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ABSTRACT
A nanosecond time-resolved imaging technique has been developed for the observation of the photo-excited charge carrier dynamics in photo-devices such as photocatalysts and solar cells. An arbitrary spatial pattern of pump pulse light excites the charge carriers, which are observed by phase-contrast imaging. This patterned excitation is preferable for various statistical image reconstruction techniques based on robust principal component analysis and the least absolute shrinkage and selection operator, which helped the enhancement of the signal-to-noise ratio and the removal of unwanted image components. By using data assimilation with the charge decay model, the lifetime and diffusion coefficients were mapped for the photo-excited electrons in a nano-particulate titanium oxide film and other photo-device materials.© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/5.0009312

INTRODUCTION
Solar-devices are in global demand to address the lack of energy resources because the sunlight could potentially provide 10 000 times more energy than the amount needed by humans. Among photo-devices, inexpensive and easily processed solar cells have been developed, including perovskite\(^{1–3}\) and sensitized solar cells.\(^{4–6}\) Photocatalysts have also been utilized for the decomposition of pollutants in air and water\(^{7}\) and have been developed intensively for the water splitting into oxygen and hydrogen these days.\(^{8}\)

Most photo-devices use semiconductor layers, which are obtained by coating dispersion solutions or reacting precursor solutions to form a light-absorption layer, a charge carrier transport layer, and a passivation layer. Various oxide or sulfuric layers have been utilized, such as TiO\(_2\), Fe\(_2\)O\(_3\), Cu\(_2\)O, PbS, CdS, and CdSe.\(^{9}\) Furthermore, various structures have been demonstrated to increase the active surface area and to enhance the transport of charge carriers, such as rods, tubes, and inverse opal structures.\(^{10}\)

In photo-devices, a key factor is how efficiently photo-excited charge carriers are separated and utilized without loss due to recombination and charge trapping in inactive trap states.\(^{11}\) In photocatalytic systems for water splitting, photo-excited electrons are used for reduction reactions, and photo-excited holes are used for the oxidation reactions, meaning hydrogen and oxygen generation. The lifetime and transport properties of charge carriers need to be obtained to understand the charge separation processes, improve them, and prevent recombination.

If we would only need the physical properties such as lifetime and mobility of charge carriers, referring from the literature values of single crystals, there would not be a difficult problem, but it is noted that the layers in photo-devices are usually porous and rough on the surface because they are made from nano-particles. A 1-cm\(^2\) film could have millions of interfaces in a single dimension, causing various interfaces, aggregates, cracks, and scratches at multiple scales, which are defects that greatly affect the charge carrier behavior. Various photocatalytic materials show multi-order exponential decay of photo-excited charge carriers from femtoseconds to milliseconds, such as TiO\(_2\),\(^{12–15}\) SrTiO\(_3\),\(^{16,17}\) BiVO\(_4\),\(^{18}\) WO\(_3\),\(^{19}\) and Fe\(_2\)O\(_3\).\(^{20–22}\) However, for a single-crystalline solid, the decay of charge carriers shows a single exponential decay mostly within nanoseconds.\(^{23}\)
indicates that the charge carriers of particulate films are trapped in different types of traps, making the decay processes unique for each sample. To elucidate the problem, only the average time-response for the charge carriers is not sufficient to understand their behavior; instead, we need to observe the charge carriers locally according to the structure and/or position. Since the charge carriers in particulate films are trapped at various defects and could have various orders of lifetimes, they could be locally confined and also be transported.

There are several approaches to study these issues by combining time-resolved methods with microscopy. Transient absorption (TA) microscopy has been well established and used for studying nanomaterials and the diffusion of photo-excited carriers on an ultrafast time scale for the silicon nanowire and perovskite thin film. Charge carrier diffusion was analyzed using the shape change of a spot illuminated by a focused pump light on an ultrafast time scale, and multi-spot excitation by diffractive optics was also demonstrated. TA microscopy has also been improved by combination with super-resolution microscopy methods, such as stimulated emission depletion (STED) and structured illumination. This has allowed for the observation of smaller regions at faster time scales. However, it has not been utilized for time scales below the nanosecond time scale and large-area observation. Photoluminescence response has also been observed with a microscopy technique. In this technique, light emitted from photo-excited carriers is mapped out, and charge trapping locations are obtained. However, there are many non-radiative processes in the charge carrier dynamics, and only a part of the information about the charge carriers is obtained.

We have studied the charge dynamics for dye or quantum-dot-sensitized solar cells and water splitting materials using the transient grating (TG) method. In this method, the refractive index is used to monitor the photo-excited charge carrier dynamics. The change in refractive index provides a broad wavelength response and is sensitive to the dipole change at the interfaces, which is preferable for observing the charge transfer dynamics at interfaces. To study inhomogeneous charge decay processes in a wide temporal range, especially at a slower time scale, we used a measurement method with a wide temporal range and combined it with an analysis of the nonlinear least-square minimization with the maximum entropy (ME) for regularization. This provided the lifetime distribution instead of a single decay time and has been applied for the analysis of photocatalytic reactions at interfaces.

In this study, we developed a new type of microscope based on the refractive index measurement for a wide temporal range extending to the second order, where the local responses can be observed, including the charge carrier decay with transport processes. Furthermore, a wide spatial region on the order of hundreds of micrometers was imaged at once by introducing the whole-region imaging instead of the focused-beam scanning, which is typically used in the ultrafast TA microscopy and photoluminescence imaging. In our setup, both the pump light and the illumination light were wide-field illumination, although the pump light consisted of a series of point-sources generated by using a digital micro-mirror. The measurement time could be reduced without scanning the illumination light, and the pump light can cover the whole region by merely changing the patterns of the digital micro-mirror, controlled by a computer. We enabled this new imaging technique by utilizing various image reconstruction techniques that have been applied in the field of image recovery in data science. In addition, the physical properties were obtained using the data assimilation technique for mapping. The hardware and software of this new technique are introduced, and an example is demonstrated.

**PRINCIPLES AND EXPERIMENT**

Figure 1 shows the general concept of how to extract the charge carrier behavior at local positions. A particulate film substrate is illuminated with an arbitrary light pattern for the photo-excitation of charge carriers. The charge carriers decay or diffuse over time due to recombination, charge trapping, and transport, and the pattern of the charge carrier distribution varies over time. The distribution of the photo-excited charge carriers is observed via the change in refractive index by phase-contrast imaging. By observing the pattern changes, the decay time and the diffusion coefficient can be estimated. The pattern illumination is preferable not only for observation of the charge carrier diffusion but also for image processing, as will be explained below.

In general, the photo-excited charge carriers are separated into electrons and holes and are subject to decay processes, such as various trapping and recombination. The phenomenological decay processes of the charge carriers are expressed as

\[
\frac{\partial^2 N(r,t)}{\partial t^2} = D(\text{direction})\nabla^2 N(r,t) - \frac{N(r,t)}{\tau},
\]

where \(N(r,t)\) is the charge carrier density according to the position and time, \(D(\text{direction})\) is the direction-dependent

![FIG. 1. General concept of the pattern-illumination time-resolved phase microscopy. A pattern of illumination excites photo-excited charge carriers, causing the refractive index change in the same way as the pattern. The pattern change during the charge carrier decay is imaged via phase-contrast imaging. When the charge carriers diffuse, the refractive index pattern changes over time.](image-url)
The diffusion coefficient, and $\tau$ is the decay time. The diffusion coefficient is related to the mobility of charge carriers by Einstein’s relation as

$$\mu = \frac{e}{k_B T} D,$$

where $e$ is the unit charge and $T$ is the temperature.

For the demonstration of the measurement concept, a stripe pattern was used, which is the same as the transient grating excitation. The pattern was used to see if our concept would work for the analysis of photocatalytic materials. The optical setup of this method is shown in Fig. 2. The pump light was the third harmonics of an Nd:YAG pulse laser (pulse width: 5 ns, wavelength: 355 nm) (GAIA, Rayture Systems), and the probe light was the second harmonics of an Nd:YAG pulse laser (pulse width: 5 ns, wavelength: 532 nm) (GAIA, Rayture Systems).

The timing of these pulses was controlled by two function generators (WF1968, NF) triggered by a base clock (DF1906, NF). Each function generator controlled both the timing of the flash lamp and the Q-switch with a time resolution of 100 ps. The pump pulse light was reflected by using a digital micromirror device (DMD) (Light Crafter 4500, Texas Instruments), and the pattern was arbitrarily controlled by a computer. The image of the DMD mirror was relayed with a lens ($f = 100$ mm) and an objective lens (LUCPLFLN20x, Olympus) to irradiate the same pattern but reduced in size (1/14) onto a sample.

The pulsed illumination light was collimated with the pump light at a dichroic mirror and used to illuminate a sample. The transmitted light was imaged by using an objective lens (LUCPLFLN20x, Olympus) and a tube lens (TTL180-A, Thorlabs). A CMOS camera (MV1-D1024E-160, Photon Focus) with a sensor area of $10.9 \times 10.9$ mm$^2$ ($1024 \times 1024$ pixels$^2$) was used to obtain recordings. The central region in the vertical direction ($200 \times 1024$ pixels$^2$) was recorded to reduce the computation burden. Each image was averaged 3–5 times, depending on the S/N ratio of the image, and it takes about 5 s–10 s for the acquisition of each image.

The refractive index change can be imaged without apparent optical interference: Talbot self-imaging and the Schlieren imaging. At first, the time-resolved refractive index image was obtained by using the Schlieren imaging, where a part of the illumination light was phase-shifted to change the phase image into an amplitude image and was demonstrated for the millisecond dynamics of photo-responsive liquid crystals. However, we figured out that the quality of the time-resolved refractive index image obtained by the Talbot self-imaging was the same as the Schlieren imaging in the previous paper. In this technique, the image was defocused by a few micrometers to change the phase image into the amplitude image, and this led the spatial resolution about $3 \mu m$ under our optical setup. The refractive index imaging was optimized by maximizing the acoustic and the thermal gratings when the stripe pattern of the pump illumination was used, which was described in the previous paper. The density change due to the acoustic wave and the temperature change purely induces the refractive index change, which assures that the refractive index change was maximized to observe.

Even for the optimized condition for the refractive index imaging, it cannot avoid including the transient absorption response because the optical configuration for our measurement is almost the same as the transient absorption method. The inclusion of the transient absorption signal was avoided by the selection of the illumination light. At this probe wavelength, the transient absorption signal can be neglected based on the previous report. This could
be further confirmed by matching the focus position where only the transient absorption change could be imaged, but the signal response was negligible.

The diameter of the area irradiated by the pump pulse was 0.5 mm. The pump light intensity was 0.8 mJ/pulse, and the probe light intensity was 0.02 mJ/pulse, respectively. While varying the time delay between the pump and the probe pulse, a sequence of images was obtained and stored on a computer. The time resolution was limited by only the pulse width of the pump and probe light (5 ns).

For the demonstration measurement, a titanium dioxide (TiO$_2$) film with a thickness of $\sim$5 μm was utilized. A titania nanoparticle paste with anatase structure (PST-18NR, JGC Catalysts and Chemicals) was used for the deposition of a TiO$_2$ nano-particle film. It was coated on a glass slide (Matsunami Glass) with the doctor-blade technique, and it was sintered at 450°C for 2 h to remove all the solvents and chemicals included in the paste.

For other demonstrations, we used hematite ($\alpha$-Fe$_2$O$_3$) and a perovskite film made of methylammonium lead iodide (MAPI). For the preparation of a hematite film, $\beta$-FeOOH was grown on the fluorine-doped tin oxide (FTO) substrate ($\sim$7 Ω/sq, SOLARONIX) in a solution consisting of 0.15M iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O, 99.9%, Wako) and 1M sodium nitrate (NaNO$_3$, 99.9%, Wako), which was conducted at 100°C for 1 h. After rinsing, $\beta$-FeOOH was converted into hematite ($\alpha$-Fe$_2$O$_3$) by sintering the sample in a furnace at 650°C for 30 min in Ar gas. The thickness was about 500 nm.

For the preparation of MAPI, a precursor solution was prepared with lead iodide (PbI$_2$) and methylammonium iodide (MAI) mixed with dimethylformamide (DMF) (Tokyo Kasei). The solution was spin-coated on a substrate and recrystallized with diethyl ether. After annealing the substrate, a MAPI film with a thickness of 500 nm was obtained.

RESULTS AND DISCUSSION

Performance of microscopy: Spatial and temporal resolution

Image acquisition utilizing a general fast CMOS camera limits the time resolution to the millisecond order, which is not sufficient for the observation of the photo-excited charge carrier dynamics. Furthermore, the signal-to-noise (S/N) ratio becomes worse because of fewer photons in general fast image acquisition when the time resolution of the camera is reduced by decreasing the light exposure time. These problems could be solved by utilizing the pump-probe pulse imaging technique. The time resolution can be defined by the pulse width, and the number of photons is not sacrificed because the photons are confined during the pulse duration.

The spatial resolution for the charge carrier dynamics was on the order of ~20 μm in our previous transient grating setup. In this new setup, the pump light pattern was controlled by using a DMD mirror, and the DMD image was used to irradiate a sample surface, which provided better pump resolution. For the microscopy imaging, a general combination of an objective lens and a tube lens has improved the spatial resolution. For these combinations, the spatial resolution of the photo-excited charge carriers and the imaging quality have been improved.

Figure 3 shows sample image sequences for the line-pattern excitation and the dot-pattern excitation for a TiO$_2$ nanoparticulate film. The change in refractive index due to the decay of the photo-excited carriers was clearly observed. The line width and the dot diameter of the change in refractive index due to the photo-excited carriers were 3 μm, and the contrast was clear enough to analyze the charge carrier distribution.

Image reconstruction from noisy images

Depending on the image quality, we utilized three types of image recovery/correction calculations: (1) flat field correction,
(2) image reconstruction by the robust principal component analysis (RPCA), and (3) sparsity-based image recovery in the spatial frequency domain. These image recovery techniques have been developed in the field of the “image recovery” and are different from the data analysis techniques, conventionally used for the time-resolved spectroscopy such as the global analysis, where the temporally relevant spectral data are analyzed by various matrix decomposition techniques.

In the flat field correction, image flickering was removed, which is inevitable when using pulse-light illumination because it inherently includes fluctuations due to the pulse intensity and the heterogeneous spot intensity. To solve this problem, the background intensity was subtracted with a mean-value filter with a user-specified kernel function. Typical images before and after the processing are shown in Fig. S1 in the supplementary material. By applying this image processing, the background intensities were adjusted homogeneously, and the intensities in the excited regions were standardized.

In the second processing method, random patterns/noise can be removed from the image by judging the sparsity structure in each image, which have been typically used for the image reconstruction. In this processing, the image data are considered as a matrix \( A (M \times N = 200 \times 1024 \text{ pixels}) \), and the \( r \)-th largest PCA components in the matrix are kept after applying the following calculation:

\[
\text{Minimize } \| A - L \|_F \text{ subject to rank}(L) \leq r,
\]

where \( F \) indicates the Frobenius norm of the matrix and \( L \) is an image matrix consisting of the principal components with the same size as \( A \).

In this calculation, the error between the original image \( A \) and the low-rank image \( L \) is evaluated by the Frobenius norm. However, this calculation frequently does not work when outlier values are included. In the robust PCA (RPCA), the low-rank matrix and the error matrix are characterized by the following equation:

\[
\text{Minimize } \text{rank}(L) + \lambda \| S \|_0 \text{ subject to } A = L + S.
\]

However, the 0th norm and the rank function are difficult to solve because they are non-convex functions. Therefore, the calculation was modified as

\[
\text{Minimize } \| L \|_* + \lambda \| S \|_1 \text{ subject to } A = L + S,
\]

where \( S \) is the sparsity matrix of the image corresponding to the noise matrix and * indicates the nuclear norm of the matrix.

The image data have several patterns of numbers, which are regarded as components of the image data, and the data were categorized by using principal components included in the image data. The image data can be decomposed by the singular value decomposition with \( U \ast S \ast V \) matrix, where \( S \) is the eigenvalue matrix, \( U \) is the vertical line matrix, and \( V \) is the horizontal line matrix.

The image is regarded as a combination of the outer product of the vertical line vector of \( U \) and the horizontal line vector of \( V \). In this calculation, the principal and sparse noise components in the image can be iteratively separated. This separates the random structure due to error into a sparsity matrix, while the principal structure is maintained with the smallest number of structures. We know the optimal signal image because the pump intensity pattern is decided in advance, so we can adjust the hyperparameter in the algorithm to separate the signal and noise structures in matrices \( L \) and \( S \) (an example code is included in the supplementary material).

We found that the RPCA can be applied successfully to separate the structured pattern and coherent noise patterns without any prior information. One of the example images is shown in Fig. 4. The corresponding scree plot is also included, and it could be confirmed that the image could be recovered by several PCA components. In the coherent imaging, a laser was utilized for the illumination of a sample, where ring-patterns are usually observed due to dust or other objects in the optical path. This causes a type of light diffraction called a coherent moiré pattern, which is detected by a camera.
In the original PI-PM image, these coherent moiré patterns were recognized and separated by this process and could be removed.

The noise removal of the data for the dot-pattern excitation is shown in Fig. S2 in the supplementary material. The data were processed by the flat field correction and the RPCA reconstruction. Similar to the line-pattern excitation, the background correction and the noise reduction were properly applied for the dot-pattern excitation.

Another effective approach is image reconstruction using the least absolute shrinkage and selection operator (LASSO) in the spatial frequency domain. LASSO has recently been used for imaging applications in astronomy and material science for the selection of important structures or frequencies in the images, where sparse components are selected with an enhancement. In the PI-PM method, samples are excited with a periodical pattern of the pump light, and the distribution of the photo-excited charge carriers should have a similar pattern to the pump light pattern. Using this prior knowledge, the PI-PM image should have sparsity in the frequency domain in the lateral direction.

As an example, an image with a stripe-pattern excitation is shown in Fig. 5. Since the image has a periodic pattern in the lateral direction, the spatial frequency in the direction should be sparse, and the reconstruction calculation was processed as follows:

$$\text{Minimize} \| A_{true} - A \|^2 + \lambda \| \Phi(A) \|_1,$$

where $\Phi(A)$ indicates the Fourier spectrum of the image data in the lateral direction (example code is included in the supplementary material). However, this reconstruction technique could be applied in the case of periodic line-pattern excitation, but not for the dot-pattern excitation, obviously because it does not always have a periodic pattern in the lateral direction.

By the selection of combination of image processing techniques, the image was recovered with less noise and enhanced periodical components, as shown in Fig. 3. We always applied the flat field correction, which provided a positive effect on the improvement of the images. After this processing, we utilized either the RPCA or the LASSO-based method for the improvement of the images. The selection of the second processing method depends on the features of the images. When they include coherent moiré patterns, the RPCA method was preferred. When the S/N ratio of the images was comparatively low, the LASSO-based recovery was used. We did not use both the processing methods because some of the small image features may be lost.

**Estimation of physical parameters using data assimilation**

To derive the physical parameters of charge carriers, we need to analyze the spatio-temporal change of the charge carrier distribution, as explained for Eq. (1). As shown in Fig. 6, each local position in the PI-PM sequence has information on the charge carrier response. For example, a section profile at the indicated line in Fig. 6 shows a change in charge distribution due to decay and diffusion, and the profile intensity gradually became weaker with an increase in width. This distribution change over time was analyzed with Eq. (1).

For the analysis, we used data assimilation, which is a statistical data analysis method using Kalman filtering studied extensively in the 1980s and 1990s in analytical chemistry for an estimate of parameters, and has been frequently utilized for weather forecasting, earthquakes, and tsunamis these days. In the data assimilation based on the previously measured observables, the observable at the next time step is predicted with the prediction and measurement (observation) steps under the assumption of errors of a physical model and a measurement (observation). This technique can be used for the estimation of parameters included in the model during the prediction process.

In our application, data assimilation was performed for each section profile [Fig. 6(b)] at local positions based on the physical model with Eq. (1). For example, the section profile is made up of 25–50 data points, representing the charge carrier distribution, given that the measured data and the actual charge distribution are represented by vectors $M(t)$ and $N(t)$. The distribution at the next time step is calculated with a numerical calculation based on Eq. (1) with an allowable error included in the physical model, and $N_{t+1}$ is obtained by a calculation using a prediction matrix, which is called the state estimate: the system dynamics matrix form is shown in the supplementary material.

From $N_{t+1}$, $M_{t+1}$ is estimated by an observation matrix, including an allowable measurement error, which is called the measurement update: the observation matrix form is shown in the supplementary material. The error matrix is made of a diagonal matrix with a noise dispersion, which can be easily estimated from the actual measurement data (5%). In the estimation of the model parameters, the physical model parameters are added in the data vector, and not only $M(t)$ but also the physical parameters are estimated by both the prediction and observation matrices. In the actual calculation, the initial distribution of the charge carriers $M_0(t)$ is given, and $N_1(t)$ and $M_1(t)$ are predicted. The measured data and the model parameters with the highest probability are predicted by the random sampling of the physical parameters at each time step. In our calculation, the decay rate and diffusion coefficients in the right and left directions were selected as physical parameters (example code is included in the supplementary material).

An example of the predicted distribution is shown in Fig. 6(c). The overall trend of the distribution was successfully recovered. This calculation process was performed throughout the photo-excitation.
regions (200 pixels in the vertical direction × 10–30 stripes). The estimated average diffusion coefficients in the left and right directions and the decay rate (1/decay time) are mapped out in Fig. 7. It is noted that the anisotropic diffusion in the right and left directions are easily affected by the optical alignment (e.g., tilting of a sample, an illumination light, and imaging lenses). This was confirmed by the fact that the direction of this anisotropic decay became opposite by a slight alignment change. This anisotropic decay was not recognized for the overall image but was noticed when the local response change was analyzed, and this issue will be fixed in the near future.

We will discuss only the average diffusion coefficient here. The average diffusion coefficient was 1.28 μm²/μs (0.0128 cm²/s), which is on the same order as that previously reported for the photo-excited electrons in a TiO₂ particulate film. The lifetime corresponding to the inverse of k was much shorter in many places at this time scale (microsecond order).

Based on the previous research studies, the decay corresponds to the recombination of the photo-excited charge carriers, and in this case, photo-excited electrons, although the order of the reported decay time ranges from nanoseconds to microseconds. The diffusion coefficients for the photo-excited electrons were 0.3 cm²/s from the photovoltage measurement and 0.01 cm²/s was obtained from the spectroscopic information. The ones in electrolyte solutions showed much lower diffusivity, and the literature values showed a large discrepancy depending on the measurement technique and sample conditions. This probably occurred because the physical properties of photo-excited charge carriers depend on the interfacial conditions and structures. At least, we can say...
that our results fall into the range of the previously reported values.

Furthermore, it is clear that the physical parameters had a wide range of values, and the effectiveness of the physical property mapping is recognized. To clarify the reason for the discrepancies of the reported physical property values and for their large dispersion in the imaged area, the correlation between the structure and the physical properties must be studied extensively. Such efforts are under way for a variety of different sample conditions.

CONCLUSION

We have developed a new microscopy technique to visualize the charge carrier response for photo-devices such as photocatalysts and solar cells. Since the charge carrier response depends on the local structure especially for nano-particleulate films, which have been utilized in most photo-devices, it is a key issue to correlate the charge carrier response and the local structure. In this study, we could observe the local charge carrier response by a combination of pattern-illumination for the photo-excitation of charge carriers and observation via the change in refractive index due to the charge carriers. The obtained images were refined by a combination of image reconstruction techniques, and physical parameters were obtained by a data assimilation technique, which provided the physical value mapping on the sample surfaces.

This method could be applied for many photo-device materials such as hematite (a photoanode) and a MAPI (a perovskite solar cell). The corresponding PI-PM image sequences are included in Movies S2 and S3. Analyses of the charge carrier behavior are underway. This method could help in understanding the mechanism of photocatalytic and photovoltaic charge behavior and developing new devices and materials.

SUPPLEMENTARY MATERIAL

See the supplementary material for an example of the images before and after the flat field correction (Fig. S1); an example of the images before and after the image recovery process in the case of the dot-pattern excitation (Fig. S2); an example of the prediction and measurement matrix for the data assimilation (Fig. S3); an example of the PI-PM image sequence for a TiO$_2$ film after the image processing (Movie S1); an example of the PI-PM image sequence for a hematite film for a dot-pattern excitation (Movie S2); an example of the PI-PM image sequence for a methyl ammonium lead iodide film (Movie S3); and example MATLAB codes for the RPCA image recovery, the sparsity-based image recovery, and the model parameter estimation by data assimilation.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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