

Supporting Information

Non-Seed Chemical Bath Deposition of ZnO Films in a Rotating Continuous Flow Reactor with Various Carboxylic Acids and Their Application to Transparent Conductive Films

Hajime Wagata,^{1} Naoya Shioiri,¹ Yuya Tanaka,² Ryo Yokogawa,^{3,4} Atsushi Ogura^{3,4}*

*¹ Department of Applied Chemistry, School of Science and Technology,
Meiji University, Kawasaki 214-8571, Japan*

*² Laboratory for Chemistry and Life Science, Institute of Innovative Research,
Tokyo Institute of Technology, Yokohama 226-8503, Japan*

*³ Department of Electronics and Bioinformatics, School of Science and Technology,
Meiji University, Kawasaki 214-8571, Japan*

⁴ Meiji Renewable Energy Laboratory, Meiji University, Kawasaki 214-8571, Japan

Tel.: +81-44-934-7208

Fax: +81-44-934-7906

*E-mail address of corresponding author: wagata@meiji.ac.jp

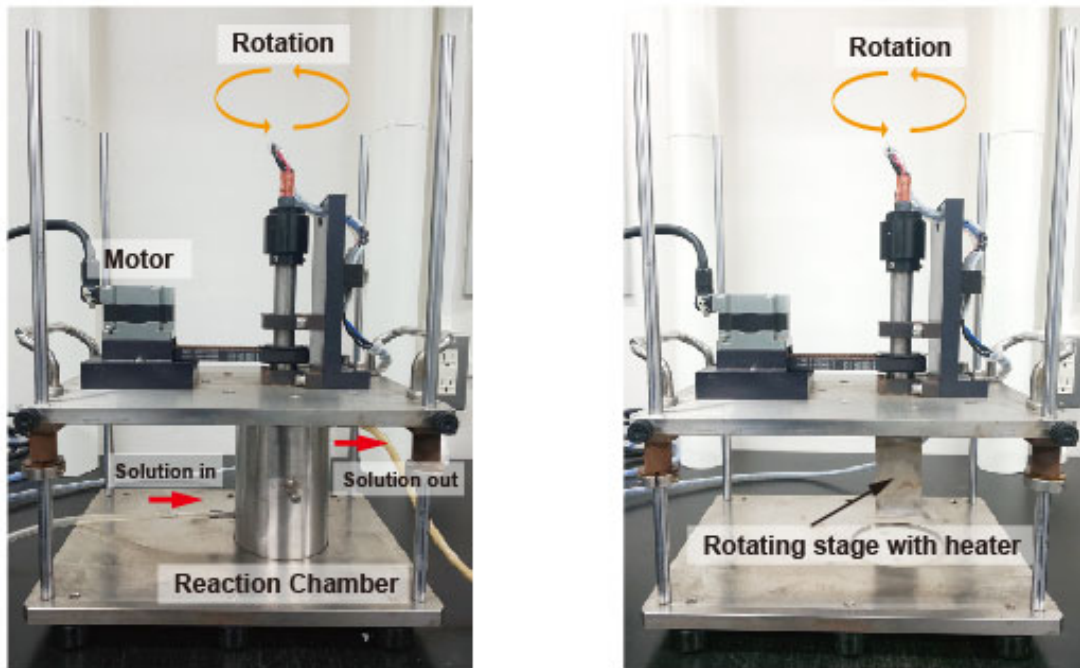


Figure S1 Photographs of a rotating continuous flow reactor used in this study;(left) with a reaction chamber and (right) without a reaction chamber.

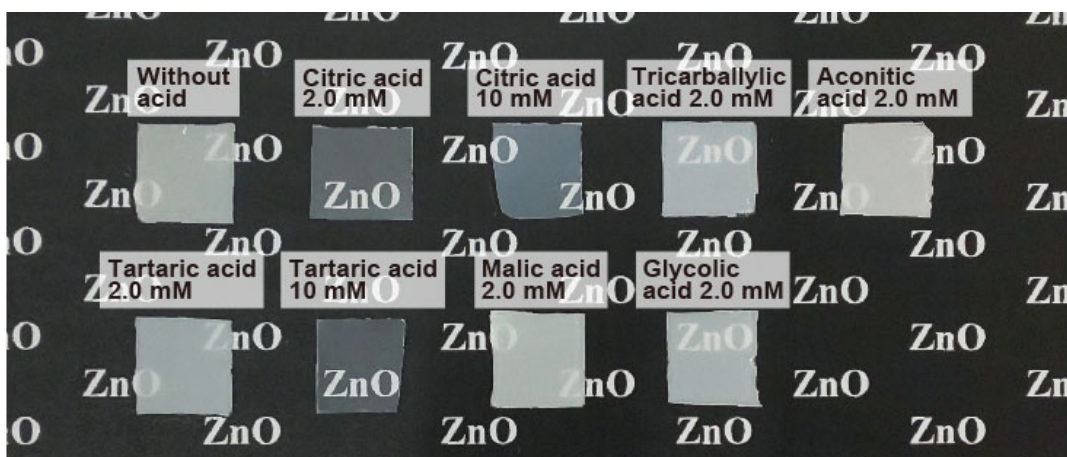


Figure S2 Photographs of the films prepared by non-seed CBD without acid and with various carboxylic acids. $10 \times 10 \text{ mm}^2$ -sized samples were cut out of $40 \times 30 \text{ mm}^2$ -sized samples.

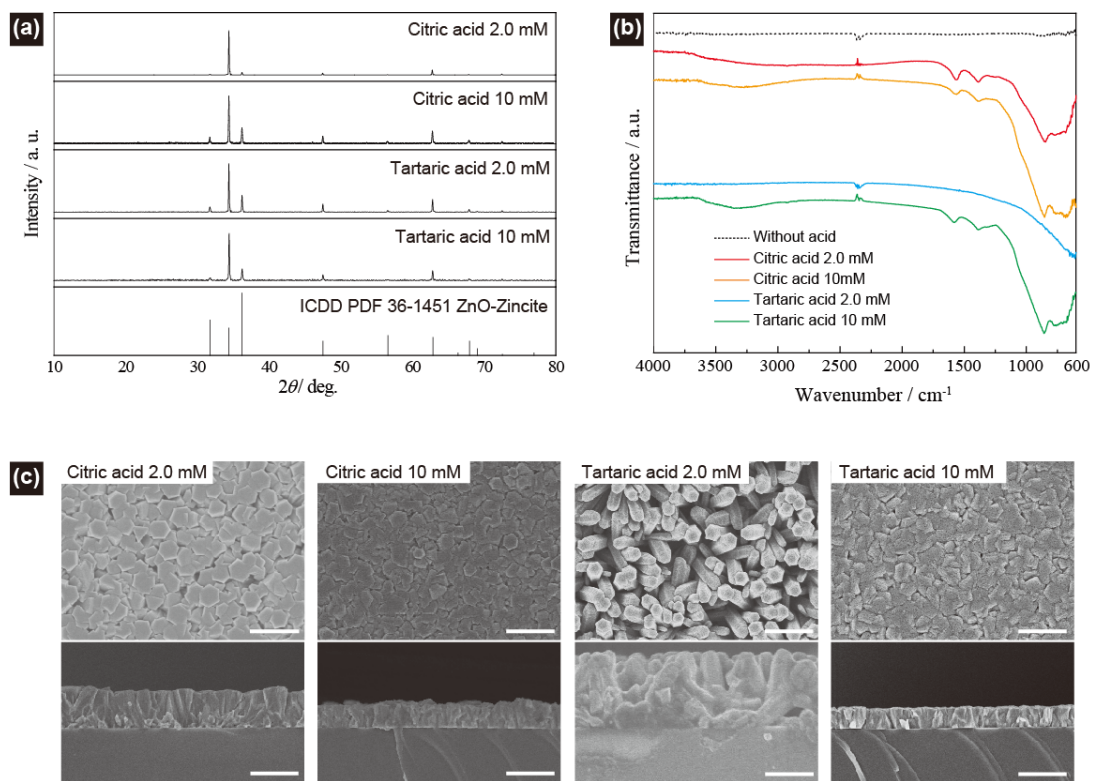


Figure S3. Comparison of the films prepared with 10 mM and 2.0 mM of citric acids tartaric acids; (a) XRD patterns, (b) FT-IR spectra, and (c) surface and cross-sectional SEM images. All the bars in the SEM images indicate 2.0 μm .

Crystallite sizes “*D*” of the dense ZnO films are calculated by Scherrer’s equation (ref. 56) shown below;

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of the X-ray (Cu $K\alpha = 1.5405981 \text{ \AA}$), β is the full width at half maximum (FWHM) of the diffraction peak in radians and θ is Bragg diffraction angle. The XRD peaks of {112} of ZnO were used for the calculation.

Lattice parameters “*a*” and “*c*” of the films were calculated by the following relations (ref.56);

$$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{1}{c^2}$$

Where *d* is the interplanar distance and (*hkl*) is miller indices. The XRD peak of {101} and {112} of ZnO were used for the calculation.

The crystallite sizes and lattice parameters were summarized in Table S1.

Table S1. Crystallite sizes and lattice parameters calculated from XRD data of the films

	Crystallite size / nm	Lattice parameters	
		<i>a</i> / \AA	<i>c</i> / \AA
Citric acid 2.0 mM	82	3.244	5.255
Citric acid 10 mM	61	3.252	5.207
Tartaric acid 10 mM	47	3.249	5.211
ZnO (ICDD-PDF 36-1451)	-	3.249	5.206

Optical band gap of the dense ZnO films were estimated by Tauc plot (ref.58);

$$(\alpha h\nu)^2 = C(E_g - h\nu) \quad (1)$$

Where α is the absorption coefficient, h is Planck's constant, ν is the frequency of photon, $h\nu$ is the energy of the photon, E_g is the optical band gap, and C is a constant.

The measured diffuse reflectance spectra were transformed to corresponding absorption spectra by applying Kubelka-Munk function (ref.58);

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (2)$$

where $R_\infty = \frac{R_{sample}}{R_{standard}}$ is the reflectance of an infinitely thick specimen, while K and S are the absorption and scattering coefficients. Putting $F(R_\infty)$ in eq (1) yields the eq (3);

$$(F(R_\infty)h\nu)^2 = C(E_g - h\nu) \quad (3)$$

The E_g value can be obtained by extrapolating the linear portion to the photon energy axis in figures shown below.

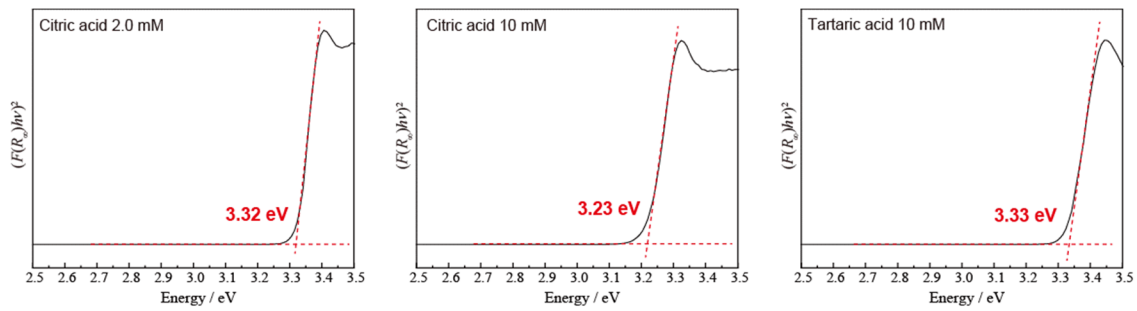


Figure S4 $(F(R_\infty)h\nu)^2$ near the absorption edge as a function of the photon energy for the films prepared with 2.0 mM of citric acid, 10 mM of citric acid, and 10 mM of tartaric acid. The optical bandgap values are also shown in the figures.