Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Dielectric and current-voltage characteristics of flexible Ag/BaTiO$_3$ nanocomposite films processed at near room temperature

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1) Estimation of porosity level in the thick films

We evaluated the porosity level of thick films by using the image analysis from the cross-sectional SEM images corresponding to Fig. 2(d,e,f). Fig. S1 represents the results of the image analysis where the blue highlighted section is roughly assumed as the section of open pores. The porosity depends on the size and content of ceramic fillers as expected.

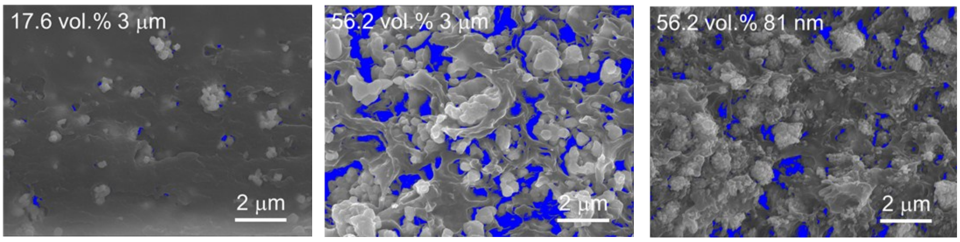

Fig. S1 Estimated section of pores as highlighted as blue color from the cross sectional images of Fig. 2(d,e,f) of the manuscript, which were calculated to have the porosity of ~1.2 %, ~12.8 % and ~3.7 % in order.

2) Evaluation of dielectric properties under bending stress

Flexibility of the composite film was evaluated by applying bending with a known curvature to confirm the change in dielectric properties under bending condition. Fig. S2 shows the variations of dielectric constant and dielectric loss of the 56.2 vol% 81 nm sample when an external bending was applied from 0 to ~1.7 % strain, with the schematic of bending curvature and a photo of real sample. The applied strain value was calculated by a simple known relation with the bending radius R as reported.[1,2] The values were almost consistently kept with increasing strain, indicating that the samples are bendable in this strain range without causing dielectric degradation. Bonding between the UV-polymer and filler particles is likely to be robust enough to resist against the tensile stress upon the bending operation.

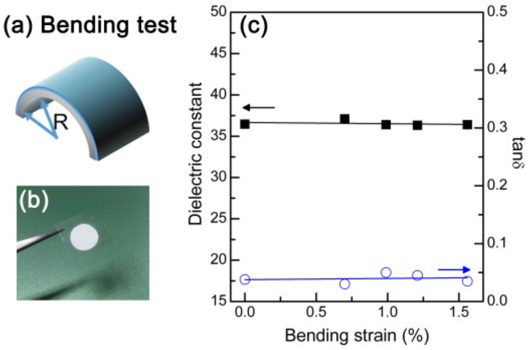

Fig. S2 (a) a bending schematic, (b) an actual samples printed/cured on a PET substrate, and (c) changes in dielectric constant and loss under applied bending strains

Estimation of effective dielectric constant by the prediction models

Effective dielectric constant of the $BaTiO_3$-polymer composites was estimated by two prediction models, such as Maxwell-Garnett model[3] and effective medium theory (EMT) model[4], which are known to be applicable selectively for high and low dielectric constant mixture composites. Fig. S3 shows the results of the variations of effective dielectric constant estimated by the models as a function of filler content for the 100 nm and 3 um $BaTiO_3$ composites. According to the Maxwell-Garnett model for dispersed dielectric spheres in a continuous dielectric matrix, the effective dielectric constant ε_{eff} of the composite is given by

$$\varepsilon_{eff} = \varepsilon_1 \left[1 + \frac{3f\left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\right)}{1 - f\left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\right)} \right] \tag{1}$$

where f, ε_1 and ε_2 are the volume fraction of filler and the dielectric constant of the polymer and filler, respectively. ε_2 and ε_1 were assumed to be ~2000 and 4.9 as representative values at 10 kHz.[5] The estimation of this model did not fit well by showing largely deviated values of dielectric constant as seen in Fig. S3.

On the other hand, the EMT model is known to represent the case of embedded ceramic filler by introducing a fitting parameter n as expressed by

$$\varepsilon_{eff} = \varepsilon_1 \left[1 + \frac{f(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + n(1-f)(\varepsilon_2 - \varepsilon_1)} \right] \tag{2}$$

where n is the morphology fitting factor of ceramic filler. A small value of n indicates near-spherical shape with a smaller particle size. The EMT model was best suitable to the 3 μm $BaTiO_3$ composites when n was 0.8 as shown in Fig. S3. The fitting factor needs to be 0.2 for the optimal approximation to cover the range of the ε_r values in the case of 100 nm $BaTiO_3$ composites. The decreased number of n reflects well the smaller particle size of $BaTiO_3$ with more symmetrical morphology. It is assumed that the single parameter n cannot represent the variation of the ε_r values in the broader range of particle size and volume fraction.[4,6]

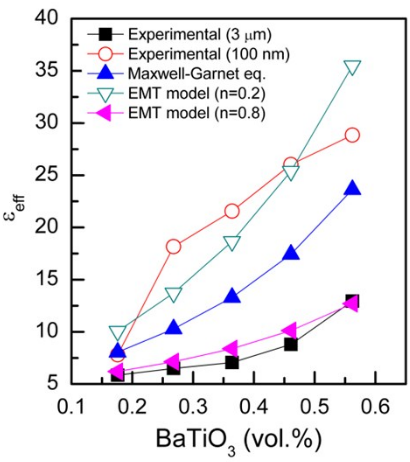

Fig. S3 Variations of effective dielectric constant in the composite films as a function of $BaTiO_3$ content as a result of estimation by the Maxwell-Garnett and the effective medium theory (EMT) model, with the plots of measured dielectric constant for the 100 nm and 3 μm $BaTiO_3$ composite samples.

Estimation of effective dielectric constant by the prediction models

Fig S4 shows the elemental distribution of the 30 vol. % Ag thick films as an example. Even though some agglomerates of Ag can be seen, overall distribution of Ag seems to be quite uniform over the sample surface area.

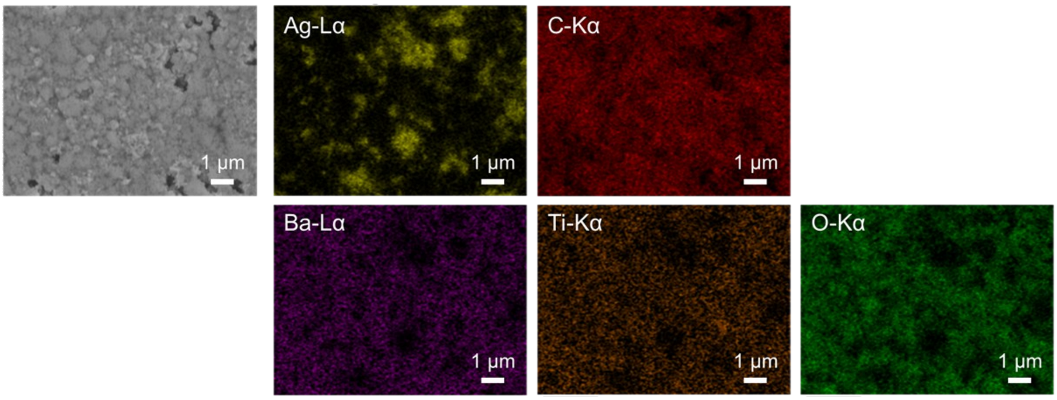

Fig. S4 The SEM-EDS elemental distribution images for the 30 vol. % Ag thick film sample

References

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