Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information

An *in-situ* And Rapid Self-Healing Strategy Enabling Stretchable Nanocomposite with Extremely Durable and Highly Sensitive Sensing Features

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1. Experimental Section

1.1 Raw Materials

AgNWs were purchased from Zhejiang Kechuang Advanced Materials Co., Ltd with an average diameter of 40 nm and a length of 20 µm. Poly(vinyl alcohol) (PVA, molecular weight 24000), succinic anhydride, 6-monodeoxy-6-monoamino-*β*-cyclodextrine (NH_2-CD), amantadine (NH_2-AD), *p*-toluenesulfonyl chloride, *N*-(3-(dimethylamino)propyl)-*N′*-ethylcarbodiimide hydrochloride (EDC), 1-hydroxybenzotriazole hydrate (HOBt), *N,N*-Diisopropylethylamine (DIPEA), glycerol (GL) and *p*-toluenesulfonic acid (TSA) were purchased from Aldrich and used without further purification. Polyurethane (4055IC) was sourced from Yantai Wanhua Polyurethane Co., Ltd. Deionized water was used throughout the work. The giant GO was prepared via the modified Hummers' method. Membrane tubes (ZelluTransRoth, 10000 MWCO, Carl Roth GmbH & Co, Karlsruhe, Germany) for dialysis were used after washing with deionized water.

1.2 Synthesis of PVA-acid

4 g PVA, 455 mg succinic anhydride, and 13 mg *p*-toluenesulfonic acid were added into the DMSO solution and kept at 50 °C for 48 h. Then impurities were removed through dialysis for five days in water. PVA-acid shown in Figure S1 was obtained by drying the dialyzed solution. The grafting ratio of carboxylic acid was estimated to be about 5.7%.

1.3 Synthesis of PVA-AD

200 mL DMF, 500 mg PVA-acid, 32 mg NH_2-AD (96 mg, 0.4 equiv to acid groups), 53 mg EDC, 43 mg HOBt, and 55.8 mg DIPEA were added into the 500 mL round-bottom flask equipped with a magnetic stirrer. The mixture was immersed in a preheated oil bath at 70 °C for 24 h. The crude product was purified by dialysis toward deionized water for five days.

1.4 Synthesis of PVA-CD

200 mL DMF, 500 mg PVA-acid, 245 mg NH_2-CD, 53 mg EDC, 43 mg HOBt, and 55.8 mg DIPEA were added into the 500 mL round-bottom flask equipped with a magnetic stirrer. The mixture was immersed in a preheated oil bath at 50 °C for 24 h. The crude product was purified by dialysis toward deionized water for five days.

1.5 Preparation of GO:AgNW/PVA-AD:PVA-CD Gel-like Ink.

In a typical preparation, 2 mg/mL GO dispersion was made by first dispersing GO in distilled water via sonication for 30 min. After sonication, the pH value was adjusted to 6.5 by adding 0.2 M NaOH aqueous solution. Subsequently, the AgNW solution was added into the GO solution at an AgNW to GO weight ratio of 20:2.5. After sonication for 10 min, the AgNW and GO mixture was vacuum filtrated using a PTFE membrane filter with a pore size of 0.45 µm and washed with 200 mL of distilled water. The resulting precipitate was redispersed in distilled water through strong agitation using a VORTEX mixer at 1000 rpm for 2 h to obtain the final homogeneous GO:AgNW (mass ratio of GO:AgNW=5:40) ink. A certain amount of glycerol was added to solve the following PVA-AD:PVA-CD mixture. PVA-AD, PVA-CD and glycerol was added to the ink at a final mass ratio GO:AgNW:PVA-AD:PVA-CD:glycerol = 5:40:0.05:0.1:0.5.

1.6 Construction of the Strain Sensor

The strain sensor was fabricated through a screen-printing technique with the printing force, speed, and angle between the squeegee and stencil optimized specifically for the GO:AgNW based inks. The screen-printing plate with an appropriate pattern was first installed in the screen-printing machine (TC-4060k screen printer, Dongguan Ta Chen Screen Printing Machine & Materials Co., Ltd.). Following installation, the gel was spread onto the screen-printing plate and printed by sliding the squeegee over the stencil. After printing, the sensor patterns were dried under ambient conditions for 10 min to evaporate the water before tests were conducted. The thickness of the strain sensor could be adjusted by changing the weight percentage of the DI water. All electromechanical measurements were conducted parallel to width direction.

1.7 Characterizations

The resistance change was measured with a Keithley 2000 digital multimeter. Stretching tests and cyclic strain tests were performed on a motorized linear stage with built-in controller (Zolix Inc.). Strain and resistance data were recorded with a custom-made LabViewcode. The morphology and mapping of the GO:AgNW/PVA-AD:PVA-CD nanocomposite film was imaged using a JSM-7800 SEM machine. X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max-2500 diffractometer with Cu-Ka radiation. The functional groups of the specimens were recorded on a BRUKER TENSOR27 FT-IR spectrometer in the 4000-400 cm^{-1} range. A total of 60 scans were averaged to yield the final spectra with a resolution of 2 cm^{-1}. Rheological behavior of the formulated inks was probed using a DHR-2 rheometer (TA Instruments) with a 25 mm plate system and 900 µm gap. All of the tested ink samples were tested under the same solid content and at room temperature (25 °C). A preconditioning step at a shear rate of 0.1 s^{-1} for 10 s was applied prior to each test. A steady-state flow step test was performed to measure the shear viscosity of the inks at shear rates of 0.1-1000 s^{-1}, and a peak hold step test was performed with constant shear rates in three intervals (0.1 s^{-1} shear rate for 60 s, 200 s^{-1} for 60 s, and 0.1 s^{-1} for 130 s) to simulate the screen-printing process. The stress sweep step test was performed with an oscillation stress of 1-1000 Pa at a frequency of 1 Hz. ^{1}H NMR spectra were recorded on a Bruker(^{1}H, 400 MHz) spectrometer using tetramethylsilane as the internal standard.

2. Supporting Figures and Tables

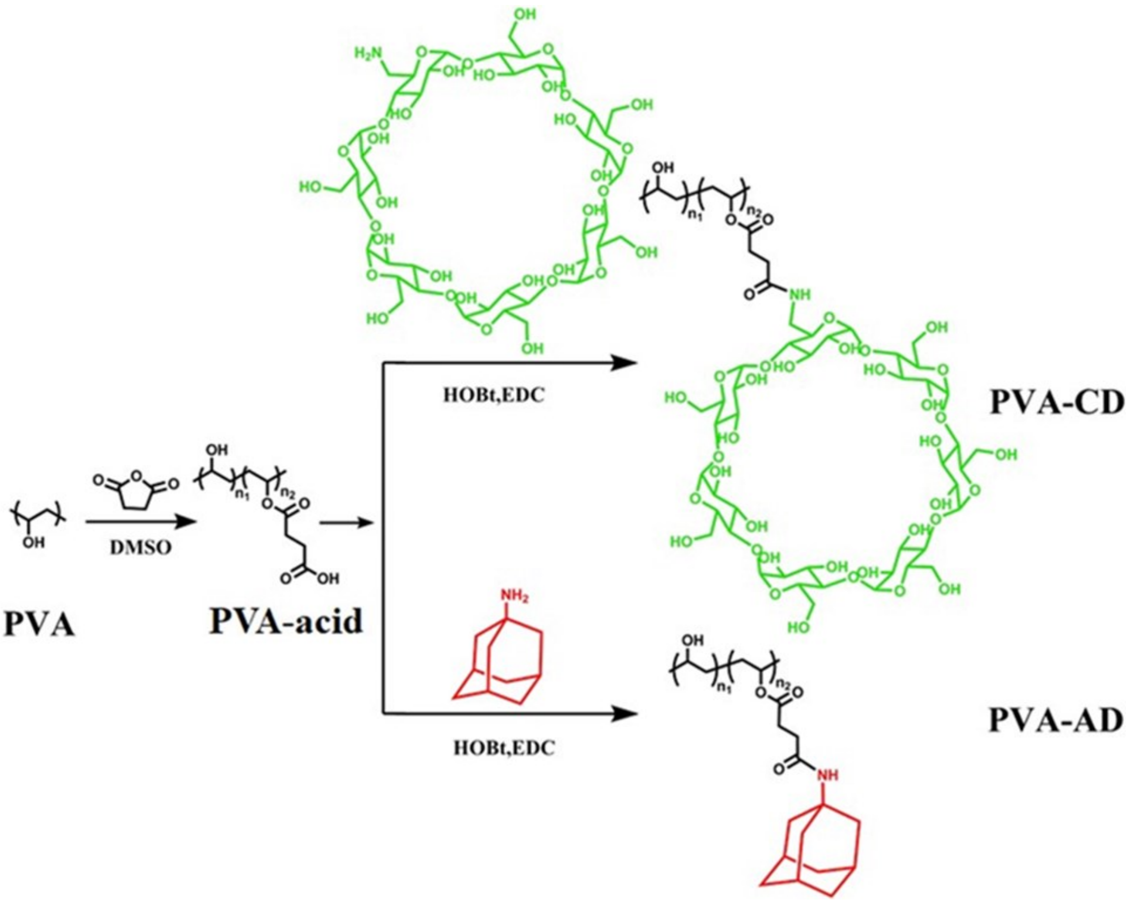

Fig. S1. General synthetic routes for target materials PVA-AD and PVA-CD.

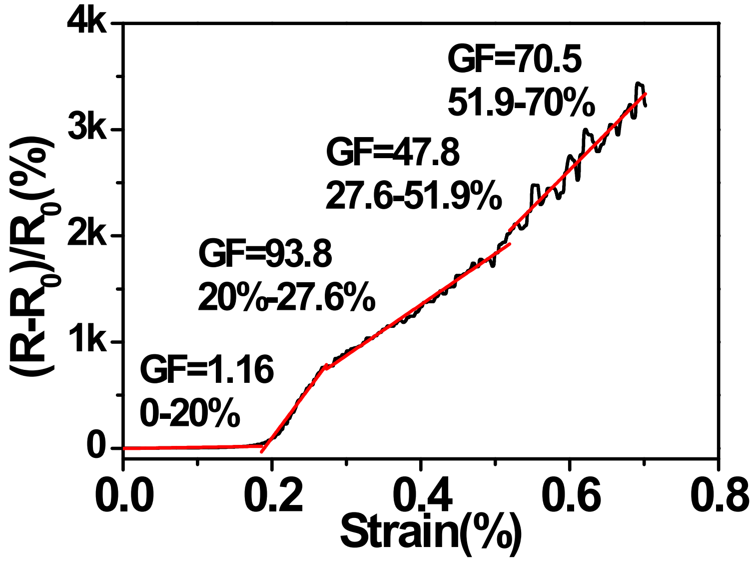

Fig. S2. Typical relative resistance change as a function of applied strain curves of GO:AgNW/PVA-AD:PVA-CD sensors with the weight ratio of GO:AgNW:PVA-AD:PVA-CD:glycerol = 5:40:0.5:1:5.

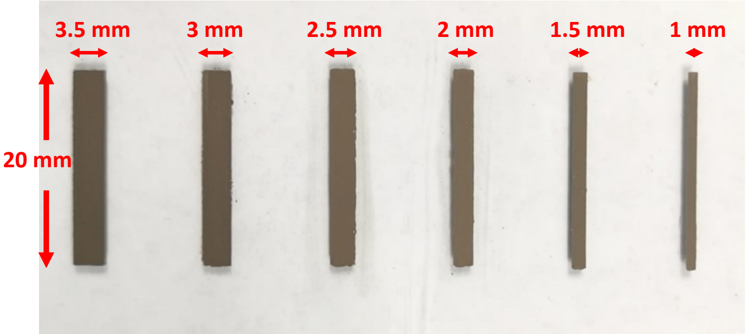

Fig. S3. Photographic images of the GO:AgNW/PVA-AD:PVA-CD sensors with various width.

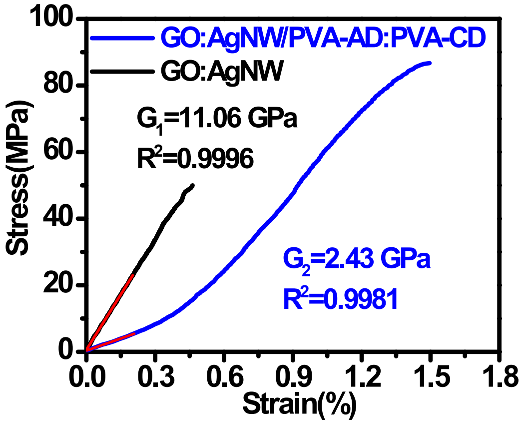

Fig. S4. The strain–stress curves of freestanding freestanding GO:AgNW/PVA-AD:PVA-CD and GO:AgNW films.

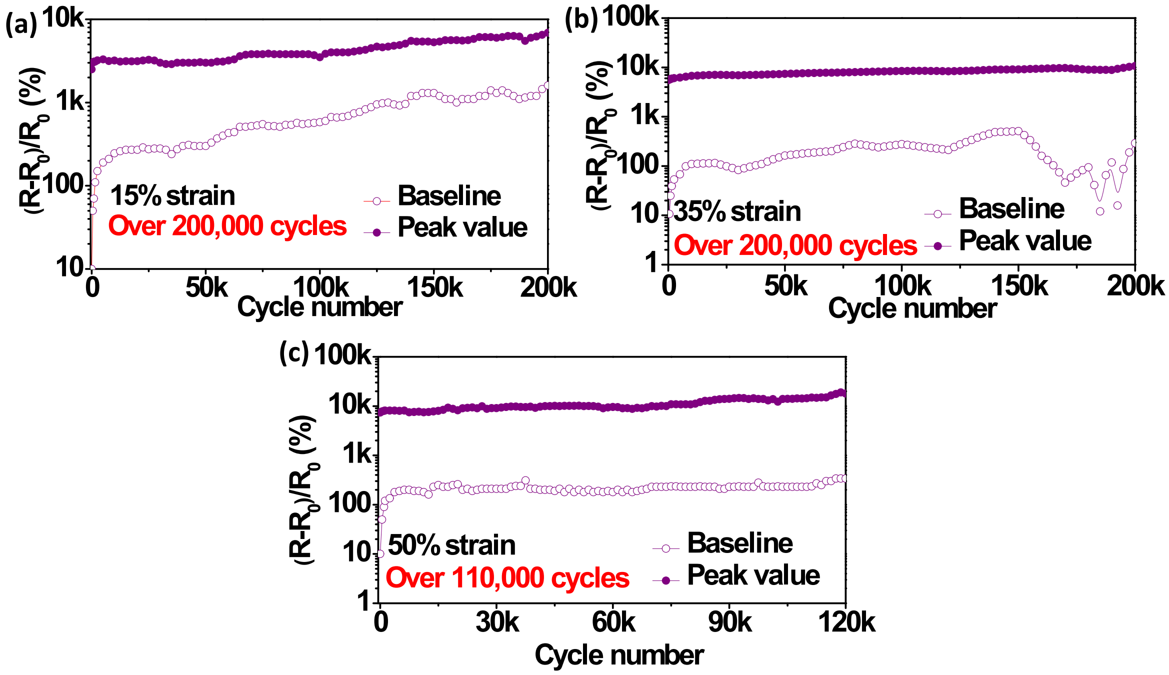

Fig. S5. Cyclic durability of GO:AgNW/PVA-AD:PVA-CD sensors under various applied strain ratios between (a) 0-15%, (b) 0-35%, and (c) 0-50%.

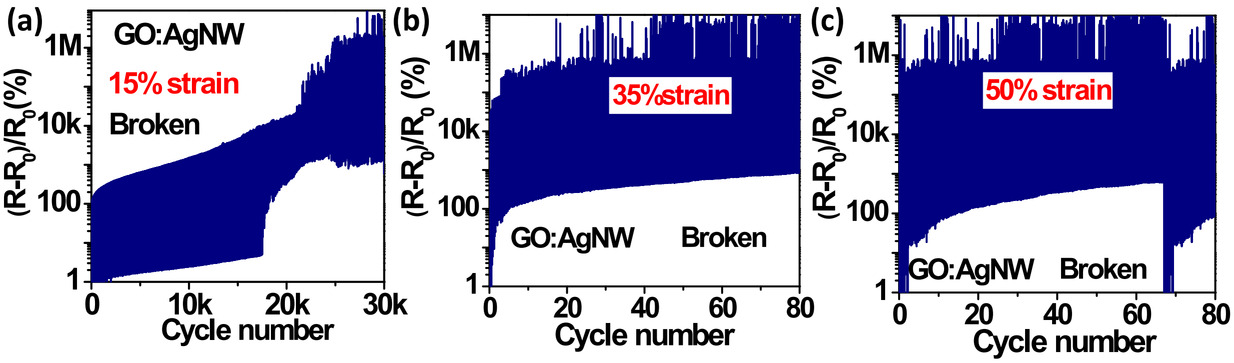

Fig. S6. Cycling performance of GO:AgNW sensors under (a) 0-15% strain, (b) 0-35% strain, and (c) 0-50% strain, respectively.

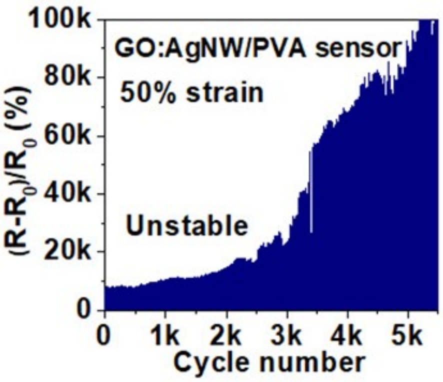

Fig. S7. Cycling performance of GO:AgNW/PVA sensor under 0-50% strain.

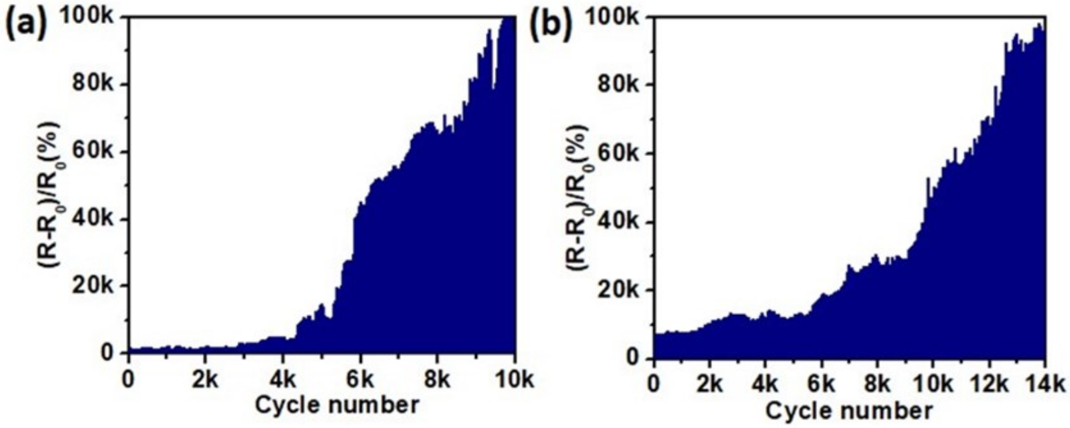

Fig. S8. Cycling performance of (a) GO:AgNW/PVA-AD, and (b) GO:AgNW/PVA-CD strain sensors under 0-35% strain.

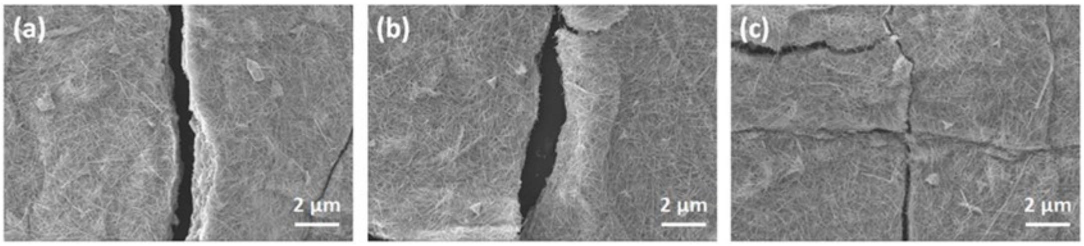

Fig. S9. SEM images of unhealable strain sensors of (a) GO:AgNW/PVA, (b) GO:AgNW/PVA-AD, and (c) GO:AgNW/PVA-CD after 100 stretch-release cycles between 0-35% strain, then left to released state for 10 days.

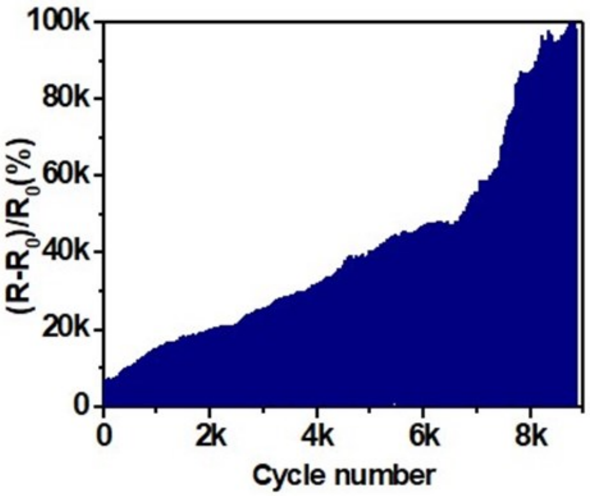

Fig. S10. Cycling performance of the GO:AgNW/PVA-AD:PVA-CD strain sensor after adding small molecular AD addition under 0-35% strain.

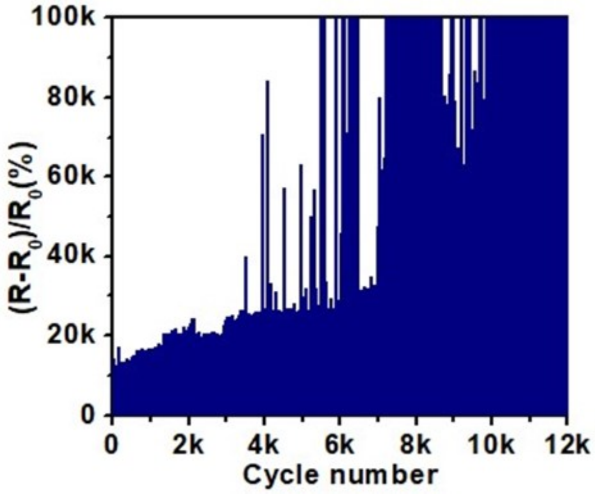

Fig. S11. Cyclic durability of the GO:AgNW/PVA-AD:PVA-CD strain sensor without the addition of glycerol under 0-35% strain.

Table S1 The sensing performance of other reported typical resistive-type strain sensors and our healable GO:AgNW/PVA-AD:PVA-CD strain sensor.

Sensing material or Sensing structure	Maximum strain	Maximum gauge factor	Healable	Reference
Carbon black/thermal plastic elastomer composite	80%	20	No	Ref 1
Nanohybrid of Carbon Nanotubes and Conductive	100%	62	No	Ref 2

Elastomers				
Graphene-Based Fiber	100%	3.7	No	Ref 3
AgNW elastomer nanocomposite	70%	2-14	No	Ref 4
Graphene-based film	<5%	10-150	No	Ref 5
carbon nanotubes based strain sensor	150%	0.0041	No	Ref 6
Fragmentized Graphene Foam strain sensor	70%	15-29	No	Ref 7
MXene/CNT films	30-130%	4.4-772.6	No	Ref 8
RGO Microtubes-Elastomer Composite	>50%	630	No	Ref 9
CNT based Thickness-Gradient Films	150%	0.58	No	Ref 10
Carbonized Cotton Fabric	140%	64	No	Ref 11
Carbonized Cotton Fabric	500%	37.5	No	Ref 12
Prestrained AgNW percolation network	35%	20	No	Ref 13
PDMS fiber coated with Au film	120%	33	No	Ref 14
RGO decorated electrospun polymer fibrous mats	100%	79	No	Ref 15
aligned SWCNT thin films	200%	2	No	Ref 16
MWCNT network with much pore	70%	56	No	Ref 17
3D Graphene Film	187%	1500	No	Ref 18
buckled sheath-core fiber	1135%	34.22	No	Ref 19
Liquid films based on biomimetic microvilli structure	200%	3.4	Yes	Ref 20
CNT embedded in PVA	1000%	2.25	Yes	Ref 21

hydrogel				
Brick and mortar structure	52%	3500	Yes	Ref 22
GO:AgNW/PVA-AD:PVA-CD	**58%**	**1591**	**Yes**	**This work**

3. Supplementary References

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