A mechanically adaptive hydrogel with a reconfigurable network consisting entirely of inorganic nanosheets and water

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Although various biomimetic soft materials that display structural hierarchies and stimuli responsiveness have been developed from organic materials, the creation of their counterparts consisting entirely of inorganic materials presents an attractive challenge, as the properties of such materials generally differ from those of living organisms. Here, we have developed a hydrogel consisting of inorganic nanosheets (14 wt%) and water (86 wt%) that undergoes thermally induced reversible and abrupt changes in its internal structure and mechanical elasticity (23-fold). At room temperature, the nanosheets in water electrostatically repel one another and self-assemble into a long-periodic lamellar architecture with mutually restricted mobility, forming a physical hydrogel. Upon heating above 55 °C, the electrostatic repulsion is overcome by competing van der Waals attraction, and the nanosheets rearrange into an interconnected 3D network of another hydrogel. By doping the gel with a photothermal-conversion agent, the gel-to-gel transition becomes operable spatiotemporally on photoirradiation.
In scientific fiction and mythology, inorganic creatures often appear. These stories present us with a new challenge in materials science of how to produce life-like materials entirely from inorganic substances. This seems considerably difficult because living organisms usually consist of water-rich flexible solids with a structural hierarchy that are capable of responding to stimuli, unlike inorganic materials, which generally exhibit poor processability, low flexibility, and a lack of responsiveness. Indeed, previous studies on biomimetic soft materials have almost exclusively involved the use of organic constituents1–8, as typi- cally represented by mechanically adaptive hydrogels based on thermoresponsive organic polymers such as poly(N-isopropylacrylamide)7–13. However, if counterparts of these hydrogels consisting entirely of inorganic materials were to become available, they could expand the scope of materials science by adopting a complementary role to organic-based biomimetic soft materials in providing such characteristics as good mechanical properties, long-term durability, and low environmental burdens14–16.

For the creation of inorganic-based biomimetic soft materials, the most promising constituents are inorganic nanomaterials such as nanoparticles, nanofibers, or nanosheets17. When these inorganic materials self-assemble to form 3D architectures in water, they sometimes afford hydrogels18–25. In most cases, the inorganic nanomaterials aggregate through attractive interactions, such as van der Waals attraction or electrostatic attraction, to form interconnected 3D networks that can hold large quantities of water; these materials are referred to as attraction-dominant gels (Fig 1e–g)18–22. However, inorganic nanomaterials can also participate in another type of self-assembly to produce a 3D architecture that is capable of exhibiting a gel-like behavior, although previous examples are limited to only a few examples on charged inorganic nanosheets23–25. If charged nanosheets exhibit a sufficiently strong mutual electrostatic repulsion, they can spontaneously self-assemble into a long-periodicity lamellar architecture in which their mobility is restricted. As a result, their aqueous dispersions can exhibit a gel-like behavior and such materials are referred to as repulsion-dominant gels (Fig 1b–d).

Although these two types of inorganic-based hydrogel have been studied separately by using various nanomaterials, we conjectured that a single aqueous system containing charged nanosheets might be capable of reversibly forming both types of hydrogel through careful tuning of the intensity of the competing attractive and repulsive forces according to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory26,27. Such a hydrogel might be endowed with responsiveness to stimuli, despite its inorganic composition.

In this work, by adopting the above strategy, we succeeded in developing a stimuli-responsive hydrogel consisting of anionic nanosheets of titane17–20 (TiNSs; 14 wt%) and water (86 wt%) that, depending on the temperature, can reversibly adopt one of two hydrogel states: a repulsion-dominant state or an attraction-dominant state (Fig 1). In this gel-to-gel transition driven by tuning of the electrostatic repulsion between TiNSs, the topology of the internal structure of the hydrogel changes abruptly (Fig 2). Owing to the 2D shape of TiNSs, which prevents the possibility of entanglement, and the particular thermoresponsive nature of TiNSs, the gel-to-gel transition occurs rapidly with little hysteresis and without deterioration upon repetition (Fig 3). Because of the abrupt topological reconfiguration of the internal structure of the material, the gel-to-gel transition is accompanied by a 23-fold change in the hydrogel's mechanical elasticity, reminiscent of that of sea cucumbers (Fig 4)31,32. Furthermore, by doping with a small number of gold nanoparticles that act as photothermal converters33, the hydrogel can become responsive to photo stimuli33–36, permitting the gel-to-gel transition to occur in a spatiotemporally controlled manner (Fig 5). Importantly, it is usually difficult to construct a gel that displays such a topological reconfiguration, even by using organic materials37,38.

Results
Preparation and characterization of a hydrogel consisting of titane nanosheets in the repulsion-dominant state (TiNS-GelRepuls). The key to our achievement was the use of a particular nanosheet of titane (TiNS) characterized by its ultra-thin (0.75 nm) and extra-wide (several micrometers) dimensions (Fig 1a and Supplementary Fig. 1)27–30. TiNS is densely populated with negative charges (1.5 C m⁻²) that are surrounded by tetra- butylammonium counterions. By using TiNS as a constituent, a repulsion-dominant hydrogel, denoted as TiNS-GelRepuls, was prepared as follows. A 0.4 wt% aqueous dispersion of TiNS (30 mL) was centrifuged at 20,000 g for 1 h, so that the dispersion became segregated into a TiNS-free supernatant (~29 mL) and a water-rich sediment ([TiNS] = 14 wt%; 0.86 mL). In this sediment, TiNSs were confined close to one another so that their mutual electrostatic repulsion became strong enough to restrict their mobility. Consequently, the sediment existed as a physical gel (Fig 1b–d; TiNS-GelRepuls)23–25 that could be isolated from the supernatant and removed from the centrifugation tube. Upon dilution with water, TiNS-GelRepuls retained its gel-like behavior up to a TiNS concentration of 8 wt%, but turned into a sol on further dilution (Supplementary Fig. 2).

TiNS-GelRepuls thus obtained showed structural profiles consistent with its supposed gelation mechanism as described above (Fig 2a). In small-angle X-ray scattering (SAXS) measurements at 25 °C, TiNS-GelRepuls exhibited multiple scattering peaks with q value ratios of 1, 1/2, 1/3, …, and1/x, suggesting the formation of a lamellar architecture of TiNSs with a uniform and large interlamellar distance of 11.8 nm (Fig 2b). This distance is 16 times larger than the thickness of TiNS (0.75 nm), indicating that TiNSs were not in contact due to their mutual electrostatic repulsion (Fig 1d). In a polarized optical microscopy (POM) study at 25 °C, TiNS-GelRepuls exhibited a strong birefringence under crossed Nicols (Fig 2c), which also confirmed the existence of a liquid-crystalline lamellar architecture in TiNS-GelRepuls (Fig 1c). Furthermore, scanning electron microscopy (SEM) observations of a freeze-dried sample of TiNS-GelRepuls showed the presence of a layered arrangement of TiNSs (Fig 2d), probably originating from a lamellar architecture of TiNSs before freeze drying.

Preparation and characterization of a hydrogel consisting of titane nanosheets in the attraction-dominant state (TiNS-GelAttract). We previously reported that the electrostatic repulsion between TiNSs becomes attenuated upon raising the tempera- ture27. Although this tendency had been observed in aqueous TiNS dispersions, we conjectured that a similar phenomenon might occur in a hydrogel of TiNSs (TiNS-Gel). Indeed, when TiNS-GelRepuls was heated from 25 to 90 °C, it changed into another type of hydrogel with a different internal structure and different physical properties (Fig 2e–h). Throughout this transition, exudation of water from the hydrogel was not observed at all, suggesting that the volume of the hydrogel remained. Because the formation of this hydrogel was dominated by attractive forces between TiNSs, as later discussed (see Fig 6a–c below), this hydrogel is denoted as TiNS-GelAttract.

In the SAXS profiles of TiNS-GelAttract at 90 °C, the sets of diffractions due to the lamellar architecture of TiNSs with a periodicity of 11.8 nm, characteristic of TiNS-GelRepuls, disappeared, while a single diffraction corresponding to a periodicity of 2.6 nm emerged (Fig 2f). The new periodicity was similar to that
of aggregates of TiNSs prepared by drying an aqueous TiNS dispersion ([TiNS] = 0.4 wt%) at a relative humidity of 95% for 12 h \( (d \approx 2.7 \text{ nm}) \). When the electrostatic repulsion between TiNSs in an aqueous dispersion is strong enough, TiNSs spontaneously self-assemble into a long-periodicity lamellar architecture in which their mobility is mutually restricted. As a result, their aqueous dispersion can exhibit a gel-like behavior, denoted as TiNS-GelRepuls. When TiNS-GelRepuls is heated above a critical temperature, the electrostatic repulsion becomes weaker than the competing van der Waals attraction, so that TiNSs abruptly stack tightly to form an interconnected 3D network that can hold large quantities of water, denoted as TiNS-GelAttract. Because of the large difference in the topology of the internal structure between TiNS-GelRepuls and TiNS-GelAttract, this gel-to-gel transition is accompanied by drastic changes in the optical and mechanical properties.

**Thermoresponsive transition between TiNS-GelRepuls and TiNS-GelAttract.** We then performed a detailed investigation of how the transition between TiNS-GelRepuls and TiNS-GelAttract occurs. First, we examined TiNS-Gel (([TiNS] = 14 wt%) by differential scanning calorimetry at temperatures between 25 and 90 °C at a scanning rate of 1 °C min\(^{-1}\) (Fig. 3a). A sharp single peak was observed at \(~55 \text{ °C}\) during both heating and cooling of the gel (Fig. 3b), confirming that the transition between TiNS-GelRepuls and TiNS-GelAttract is a first-order phase transition that occurs at \(~55 \text{ °C}\).

To clarify how the internal structure changed in the gel-to-gel transition, we monitored the SAXS profiles of TiNS-Gel ([TiNS] = 14 wt%) while performing a temperature sweep between 25 and 90 °C (Fig. 3c and Supplementary Fig. 3). As described above (Fig. 2b), TiNS-GelRepuls at 25 °C showed a set of diffractions...
The Young moduli (\(G_{\text{TiNS-GelRepuls}}\)) and an attraction-dominant state (\(\text{TiNS-GelAttract}\)) were 26 kPa and 14 wt% at 25 °C, respectively. In a frequency sweep (frequency = 0.1–10 rad s\(^{-1}\)) of the TiNS-Gel (Fig. 4a), the storage moduli (\(G'\)) that were higher than its loss moduli (\(G''\)) over the entire frequency range, confirming its gel-like properties. The Young’s modulus of TiNS-Gel (\([\text{TiNS]} = 14 \text{ wt%}\)) increased from 1.3 to 20 kPa when it underwent a transition from TiNS-GelRepuls to TiNS-GelAttract, demonstrating the excellent reversibility and rapidity of this mechanical-property switching.
**Temperature-dependent SAXS of TiNSs, and excellent photothermal-conversion ability**

Thus, (AuNPs) because of their water dispersibility, compatibility with appropriate photothermal converter.

produce a photoresponsive version by the addition of an appropriate photothermal converter. Distance was determined by SAXS measurements.

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**Spatiotemporal controllability of a TiNS hydrogel.** The results reported above prompted us to attempt to produce a more life-like smart material from TiNS-Gel by expanding the range of stimuli capable of inducing the gel-to-gel transition. In particular, the use of light as a stimulus is an attractive option that should permit the gel-to-gel transition to occur in a spatiotemporally controlled manner (Fig. 5a), similar to some biological systems. Because TiNS-Gel itself is thermoresponsive, it might be modified to produce a photoresponsive version by the addition of an appropriate photothermal converter.

As a photothermal converter, we chose gold nanoparticles (AuNPs) because of their water dispersibility, compatibility with TiNSs, and excellent photothermal-conversion ability. Thus, TiNS-Gel_Rpuls (TiNS = 14 wt%) was doped with monodisperse AuNPs (AuNP = 0.05 wt%) with an average diameter of 17 nm (Fig. 5b, c). The mechanical properties and thermoresponsiveness of AuNP-doped TiNS-Gel were well preserved (Supplementary Fig. 5). Also, the photothermal-conversion ability of AuNPs was preserved throughout the hybridization; when AuNP-doped TiNS-Gel was irradiated with 445-nm laser light (power density = 5.6 W cm⁻²), the temperature of the irradiated region increased from 25 to 82 °C within 40 s, as monitored by a thermal-imaging camera (Fig. 5d, right). Because AuNP-free TiNS-Gel did not show any temperature change under the same photoirradiation condition (Fig. 5d, left), the present photothermal conversion can be ascribed to the effects of AuNPs exclusively. When the light was turned off, the irradiated region of AuNP-doped TiNS-Gel was air-cooled to 25 °C within 60 s. The light-on/light-off cycle could be repeated many times without detectable deterioration (Fig. 5e).

As we envisioned in Fig. 5a, POM observation of these temperature-changing processes showed that AuNP-doped TiNS-Gel underwent a transition between TiNS-Gel_Rpuls and TiNS-Gel_Attract rapidly, reversibly, and in a spatiotemporally controlled manner (Fig. 5f). On photoirradiation of TiNS-Gel_Rpuls with 445-nm laser light (power density = 5.6 W cm⁻²; irradiated region = 2 × 4 mm) for 40 s, the irradiated region was selectively transformed into TiNS-Gel_Attract with no birefringence, whereas upon ceasing photoirradiation, the irradiated region returned to TiNS-Gel_Rpuls with a large birefringence within 4 s (Supplementary Movie 1). Detailed studies revealed that (i) the transition from TiNS-Gel_Rpuls to TiNS-Gel_Attract under this condition was finished within ~2 s and (ii) the transition speed can be tuned by changing the light power density (Supplementary Fig. 6b) and AuNP concentration (Supplementary Fig. 6c). This dynamic structural change, which is highly controllable in both time and space, is reminiscent of the responsive behaviors of living organisms, despite the inorganic composition of TiNS-Gel.

**Key parameters for TiNSs to form a mechanically adaptive hydrogel.** Although many hydrogels consisting entirely of such inorganic nanomaterials as nanoparticles, nanofibers, or nanosheets have been developed, TiNS-Gel is the only known hydrogel that is capable of reversibly adopting one of two hydrogel states. To clarify which are the key factors underlying this property, we conducted systematic studies on the characteristic profiles of TiNSs in terms of (i) its large and tunable...
electrostatic repulsion and (ii) the ultra-thin and extra-wide 2D shapes of its nanosheets, as described below.

TiNSs carry a dense array of negative charges (1.5 C m⁻²) and they intrinsically show a large mutual electrostatic repulsion, which is essential in permitting the formation of TiNS-GelRepuls (Fig. 1b–d). For the reversible transition between TiNS-GelRepuls and TiNS-GelAttract, the electrostatic repulsion should be tunable (Fig. 1e–g). We found that the required tunability was provided by the thermoresponsive behavior of the TiNS surfaces, where tetrabutylammonium counterions (T⁺) and protons (H⁺) form ion pairs with surface anions (Ti–O⁻), as shown in Fig. 6a. When an aqueous dispersion of TiNSs is heated from 25 to 90 °C, the countercations Ti⁺ (1.5 C m⁻²) upon repeated thermal scanning between 25 and 90 °C.

The gel-to-gel transition was accompanied by marked changes in the birefringence and the mechanical properties (Fig. 4). The gel-to-gel transition was followed by measurements of the zeta potential (Fig. 6c). According to the DLVO theory, both of these heat-induced changes should contribute to an attenuation of the electrostatic repulsion between TiNSs, thereby explaining the mechanism of the transition from TiNS-GelRepuls to TiNS-GelAttract. Upon heating from 25 °C, the electrostatic repulsion between TiNSs is gradually attenuated and eventually, at ~55 °C, becomes weaker than the competing van der Waals attraction, so that TiNSs abruptly stack tightly to form an interconnected 3D network, resulting in a transition from TiNS-GelRepuls into TiNS-GelAttract. Note that the thermoresponsive changes in the free-ion concentration (Fig. 6b) and surface-potential intensity (Fig. 6c) are reversible and show little hysteresis, which is consistent with the reversible and little-hysteresis nature of the transition between TiNS-GelRepuls and TiNS-GelAttract as confirmed by the SAXS (Fig. 3c) and rheological measurements (Fig. 4c).

To clarify the roles of another key property of TiNSs, their ultra-thin and extra-wide 2D shape, we constructed a thermal phase diagram of TiNSs dispersed in water ([TiNS] = 14 wt%) with systematic changes in the size of TiNSs (Fig. 6d). Aqueous dispersions of TiNSs of various sizes were prepared by sonication of an as-synthesized aqueous TiNS dispersion ([TiNS] = 0.4 wt%; original hydrodynamic size = 1.9 µm). The resulting TiNS dispersions were then concentrated to [TiNS] = 14 wt% by centrifugation as described above. When the size of TiNSs was sufficiently large (hydrodynamic size = 1.2–1.9 µm), the TiNS dispersion formed TiNS-GelRepuls in the low-temperature region below 55 °C (Fig. 6d, #1, #2, #5, and #6) and TiNS-GelAttract in the high-temperature region above 55 °C (Fig. 6d, #3, #4, #7, and #8). However, when the size of TiNSs was moderate (hydrodynamic size = 0.18–0.47 µm), the TiNS dispersion did not form TiNS-GelRepuls in the low-temperature region but, instead, existed in a sol state (Fig. 6d, #9, #10, #13, and #14), probably because a reduction in the size of TiNSs enhanced their mobility, even though a strong electrostatic repulsion between TiNSs was present. In consistency with this, our previous report on an aqueous dispersion of TiNSs with relatively small size (~1 µm) showed a lower tendency of forming a lamellar architecture than that of this work. Meanwhile, in the high-temperature region, moderate-sized TiNSs (hydrodynamic size = 0.18–0.47 µm) were still capable of forming TiNS-GelAttract (Fig. 6d, #11, #12, #15, and #16). When the size of TiNSs was further reduced (hydrodynamic size = 0.11 µm), the TiNS dispersion did not form a hydrogel in either the low-temperature region or the high-temperature region (Fig. 6d, #17–#20), probably because the size of TiNSs was so small that their heat-induced aggregation did not result in an interconnected 3D network, but instead resulted in the possible formation of densely packed columnar stacks of TiNSs.

Overall, a large lateral size of TiNSs is essential for the formation of TiNS-GelRepuls and TiNS-GelAttract and the size of nanosheets required for the formation of TiNS-GelRepuls (~1 µm) is much larger than that required for the formation of TiNS-GelAttract (~0.18 µm).

Discussion

We have developed a stimuli-responsive hydrogel (TiNS-Gel) consisting of inorganic constituents (14 wt% TiNSs and 86 wt% water). In response to temperature changes, TiNS-Gel reversibly adopts one of two hydrogel states (TiNS-GelRepuls or TiNS-GelAttract) that have totally different internal structures: a lamellar architecture and an interconnected 3D network, respectively. The gel-to-gel transition proceeds within a narrow temperature range (55 ± 2 °C) and with excellent rapidity (within ~2 s) and perfect reversibility (little hysteresis and no deterioration upon repetition). The gel-to-gel transition was accompanied by marked changes in the optical properties (strong birefringence to no birefringence) and the mechanical properties (G' = 26 kPa to G' = 600 kPa) of the gel. Thus, the mechanical properties of TiNS-Gel changed considerably and rapidly as a result of...
The keys to this achievement are the characteristic profiles of TiNSs, which have an ultra-thin and extra-wide 2D shape and large and tunable electrostatic repulsion. Their shape endows TiNSs with the ability to form self-assembled 3D structures that contain abundant water efficiently, while their electrostatic properties permit the topology of these 3D structures to change in response to thermal stimuli. The 2D shape of TiNSs, which eliminates the possibility of entanglement, may be the reason for the excellent rapidity and reversibility of the thermal response of TiNS-Gel. These properties appear to be superior to those of conventional hydrogels based on 1D materials such as organic polymers or nano-fibers. Although poly(N-isopropylacrylamide) and related organic polymers have long been the components of choice for smart soft materials, we have demonstrated that TiNS can serve as an alternative to such organic polymers. This work will surely expand the scope of adaptive materials of the next generation, possibly even leading to the creation of ‘inorganic life’.

**Methods**

**Preparation of the hydrogel of TiNS (TiNS-Gel).** In a typical procedure, an aqueous dispersion (30 mL) of TiNS ([TiNS] = 0.4 wt%, [C6H13N+4OH−] = 90 mM) in a 50-mL centrifuge tube was centrifuged at 20,000 g for 1 h. From the resultant segregated mixture, the supernatant (~29 mL) was removed by pipetting, and the precipitate (0.86 mL) was collected as the hydrogel of TiNS in the repulsion-dominant state (TiNS-GelRepuls). Because the amount of TiNS included in the supernatant was negligibly small, the TiNS content in the resultant gel was calculated to 14 wt%. TiNS-GelRepuls doped with AuNPs was prepared in a similar procedure, except for adding an aqueous dispersion of AuNPs ([AuNP] = 0.05 wt%). This cycle could be repeated many times without deterioration (Supplementary Movie 1). Scale bars: 100 nm (c); 2 mm (d, f).

**Synthesis of gold nanoparticles (AuNPs).** An aqueous dispersion of gold nanoparticles (AuNPs) were synthesized according to the literature. Typically, a solution of HAuCl4⋅3H2O in water (0.01 wt%, 50 mL) was heated to reflux. To the resulting mixture, a solution of sodium citrate in water (1.0 wt%, 1.0 mL) was quickly injected. The color of the mixture turned to a brilliant red after 2 min, and its reflux for additional 3 min afforded an aqueous dispersion of AuNPs. Thus obtained AuNPs were monodisperse with an average diameter of 17 nm, as determined by TEM.

**Characterization of gold nanoparticles (AuNPs; average diameter = 17 nm).** UV–Vis absorption spectrum of an aqueous dispersion ([AuNP] = 0.005 wt%; [AuNP] = 0.05 wt%), pictures of the samples in a 1.5-mm diameter glass capillary (left) and their thermal imaging camera images before (mid) and after (right) 40 s light irradiation. Time-course temperature changes of TiNS-Gel ([TiNS] = 14 wt%) without (pink dots) and with (navy dots) 0.05 wt% AuNPs upon repeated turning on and off of the 445-nm laser light, which were monitored by a thermal-imaging camera. Photoinduced changes in POM images under crossed Nicols of TiNS-Gel doped with AuNPs ([TiNS] = 14 wt%; [AuNP] = 0.05 wt%). When TiNS-GelRepuls in a 0.2-mm-thick glass container was irradiated with the 445-nm laser light (irradiated region = 2 × 4 mm) for 40 s, the irradiated region was selectively transformed into TiNS-GelAttract with a large birefringence. Upon ceasing photoirradiation, the irradiated region returned to TiNS-GelRepuls with a large birefringence within 4 s. This cycle could be repeated many times without deterioration (Supplementary Movie 1). Scale bars: 100 nm (c); 2 mm (d, f).
The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. All other information is available from the corresponding authors upon reasonable request.

Received: 20 June 2020; Accepted: 27 October 2020; Published online: 27 November 2020

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Acknowledgements
This work was financially supported by a JSPS Grant-in-Aid for Scientific Research (S) (18H05260) and a JSPS Grant-in-Aid for Scientific Research (B) (20H02791). We also acknowledge JST CREST Grant Number JPMJCR17N1, Japan. K.S. thanks JSPS for Grant-in-Aid for Research Activity Start-up (19K23642) and Young Scientists (20K15350) and Kurita Water and Environment Foundation (KWEF, Japan). K.S. also acknowledges RIKEN for the Special Postdoctoral Researcher Program. The small-angle X-ray scattering measurements were performed at BL45XU in SPring-8 with the approval of the RIKEN SPring-8 Center (proposal 20180067).

Author contributions
K.S. conceived the project and designed the experiments. K.S. and N.I. performed all experiments. T.A. and Y.I. co-designed the experiments. Y.E. and T.S. prepared colloidally dispersed TiNSs. T.H. supported the small-angle X-ray scattering measurements at SPring-8. K.S. and Y.I. analyzed the data and wrote the manuscript with the input of all other authors. The manuscript reflects the contributions of all authors.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-19905-4.

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Peer review information Nature Communications thanks Subi George, Myongsuo Lee and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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