Supplementary Materials for

Unraveling the physiochemical nature of colloidal motion waves among silver colloids

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Published 25 May 2022, Sci. Adv. 8, eabn9130 (2022)
DOI: 10.1126/sciadv.abn9130

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Other Supplementary Material for this manuscript includes the following:

Movies S1 to S11
**Supplementary Text**

**Ballistic wave at low population density**

PMMA-Ag colloids (population density $\phi$ of 1.3%) were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$, 400 µM KCl, under UV illumination of 230 mW/cm$^2$. Fig. S2, A and B shows activated colloids at a wavefront move ballistically in all directions prescribed by their own Janus interfaces as a result of their phoretic self-propulsion.

**Swarming wave at high population density**

Janus PMMA-Ag microspheres of a population density of 26% were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$ and 200 µM KCl under UV illumination of 43 mW/cm$^2$, and colloidal waves emerged. Fig. S2, C and D shows Janus colloids in the wavefront collectively moving towards the incoming wave regardless of their Janus interface. The moving direction of a colloid is aligned to the wave direction rather than their own Janus interfaces.

**Coexisting feature of ballistic wave and swarming wave**

The results of coexisting feature of ballistic wave and swarming wave at an intermediate population density (11.6%) are shown in fig. S2E. There is the feature of a ballistic wave in fig. S2F where a Janus colloid at a wavefront moves away from its Ag cap. There is also the feature of a swarming wave where a second Janus colloid at the same wavefront moves towards the incoming wave regardless of their Janus interface in fig. S2G.

**Definition of amplitude, phase, and speed of colloidal wave**

From Fig. 3B, we can find a set of time $t_i$ when particle velocity in this position reaches maximum speed. For each point in time, we can define the phase of the system with following equation:

$$\phi = 2\pi \frac{t-t_i}{t_{i+1}-t_i} \ (t_{i+1} > t > t_i) \quad \text{Eqn. S1}$$

In our system, we define the amplitude $y_{peak}$ of colloidal wave as peak velocity of particle along the y direction at certain time in Fig. 3C. As a result, the instantaneous propagation speed of a wave is:

$$v_{wave} = \frac{dy_{peak}}{dt} \quad \text{Eqn. S2}$$

**Calibration of the fluorescent intensity of Solvent Green 7 in different pH**

A series of standard pH solutions were prepared and mixed with 100 µM of Solvent Green 7. We then applied blue light (475 nm, 75 mW/cm$^2$) produced by filtering a halogen lamp light via fluorescent cube (model FITC) to excite the dye solution in different pH, and recorded with imageJ the average fluorescent intensity defined by the pixel grey value of optical micrographs captured at different pH. Results are shown in fig. S3.

**Experimental validation of equation 1 and 2 by pH measurement**
The change in solution pH was measured by a pH meter (PHS-3E, Shanghai Leici) during the photodecomposition of AgCl (Eqn. 1 in the main text) and the oxidation of Ag back into AgCl (Eqn. 2). For Eqn. 2, we added an 0.5 w.t.% H$_2$O$_2$ solution to a suspension of Ag colloids and 200 μM KCl in the absence of light. As shown in fig. S5A, the solution pH value increased from 5.9 to 9.6 in 1 min upon addition of H$_2$O$_2$, consistent with the oxidation of Ag into AgCl by H$_2$O$_2$ that releases OH$^-$. For Eqn. 1, we measured the pH of AgCl colloids suspended in DI water. As shown in fig. S5B, the global pH value decreased from 6.5 to 4.6 upon turning on UV light of 43 mW/cm$^2$, consistent with the photodecomposition of AgCl into Ag that releases H$^+$. Numerical method of simulation based on the reaction-diffusion model

Numerical simulation was performed on a 256×256 grid on a 2D plane. The length unit in the simulation is the width of the grid, noted dx. For any position $X(x, y)$ in this area ($0 < x < 256dx, 0 < y < 256dx$), $I_{\text{pattern}}(X)$ shows the light distribution:

$$I_{\text{pattern}}(X) = \begin{cases} 1 & (X \text{ in the lighted region}) \\ 0 & (X \text{ in the dark region}) \end{cases}$$

Eqn. S3

The concentration of the activator and inhibitor are functions of time and position, termed $u(X, t)$ and $v(X, t)$. Rogers-McCulloch model shows the concentration distribution as follows:

$$u(x, y, t + \tau) - u(x, y, t) = D\tau(u(x + dx, y, t) + u(x - dx, y, t) + u(x, y + dx, t) + u(x, y - dx, t) - 4u(x, y, t))dx^{-2} + c_1u(x, y, t)(u(x, y, t) - u_c)(1 - u(x, y, t))I_{\text{pattern}}(x, y)\tau - c_2u(x, y, t)v(x, y, t)I_{\text{pattern}}(x, y)\tau$$

Eqn. S4

$$v(x, y, t + \tau) - v(x, y, t) = \varepsilon(u(x, y, t) - kv(x, y, t) - b)I_{\text{pattern}}(x, y)\tau$$

Eqn. S5

with a closed boundary condition:

$$\frac{\partial u}{\partial n} = 0$$

Eqn. S6

The initial value is set as follows:

$$u(X, 0) = \begin{cases} 1 & (X \text{ in the source region}) \\ 0 & (\text{otherwise}) \end{cases}$$

Eqn. S7

$$v(X, 0) = 0$$

Eqn. S8

For plane and spiral waves, the source region is one or two columns of the grid on the boundary. For target wave, the source region is a circular region at the center of the grid.

Then we use three major characteristic quantities to determine the parameters in this model:

1) The width of wave peak

Based on the Micro-PIV results from the rectangular light channel experiment, we can simulate the distance between the positive and negative maximum values of the chemical gradient in the
numerical model and determine the width of wave peak in simulation. This characteristic quantity determines the spatial scale in the numerical model.

(2) The wave speed in a rectangular light channel

After the spatial scale is determined, we can match the light pattern of the numerical model with the experiment setup. As shown in Fig. 8D, when the light channel width is above a certain value, the wave speed in the channel is a constant. Then we can extract the wave speed to determine the time scale in the simulation.

(3) The ratio of particle speed from both sides of wave peak

The shape of the wave peak in the simulation is determined by the ratio of particle speed from both sides of the wave peak in the rectangular light channel experiment. This characteristic of wave peak shape is shown intuitively in Fig. 6.

Using these three characteristic quantities, the parameters of the model is chosen as follows: \( u_c = 0.0075, c_1 = 2.5, c_2 = 2.4, \epsilon = 0.033, k = 0.25, b = 0, D = 1.2 \). Moreover, \( dx = 1 \) represents 2.083 \( \mu \text{m} \) in the experiment and \( \tau = 0.15 \) represents 1.79 ms in real time.

To simulate spiral waves or waves traveling in ring-shaped patterns, we need to break the symmetry of the wavefront. First, we set \( u(x < 2dx, 0) = u_c \) and created a plane wave that travels along the X-axis. When the wavefront position is about 128dx at a certain time point \( t_c \), we reset \( u(y > 128dx, t_c) = 0 \) and \( v(y > 128dx, t_c) = 0 \). Then we can get spiral waves in the uniform light region and traveling waves in ring-shaped patterns.

To trigger the wave periodically, we applied a constant potential gradient of \( u \) on the source region, whose value is the maximum gradient in the wave direction. This gradient can continuously produce a constant \( u \) value, while it can be erased by \( v \). After \( v \) is below a certain value, \( du/dt \) on the left boundary can be above zero, then another wave is triggered. This wavelength shows the intrinsic period of the chemical reaction. The region of the simulation zone can be altered if necessary.

Because no wave was generated out of a background of a uniform concentration of activator, we suspect that both types of waves originate from a denser patch of colloids as a result of the inevitable fluctuation of population density in an experiment.

**Numerical simulations containing discrete micro-objects**

Discrete micro-objects with 4dx diameter circles are generated by a series of points with their coordinates \( \mathbf{r}_i \) (i is the serial number of the object). These points are randomly positioned in the simulation zone by \textit{rand function} with around 50% packing fraction (fig. S11A). We use binarized variables \( P_{\text{pattern}}(\mathbf{X}) \) to define whether one point is in the neighborhood of a micro-object or not.

\[
P_{\text{pattern}}(\mathbf{X}) = \begin{cases} 
1 & (\exists i, |\mathbf{X} - \mathbf{r}_i| \leq 2dx) \\
0 & (\text{otherwise}) 
\end{cases}
\]

Eqn. S7

Then we use \( I_{\text{pattern}}(\mathbf{X}) \) instead of \( I_{\text{pattern}}(\mathbf{X}) \) to make sure the chemical reaction only takes place near the surface of micro-objects. The propagation of wave through discrete micro-objects is similar to our homogeneous model (fig. S11B), with a slightly lower wave speed.
Quantitative agreement of wave speeds between experiment and simulation in ring-shaped patterns

The wave speeds obtained from experiments and simulation in the ring-shaped pattern are shown in fig. S8. Using structured light, oscillating colloids were exposed to a ring-shaped illuminated pattern with an outer and inner radius of 200 and 100 μm, respectively (fig. S8A). In the beginning, waves originated at random positions and traveled along the circle with no preferential chirality. After fusion and annihilation over time, waves began to rotate persistently around the annular ring (fig. S8, B and C), with a clockwise or counter-clockwise handiness in equal probabilities. Moreover, as with the case of rectangular patches (Fig. 7D in the main text), waves in rings of larger diameters traveled faster, but only for annular rings with a fixed outer radius and a varying inner radius (fig. S8G). On the other hand, wave speed was not sensitive to the change of the outer radius if the inner diameter is fixed (fig. S8H). We note that our numerical model reproduces traveling waves in ring-shaped pattern in fig. S8, D-F and predicts a slightly higher (6%) angular velocity than experiments for waves traveling in annular rings with varying outer diameters (fig. S8E), possibly because of the inevitable consumption of H$_2$O$_2$ over the course of the experiment, which is not considered in our models.

Colloidal waves produced by pure Ag particles and an Ag-coated glass slide

fig. S12A shows a colloidal wave propagating across a population of pure Ag particles in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 400 μM when illuminating UV light at 200 mW/cm$^2$. The Ag-coated substrate was prepared by sputtering 20 nm Ag on a typical glass slide. A solution containing 200 μM KCl, 0.5 w.t.% H$_2$O$_2$, and 2 μm SiO$_2$ tracer particles was transferred onto the Ag-coated slide. Upon illumination of UV light with 43 mW/cm$^2$, traveling motion waves of SiO$_2$ tracers can be observed in fig. S12B. See also Video S10.
Fig. S1. Waves under different light intensities in the experiment (18% population density, 0.5 wt% H$_2$O$_2$, and 200 μM KCl). More chaotic waves are found at higher light intensity.
Fig. S2. Propagation of a ballistic wave (A, B), a swarming wave (C, D) and a wave exhibiting both features (E-G). (A, B) Optical micrograph (A) and schematic (B) of a ballistic wave where Janus particles at wavefront move in directions prescribed by their own Janus orientations. (C, D) Optical micrograph (C) and schematic (D) of swarming wave where Janus particles at a wavefront move towards the incoming wave regardless of their Janus interfaces. (E) Optical micrograph of a colloidal wave exhibiting both features. (F) a Janus particle circled in (E) moves away from its metal cap. (G) a Janus particle at the same wavefront moves in a direction unrelated to its Janus interface. In all figures, Janus particles moving faster than 6 µm/s are marked as red dots and their instantaneous velocities (both the direction and the magnitude) are marked as blue arrows. Particle population density $\phi$ is 1.3% in a), 26% in c) and 11.6% in e).
Fig. S3. Calibration curve of the relationship between the fluorescence intensity of 100 μM Solvent Green 7 and solution pH. Inset: optical micrographs of fluorescence dye solution at different pH (scale bar=5 μm). Error bars are the standard deviation of ~10000 pixel grey values in the optical micrographs. The red line is sigmoidal fit.
**Fig. S4.** Optical micrographs of the pH profile overlaid with micro-PIV tracking of a colloidal wave. PMMA-Ag colloids (population density $\phi$ of 25%) were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$, 200 $\mu$M KCl, and 100 $\mu$M Solvent Green 7, under UV illumination of 43 mW/cm$^2$. The color legend to the right corresponds to PIV tracking.
Fig. S5. Experimental validation of equation 1 and 2 by pH measurement. (A) pH measurement of adding 0.5 w.t.% H$_2$O$_2$ into an aqueous suspension of Ag colloids and 400 μM KCl in the absence of light. (B) pH measurement of illuminating an aqueous solution containing AgCl colloids in the absence of H$_2$O$_2$ with UV of 43 mM/cm$^2$. 
Fig. S6. Oscillation frequency of individual PMMA-Ag micromotor (red) and colloidal wave (blue) at different concentrations of NaOH. Colloids were suspended in an aqueous solution containing 0.5 w.t.% H₂O₂ and 400 μM KCl under UV illumination of 500 mW/cm² for single motor experiments, and colloids (population density $\phi$ of 13.1%) were suspended in an aqueous solution containing 0.5 w.t.% H₂O₂ and 200 μM KCl under UV illumination of 43 mW/cm² for experiments of colloidal waves.
Fig. S7. The relationship between speeds of PMMA-Ag particles at a ballistic wavefront and salt concentration (KNO₃) in the bulk solution. Inset shows the linear relationship between particles speed and the inverse of the salt concentration. Red dash line is a linear fit through the origin. PMMA-Ag Janus particles (population density ϕ of 1.2%) were suspended in an aqueous solution containing 0.5 w.t.% H₂O₂, 400 μM KCl under UV illumination of 230 mW/cm².
Fig. S8. Dynamics of waves in ring-shaped light patterns. (A) A ring-shaped light pattern with (B) Micro-PIV of a colloidal wave propagating in the ring-shaped light pattern described in a). (C) Kymograph generated by the circumferential midline of the ring in (B). (D-F) Simulations corresponding to (A-C). (G, H) Experimental (points) and simulated (lines) wave speeds in ring-shaped patterns with a fixed outer radius (400 μm) and a varying inner radius (G), and in ring-shaped patterns with a fixed inner (150 μm) radius and a varying outer radius (H). In all experiments, PMMA-Ag colloids of a population density of 19% were suspended in an aqueous solution containing 0.5 w.t.% H₂O₂ and 200 μM KCl under 405 nm illumination of 1.6 W/cm².
Fig. S9. Waves in a rectangular light pattern with a dark segment. (A) Schematic of a rectangular-shaped light pattern of 490×100 μm with a dark segment of 75×100 m μm in the middle. (B) Micro-PIV generated image of wave propagating (left), fading (middle), and disappearing (right) in the rectangular-shaped light pattern.
Fig. S10. A wave stopping at an illuminated slit of 5 (A, B) or 20 (C, D) µm in width. (A) Schematic of a rectangular-shaped light pattern of 490×100 µm with a bright slit of 5 µm in width in the middle. (B) Micro-PIV generated image of wave propagating (left), fading (middle), and disappearing (right) at the narrow light channel. (C, D) Similar results from a 20 µm slit.
Fig. S11. Simulated chemical waves traveling in homogeneous (top) and heterogeneous (bottom) media. For the latter case, simulations were performed with 15000 micro-objects of 4dx diameters arranged randomly (see supplemental text for details).
Fig. S12. Optical micrograph overlaid with micro-PIV tracking showing the propagation of a motion wave of pure Ag particles (A) and SiO$_2$ tracer particles on a Ag-coated glass slide (B). Pure Ag particles with $\phi$ of 28% were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$ and 400 μM KCl under UV illumination of 200 mW/cm$^2$. SiO$_2$ tracer particles with $\phi$ of 18% were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$ and 200 μM KCl under UV illumination of 43 mW/cm$^2$. See supplemental text for fabrication details.
**Movie S1.**
Typical dynamics of oscillating PMMA-Ag Janus micromotors. PMMA-Ag Janus micromotors exhibit oscillatory motion in an aqueous solution containing 1 wt % H$_2$O$_2$ and 400 μM KCl, illuminated with a UV LED lamp at 365 nm and 500 mW/cm$^2$ intensity applied from above. Video plays at 5 times faster.

**Movie S2.**
A representative “ballistic wave” among Janus PMMA-Ag colloids. PMMA-Ag Janus microspheres (population density of 1.3%) were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$ and 400 μM KCl, and illuminated with UV of 230 mW/cm$^2$. The left panel shows the original video. In the right panel, the active Janus particles (speed above 5 μm/s) and their velocity vectors are marked with light blue dots and orange arrows, respectively.

**Movie S3.**
A representative “swarming wave” among Janus PMMA-Ag colloids. PMMA-Ag Janus microspheres (population density of 29%) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 200 μM, and illuminated with UV LED lamp operating at 43 mW/cm$^2$. The left panel shows the original video where colloids sequentially move from top to bottom. In the right panel, particles velocity (both the magnitude and the direction) were labeled with arrow, so that those moving towards an incoming wave and faster than 4.3 μm/s were in orange and those trailing a wave faster than 2.2 μm/s were in dark blue. Speed cutoff values are arbitrary.

**Movie S4.**
A presentative wave exhibiting both ballistic and swarming features. PMMA-Ag Janus microspheres (11.6% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 400 μM, and illuminated with UV LED lamp operating at 230 mW/cm$^2$. The left panel shows the original video where colloids sequentially move from top to bottom. In the right panel, the active Janus particles (speed above 5 μm/s) and their velocity vectors are marked with light blue dots and orange arrows, respectively.

**Movie S5.**
Colloidal waves under different UV intensities. At a low light intensity of 14 mW/cm$^2$, a colloidal wave propagates outward in a concentric circle without encountering other waves. Upon increasing light intensity, more colloidal waves are generated and annihilate with each other over time, resulting in many scattered spiral waves in the field of view. Wavefronts in the experiment were visualized by micro-PIV so that color-coded arrows indicate the local flow velocities. PMMA-Ag colloids (18% population density) were suspended in an aqueous solution containing 0.5 w.t.% H$_2$O$_2$ and 200 μM KCl, and illuminated by UV light at labeled intensities.

**Movie S6.**
Green fluorescent waves across a dark background during the propagation of colloidal waves. PMMA-Ag Janus colloids (25% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.%, KCl of 200 μM and 5mM pH-sensitive fluorescence dye Solvent Green 7, and illuminated with a blue light source (470 nm, 75 mW/cm$^2$). The left panel shows a green wave across a relatively darker background. The right panel shows a colloidal wave (wavefronts were visualized by color-coded arrows from the Micro-PIV technique) across the population of Janus colloids for the same video.
**Movie S7.**

Bubbles are produced primarily at wavefronts when colloidal waves sweep across a population of Janus colloids. PMMA-Ag Janus microspheres (25% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 1 w.t.% and KCl of 200 µmol/L, and illuminated with UV LED lamp operating at 200 mW/cm$^2$.

**Movie S8.**

A single propagating green fluorescent wave generated upon turning off the UV light. PMMA-Ag Janus colloids (24% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.%, KCl of 200 µM, and 100 µM fluorescent dye of Solvent Green 7. They are illuminated with two lamps: a blue light (470 nm, 10 mW/cm$^2$) that is capable to excite the dye molecules but incapable of generating the colloidal wave, and a UV light (365 nm, 43 mW/cm$^2$) that is capable of generating the colloidal wave. When the UV lamp is turned off, A single propagating green fluorescent wave is generated that sweeps across the colloidal population.

**Movie S9.**

Janus colloids moving upward and out of focus at a wavefront. PMMA-Ag Janus microspheres (14% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 200 µM, and illuminated with UV LED lamp operating at 43 mW/cm$^2$. Upon meeting a wavefront, Janus colloids move upward and out of focus, and settle back down after the wave passes.

**Movie S10.**

Qualitative comparison between simulation and experiments for target waves (a), spiral waves (b), annihilation of two waves (c) and periodic waves (d). Wavefronts in the experiment were visualized by color-coded arrows that indicate the local velocity from the Micro-PIV technique. All experiments were performed at 20% population density, 0.5 wt% H$_2$O$_2$, 200 µM KCl, 43 mW/cm$^2$ light intensity, except for S10a and d, which had a population density of 15% and 23%, respectively.

**Movie S11.**

Colloidal waves propagating across a population of pure Ag colloids (left), and SiO$_2$ tracer particles on the Ag-coated substrate (right). Pure Ag microspheres (19% population density) were suspended in an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 400 µM, and illuminated with a UV LED lamp operating at 200 mW/cm$^2$. 2 µm SiO$_2$ tracer particles were transferred into a chamber containing Ag-coated substrate prepared by sputtering 20 nm Ag layer and an aqueous solution containing H$_2$O$_2$ of 0.5 w.t.% and KCl of 200 µM, and illuminated with UV LED lamp operating at 43 mW/cm$^2$. Video plays 3 times faster.