

Supporting Information

Remote Control of Electron Transfer Reaction by Microwave

Irradiation: Kinetic Demonstration of Reduction of Bipyridine

Derivatives on Surface of Nickel Particle

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Experimental Section

Nickel powder (3-7 μm , 99.8 %), *N,N*-dimethyl-4,4'-bipyridinium dichloride (98 %, MV^{2+}), and 4,4'-bipyridine were purchased from Sigma-Aldrich Co. LLC. and used as received. *N,N*-ethylene-2,2'-bipyridinium dibromide (DQ^{2+}), 2,2'-bipyridine, 1,3-dibromopropane, acetone, and 1,3-propanesultone were purchased from Wako Pure Chemical Industries, Ltd. and used as received.

3DQ^{2+} was synthesized according to a procedure adapted from previous report^[S1]. 2,2'-bipyridine (19.2 mmol, 3.0 g) was added to 1,3-dibromopropane (98.5 mmol, 19.89 g, 10 ml). The mixture was heated at 440 K and for 16 h under reflux. After cooling, the precipitate was filtered and washed with acetone. The product was then recrystallized from water and acetone. The product was identified by ^1H NMR (Bruker Co.). ^1H NMR (D_2O , 300 MHz): δ (ppm) = 9.3 (2H, d, J = 6.0 Hz); 9.0 (2H, m), 8.6 (2H, m), 8.5 (2H, m), 5.1 (2H, m), 4.6 (2H, m), 3.0 (2H, m).

A water dispersion of nickel powders (0.065 g/mL) contained in three-neck test tube made of quartz (Figure S7(a)) was purged with Ar bubbling for 15 minutes to remove the dissolved oxygen. After the purging, the pipe for Ar introducing was raised above the water surface. During the all experiment, Ar was flowed continually to prevent an invading of oxygen into the test tube. Then, the test tube was inserted in a microwave irradiation chamber or an oil bath, and heated to reaction temperature. The temperature of the dispersion was measured by an optical fiber thermometer (Opsens,

Picosens). After the temperature of the dispersion was stabilized, a drop of the aqueous solution of $3DQ^{2+}$, MV^{2+} , DQ^{2+} or PVS, whose volume was one tenth of the dispersion of Ni, was added to the dispersion. The amount of produced reductant of Bpy were determined by UV-vis optical measurement. BPS101 Tungsten halogen Light Source (B&W Tek.) was used as the light source. The light was guided to Quest X CCD Array Spectrometer (B&W Tek.) through an all quartz immersion probe (with the window pitch of 5 mm, Hellma Analytics Co.) which is immersed in the reaction liquid. All experiments were performed triplicate.

For the microwave irradiation, the two types of microwave resonator were used. The one is an ellipsoidal microwave applicator (CHRONIX Ltd.) as shown in Figure S7(b). A microwave antenna is embedded at one of the focal point of ellipsoidal cavity, and an insertion site to introduce the samples are located at the other focal point. The microwave antenna is connected to a 2.45 GHz microwave generator with a semiconductor oscillator via an impedance matching device. In this cavity, TM_{110} mode of standing microwave can be generated, and the sample insertion site is the antinode of the alternating electric field and node of the alternating magnetic field. The other one is a waveguide type microwave resonator (Fuji Electronic Industrial Co. Ltd) as shown in Figure S7(c). The microwave antenna is placed at the endpoint, connected to the 2.45 GHz microwave generator with a semiconductor oscillator. A plunger at the other endpoint and three stub tuner at the middle are

60 equipped for the impedance matching. TE_{103} mode of standing microwave can be generated in the
61 cavity. Hence the electric field component of this standing wave is made out of phase with the magnetic
62 one by 90 degrees, separating the positions of the antinode of the electric field (E field) and the
63 magnetic field (H field).

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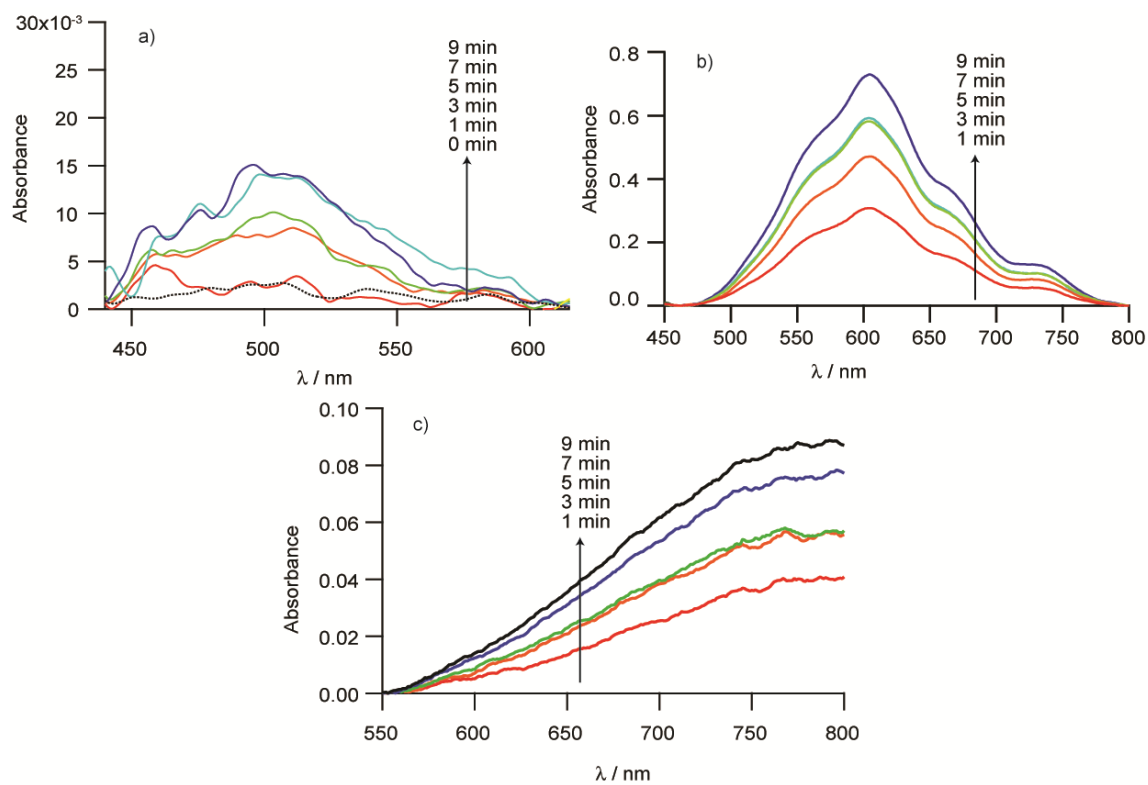


Figure S1. The alternation of the UV/Vis absorption spectra during the reaction between Ni particles and (a) 3DQ⁺ (b) MV⁺, and (c) DQ⁺ under oil bath heating

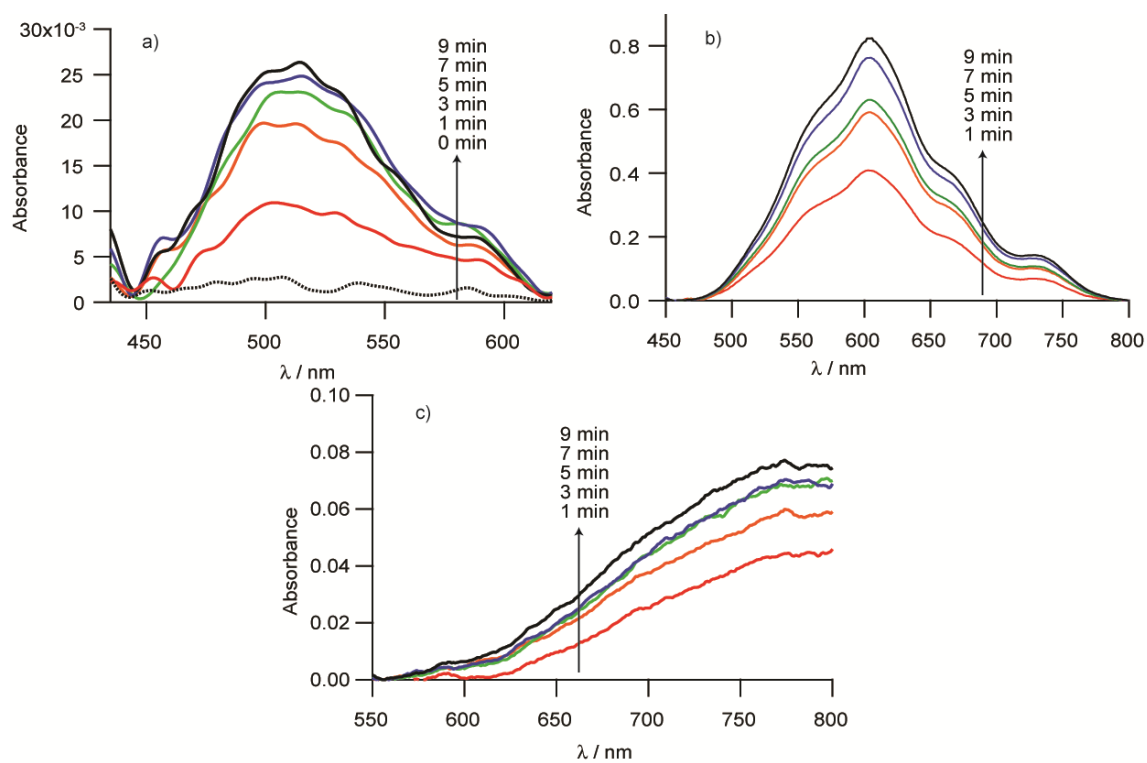


Figure S2. The alteration of the UV/Vis absorption spectra during the reaction between Ni particles and (a) 3DQ⁺ (b) MV⁺, and (c) DQ⁺ under microwave heating.

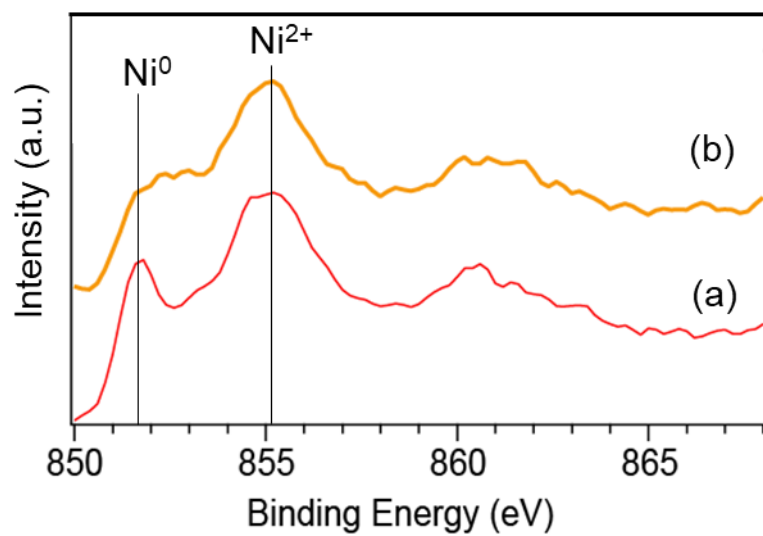


Figure S3. Ni 2p_{3/2} XPS spectra of powder (a) before and (b) after the reaction with *Bpys*²⁺.

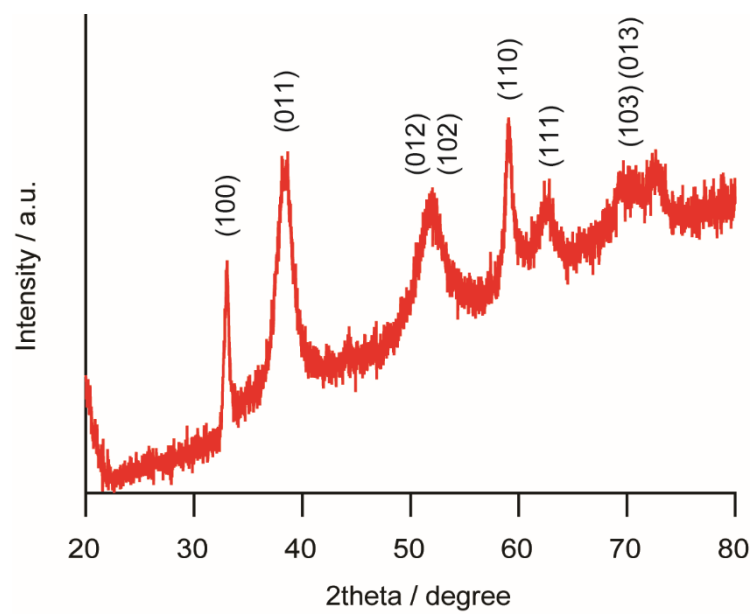


Figure S4. XRD patterns of precipitated white powders after the electron transfer reaction between Ni powders and MV^{2+} in aqueous solution.

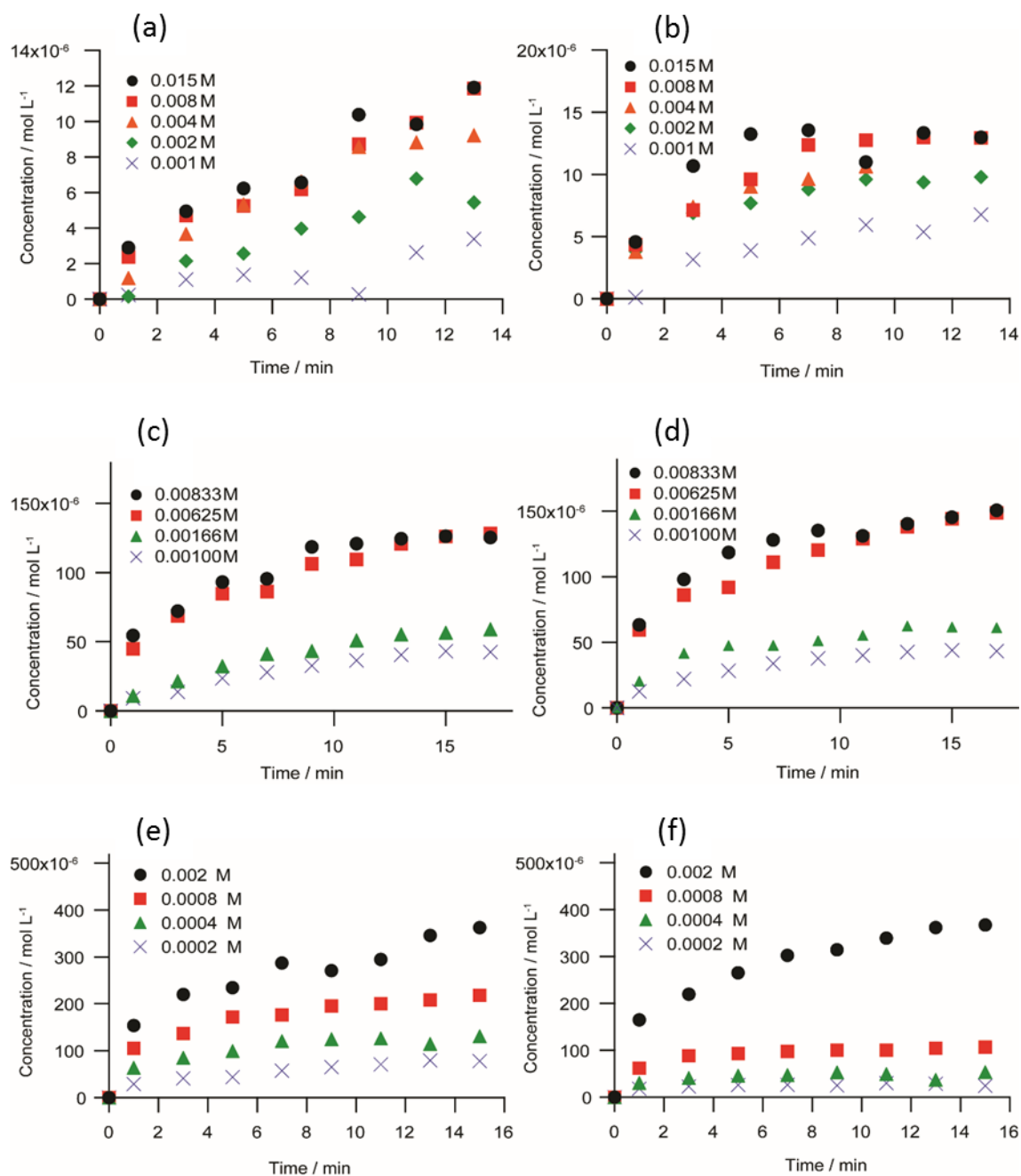


Figure S5. The dependence of the concentration of the produced radical cations on the initial concentration of the 3DQ²⁺ under (a) oil bath heating and (b) microwave heating, MV²⁺ under (c) oil bath heating and (d) microwave heating, and DQ²⁺ under (e) oil bath heating and (f) microwave heating.

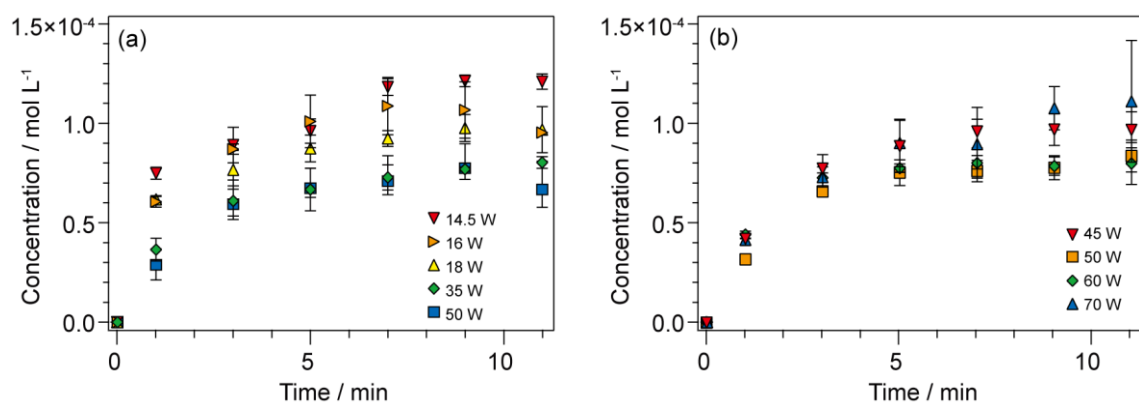


Figure S6. Change of the concentration of MV^{++} vs. the reaction time under (a) at the antinode of the alternating electric field and (b) at the antinode of the alternating magnetic field in the TE_{103} mode of 2.45 GHz microwaves.

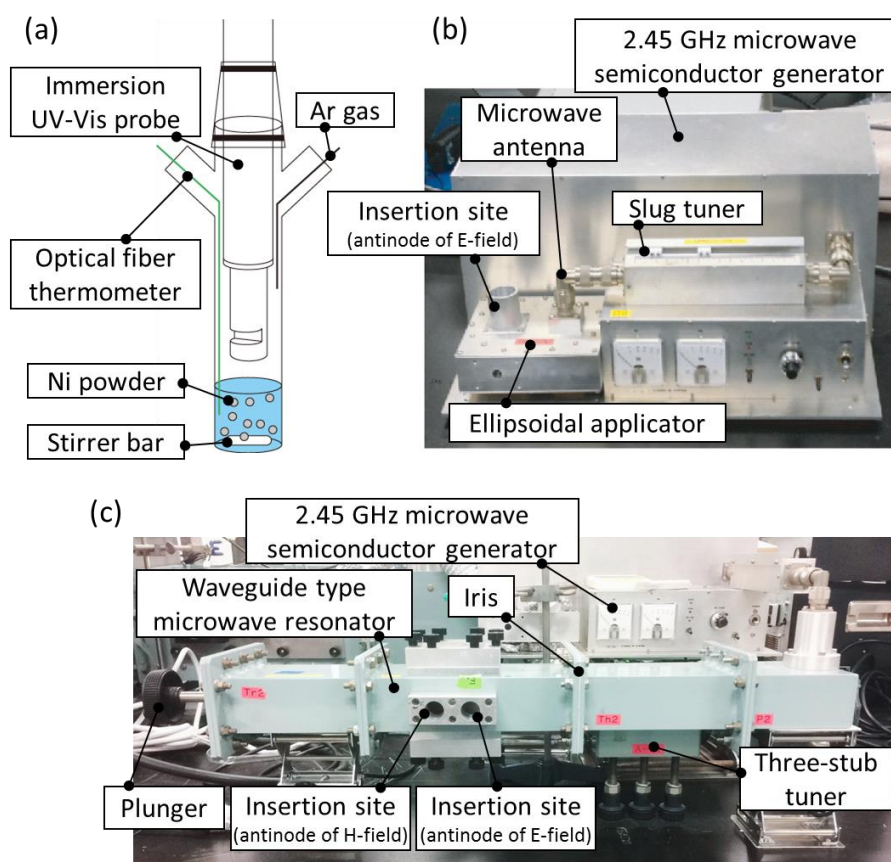


Figure S7. (a) Illustration of the reaction vessel. Photograph of microwave irradiation systems equipped with (b) an ellipsoidal microwave applicator, and (c) a waveguide type microwave resonator.

Reference

- [S1] Homer, R. F.; Tomlinson, T. E. The Stereochemistry of the Bridged Quaternary Salts of 2, 2' -Bipyridyl. *J. Chem. Soc.*, **1960**, 2498-2503.