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A Photowelding Strategy for Conductivity Restoration in Flexible Circuits

Yunyu Sun, Mingcheng Yang, Yutong Guo, Mengjiao Cheng, Bin Dong,* Feng Shi*

Abstract: Light-driven micropumps, which are based on electro-osmosis with the electric field generated by photocatalytic reactions, have been developed as one of the most attractive research topics in chemical micromotors. Until now, most researches in this field mainly focused on directional motions or collective behaviors of microparticles, which lack practical applications. In this paper, we have developed a photowelding strategy to realize photoinduced conductivity recovery of cracked flexible circuits repeatedly. We immerse the circuit in suspension of conductive healing particles and apply photo-illumination to the crack; photocatalysis of pre-deposited pentacene (PEN) layer triggers electro-osmotic effects to gather conductive particles at the crack, leading to conductivity recovery of the circuit. This photowelding strategy has exploited a novel application of light-driven micropumps and photocatalysis in conductivity restoration.

Photocatalysis based on photoinduced charge separation has long advanced the frontier of converting light energy into chemical potential energy, leading to fantastic applications, such as H_2 production,[1] organic synthesis,[2] water treatment,[3] etc.[4] Light-driven micropumps, representing an important progress of photocatalysis, generate local electric field upon photocatalytic reactions and meanwhile produce electro-osmotic effects.[5] Current works on light-driven micropumps have been limited to fundamental studies including fluid motion,[6] manipulation of microparticles,[7] etc. To facilitate the practical use of this field, it is significant to exploit applicable scenes that could fully demonstrate the advantages of photo manipulation of microparticles in a switchable and precisely controllable way.

Flexible circuit is a revolutionary technology to assemble electronic circuits on flexible substrates for advanced products of flexible displays,[8] flexible sensors,[9] etc.[10] However, one bottleneck problem in practical uses of flexible circuit is the high risk of cracks and conductivity failure caused by frequent bending, stretching and possible scratching. Currently, several strategies have been proposed for conductivity restoration including self-healing based on dynamic chemistry,[11] pre-loading of microcapsules containing conductive matters,[12] etc. These innovative strategies have brought 'smart' features to flexible circuits, i.e. the circuits self-heal upon being damaged. However, these strategies have some restrictions under certain application conditions, such as dependence of healing ability on crack depth, low mechanical strength as a compromise of using reversible interaction, limited healing times, low compatibility with existing fabrication of flexible circuits, etc. Therefore, developing new methods for conductivity restoration of flexible circuits is urgent to address the above problems to facilitate practical uses of flexible electronics.

In this paper, we apply light-driven micropumps based on photocatalytic reactions to conductivity restoration of flexible circuits (defined as photowelding strategy). A thin PEN layer is pre-deposited on top of a circuit without disturbance to the circuit. Once cracks occur, we immerse the circuit into a suspension of healing agents and irradiate the crack; the resulted electro-osmosis effect generated by the diffusion of photocatalytic products (H^+ and $\cdot O_2^-$) could gather healing particles at the crack to recover conductivity. Because healing agents are externally accessible and photocatalyst is not consumed, we could heal cracks for many times. The minimum distance between adjacent conductive and broken lines reaches 100 μm for successful repair, the smallest width of healable crack is 10 μm, and a 300-μm cut is healed in ~8 min under a 1.2-W/cm^2 irradiation. Even with a protective layer on circuits, in situ healing is still possible. We envision this photowelding strategy may exploit a promising application of light-driven micropumps and photocatalysis in conductivity restoration of flexible circuits due to advantages of being independent on crack depth and storage of healing agents, cost-effective, compatible with existing fabrication of flexible electronics (Section S1, S2).

To demonstrate the photo-welding strategy, we have built a model flexible circuit (Figure 1a) consisting of a direct power source, an LED light bulb and a polydimethylsiloxane (PDMS) substrate with a gold wire (200-nm thick and 200-μm wide) covered with a PEN layer (75-nm thick and 200-μm wide). Note that the PEN layer has negligible influence on the performance of the circuit (Figure S1). The originally intact flexible circuit lights up a green LED bulb (Figure 1b) and shows a low resistance of 46 Ω (Figure 1g red line). Then, we scratch the circuit using a diamond knife to generate a ~120-μm crack (Figure 1c inset). This damage results in disconnection of the circuit (Figure 1c), lighting out of the bulb (Figure 1d) and sharply increased resistance (Figure 1g blue and orange lines).

To in situ heal the crack, we apply the photowelding strategy by dropping PS@Au microparticles suspended in deionized water at the crack and then irradiate the cracked spot for 4 min with a 1.2-W/cm^2 intensity (Video S1). After drying, the crack is completely filled with microparticles and the LED bulb lights up again, indicating the conductivity recover (Figure 1e,f). The resistance of the circuit dramatically drops to nearly 18 MΩ (the resistance of deionized water, Figure 1g purple line) upon applying the PS@Au microparticle suspension. Later, the resistance decreases gradually over the next 23 min in the presence of water. This is because the microparticles continuously and gradually aggregate and the water evaporation

[a] Y. Y. Sun, Y. T. Guo, Prof. B. Dong
Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, Jiangsu, China
E-mail: bdong@suda.edu.cn
[b] Dr. M. J. Cheng, Prof. F. Shi
Beijing Laboratory of Biomedical Material & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
E-mail: shi@mail.buct.edu.cn
[c] Prof. M. C. Yang
Beijing National Laboratory for Condensed Matter Physics and CAS Key Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China and School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

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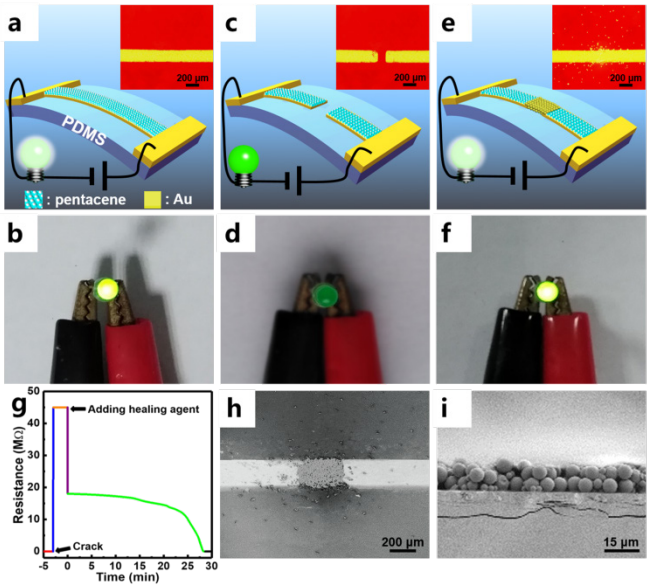

Figure 1. The photowelding strategy. Schematic illustration, microscopic photos (insets) and LED bulb states of the a,b) as-prepared, c,d) damaged and e,f) repaired model flexible circuit. g) Resistance changes during the connection-disconnection-reconnection process. h) Top and i) side view SEM images of the PS@Au microparticle aggregation in the cracked area.

is slow. After totally dried, the crack is filled by multilayer microparticles (Figure 1h,i), leading to a circuit resistance of ~100 Ω (Figure 1g black line). Compared with the original value (46 Ω), the slight resistance increase is caused by the contact resistance between different microparticles (Figure S2). The aggregation size at the healed crack is highly relevant to the illumination time, intensity and the microparticle concentration (Figure S3). As a result, cracks with different sizes ranging from 10 μm to 650 μm can be repaired by tuning these parameters (Figure S4, S5). The reparation speed is irrelevant to microparticle size (Figure S6). The healing process can be well repeated for at least 40 times of crack-heal cycles at the same position of the circuit (Section S7). In addition, irregular crack can also be repaired (Figure S9); the healing agent suspension brings little damage to circuit performance (Figure S10); the adhesion between PS@Au microparticle aggregation and PDMS substrate is van der Waals force, which is strong enough to keep particles gathered even in repetitive bending (Figure S11). Moreover, the photowelding strategy is versatile regarding flexible substrate (Figure S12), circuit (Figure S13), photocatalyst (Figure S14) and healing microparticle types (Figure S15, S16).

The mechanism of the above photowelding method is interpreted as follows. As illustrated in Figure 2a,b, the irradiated PEN layer can generate photoinduced excitons[13] to cause charge separation. The holes generated in PEN oxidize water, resulting in H^+ and hydroxyl radicals (·OH); and the generated electrons injected from the conduction band of PEN to the underlying Au layer reduce O_2 to $\cdot O_2^-$. The quantum yield of the reaction is estimated to be ~0.27% (Section S12). Because of the concentration gradient of the formed H^+ and $\cdot O_2^-$ from the crack to other area, H^+ and $\cdot O_2^-$ diffuse into the ambient solution (Figure 2c). Because H^+ moves faster than $\cdot O_2^-$ (Figure 2d), an

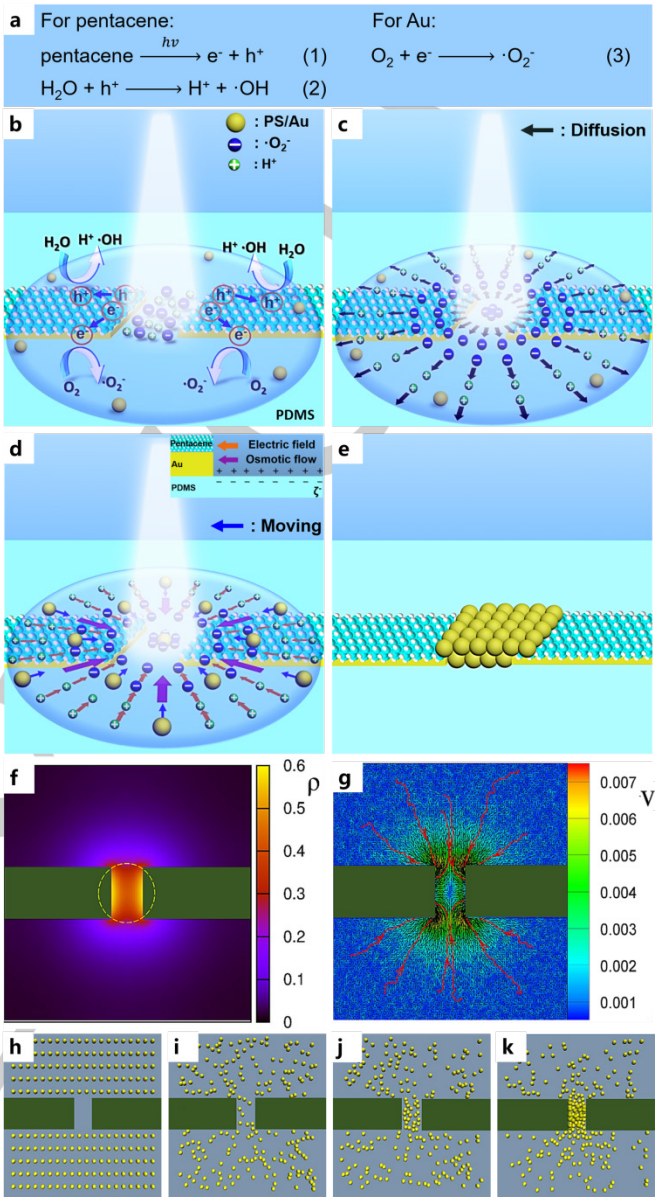

Figure 2. Underlying mechanism of the photowelding strategy. a) The possible photocatalytic reactions near the crack. b) Under photoirradiation, H^+ and $\cdot O_2^-$ are generated. c) H^+ diffuses faster than $\cdot O_2^-$, inducing an inward electric field, d) causing electro-osmotic flow (d inset) and moving PS@Au microparticles toward the irradiation center. e) PS@Au microparticle aggregates near the illumination center. f) Simulation showing the relative concentration distribution of the reaction products on the substrate surface. Green square and circle refer to the PEN layer and the illumination region, respectively. g) The generated osmotic flow on the substrate surface in the absence of colloidal particles with red and black lines indicating the streamlines and the flow velocity, respectively. h-k) Snapshots of the PS@Au particles driven by osmotic flow to aggregate in the cracked area.

inward electric field is formed; meanwhile, the negatively charged PDMS surface[14] forms a double layer with positive charges on the outer layer, resulting in fluid flow along the PDMS surface toward the irradiation center based on electro-osmosis (Figure 2d inset).[5] Taken together, PS@Au microparticles in the suspension are moved to the irradiated

crack spot driven by the above electro-osmosis fluid flow. After approaching the crack, the PS@Au microparticles settle down to form aggregation because of their larger density than that of water (Figure 2e); with sufficient conductive PS@Au microparticles filling the crack, the conductivity of the cracked circuit is recovered.

The mechanism is further supported by particle-based mesoscale fluid simulations (Section S13).[15] The photocatalytic reaction creates high concentration reaction products around the cracked area (Figure 2f). Because of the concentration gradient of photocatalytic products and their different diffusion rates, the generated electric field drives an electro-osmotic flows from the outside toward the illuminated reaction region (Figure 2g), which continuously transports the microparticles to the cracked area (Figure 2h-k). The above mechanism is also confirmed by other control experiments (Figure S17, S18). Besides, we conduct control experiments to clarify contributions from other effects to particle transportation: even though slight local temperature increase is observed, photo-thermal effect is too weak to transport any particles (Figure S19); water surface tension does not influence microparticle aggregation process (Figure S19).

The concept of photowelding has been demonstrated as above with a simple circuit, i.e. one single conductive path, similar to most previous methodologies for conductivity restoration. However, practical circuits are more complex with dense conductive paths, thus urgently requiring precise repair to avoid possible short cut. Besides, the ability to heal complex circuits remains to be clarified. Here we design two closely and parallelly aligned gold lines (500 μm apart) with four terminals (A-D in Figure 3a). After a crack is generated between terminals A and B, the photowelding strategy is used to precisely restore conductivity only at the damaged spot, while leaving the parallel gold line undisturbed, i.e. no extra PS@Au microparticles covering both lines to cause short cut (Figure 3a,b, Figure S20 and Video S2). The minimum spacing distance between these two parallel conductive lines can reach 100 μm (Figure S21, S22).

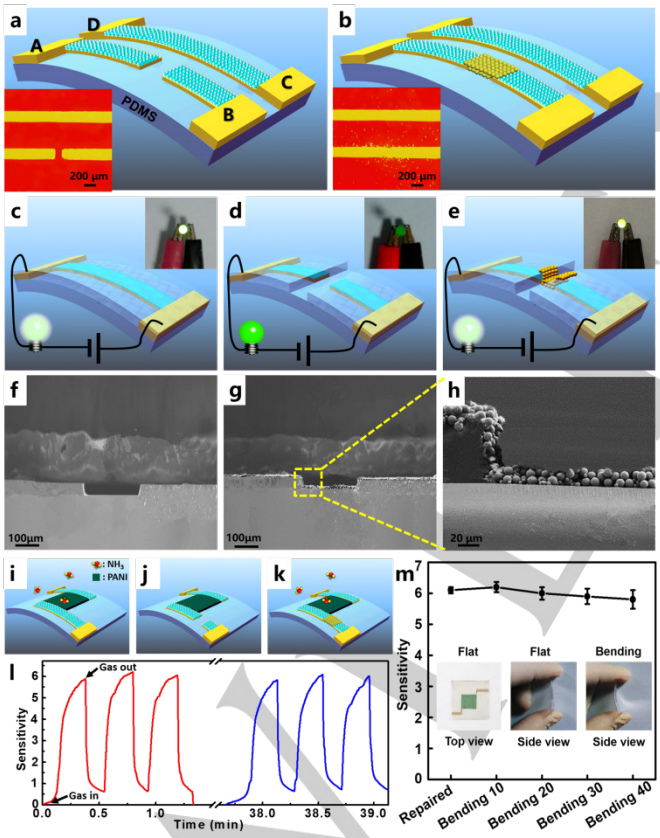

Figure 3. Capability of the photowelding method for conductivity restoration. a,b) Schematics and optical microscopic images (insets) showing precision reparation of a crack in one of two adjacent circuits. c-e) Schematics, LED status (c-e insets) and f-h) side view SEM images indicating the reparation of a flexible circuit sealed by a PDMS surface coating. i-k) Schematics, l) sensitivity changes and (m and its insets) flexibility test result demonstrating the reparation of the flexible sensing device.

Considering practical using situation of flexible circuits packed with an inert layer, we further demonstrate the conductivity restoration of our photowelding method even under a protective coating of PDMS (Figure 3c-e, Section S18). After mechanical damage, the LED bulb, which is initially on (Figure 3c inset), goes off (Figure 3d inset). A reconnection is realized based on the photowelding process, as indicated by the lighted LED (Figure 3e inset). The successful repair is also reflected in the SEM images, which shows that the clear gap caused by scratching (Figure 3f) is filled with PS@Au microparticles (Figure 3g,h). Thus, exposed PEN at the cracked area can still function and induce microparticle aggregation near the damaged area under light irradiation, leading to conductivity recovery.

In practical use, flexible electronics have been frequently used for sensing; therefore, we check whether the photowelding strategy could also recover designated function of certain flexible electronics after conductivity restoration. The model system is constructed by sandwiching a sensing material, i.e. polyaniline (PANI), which is known to be sensitive to ammonia gas,[16] between the PEN-coated gold electrodes (Figure 3i). This sensing device displays reversible resistance change under repetitive exposure to 50 ppm ammonia gas (Figure 3l red curve). After mechanical damage (Figure 3j) and reparation utilizing the photowelding strategy (Figure 3k), the gas sensing ability of the repaired sensor device is recovered (Figure 3l blue curve). Additionally, the restored device could withstand multiple bending cycles without experiencing apparent changes in sensitivity (Figure 3m), thus confirming the ability of photowelding in recovering both function and circuit conductivity of flexible devices.

In conclusion, we have developed a novel photowelding strategy based on light-driven micropump for the restoration of conductivity crack in flexible circuits; this strategy is precise and controllable to repair local circuit damage without disturbing nearby functional parts. The reparation mechanism is interpreted by photocatalysis-triggered electro-osmosis flows directionally gathering external conductive healing agents (i.e. PS@Au microparticles which are cost-effective and highly efficient (Section S19)) to photo-irradiated crack spot. Because this photowelding is proven to heal circuits even under protective encapsulation coating or specific functions of certain sensing flexible devices with crack depth independent healing capability, good repeatability and compatibility with the existing fabrication strategy, we envision its promising future in practical uses of

repairing conductive failure of flexible electronics, especially at microscale.

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Keywords: photowelding • conductivity restoration • precision reparation • aggregation

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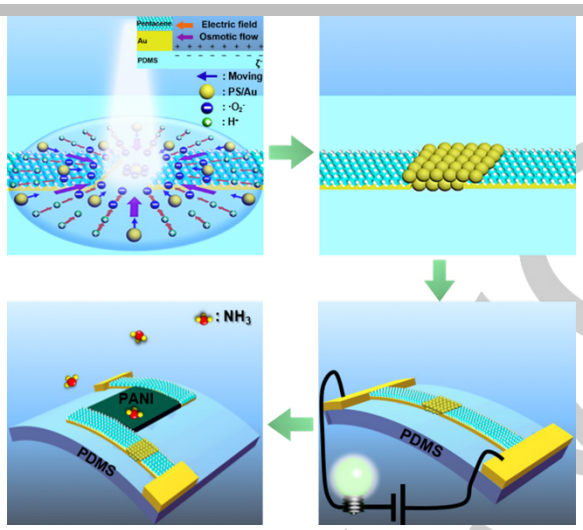
COMMUNICATION

The pentacene based photocatalysis is applied in the conductivity restoration of flexible circuits (coined as photowelding) for the first time. Photoinduced charge separation and the resulting photocatalytic products generated near the locally irradiated superficial organic semiconductor layer enable the agglomeration of the healing agent at the cracked area, leading to the successful reparation of the damaged circuit.



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