Electronic Supplementary Information

Liquid metal catalyst for the conversion of ethanol into graphitic carbon layers under ultrasonic cavitation field

Hideya Kawasaki*[1], Tomoko Otsuki[1], Fumiya Sugino[2], Ken Yamamoto[2], Tomoharu Tokunaga,[3] Rintaro Tokura,[4] Tetsu Yonezawa*[4]

[1]Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita-shi, Osaka 564-8680, Japan

[2]Department of Pure and Applied Physics, The Faculty of Engineering Science, Kansai University, Suita-shi, Osaka 564-8680, Japan

[3]Department Materials Science and Engineering, Faculty of Engineering, Nagoya University, Furo-Cho, Nagoya 464-8603, Japan

[4] Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Corresponding authors: (H.K) hkawa@kansai-u.ac.jp; (T.Y) tetsu@eng.hokudai.ac.jp

Authorship contributions

H. Kawasaki: the conceptualization of this study and approval of the final draft, T. Otsuki: synthesis of LMP, F. Sugino: collection of high-speed imaging, K. Yamamoto: design on ultrasonic instruments and interpretation of high-speed imaging, T. Tokunaga: data analysis of TEM-EELS, collection, analysis, and interpretation of TEM and TEM-EELS measurement data, R. Tokura: data analysis and interpretation of TEM-EELS. T. Yonezawa: the design on the characterization of LMP and final draft approval.

EXPERIMENTAL SECTION

Materials.

Gallium (Ga) and Indium (In) were purchased from Kojundo Chemical Lab. Co., Ltd. with cited purities of 99.99%. All solvents, ethanol (99.5 %), 1-Propanol(99.5%), 1-Octanol(99.8%), and 1-Decanol (95 %) for preparation of EGaIn liquid metal particles were obtained from FUJIFILM Wako Pure Chemical Corporation. Graphene oxide and HCl ethanol solution were purchased from Sigma-Aldrich.

EGaIn particle preparation :

Ga 75.5%, In 24.5% (by weight, Ga:In = 1:1 (mol/mol)) was placed in a vessel (1.54 g Ga, 0.50 g In) and heated on a hot plate at 180 °C to produce EGaIn liquid metal. To prepare a suspension of EGaIn liquid metal particles (LMP), 0.5 g of EGaIn was added into a vial (20 mL), which was filled with ethanol to a total volume of 5 mL. We employed a two-step sonication process: forming large micron-sized particles by the ultrasonic bath (D-SONIC, SANSYO, Japan) for 15 min, followed by the sonication treatment using a high-intensity ultrasonic horn (UP200S/200 W, 24kHz, Cycle：1, Amplitude：60%, Hielscher USA, Inc.) for 120 min in an ice bath to obtain smaller particles of less than 1 μm.

EGaIn particle characterization

The suspension of LMP was deposited dropwise on a clean silicon wafer and after drying in air, the sample was examined by SEM (Scanning Electron Microscope, JEOL JSM-6380LVA/JED-2300 and JEOL JCM-6000Plus NeoScope), XPS (X-ray Photoelectron Spectroscopy, Physical Electronics, Inc.), and Micro-Raman Spectroscopy (MicroRAM-300, Lambda Vision Inc.). For TEM characterization, the suspension was cast onto a TEM carbon grid. After drying in air, the sample was probed by TEM (JEOL JEM-1400Plus) operating at 120 kV. Scanning Transmission Electron Microscope (STEM) images of LMP were collected using A Hitachi STEM (HD-2700 with a cold field emission gun operating at 200 kV). The LMP powder was embedded on Mo grids. After drying, the samples were

introduced into the STEM (JEOL ARM-200F with a cold field emission gun operating at 200 eV) column. Electron energy loss spectroscopy measurements were carried out with an EELS system (GIF Quantum, Gatan, USA) equipped with the STEM

High-speed imaging of the dynamic behavior of cavitation bubble on the surface of EGaIn liquid metal in ethanol under ultrasonication

A high-speed camera (Hyper Vision HPV-X2, Shimadzu) was placed on the LED device's opposite side. An optical lens (LEICA Z16 APO, Leica) was installed in front of the high-speed camera, operated at a frame rate of 200,000 fps and a shutter speed of 1 μs. The experiments were carried out according to the following procedure: ethanol was filled in the vessel, and one droplet of EGaIn was placed on a solid plate. The high-speed camera was switched on to record the ethanol-droplet interface. The ultrasound irradiation (26 kHz, 30 W) initiated the EGaIn droplet formation.

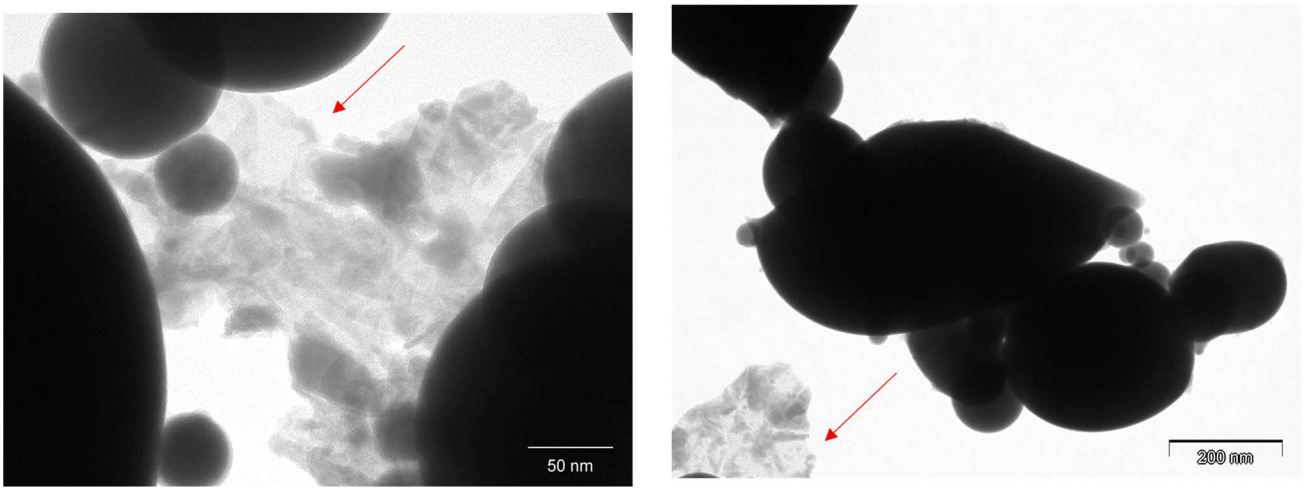
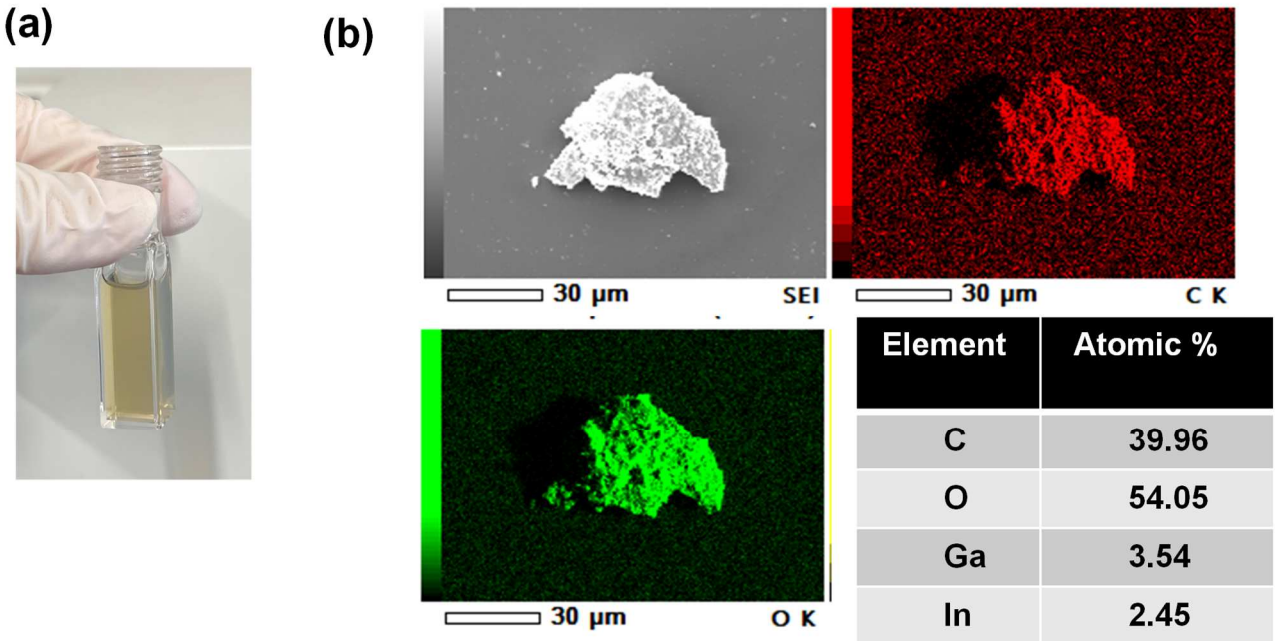


Fig. S1. TEM images of LMP(EtOH). The carbonaceous materials are seen in the TEM image as shown in red arrows.



Element	Atomic %
C	39.96
O	54.05
Ga	3.54
In	2.45

Fig. S2. (a) Photograph of supernatant obtained from LMP(EtOH) dispersion by the centrifugation for 6000 rpm for 10 min. (b) The supernatant in (a) was deposited on a clean silicon wafer. The SEM and EDS images of carbonaceous materials in the silicon wafer.

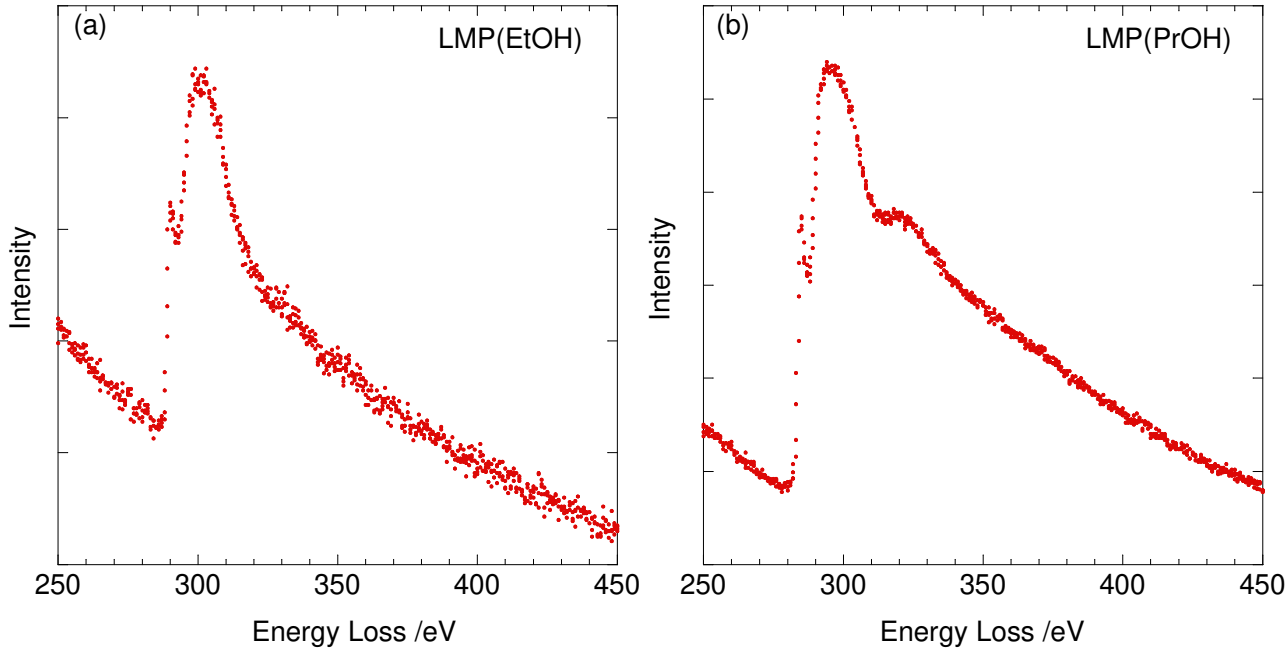
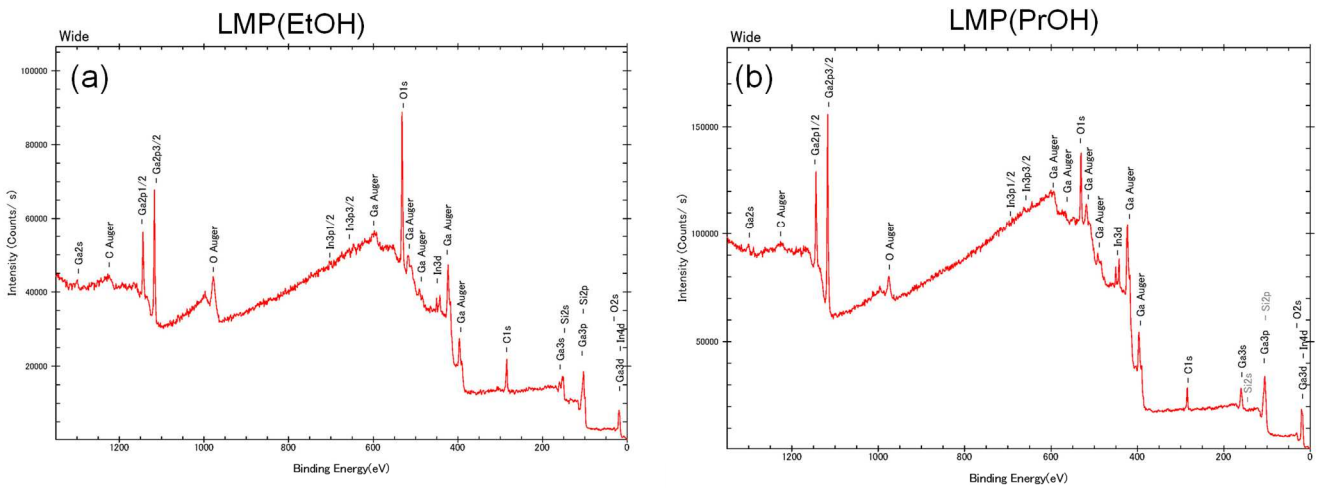


Fig. S3. EELS spectra of carbon K (1s) taken at the surface of (a) LMP(EtOH) and (b) LMP(PrOH).



Ga:12.1 (atomic %)
In:0.80 (atomic %)
O:61.3 (atomic %)
C:25.8 (atomic %)

Ga:28.1 (atomic %)
In:2.0 (atomic %)
O:46.1 (atomic %)
C:23.8 (atomic %)

Fig. S4. XPS spectra of (a) LMP(EtOH) and (b) LMP(PrOH). The atomic % ratio of Ga, In, O, and C are shown below the figures.

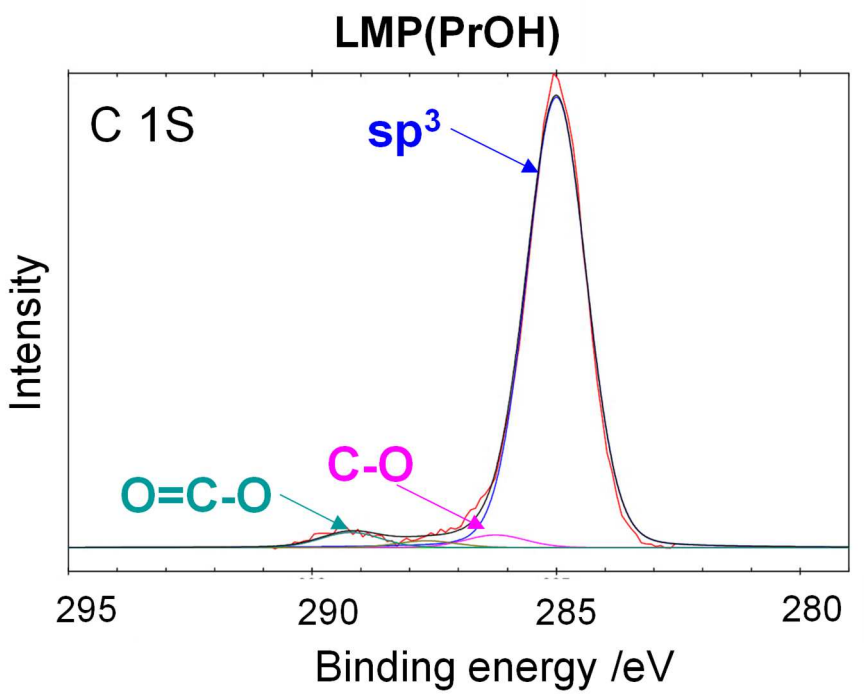


Fig. S5. XPS spectrum of the C 1s region of LMP(PrOH).

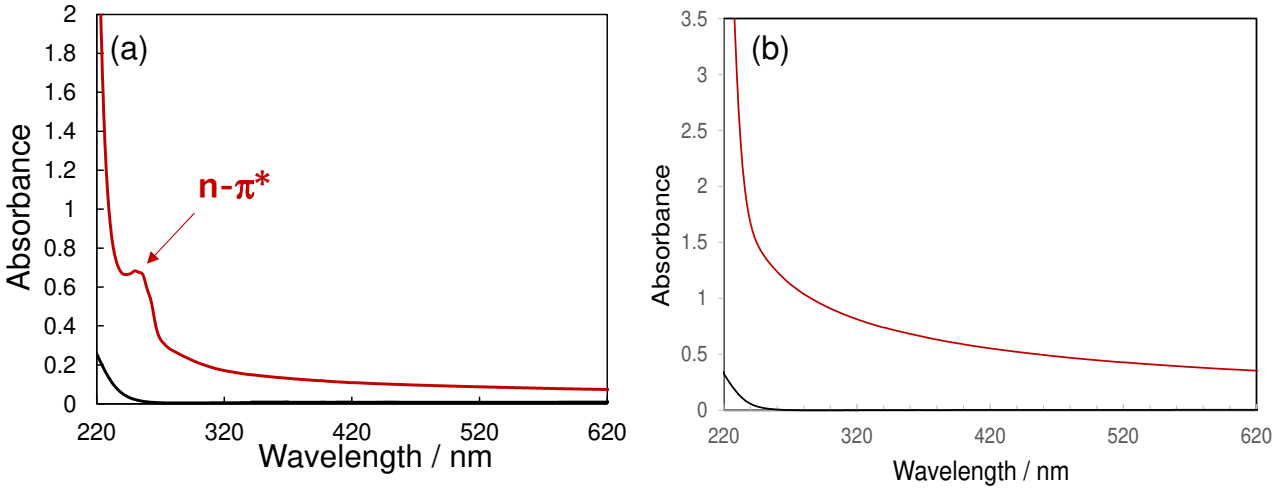


Fig. S6. (a) UV-Vis spectra of the supernatant obtained from the LMP(EtOH) dispersion in ethanol after HCl addition and subsequent centrifugation (solid red line) and that of the ethanol solution obtained under sonication conditions identical to those for LMP(EtOH) formation (solid black line) (b)The UV-Vis spectra of the supernatant solution obtained from LMP(PrOH) dispersion in ethanol by adding HCl and centrifugation (solid red line), and 1-propanol solution after identical sonication conditions to the case of LMP(PrOH) (solid black line).

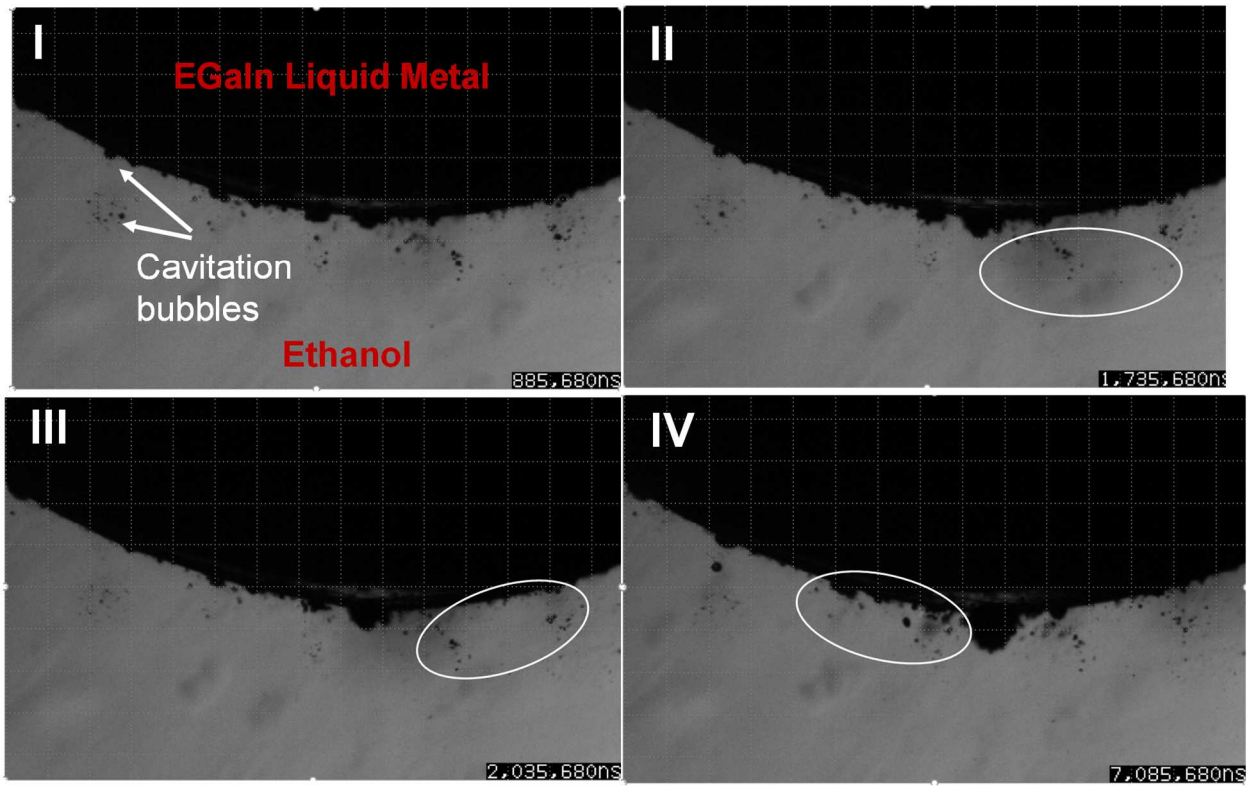


Fig. S7 Snapshots of the dynamic behavior of cavitation bubbles and the EGaIn liquid metal–ethanol interface during ultrasonication: Image I at 885,680 ns, Image II at 1,735,680 ns, Image III at 2,035,680 ns, and Image IV at 7,085,680 ns. The video images were approximately 4.24 mm in width and 2.65 mm in height. The white circles and ellipses indicate the fragmentation of liquid metals into tiny droplet

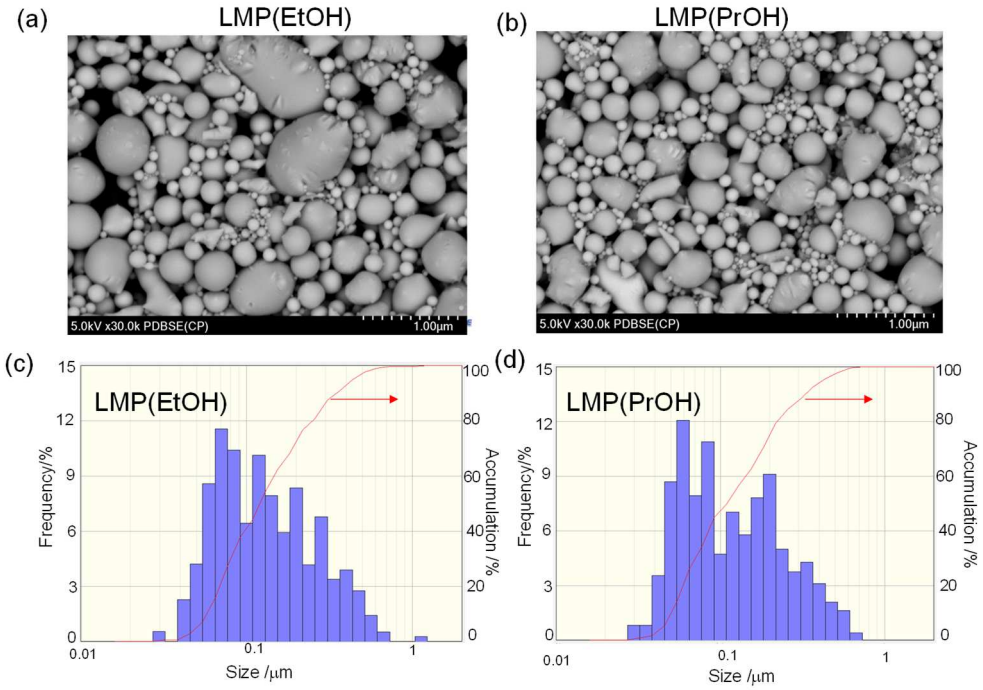


Fig. S8 SEM images and their size distributions of (a),(c) LMP(EtOH) and (b), (d) LMP(PrOH) immediately after identical sonication.

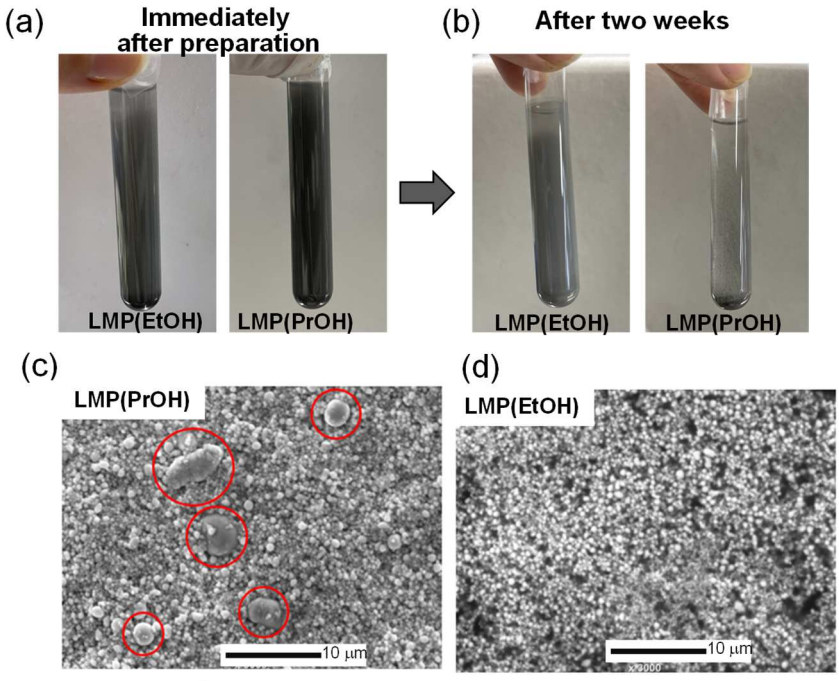


Fig. S9 Photographs of LMP(EtOH) and LMP(PrOH) (from left to right) (a) immediately after sonication and (b) two weeks later after sonication. The SEM images of sediments from (c) LMP (EtOH) dispersion in EtOH and (d) LMP(PrOH) dispersion in 1-propanol. The SEM image of sediments from LMP(PrOH) showed large particles via their coalescence and size growth, as shown in red circles.