

Supporting Information

Synthesis and Electric Field Response of Titanium Dioxide Nano-particles Dispersed in Hydrophobic Solvents

Tetsuya Kurebayashi,^a Seki Inoue,^a Yuichi Masuda,^a Hiroyuki Shinoda^a and Takehiko Sasaki^a

^a Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan

Experimental Procedures

Chemicals

Titanium tetrabutoxide, distilled water, Ethanol (super dehydrated, 99.5%), Hydrochloric Acid (36%), Octyl acetate (FUJIFILM Wako Pure Chemical Corporation), isotridecyl acid phosphate (JP-513, JOHOKU CHEMICAL CO., Ltd.) were used as received. AEROXIDE TiO₂ P90 (Evonik) was used as reference sample of IR measurement.

Synthesis of TiO₂ nanoparticle

Titanium tetrabutoxide (TTB, 80 mmol) was added dropwise to 800 mL of ethanol with 5% distilled water under vigorous stirring. TTB was hydrolyzed immediately, resulting in a white precipitate. After 1h of stirring, hydrochloric acid was added dropwise to 0.3M. The precipitate was peptized and clear solution was obtained in several minutes. After 1 hour, isotridecyl acid phosphate (8mmol) was added dropwise to this solution and white precipitation was formed. The precipitate was filtered and dried overnight at room temperature. When the resulting powder was added to toluene at 1 g/mL, it dispersed spontaneously and became a transparent solution without ultrasonication. Finally, TiO₂ nanoparticle powder was obtained by refluxing at 115°C with toluene, dehydrating, and then reprecipitating with large amounts of ethanol, washing with ethanol twice, and vacuum drying.

The nanoparticle dispersions used in the following analysis were prepared by adding solvent to the powder and shaking it, with no special dispersion treatment such as the homogenizer.

Characterization.

Fourier transform infrared (FTIR) measurements were conducted on Nicolet iS5 (Thermo Scientific). The powders were compressed and measured by ATR method. Before sample measurements, background measurement was conducted with no powder (air). Refractive Index measurements were conducted on KPR-3000 (SHIMADZU) at room temperature. Three spectrum lines: g, e and r lines were used as light source, corresponding as 435.83 nm, 456.7 nm and 706.52 nm. Liquid samples were filled in V block accessory. UV-Vis spectroscopy measurements was carried out on U-4100 (Hitachi High-Tech) with glass cuvette, which optical path length is 3mm. Before sample measurements, background measurement was conducted without cuvette. Visible light transmittance was calculated

as the integral of transmittance at 340~810 nm. Dynamic light scattering (DLS) measurement was conducted on Nanotracer wave II (Microtrac). The measurement was performed after co-washing twice with a solvent of the same composition as the dispersion. The particle size was adopted as the number average.

TEM Observation

TEM images were observed on JEOL JEM-2100 operating at 200 kV, used to obtain bright field images for all particles, at The Institute for Solid State Physics (ISSP), The University of Tokyo.

Electrochemical Measurement

Electrochemical measurements were carried out on SP-300 (Bio-Logic Science Instruments). A glass cuvette with a copper electrode attached to the inside was used as the measuring cell. A sample dispersion of 0.5 mL was added to the cell with a width of 10 mm and a distance (thickness) of 3 mm between the electrodes. The measured resistance/conductance was converted to volume resistivity/conductivity. The measurement was started at 1 MHz and swept at logarithmic intervals down to 0.1 Hz. The amplitude was set to 100 mV and the bias voltage to 0 V. The real component at 1250 Hz, where the capacitive component of the electrolyte containing nanoparticles disappeared, was used as a representative value.

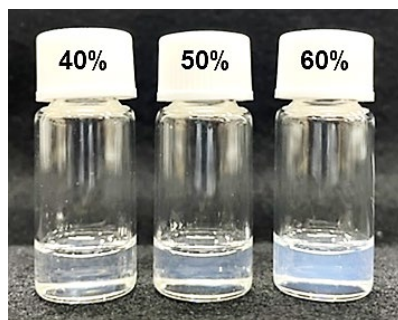


Figure S1. Photographs of dispersions with ethanol ratios of 40%, 50%, and 60%.

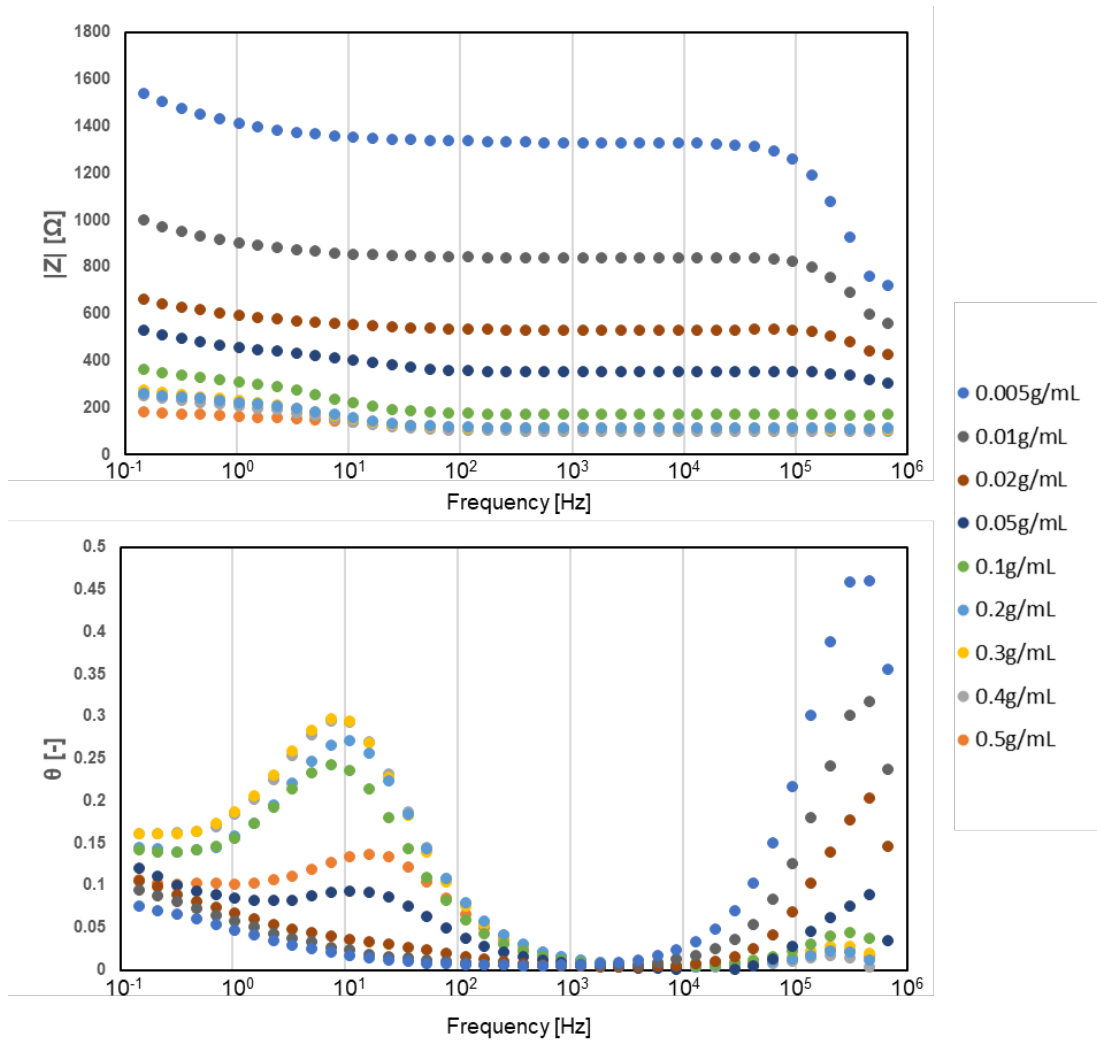


Figure S2. Bode plots at various concentrations

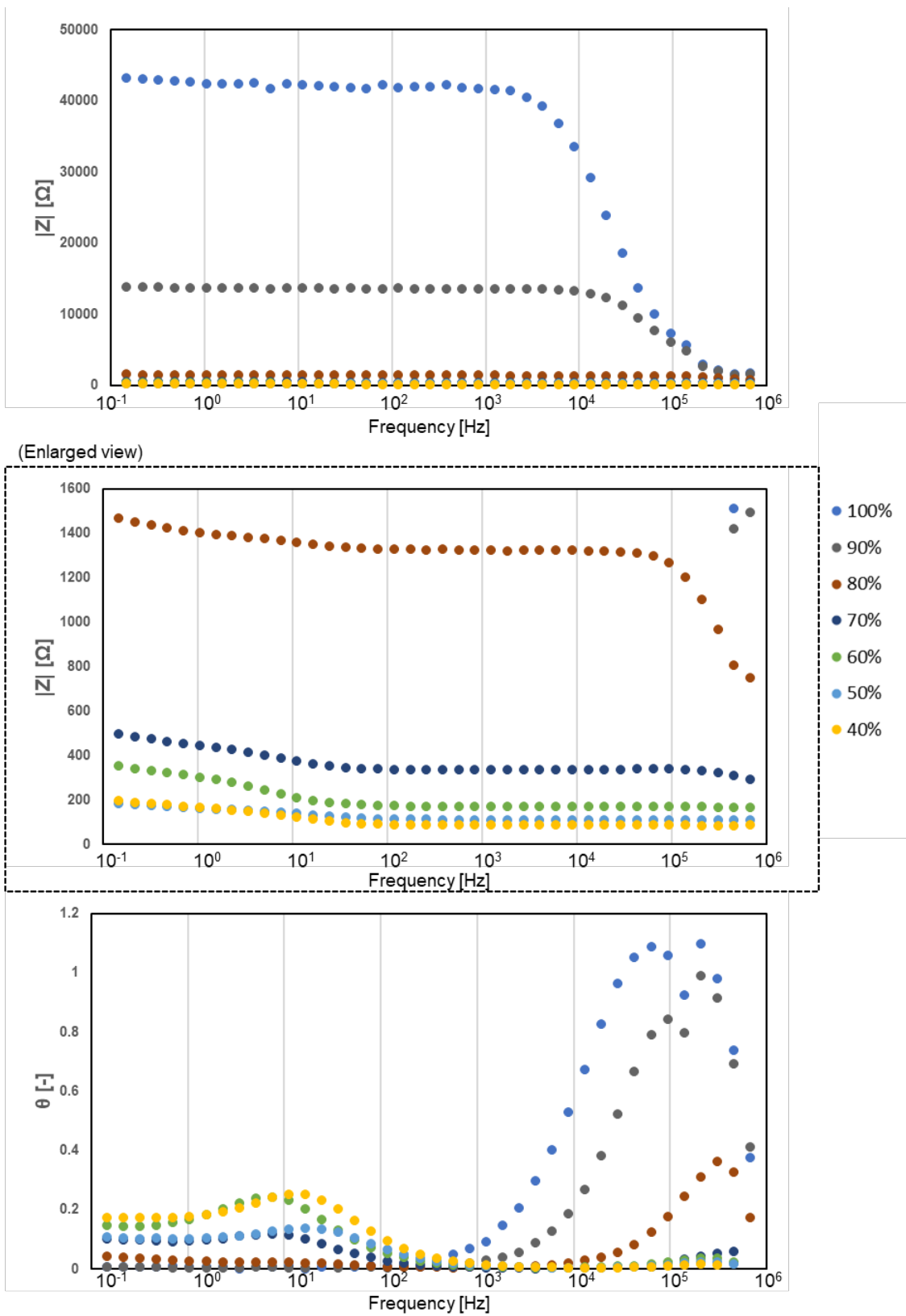


Figure S3. Bode plots at various ethanol ratio in octyl acetate. Middle plot is enlarged plot of the upper plot.

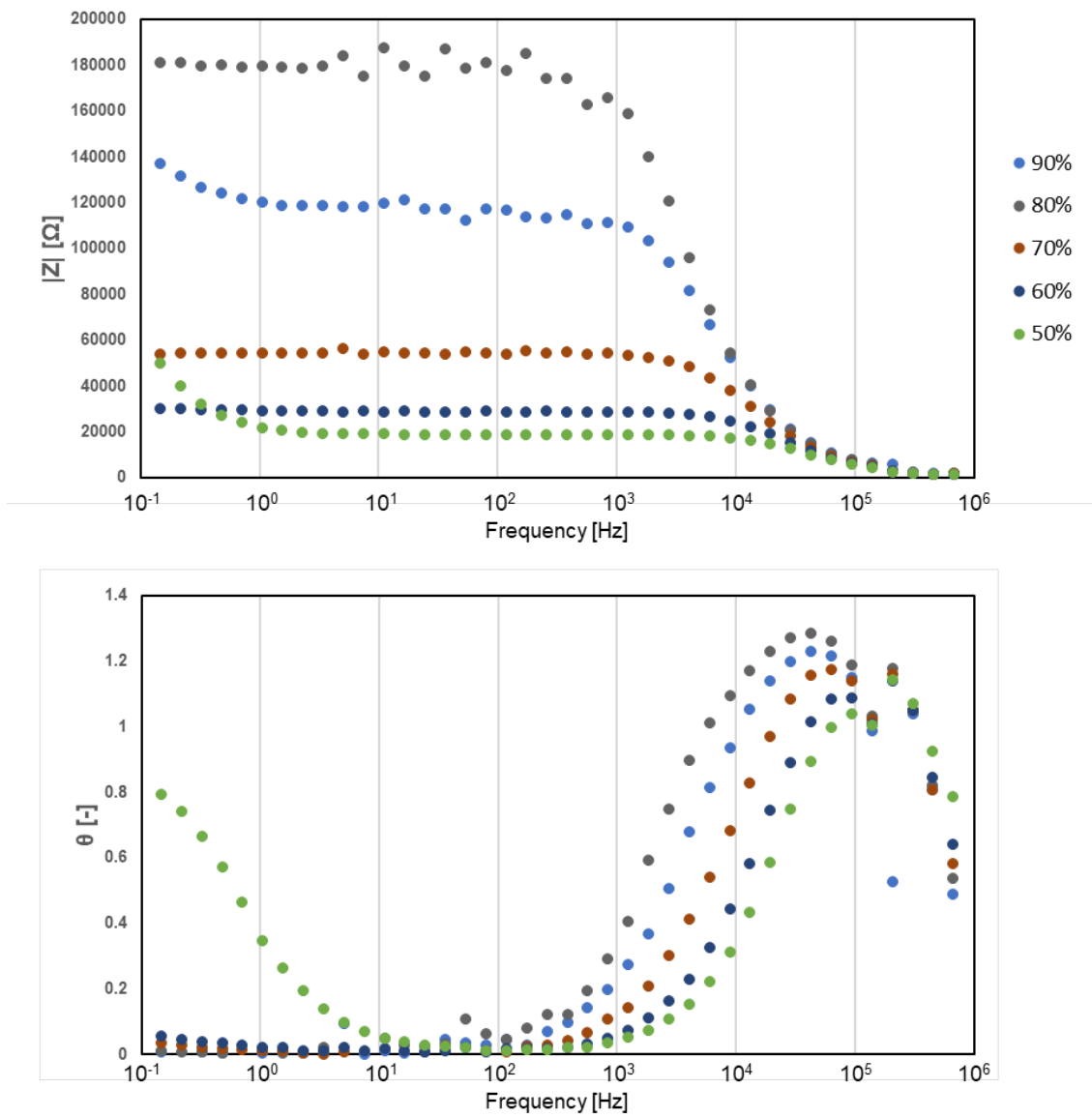


Figure S4. Bode plots of at various ethanol ratio in octyl acetate without nanoparticle.

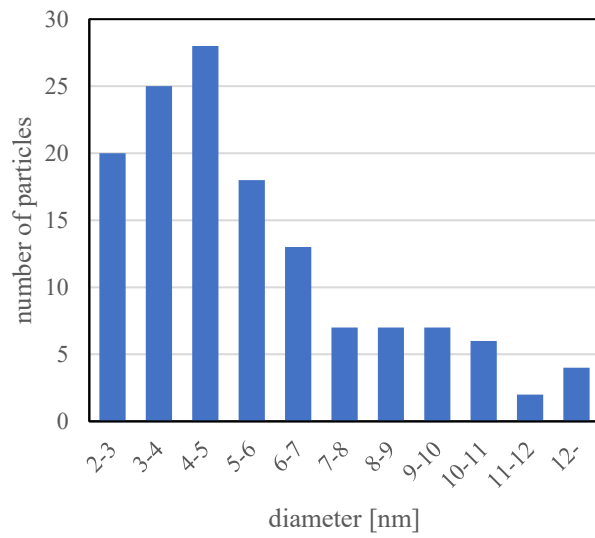


Figure S5. Particle size distribution histogram obtained by counting 137 particles with 6 TEM images measured for equivalent independent fields of view.