Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Novel Optoelectronic Rotors Based on Orthorhombic $CsPb(Br/I)_3$ Nanorods

Fei Cao, Dejian Yu, Yu Gu, Jun Chen and Haibo Zeng**

Institute of Optoelectronics & Nanomaterials, MIIT Key Laboratory of Advanced Display Material and Devices, College of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

The derivation of angular velocity of nanorod rotation: According to Ref[1], the time-average torque can be written as:

$$\Gamma =< p_{\parallel}E_{\perp} - p_{\perp}E_{\parallel} >= -\frac{1}{2}V\varepsilon_1 E^2\ \mathrm{Im}[\frac{\varepsilon_2^* - \varepsilon_1^*}{\varepsilon_1^* + (\varepsilon_2^* - \varepsilon_1^*)L_{//}} + \frac{\varepsilon_2^* - \varepsilon_1^*}{\varepsilon_1^* + (\varepsilon_2^* - \varepsilon_1^*)L_{\perp}}]$$

where

$$\varepsilon_{1,2}^* = \varepsilon_{1,2} + \frac{\sigma_{1,2}}{i\omega}$$

In the equation, V is the volume of the particle, E is the amplitude of the rotating electric field. $\varepsilon_{1,2}$ are absolute permittivity and $\sigma_{1,2}$ are electric conductivity. The subscripts 1,2 inditates the fluid and the particle respectively. Therefore, the equation becomes:

$$\Gamma = -\frac{1}{2}V\varepsilon_1 E^2\ \mathrm{Im}[\frac{\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)}{\varepsilon_1 - \frac{i}{\omega}\sigma_1 + [\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)]L_{//}} + \frac{\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)}{\varepsilon_1 - \frac{i}{\omega}\sigma_1 + [\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)]L_{\perp}}] \cdot$$

Rearranging the real and imaginary part yields:

$$\Gamma = -\frac{1}{2}V\varepsilon_1 E^2\ \mathrm{Im}[\frac{\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_{//} - \frac{i}{\omega}[\sigma_1 + (\sigma_2 - \sigma_1)L_{//}]} + \frac{\varepsilon_2 - \varepsilon_1 - \frac{i}{\omega}(\sigma_2 - \sigma_1)}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_{//} - \frac{i}{\omega}[\sigma_1 + (\sigma_2 - \sigma_1)L_{//}]}] \cdot$$

One can define the Maxwell-Wagner relaxation time as:

$$\tau_{//,\perp} = \frac{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_{//,\perp}}{\sigma_1 + (\sigma_2 - \sigma_1)L_{//,\perp}},$$

and the polarizability as:

$$\chi_{//,\perp}^0 = \varepsilon_1 \frac{\sigma_2 - \sigma_1}{\sigma_1 + (\sigma_2 - \sigma_1)L_{//,\perp}},\quad \chi_{//,\perp}^\infty = \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_{//,\perp}}.$$

The torque can be written as:

$$\Gamma = -\frac{1}{2}VE^2\ \mathrm{Im}[\frac{\chi_{//}^0 + i\chi_{//}^\infty\omega\tau_{//}}{1 + i\omega\tau_{//}} + \frac{\chi_{\perp}^0 + i\chi_{\perp}^\infty\omega\tau_{\perp}}{1 + i\omega\tau_{\perp}}]$$
$$= -\frac{1}{2}VE^2[\frac{\omega\tau_{//}}{1 + (\omega\tau_{//})^2}(\chi_{//}^\infty - \chi_{//}^0) + \frac{\omega\tau_{\perp}}{1 + (\omega\tau_{\perp})^2}(\chi_{\perp}^\infty - \chi_{\perp}^0)]$$

For a long nanowire, the depolarization factors satisfy $L_{||}<<1$ and $L_{\perp}\approx 0.5$. In our experiment, the nanowire is much more conductive than the fluid i.e. $\sigma_2>>\sigma_1$ and $L_{||}\sigma_2>>\sigma_1$. Therefore,

$$\tau_{//} \approx \frac{\varepsilon_1}{L_{//}\sigma_2} \quad \chi_{//}^\infty - \chi_{//}^0 \approx \varepsilon_1(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} - \frac{1}{L_{//}}) \approx -\frac{\varepsilon_1}{L_{//}}$$
$$\tau_{\perp} \approx \frac{\varepsilon_1 + \varepsilon_2}{\sigma_2} \quad \chi_{//}^\infty - \chi_{//}^0 \approx 2\varepsilon_1(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} - 1) = -4\varepsilon_1\frac{\varepsilon_1}{\varepsilon_2 + \varepsilon_1}$$

Torque T can be simplified as:

$$\Gamma = \frac{1}{2} V \varepsilon_1 E^2 [\frac{1}{L_{//}} \frac{\omega\tau_{//}}{1+(\omega\tau_{//})^2} + \frac{\omega\tau_{\perp}}{1+(\omega\tau_{\perp})^2} \frac{4\varepsilon_1}{\varepsilon_1+\varepsilon_2}]$$

Our experiment works in the frequency range where $\omega\tau_{||}$>>1 and the angular velocity of nanorod rotation can be written as:

$$\Omega = \Gamma / \gamma = \Omega_0 [\frac{1}{\omega\tau_{12}} + \frac{4\omega\tau_{12}}{1+(\kappa\omega\tau_{12})^2}]$$

$$\tau_{12} = \frac{\varepsilon_1}{\sigma_2} \quad \kappa = 1 + \frac{\varepsilon_2}{\varepsilon_1} \quad \Omega_0 = \frac{V\varepsilon_1 E^2}{2\gamma}$$

where γ=6$\eta Vp(R)$ is the rotational friction (or drag) coefficient. η is the viscosity of the fluid, $p(R)$ is the Perrin factor and is defined as:

$$p(R) = \frac{2}{3R} \frac{(R^2+1)(R^2-1)^{3/2}}{(2R^2-1)\ln(R+\sqrt{R^2-1}) - R\sqrt{R^2-1}}$$, where $R = \frac{l}{d}$.

As seen in figure S5, the angular velocity is almost inversely proprotional to $\omega\tau_{12}$ and therefore the angular velocity can be simplified as:

$$\Omega = \frac{E^2\sigma_2}{12\eta p(R)\omega}$$

The derivation of $L_{||}$ and $L_{\perp}$: $L_{//} = \frac{ab^2}{2}\int_0^{\infty} \frac{ds}{(s+a^2)^{2/3}(s+b^2)} = \frac{b^2}{2a^2e^3}\left[\ln\left(\frac{1+e}{1-e}\right) - 2e\right]$ and

$L_{\perp} = (1-L_{//})/2$, where $e = \sqrt{1-b^2/a^2}$. For the nanorod (high elongated), $a >> b = c > o$, so that $L_{||}$<<1 and $L_{\perp}$≈0.5.

Detailed analysis of the upper value of this transition time: The relaxation time to reach a stable excess charge carrier concentration is closely related to the lifetime of charge carriers, typically in the range of 10^{-9} s.[2] The characteristic time of charge transport inside the nanowire can be estimated as:

$$t_1 = l/(\mu E)$$

where l (~10^{-6} m) is the length of the wire, μ (~10^{-3} m^2/V/s) is the carrier mobility, E (~10^5 V/m) is the strength of the applied electric field. This characteristic carrier transport time is thereby in the order of 10^{-8} s. Meanwhile, there's another relaxation time, namely the velocity relaxation time of the colloidal particles and it can be estimated as:

$$t_2 = \rho l^2/\eta$$

where ρ (~10^4 kg/m^3) is the density of the nanowire, l (~10^{-6} m) is the length of the wire and η (~10^{-3} Pa·s) is the viscosity of the fluid. [3] This relaxation time is approximately 10^{-5}s and is obviously the slowest process. As a result, the response time between the ON and OFF states is approximately in the order of 10^{-5} s and it depends on the size, density of the particle as well as the viscosity of the fluid.

The dynamics of carrier generation and recombination: The carrier generation and recombination dynamics is typically governed by the following dynamical relation:

$$\frac{d\Delta n}{dt} = G - A\Delta n - B\Delta n^2 - C\Delta n^3$$

where G is the generation rate proportional to the light intensity, Δn is the excess carrier concentration. A, B and C are the rate coefficients for SRH trap assisted recombination, radiative recombination and Auger recombination. At steady state, $d\Delta n/dt$=0 and the excessive carrier concentration is related to the generation rate as:

$$G = A\Delta n + B\Delta n^2 + C\Delta n^3$$

When the light intensity is low, the linear term dominates and one expects a linear relation between conductivity and light intensity since $G \propto I$ and $\sigma_2 \propto \Delta n$. For more intense light, higher order terms such as radiative recombination ($B\Delta n^2$), Auger recombination ($C\Delta n^3$) start to kick in, which results in a nonlinear relation between G and Δn causing the deviation from the linear trend shown in figure 4b.

Experimental Section

Materials: cesium bromide (CsBr, 99.9%), lead iodide (PbI_2, 99.9%), dimethyl sulfoxide (DMSO, 99.8%), octadecylamine (OAm, 97%), acetate (HAc, 99.8%) and tetradecane (99%) were purchased from Aladdin and used without further purification.

Preparation of the $CsPb(Br/I)_3$ nanorods: 0.6 mmol CsBr and 0.3 mmol PbI2 were dissolved in 5 ml DMSO as precursor. 0.15 ml of the precursor was mixed with 1 ml 0.2 g/ml octadecylamine/acetic acid solution under magnetic stirring. The solution was sonicated for 15 min, then 15 ml of toluene was added into the solution. After 5 mins of reaction, the products were extracted by centrifugation (5000 rpm×1 min) and were washed using toluene, the washing-centrifugation cycle was repeated twice. The precipitates were then redispersed in 20 ml tetradecane for further characterizations. It should be noted that owing to the fast

ionic reaction process and the spontaneous phase-transformation, the obtained nanorotors own a certain digree over length and size. This provides solid experimental base for selecting nanorotors with desired sizes when exploring related phenomenon.

Preparation of perovskite nanorods film: For preparing the perovskite nanorods film, perovskite nanorods were firstly disperse in toluene, the dispersion was then dropt onto a glass substrate of 2*2 to form a dense film. The film was heated on a hot plate of 70℃ until all the toluene were evaporated.

Experiment Setup: We fabricated a quadruple electrode on the glass substrate to generate the rotating electric field. It consists of two sets of parallel electrodes and the gap between the opposite electrodes is about 2 millimeters. Two AC voltages with 90^0 phase difference are applied to the two sets of electrodes respectively. The signal generator controls the phase and frequency on the signal while the signal amplifier controls its amplitude. The perovskite nanorods colloid is dropped at the center of the quadruple electrode for test, the rotation of perovskite nanorods is recorded by an optical microscope (CORRECT SEIWA OPTICAL CO.,LTD.)

Characterizations: The XRD experiment was perfoemed using a Bruker D8 Advance XRD system. SEM images were captured by a Quant 250FEG instrument. The absorption and photoluminescence spectra were measured by a SHIMADZU UV-3600 UV-VIS-NIR spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer, respectively. All the device characterizations were conducted at room temperature in ambient air.

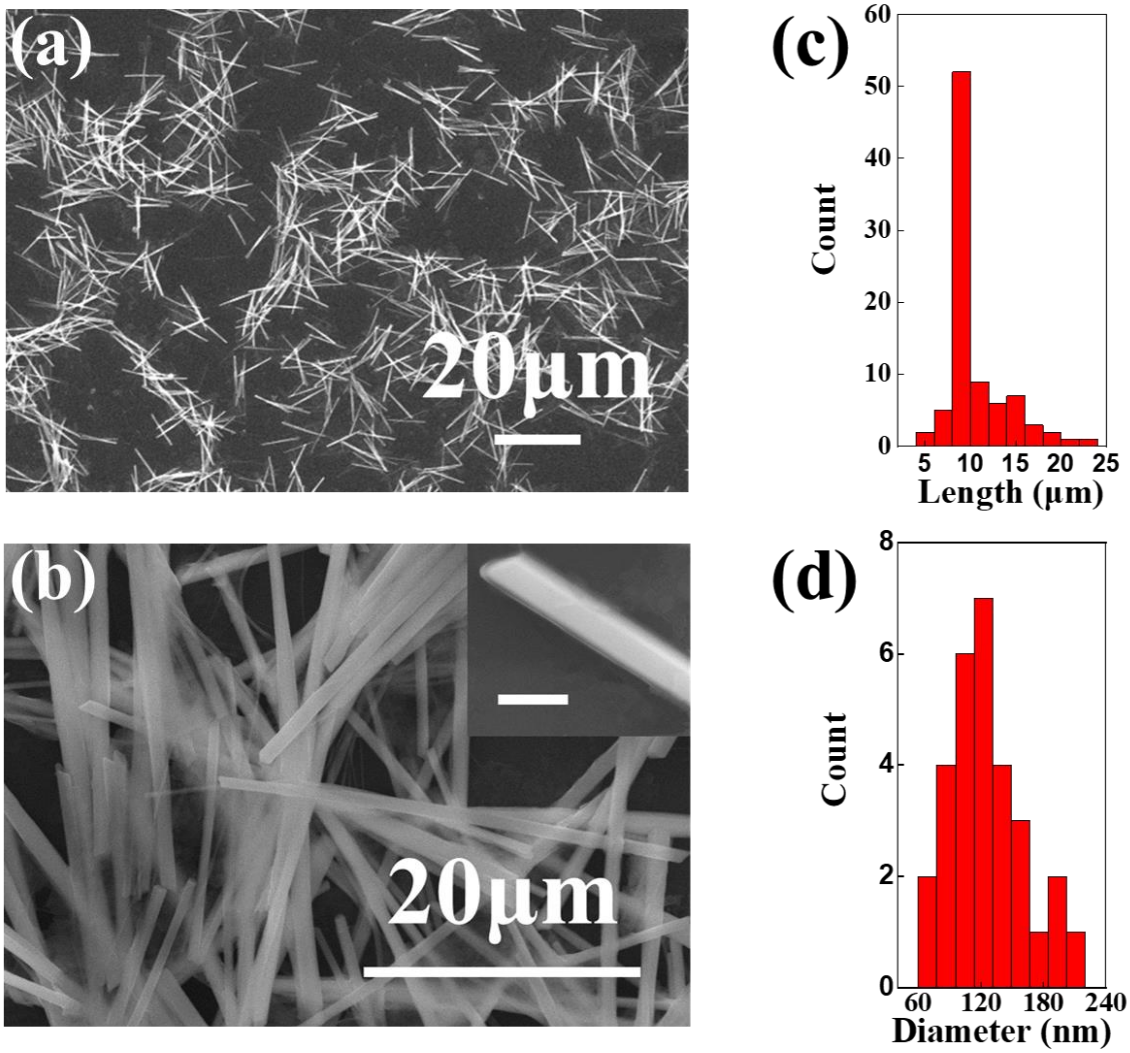

Figure S1. Characterizations of the $CsPb(Br/I)_3$ nanorods. (a) and (b) SEM image of the $CsPb(Br/I)_3$ nanorods. Inset: magnified image of individual nanorod, the scale bar is 500 nm. (c) Histogram of length distribution of the $CsPb(Br/I)_3$ nanorods. (d) Histogram of diameter distribution of the $CsPb(Br/I)_3$ nanorods.

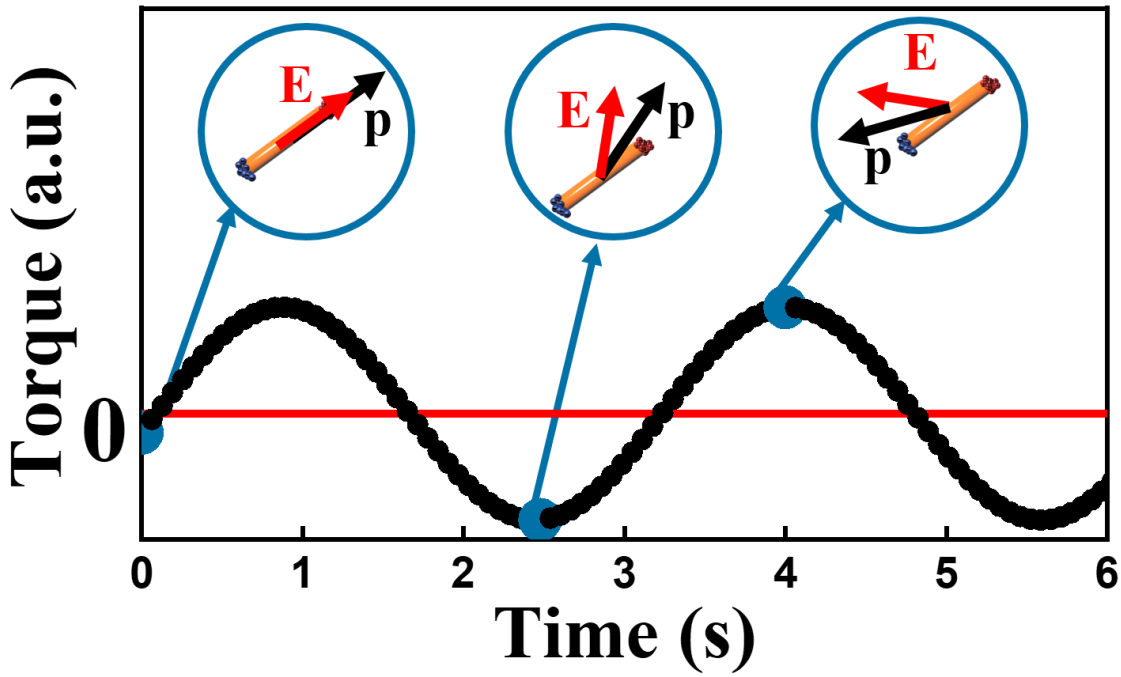

Figure S2. The instantaneous torque load on rotors. Inset: the orientation of electric field and polarization at different times.

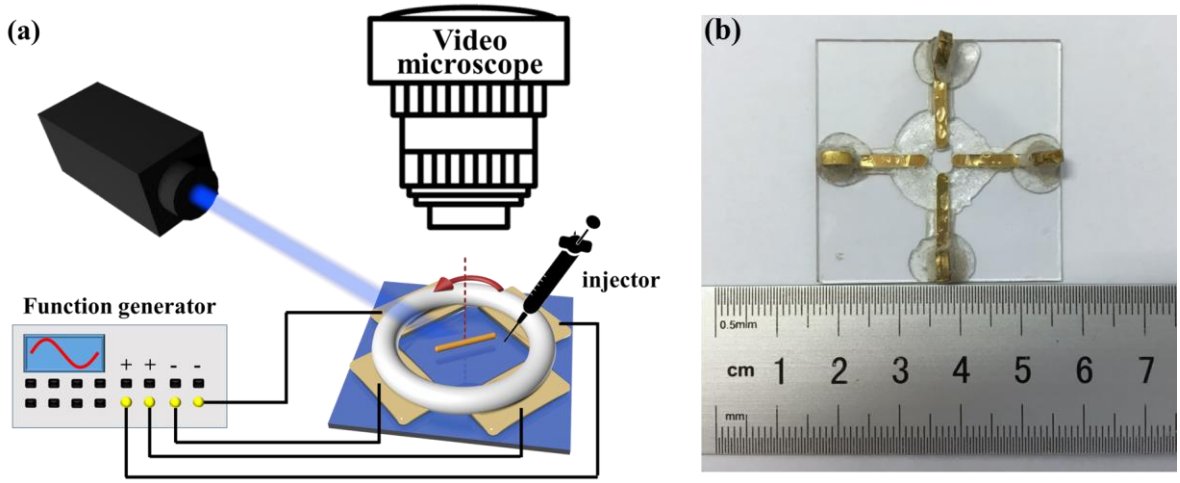

Figure S3. (a) Schematic diagram of the experiment setup. (b) Photo of the quadruple electrode

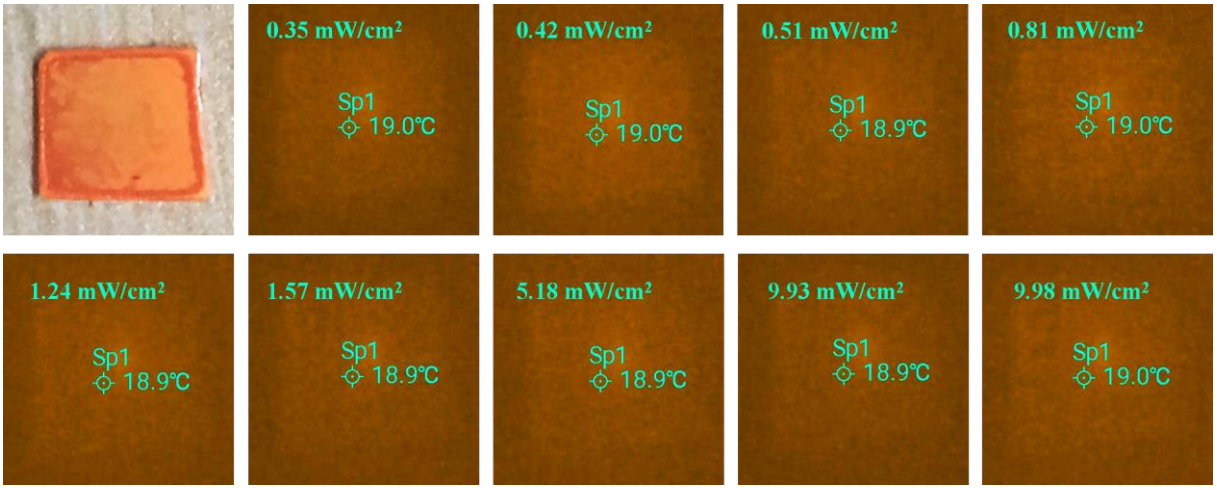

Figure S4. Infra-red photos of perovskite nanorods films under different light intensity.

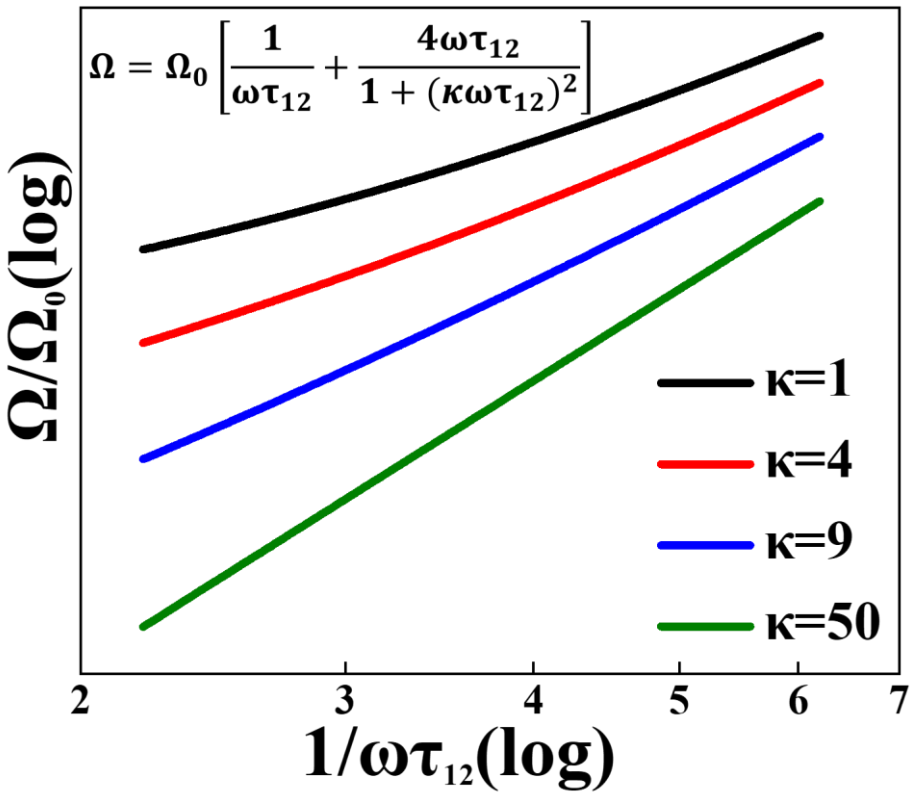

Figure S5. The curves of equation $\Omega = \Gamma / \gamma = \Omega_0[\frac{1}{\omega\tau_{12}} + \frac{4\omega\tau_{12}}{1+(\kappa\omega\tau_{12})^2}]$ with various parameter κ.

[1] T. B. Jones, *Electromechanics of particles*, Cambridge University Press, Cambridge ; New York 2005.

[2] M. B. Johnston, L. M. Herz, Acc Chem Res 2016, 49, 146.

[3] Brennen, Christopher E, *Fundamentals of multiphase flow (Reprint. ed.)*, 2005.