple chemical modifications. The recognition of an alkali metal ion was achieved based on the absorbance changes originating from particle aggregation. Further study of water-soluble Crown–SNPs containing fluorescent molecules is underway in our laboratory, aiming at more sensitive and practical detection.

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