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Supplementary Information

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Experimental section

1. Preparation of black TiO_2:

TiO_2 and $NaBH_4$ were mixed in a 4:1 ratio in a grinding bowl, thoroughly blended, and annealed at 400°C for 1 hour in a tube furnace. After centrifugation with deionized water and ethanol, the powder yielded black TiO_2 (R-P25). Additionally, TiO_2 powder was dispersed in a mixture of methanol and deionized water (volume ratio 7:3). Following methods described in the literature, the mixture was irradiated using a Ti-sapphire laser system (Spectra-Physics, Spitfire ACE). After drying, laser-modified black TiO_2 (L-P25) was obtained.

2. Preparation of photoanode

Mixtures of 0.4g each of R-P25 and L-P25 powders (in mass ratios of 3:7, 5:5, and 7:3 respectively) were prepared into slurries using the previously described method. These slurries were spin-coated onto FTO conductive glass and annealed at 450°C for 30 minutes to obtain TiO_2 films.

The CdS/CdSe QD were sensitized onto the FTO/TiO_2 photoanode using a chemical bath deposition method. The FTO/TiO_2 photoanode was sequentially immersed in a methanol solution containing 0.06 M $Cd(CH_3COO)_2$ and a methanol solution containing 0.06 M $Na_2S \cdot 9H_2O$. After soaking for 30 seconds, the photoanode was removed and rinsed appropriately with methanol. This process was repeated six times to complete the CdS quantum dot sensitization.

Next, in a three-neck flask, 25 mL of deionized water, 1.55 g Na_2SO_3, and 0.155 g Se powder were added, and the mixture was heated in an oil bath to 125°C until the

Se powder was completely dissolved. The temperature was then maintained at 125°C for 2 h, after which the flask was removed from the oil bath and cooled to room temperature. A solution containing $C_6H_6NNa_3O_6 \cdot H_2O$ and $Cd(CH_3COO)_2$ in deionized water was added, and the mixture was stirred before the FTO/TiO_2/CdS photoanode was placed in it. The photoanode was then kept in the dark at 24°C in a water bath for 2 h.

Finally, a ZnS passivation layer was prepared. The prepared photoanode was sequentially immersed in 0.1 M $Zn(CH_3COO)_2$ methanol solution and 0.1 M Na_2S methanol-deionized water (V/V, 1:1) solution. After soaking for 60 s, the photoanode was removed and rinsed with methanol. This process was repeated twice, and then the photoanode was placed in a petri dish and stored in the dark.

According to the passivation layer design specifications, the target thickness range is 20-30 nm. The measured passivation layer thickness, characterized by transmission electron microscopy (TEM), is 21±1.5 nm[1], which meets the requirements of the work performed.

3. Synthesis of AM gel electrolytes

12 g AM were dispersed in 15 mL of deionized water, heated and stirred until fully dissolved. After complete dissolution, 0.1 g of N, N'-(methylene) bisacrylamide and 0.2 g of ammonium persulfate were added. After stirring for several minutes, the mixture became a viscous system. Subsequently, it was poured into a petri dish and left at room temperature for 24 h to obtain a AM matrix.

To prepare the polysulfide electrolyte, sulfur powder and sodium sulfide were

dissolved in a mixture of deionized water and methanol. The electrolyte was then added to the AM matrix, allowed to fully absorb, resulting in the formation of the AM gel electrolyte.

4. Preparation of Carbon/Ti Counter Electrodes

The Ti mesh was cut into an appropriate size and placed in ethanol and acetone respectively for ultrasonic cleaning. After the ultrasonic treatment, the Ti mesh was rinsed with deionized water. The cleaned Ti mesh was then dried for later use.

Active carbon, conductive carbon black, and PVDF were mixed in a ratio of 8:1:1, and NMP was added to thoroughly grind the mixture into a viscous slurry. The slurry was then brushed onto the titanium mesh. After drying, the active carbon/Ti counter electrode was obtained.

5. Characterization

The equipment used for experiments and data analysis in this research:

X-ray Diffraction (Rigaku XRD): λ = 0.15406 nm, tube current = 40 mA, diffraction angle = 10°-80°; X-ray Photoelectron Spectroscopy (XPS, ESCALAB MkII); Field Emission Scanning Electron Microscope (FESEM, S4800, Hitachi); UV/Visible/NIR Spectrophotometer (UV-3150); Solar Simulator (Zolix Instruments Co., Ltd.): AM1.5, light intensity = 100 mW/cm^2; Transmission Electron Microscope (TEM, Talos F200): Accelerating voltage = 200 kV; Electrochemical Workstation (Shanghai CHI660C). These methods are used for parameter determination and structural analysis.

6. Analog calculation

Utilizing density functional theory calculations and molecular dynamics simulations to compute the interactions between AM, NaS, S, and H_2O. The wave function expansion employed a cutoff energy of 500 eV, and the energy convergence criterion was set to 10^{-6} eV to ensure high calculation precision. The exchange and correlation terms were treated with the Generalized Gradient Approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional. The Brillouin zone integrations were carried out using a 3×3×2 K-point grid. When constructing the simulation model, a 15 Å thick vacuum layer was set around the carbon-based materials to avoid interactions. The study of the interactions between the polymer and water was conducted using the Forcite module for molecular dynamics calculations and analysis.

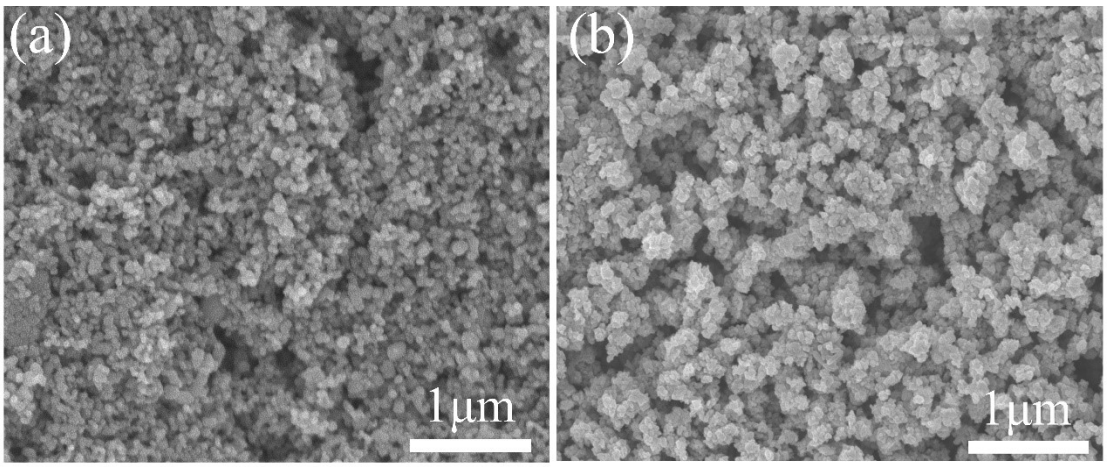

Fig. S1 SEM images in top view of two TiO_2 nanoparticle films(a-b)

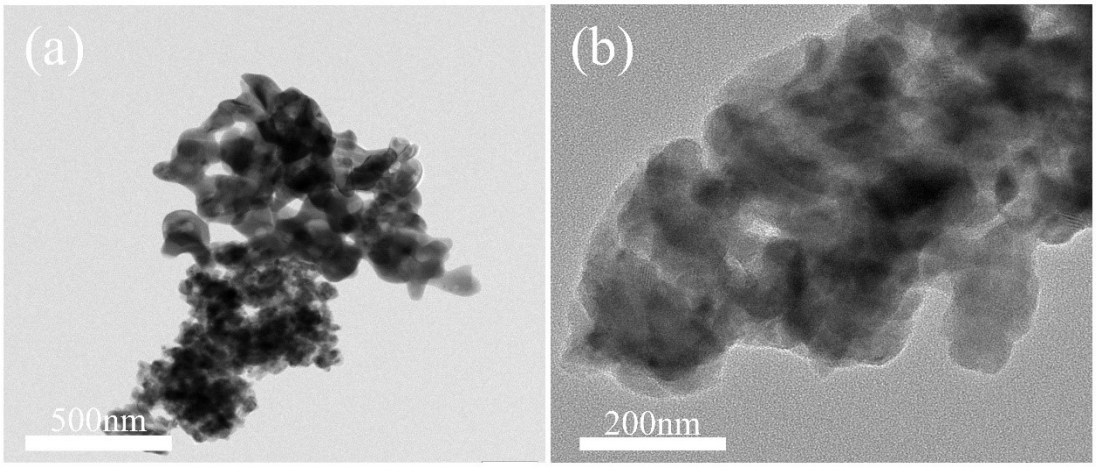

Fig. S2 TEM images of P25 TiO_2(a-b)

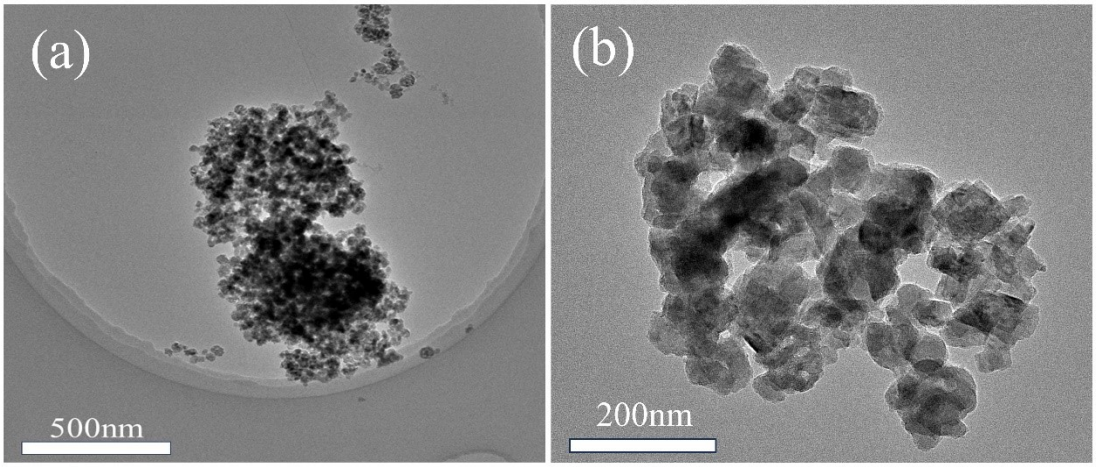

Fig. S3 TEM images of R-P25(a-b)

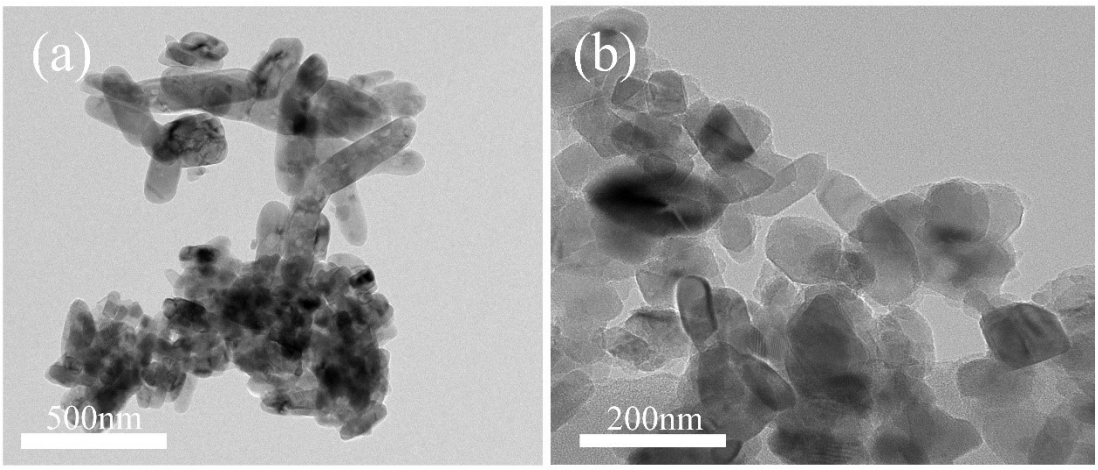

Fig. S4 The TEM images of L-P25 TiO_2(a-b)

The photoanodes were prepared using the pristine P25, L-P25, and R-P25. Additionally, L-P25 and R-P25 were mixed in ratios of 3:7, 5:5, and 7:3 to prepare photoanodes.

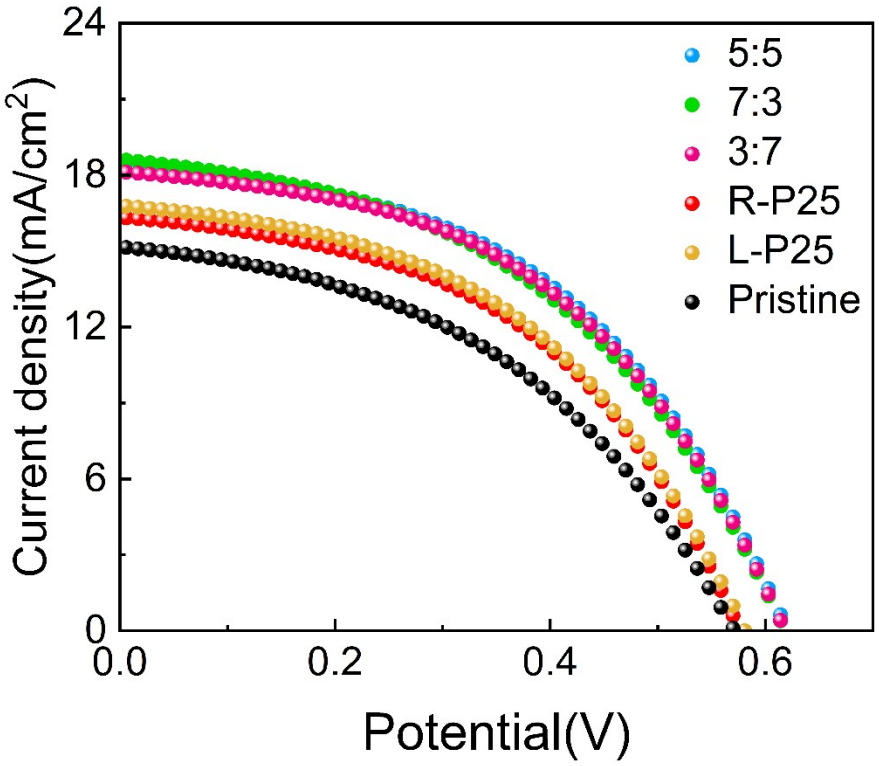

Fig. S5 The J-V curves of QDSSCs prepared using different photoanodes based on CuS CE.

Table S1. Performance parameters of five solar cells based on CuS

Sample	Jsc(mA/cm^2)	Voc(V)	FF(%)	PCE(%)
Pristine P25	15.23	0.57	43	3.80
R-P25	16.35	0.58	48	4.53
L-P25	16.84	0.58	47	4.58
3:7	18.52	0.60	46	5.35
5:5	18.34	0.61	48	5.47
7:3	18.70	0.60	45	5.28

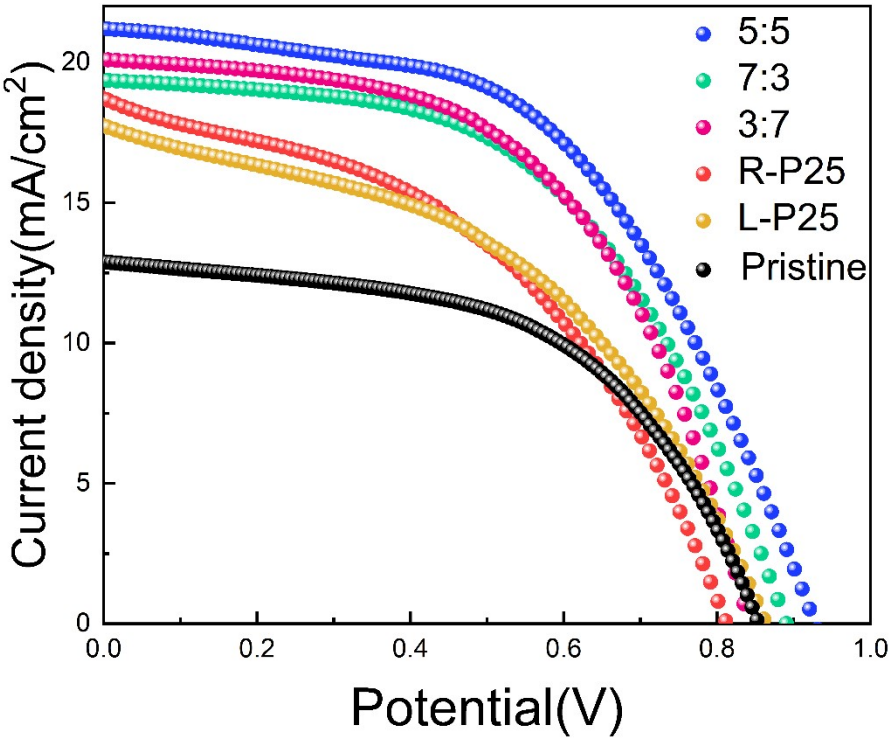

Fig. S6 The J-V curves of QDSSCs prepared with different photoanodes based on liquid electrolyte

Table S2. Performance parameters of five solar cells based on liquid electrolyte

Sample	Jsc(mA/cm^2)	Voc(V)	FF(%)	PCE(%)
Pristine P25	12.75	0.85	50	6.12
R-P25	17.93	0.81	46	7.14
L-P25	16.94	0.86	47	7.35
3:7	20.10	0.84	48	8.85
5:5	22.51	0.97	46	9.98
7:3	19.47	0.89	49	8.63

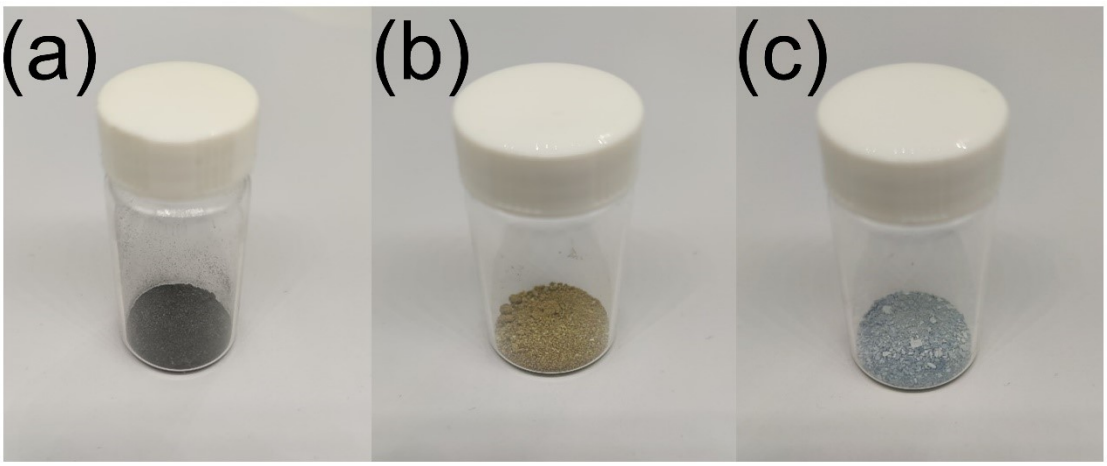

Fig. S7 Digital photos of black TiO_2 before(a) and after annealing (b, c).

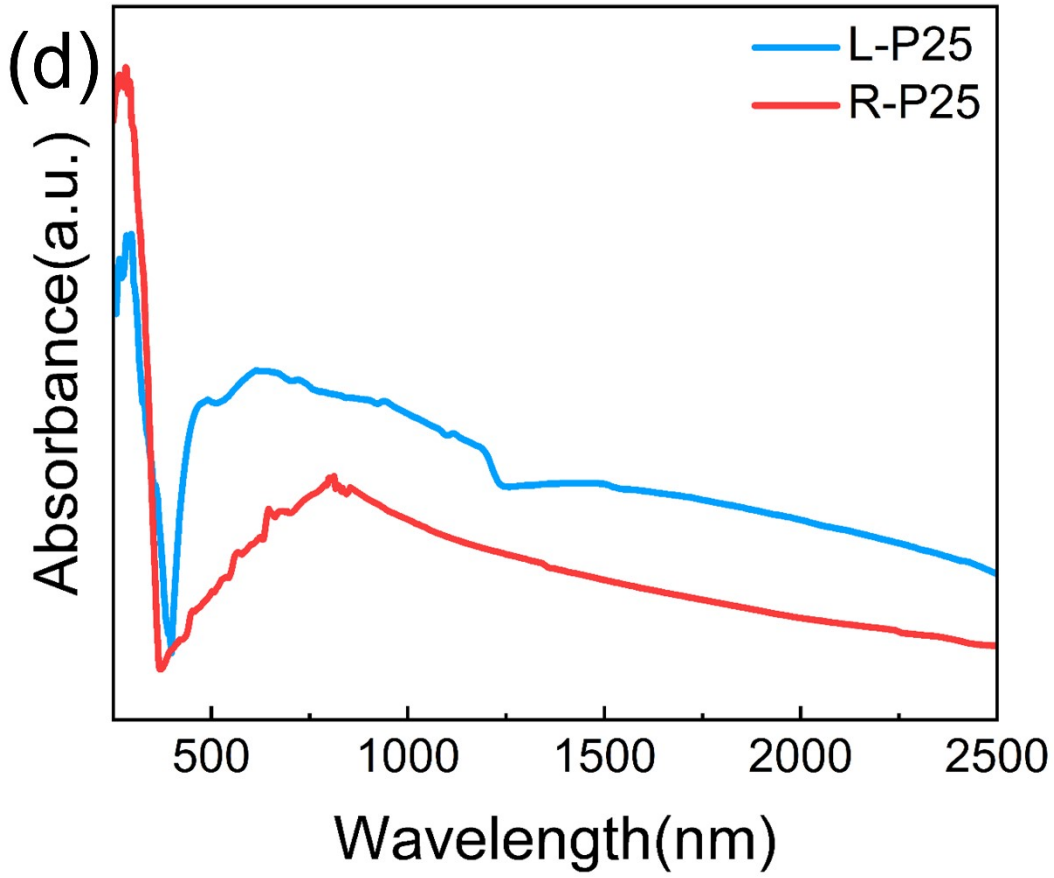

Fig. S8 The light absorption spectra of the two black TiO_2 powders after annealing.

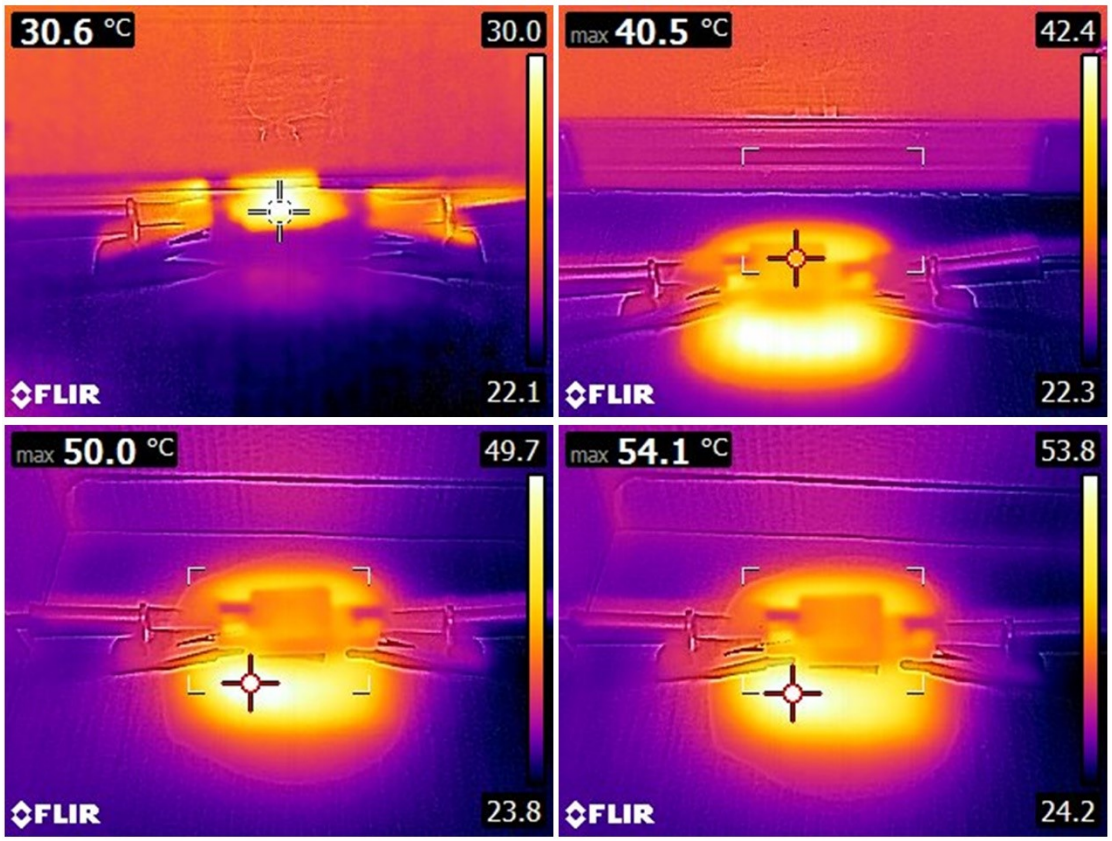

Fig. S9 Infrared thermal images at different temperatures.

Reference

1. C. Zhou, Q. Chen, G. Wang, A. Guan, L. Zhou, N. Huang and J. Xu, *Journal of Electroanalytical Chemistry*, 2016, **780**, 271-275.