# Aqueous mid-infrared electrically switchable opaque building envelopes for all-season radiative thermoregulation

<sup>1</sup>Chenxi Sui, <sup>2</sup>Jiankun Pu, <sup>1</sup>Ting-Hsuan Chen, <sup>1,3</sup>Yi-Ting Lai, <sup>1,4</sup>Yunfei Rao, <sup>1,5</sup>Xiuqiang Li, <sup>1</sup>Jiawei Liang, <sup>2</sup>Venkatasubramanian Viswanathan\*, <sup>1</sup>Po-Chun Hsu\*

<sup>1</sup>Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University

<sup>2</sup>Department of Mechanical Engineering, Carnegie Mellon University

<sup>3</sup>Department of Materials Engineering, Ming Chi University of Technology

<sup>4</sup>Zhejiang Provincial Key Laboratory of Fiber Materials and Manufacturing Technology, Zhejiang Sci-Tech University

<sup>5</sup>Institute for frontier science, Nanjing University of Aeronautics and Astronautics

\*Corresponding email: pochun.hsu@duke.edu and venkvis@cmu.edu

#### Abstract

Radiative thermoregulation has been considered a promising approach for reducing the heating, ventilation, and air-conditioning (HVAC) energy consumption of buildings and solving the global climate change issues. Electrochromism is a powerful way to dynamically control the heat balance of buildings in response to fluctuating weather conditions, but it has been largely limited to visible and near-infrared wavelength regimes. Here, we develop an aqueous flexible electrochromic system based on graphene ultra-wideband transparent conductive electrode and reversible electrodeposition, which can non-volatilely tune the thermal emissivity between 0.07 (heating) and 0.92 (cooling) with substantial long-term stability and durability. Building energy simulation demonstrates that applying our electrochromic device to building envelopes can save the year-round operational HVAC energy consumption across the U.S., especially in cold climate zone (up to 43.1 MBtu on average among climate zones 5-8). Furthermore, such a dynamic building envelope shows more profound benefits on less insulated buildings, with up to 19.44% of the year-round operational HVAC energy saving for building with only 25% insulation layer, which can serve as a technological solution to retrofit historical buildings or to complement newly constructed buildings with less insulation for lower embodied carbon.

#### Main

Buildings account for as high as 30% of the global energy consumption and emit 10% of global greenhouse gas, which causes environmental and economic challenges for a sustainable future. (1-5) Among such colossal energy consumption, approximately 48% is for space heating and cooling alone (6), calling for innovation to sustainably manage the building temperature and create net-zero-energy buildings. Radiative cooling materials have been developed to provide an effective approach to utilizing the coldness of outer space. (7-16) By reflecting the solar radiation and emitting heat to the sky, radiative cooling material can save the air-conditioning energy consumption of buildings in the hot summer. Apart from supplying cooling power to cool the buildings, low-emissivity (low-e) building envelopes can also conserve the HVAC (heating, ventilation, and air-conditioning) energy consumption by suppressing the radiative heat loss in cold climates. (17-27) However, the applicability of the abovementioned roof/wall envelopes with static radiative properties is restricted by the spatially and temporally variable weather. (6) Additionally, global warming causes increasingly frequent extreme weather events, (28-30) urgently demanding smarter and wider adaptability to different weather for buildings. A promising future net-zero-energy building should be able to dynamically tune its thermal emissivity in accordance with the weather conditions and occupants' demands. (31-33) To provide buildings with weather adaptability, Wang et al.(34) and Tang et al.(35) successfully demonstrated thermochromic materials based on tungsten-doped vanadium dioxide to passively shut down the radiative cooling in cold seasons, showing promising energy saving potential and functionality. The tuning criterion is a fixed phase change temperature, and it would be a step further to develop dynamically on-demand programmable radiative thermoregulation. Mechanical methods (6, 36, 37) have been demonstrated to dynamically switch between solar heating and radiative cooling, but the requirement of mechanical moving parts inevitably results in challenges in wide employment, such as transportation, storage, and installation.

Electrochromic devices can dynamically manage buildings' optical and thermal properties without mechanical force. Substantial progress has been made in both fundamental electrochemistry and commercialization.(*38-57*) However, it is still challenging to realize large mid-infrared (mid-IR) emissivity tuning contrast and long-term durability. In addition, for building applications, the usage of costly and flammable electrolytes will limit the scalability and create safety concerns. (*52*) Indeed, creating energy-efficient, durable, economical, and electrically switchable building envelopes for radiative thermal

management requires a rational systematic design of electrochemical redox reactions, electrolyte, and electrode materials.

Here, to tackle the bottleneck, we design a cost-effective Cu-based aqueous electrochromic mid-IR building envelope. The adoption of aqueous cupric solution makes the electrochromic device non-flammable and much more cost-effective than its counterparts, and using the ultra-wideband transparent conductive electrode allows considerable dynamic range of thermal emissivity tunability from 0.07 to 0.92. (*52*) The switching is stable, non-volatile, efficient, and mechanically flexible. After 1,800 deposition-stripping cycles, the emissivity contrast only reduces by 21%, thanks to the ultrathin Pt catalyst layer. The density functional theory (DFT) calculation also confirms the uniform and durable deposition of Cu on the Pt-modified electrode. Finally, the rigorous building energy calculation shows that our aqueous dynamic building envelope can save 8.4% of the U.S. buildings' HVAC energy consumption on average among climate zones 5-8 and reduce the embodied carbon of the insulation layer.

#### Aqueous electrolyte for electrochromism

As shown in Figure 1a, the electrochromic device contains a Pt-modified ultra-wideband transparent electrode as the working electrode, which is made of polyethylene, gold gird, monolayer graphene, and 2 nm sputtered Pt. The counter electrode is Cu foil for reversible Cu electrodeposition. The Pt-modified ultra-wideband transparent conductive electrode is optimized to maintain high mid-IR transmission. According to Kirchhoff's radiation law, emissivity is equal to absorptivity at thermal equilibrium, so the underlying IR-absorbing aqueous electrolyte will dominate the device's emissivity, screening the influence of the Cu foil. At the stripped state (pristine or +1 V bias versus Cu foil), the device exhibits high emissivity due to the electrolyte, leading to a cooling state that enhances the heat exchange between the buildings and the outer space through the atmosphere transparent window. At -0.7 V (versus Cu foil) bias, the device can switch to the low-e heating state by electrodepositing Cu on the ultra-wideband transparent electrode, thereby suppressing the radiative heat loss of the building.

This Cu-aqueous electrolyte possesses three advantages for the wide-range and large-scale applicability for thermal management: (i) nonflammability, (ii) lower price, and (iii) outstanding electrochromic performance (high tunable mid-IR contrast, non-volatile state retention, and long-term durability). A flammability test was conducted to examine the safety of the Cu-aqueous electrolyte compared with Ag-DMSO electrolyte that has been used for mid-IR tuning in prior reports(*40, 52*) (Figure 1b). Combustion occurred when the traditional Ag-DMSO electrolyte was exposed to fire, clearly confirming the better safety of Cu-aqueous electrolyte. Cost-effectiveness is another benefit of Cu-aqueous electrolyte. We calculate the price of the Cu-aqueous and Ag-DMSO electrolytes, and the results show that Cu-aqueous is 79.3% cheaper due to the lower cost of solvent and metal salt, as shown in Figure 1c (the detailed price of each component in the electrolyte is provided in the *Method*).

To achieve effective thermal management through the mid-IR modulation, an electrochromic device needs to perform the tunability in an extensive mid-IR range. Thanks to the high transmission of the graphene-based ultra-wideband transparent conductive electrode, the device can switch between the heating (low-e) and cooling mode (high-e) by depositing and dissolving the Cu film. Figure 1d shows the Fourier-transform infrared spectroscopy (FTIR) of the device at two states. The building envelopes can switch between cooling mode ( $e_{7.5-13\mu m} \approx 0.92$ ) and heating mode ( $e_{7.5-13\mu m} \approx 0.07$ ). The thermal emissivity contrast of  $\Delta e \approx 0.85$  is the highest among the reported non-mechanical mid-IR switching devices, including both thermochromic and electrochromic devices.(*34, 35, 40, 45, 53, 56, 58*) (Figure 1e) The more detailed comparison is shown in *Supplementary Information*. (Table S1)

Non-volatile switching is another key criterion for smart building envelopes. Prior reports of Ag-DMSO electrolyte system (40, 52) require supplying a small bias to maintain the deposited (low-e) state, due to the excessive bromide and silver-bromide complex ions. This self-dissolution can lead to considerably low tuning efficiency at the low-e state because of the excessive electricity consumed to compensate for the loss of metal film. In contrast, the Cu-aqueous electrolyte can bypass this limitation by using the  $Cu^{2+}/Cu$  (metal film) rather than the Br<sub>3</sub>/Br as the counter electrode redox couple. In Figure 1f, 400 s negative bias of -0.7 V and -1.5 V were applied respectively on the electrochromic devices with Cuaqueous and Ag-DMSO electrolyte and subsequently left them at open-circuit. The as-deposited Ag film with the Ag-DMSO electrolyte quickly dissolved back into the electrolyte in only 100 s; in contrast, the as-deposited Cu film can stay for more than 5.5 hours in the Cu-aqueous electrolyte, confirmed by the stable low emissivity. This result allows us to safely assume that the electrical energy consumption to maintain the emissivity states is negligible and calculate the required annual electricity to switch the entire building envelope, as shown in Figure 1g. The calculation method is described in Supplementary Note 1. The result shows that, even under the conservative assumption that the building envelope is switched three times a day with a large emissivity contrast of 0.80, the required annual electricity is negligible (only 0.13%) compared to the annual electricity usage of a baseline residential building. (59)



Figure 1. Concept and advantages of electrochromic mid-IR modulation system with an aqueous electrolyte. (a) Schematic demonstration of the electrochromic system. The device can be tuned between the heating mode (Cu-deposited) and the cooling mode (Cu-stripped). (b) Flammability test of Cu-aqueous and Ag-DMSO electrolyte. (c) Price analysis of Cu-aqueous and Ag-DMSO electrolyte. The total price is divided into four parts (acid, solvent, salt, and polymer inhibitor) to clearly show that aqueous electrolyte is more cost-effective. (d) FTIR spectra for the heating mode) to 0.92 (cooling mode). The green shaded area is the atmospheric transparent window. (e) The comparison of tunable emissivity contrast with different strategies: thermochromic  $VO_2(34)$ , thermochromic  $W_xV_{1-x}O_2(35)$ , thermochromic hydrogel(*58*), electrochromic graphene devices #1(*56*) and #2(*53*), electrochromic

conductive polymer devices(45), and reversible electrodeposited Ag device(40). The comparison chart shows that our emissivity tunability range is the highest, with  $\Delta e = 0.85$ . (f) Non-volatility test of heating mode (metal-coated). Without the Br<sub>3</sub><sup>-</sup>/Br<sup>-</sup> redox couple in the Ag-DMSO electrolyte, the electrochromic system can maintain its heating mode (low-e state) for 5.5 h without considerable decay.  $\lambda = 10 \ \mu m$ . (g) Annual electricity consumption for an aqueous device switching to different emissivity. We assume three times of switching each day. The red dash line represents the annual electricity usage of a baseline buildings.(59) The annual electricity consumption of the device switching to different emissivity states as a percentage of the annual electricity usage of a baseline building is labeled on the bar.

#### Elemental characterization and mid-IR tunability analysis for electrodeposition

To further investigate the emissivity tuning mechanism, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to characterize the surface morphology and elemental composition of the electrodeposited metal film. (Figure 2a) It shows that Cu can be deposited uniformly due to the introduction of the Pt-modification and polymer inhibitor.(*52, 54*) The composition of the deposited metal film was characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). In Figure 2b, the peaks at 932.5 and 952.5 eV in the Cu 2p scan confirm the existence of the metallic Cu(0). The shifted Cu 2p<sub>3/2</sub> peak at 934.5 eV and the satellite around 944 eV correspond to the small amount of CuO.(*60*) The composition analysis of Cu shows that there is 25.11% CuO. After electrodeposition, XRD analyses reveal peaks at 43.4° and 50.5° appearing on the ultra-wideband transparent electrode can be assigned to the Cu (111) and Cu (200),(*61, 62*) as shown in Figure 2c. There is no signal for the crystallized CuO in the XRD data. Since the XPS analyzes the top surface layer of the sample and XRD delivers the much deeper measurement, we infer that the CuO only exists in the top surface layer, which elucidates that the metallic Cu dominates the electrodeposition process and results in low emissivity.

For practical applications as the building envelope, the electrochromic device must have long-term durability. Figures 2d and e show the cycle test of the mid-IR emissivity tuning. The large emissivity contrast can be maintained for 1000 cycles and only degrade 21% after 1800 cycles, which exhibits a significant improvement from the previous reports using Ag-DMSO electrolyte (only up to 300~400 cycles).(*40, 52*) The emissivity spectra maintain their broadband feature after 2500 cycles (Figure 2e). It is noteworthy that the heating mode (low-e state) degrades faster than the cooling mode (high-e state), which could be attributed to the irrecoverable absorption of Cl<sup>-</sup> ions on the working electrode and the

oxidation of the metal film.(47, 52) It should be mentioned that the deposition and stripping potentials are carefully selected to avoid hydrogen and oxygen evolution reactions (HER and OER).(47) As shown in the cyclic voltammetry test (Figures S2 and 3), there is no noticeable current increment related to HER or OER within the deposition and stripping potentials range for both 2-electrodes and 3-electrodes systems.

To quantitively explain the monotonic trend of the decreased emissivity with the increased amount of electrodeposited Cu, one needs to consider the convoluted effect of volume fraction and thickness. During the initial electrodeposition process,  $Cu^{2+}$  ions can either be reduced onto the existing Cu nanoparticle (increase thickness) or nucleate on the bare substrate (increase volume fraction). While it is intuitively straightforward to understand the negative monotonic correlation between the amount of Cu and the emissivity, the real question is how to derive the quantitative explanation of the experiment. Considering the porous nature of the electrodeposited Cu nanoparticle film and the large dimensional difference between the nanoparticles and thermal radiation wavelength, we adopt the effective medium theory (EMT) to fit the experimental results and obtain the relationship between the emissivity and the Cu film thickness with different volume fractions (Figure 2f). The effective permittivity  $\varepsilon_{eff}$  of the porous Cu film is calculated by Bruggeman's EMT (eq. 1):(63)

$$f\frac{\varepsilon_{\rm Cu} - \varepsilon_{\rm eff}}{\varepsilon_{\rm Cu} + 2\varepsilon_{\rm eff}} + (1 - f)\frac{\varepsilon_{\rm air} - \varepsilon_{\rm eff}}{\varepsilon_{\rm air} + 2\varepsilon_{\rm eff}} = 0$$
(1)

where *f* is the volume fraction of the Cu nanoparticles,  $\varepsilon_{Cu}$  and  $\varepsilon_{air}$  are the wavelength-dependent permittivity of the Cu and air, respectively. Note that it was air rather than aqueous electrolyte used for calculation because the empirical data were measured ex-situ in the dry state. Then, considering three stratified mediums (inset of the Figure 2f), the thickness-dependent reflectivity  $\mathcal{R}$  of the porous Cu film is obtained (eq. 2):(*64, 65*)

$$\mathcal{R} = \left| \frac{r_{12} + r_{23} e^{2i\beta}}{1 + r_{12} r_{23} e^{2i\beta}} \right|^2 \tag{2}$$

where  $r_{\rm mn} = (n_{\rm m} \cos \theta_{\rm m} - n_{\rm n} \cos \theta_{\rm n})/(n_{\rm m} \cos \theta_{\rm m} + n_{\rm n} \cos \theta_{\rm n})$ ,  $\beta = (\frac{2\pi}{\lambda})n_2h \cos \theta_2$ ,  $n_{\rm m} = \sqrt{\varepsilon_{\rm m}}$ , and  $\theta_{\rm m} = \sin^{-1}\left(\frac{n_1 \sin \theta_1}{n_{\rm m}}\right)$ .  $\vartheta$ , n, and h are the incident angle, refractive index, and thickness of porous Cu film, respectively. Medium 1 and 3 are polyethylene and air, and medium 2 corresponds to the porous Cu film. Finally, the emissivity is calculated by 1-  $\mathcal{R}$  based on Kirchhoff's radiation law. As shown in Figure 2f, the experimental results (red circles) are consistent with the theoretical calculations (blue

lines) by varying the volume fraction between 0.38 and 0.41. It should be noted that the initial data point for no Cu deposition is approximated by replacing the permittivity of the Cu ( $\varepsilon_{Cu}$ ) by Pt ( $\varepsilon_{Pt}$ ) in Eq. 1. The result shows that the initial Pt volume fraction  $f_{Pt}$  is about 0.70. The structure of this nanoscopic Pt is shown in the TEM image (Figure S6). When the Cu starts to deposit, the volume fraction decreases to below 0.38, and the thickness of the deposited metal layer increases to around 11 nm, which results from the sparsely packed Cu nanoparticles. As more Cu deposits, the volume fraction turns to increase together with the thickness, indicating that the Cu nanoparticles become larger and denser to block the thermal radiation.



**Figure 2. Elementary and mid-IR tunability analysis.** (a) SEM image and EDX mapping of the deposited film. The scale bar is 50  $\mu$ m. (b, c) XPS and XRD analysis of the deposited film. (d) Cycle life test of the electrochromic mid-IR system. (e) The FTIR spectra for different cycle numbers. (f) The relationship between the emissivity and the thickness of as-deposited metal film. Effective medium theory is used to fit the relationship to physically explain the mid-IR tunability. The emissivity is both measured and calculated under  $\lambda = 10 \ \mu$ m. The inset is the schematic demonstration of the electromagnetic wave propagating through the stratified medium.

#### Pt-modification for uniform electrodeposition

As stated in the previous research, the Pt-nanoparticles modification on the working electrode can enhance the uniformity and durability of the reversible metal electrodeposition. (*40, 42, 47, 48, 52*) The morphologies of electrodeposited Cu film on the bare graphene and Pt-modified substrate were characterized by SEM (Figure 3a). On the bare graphene substrate, Cu tends to become sparsely distributed large particles due to the high surface energy between graphene and metallic Cu (Figure S4). According to effective medium and percolation theory, (*63, 66, 67*) the metal film must be dense and continuous enough to reach the percolation threshold that can behave metal-like in optics (reflecting the electromagnetic wave). However, the "Cu-phobic" surface of bare graphene can only form a sparse Cu particles film, and thus the deposited film is not reflective enough for mid-IR radiation. On the contrary, the Cu can grow uniformly and coherently on the "Cu-philic" surface of the Pt-modified graphene, resulting in fast conversion to the metallic state after electrodeposition. As shown in Figure 3b, with the same charge density of electrodeposition (0.175 C/cm<sup>2</sup>), the Cu film grown on the Ptmodified surface possesses lower emissivity, contributing to a more considerable contrast in the mid-IR range.

To realize the fundamental difference between the bare graphene and Pt-modified graphene for Cu electrodeposition, we further study the heterogeneous interaction of the Cu atoms with different substrates using DFT. Adsorption free energy between substrates and Cu atoms and interaction energy between Cu-Cu adatoms are two factors to characterize the heterogeneous nucleation of Cu.(*68*) Three different systems were simulated (Figure 3c) using DFT. To evaluate the adsorption energy, we consider the following reaction mechanism, and the initial electrochemical adsorption step is given by:

$$Cu^{2+}_{(sol)} + 2e^- + * \rightleftharpoons Cu^*$$

where \* refers to an adsorption site on the bare graphene and Pt substrates. In order to avoid calculating the free energy of solution species, the limiting potential for the adsorption step can be calculated using the computational Cu electrode reference, which is given by:  $\Delta G_{Cu^{2+}} + \Delta G_{2e^{-}(U=0)} = \Delta G_{Cu}$ . The adsorption energy ( $E_{ads}^{\theta}$ ) then can be described as:

$$E_{ads}^{\theta} = \Delta G_{Cu^*} - \Delta G_{Cu}$$

where  $\theta$  is the coverage factor,  $\Delta G_{Cu^*}$  is the Gibbs free energy of the Cu adatom and  $\Delta G_{Cu}$  is the Gibbs free energy of the bulk Cu. We approximate the free energies to be equal to their DFT energies, neglecting entropic contributions:

$$E^{\theta}_{ads} = (E^{\theta}_{slab} - E^{clean}_{slab}) - E^{bulk}_{Cu}$$

where  $E_{slab}^{\theta}$  is the DFT energy of the substrate with Cu adatom,  $E_{slab}^{clean}$  is the DFT energy of the pure substrate and  $E_{Cu}^{bulk}$  is the DFT energy of the bulk Cu. Both adsorption energies of Cu to graphene and Pt were calculated at high coverage ( $\theta = 1$ ) and low coverage ( $\theta = \frac{1}{9}$ ).(69) In addition, all low index surfaces of Pt are considered for the calculation. The procedure to determine the lowest adsorption energy site is described in the *Method* section. A decrease of adsorption energy from low to high coverage can be observed across all the systems studied in the top plot of Figure 3d, indicating that the Cu adatom will adsorb on Pt and graphene surface after overcoming the initial nucleation overpotential. The results show that the adsorption energies of Cu adatom on graphene at high and low coverage are both positive, i.e., 0.98 eV and 3.10 eV, respectively, much higher than that on Pt surfaces. Cu adatom would have weak interaction with graphene and would prefer to cluster rather than form uniform films on the graphene surface. To verify that Cu indeed has a higher tendency to cluster on graphene surface, the interaction energy  $\omega$  between adatoms is further calculated by:

$$\omega = E_{slab}^{2Cu} - \left(2 * \left(E_{slab}^{clean} + E_{Cu}^{bulk}\right) + E_{ads}^{low\theta}\right)$$

where  $E_{slab}^{2Cu}$  is the DFT calculated energy of a substrate with 2 Cu atoms and  $E_{ads}^{low\theta}$  is the adsorption energy of Cu at low coverage. Thus, the interaction energy can be obtained by direct measurement of the binding energy of two Cu adatoms on a given substrate, as shown in the right part of Figure 3c. Since there are different directions of the interaction, the mean and standard deviations of the interaction energy are calculated as shown in the bottom plot of Figure 3d. The mean interaction energy of Cu adatoms on bare graphene substrate is ~2.17 eV lower than that on Pt substrate. It indicates that Cu prefers to nucleate around the random-distributed defects, causing the discrete, sparse clusters of the Cu particles on the bare graphene substrate. The defects or edges of the graphene tend to attract metal/metal oxide atoms, which might result from its dangling bonds or the termination by other reactive species.(70) A tight connection between the experiments and simulations confirms the benefit of Pt-modification for uniform electrodeposition.



Figure 3. Characterization and theoretical explanation of the performance enhancement by Pt-

**modification.** (a) SEM images of the deposited Cu morphology on the transparent electrode with and without Pt modification. The scale bars of the low and high magnification images are 10  $\mu$ m and 1  $\mu$ m, respectively. (b) The FTIR spectra of the Cu films were deposited on the bare and Pt modified graphene transparent electrode. Both samples are coated with the same charge density, 0.175 C/cm<sup>2</sup>. (c) Atomic diagrams for DFT calculation. (d) The calculated adsorption energy between substrates (Pt or graphene) and Cu atom, and the interaction energy between two adjacent Cu atoms on different substrates.

#### Smart building envelope for energy saving and carbon footprint benefit

The high-performance mid-IR electrochromism, nonflammability, inexpensiveness, and flexibility (Figures S7 and S8) of the Cu-aqueous mid-IR modulation device allow the application of smart building envelopes for thermal management by electrical bias (Figure 4a). To experimentally demonstrate such applicability, we attached the electrochromic device onto a heater and measured the heat loss through the device under different ambient temperatures (Figure 4b). Detailed experimental design is shown in the *Method*. (Figure S9) Without the ability to change the emissivity, the high-e/low-e building envelope tends to overcool/overheat the building in a cold/hot environment, confirmed by the high/low heat loss (over 100 W/m<sup>2</sup> or below 50 W/m<sup>2</sup>). In contrast, the electrochromic device can vary its emissivity in response to different ambient temperatures to maintain the constant heat loss (near 75 W/m<sup>2</sup>) for the thermal comfort of the buildings.

To comprehensively demonstrate the building HVAC energy saving ability, the remarkable optical properties of the Cu-aqueous electrochromic device are imported into EnergyPlus as the emissivity of buildings' sidewalls and roofs to calculate the year-round energy-saving. The calculation is conducted for 15 cities, corresponding to 15 climate zones in the U.S. (Figure S10), (4, 6, 71) to demonstrate the widerange applicability of this smart building envelope. In Figure 4c, we plot the operational HVAC energy saving and saving percentage of the building enveloped with the electrochromic device. The result manifests that most buildings located in weather with high variations, including daily and seasonal fluctuation, require dynamic thermal management. The dynamic emissivity tunability of the device helps the building save more energy compared to the constant low-e or high-e building envelopes (Figure S11). When the cooling load is larger than the heating load, especially in hot areas 1A and 3B, the low-e building envelopes suppress radiative heat loss to the environment, causing excessive cooling load and more energy consumption. In hot/dry areas like Honolulu, Austin, Los Angles, Phoenix, the low-e building envelope even consumes more energy than the normal values, pointing out the necessity of switchability between cooling and heating modes (high-e and low-e states). In Figures 4c and 4d, the electrochromic device adaptive to the fluctuating weather conditions can achieve higher energy saving, especially in cold areas. The building envelopes in Helena and Fairbanks can save 48.26 MBtu and 57.26 MBtu year-round HVAC energy, respectively.

In addition to the operational energy and carbon footprint due to HVAC, the building insulation material is also considered an emission source, known as embodied carbon. (72-74) Commonly used materials such as expanded polystyrene, extruded polystyrene, and polyurethane have more than 4 kgCO<sub>2</sub> eq./kg

carbon footprint, aggravating global warming. (Figure S12) (72) It is attractive to reduce the carbon emission of the thermal insulation layer during building construction. Because of our device's dynamic tunability, we anticipate it can reduce the usage of the thermal insulation layer by adapting to the varying external environment, rather than merely shielding from it. In Figure 4e, we calculate the energy saving percentage for buildings with different thicknesses of the insulation layer in Helena and their corresponding carbon footprint of the thermal insulation layer. The calculation method is shown in the *Supplementary Note 2*. In *EnergyPlus*, the insulation layer's default thickness (100%) is 0.119 m and 0.127 m for Steel Frame Wall and Roof, respectively. As we decrease the thickness of the thermal insulation layer from 100% to 25%, the embodied carbon footprint of the building can be reduced from 12170.2 to 3042.6 Kg CO<sub>2</sub> eq., and up to 19.44% of HVAC energy can be saved with the help of the Cuaqueous electrochromic device. The results demonstrate that the Cu-aqueous mid-IR modulation device can save more percentage of operational HVAC energy for low carbon footprint buildings (fewer insulation materials used), outperforming the constant low-e and high-e envelope, especially when installed on buildings with poor thermal insulations for retrofitting. (Figure S13)



**Figure 4. Smart building envelope for all-season energy saving application**. (a) Scheme for smart building envelope with radiative thermal management. By continuously tuning the emissivity, the building can maintain thermal comfort efficiently in all seasons. (b) Heat loss of building surfaces with different envelopes under different ambient temperatures. (c) The year-round operational HVAC energy saving and saving percentage of buildings enveloped with the electrochromic device. (d) Energy saving map of the building envelope by the electrochromic device for all 15 climate zones in the U.S. (e) Building corresponding carbon footprint for Helena with different thickness of insulation layer and their HVAC energy saving percentage by using the electrochromic envelope. CO<sub>2</sub> eq. means CO<sub>2</sub> equivalent.

#### Discussion

This research develops an aqueous electrically switchable electrochromic building envelope for the building thermoregulation. First, comprehensive experiments were conducted to demonstrate the benefits of Cu-aqueous electrolytes. The nonflammability and lower cost (79.3% reduction of electrolyte price compared with Ag-DMSO) provided by the aqueous electrolyte contribute to a safe and economical smart building envelope. By removing the Br<sub>3</sub><sup>-</sup>/Br<sup>-</sup> redox couple, the metal deposition shows a non-volatile tunability with significant thermal emissivity contrast (0.85 in the atmospheric transmittance window range). The low-e state in mid-IR can be maintained for 5.5 hours without significant decay under the open circuit condition. Since the aqueous electrolyte is less harmful to the working electrode, the device can switch between heating and cooling modes 1800 times with only 21% degradation in emissivity contrast, which exhibits significant improvement for long-term durability. Second, we fundamentally explain the benefit of Pt-modification for uniform electrodeposition through various characterization techniques and simulations. The calculation shows more negative adsorption energy between Pt-Cu and higher interaction energy between two Cu adatoms on Pt, indicating that Cu tends to form a uniform film on the Pt-modified graphene substrate, achieving the large emissivity contrast in mid-IR.

The building envelope can maintain a constant heat loss of the building under different ambient temperatures to avoid overheating and overcooling by tuning its emissivity. The usage of graphene as a transparent electrode also provides mechanical flexibility to the device, enabling it to retrofit the wall or roof of buildings with various shapes and be folded or rolled up for convenient transportation and storage. The building energy simulation across the U.S. further confirms such a smart building envelope can save more operational HVAC energy, especially in cold areas. It should also be noted that this electrochromic building envelope can reduce the usage of the embodied carbon of buildings' thermal insulation layer, contributing to a low-carbon sustainable future. We hope this research can pave the way for designing sustainable electrochromic devices in mid-IR modulation for smart building envelopes and deepen the fundamental understanding of the reversible metal electrodeposition.

#### Method

#### **Electrolyte preparation**

The aqueous electrolyte consists of 20 mM Cu(ClO<sub>4</sub>)<sub>2</sub>, 1 M LiClO<sub>4</sub>, 10 mM HClO<sub>4</sub>, and 10 wt.% PVA for uniform electrodeposition. The whole solution is mixed under 80 °C. The DMSO electrolyte is prepared by following the previous recipe.(*52*)

#### Electrochromic building envelope device fabrication

The monolayer chemical vapor deposited graphene on Cu is purchased from Cheap Tube Inc. For the Au grid fabrication, the photoresist (NFR-016D2) is spin-coated on the graphene and then photolithographed to form microchannels (with width and spacing of 10 µm and 1 mm, respectively). Then, 200 nm Au is evaporated (Kurt J. Lesker PVD 75) and lift-off in acetone to form the Au grid on the graphene. The graphene coated with the Au grid is hot-pressed onto the transparent PE film under 99 °C to ensure the strong bonding between graphene and polymer, and the Cu on the graphene is etched away by iron (III) chloride solution.

To fabricate the whole building envelope device, 2 nm Pt is sputtered onto the transparent conductive electrode, which serves as the working electrode. The counter electrode is Cu foil. Two electrodes with the Cu-aqueous electrolyte in between are sandwiched and sealed by acrylic tapes (3M, ~0.25mm).

#### Electrochemistry

The electrochromic performance testing is conducted via the VMP3 (BioLogic Inc.). For the constant potential electrodeposition process, the deposit potential is -0.6 V (versus Ag/AgCl) for 3-electrode system and -0.7 V (versus Cu foil) for 2-electrode device. For the constant potential stripping process, the potential is +0.3 V for 3-electrodes (versus Ag/AgCl) and +1 V for 2-electrodes (versus Cu foil) systems. The cyclic voltammetry test is scanned with a rate of 20 mV/s.

#### Characterization

FTIR characterization of the static and real-time spectra is conducted by iS50 (Thermo Scientific) equipped with a diffuse gold integrating sphere. The SEM images and EDX elements analysis of the deposited Cu nanoparticles are taken by a high-resolution field-emission scanning electron microscope (Apreo S by ThermoFisher Scientific). The XPS spectrum is obtained on the X-Ray Photoelectron Spectrometer (Kratos Analytical Axis Ultra). The infrared images are recorded using an IR camera (FLIR E60).

#### Heat transfer measurement

The heat loss of the building enveloped with the electrochromic device was measured in an acrylicenclosed chamber with cooling/heating water recirculation. The setup of this experiment is described in Figure S9. The surface temperature is controlled by the top heater. To eliminate the lateral heat loss, the temperature guard heater is heated to have the same temperature as the top heater. Both top and guard heaters are connected to a DC power supply (Rigol, DP821A). The temperatures of two heaters are measured by two thermal couples, collected by the DAQ module (MC Measurement Computing, USB-2408). Such a process is achieved by the PID control system, coded by LabView. By doing so, the heat will transport vertically in a 1D direction. The building envelops sample, heaters, and vacuum insulation panel are attached by thermal paste. The ambient temperature was controlled by recirculating water pipes. To simulate the real building in all seasons, we choose five ambient temperatures: 10 °C, 15 °C, 20 °C, 25 °C, and 30 °C. For these ambient temperatures, we set the surface temperature to be 23 °C, 27 °C, 30 °C, 33 °C, and 37 °C. Since the building surface temperature is always higher than the ambient temperature, the building will lose heat to the environment. The measurement is conducted under the thermal equilibrium (wait 10 mins after the initial temperature raise peak), so the heat loss through the building envelope is equal to the power density of the top heater.

#### **Electrolyte price calculation**

The industrial-scale price of the chemicals used to prepare the electrolyte is obtained on the Alibaba ecommerce website and is shown in the sheet below. (<u>https://www.alibaba.com</u>) The blue and red shadows represent the chemicals used in Cu-aqueous and Ag-DMSO electrolytes, respectively.

| Chemical's name                    | Price (US \$/gram) |  |  |  |
|------------------------------------|--------------------|--|--|--|
| PVA                                | 0.0022             |  |  |  |
| HClO₄                              | 0.005              |  |  |  |
| Cu(ClO <sub>4</sub> ) <sub>2</sub> | 0.01               |  |  |  |
| LiClO <sub>4</sub>                 | 0.015              |  |  |  |
| Water                              | 0.00084            |  |  |  |

| AgNO <sub>3</sub> | 0.5    |  |  |  |
|-------------------|--------|--|--|--|
| CuCl <sub>2</sub> | 0.006  |  |  |  |
| TBABr             | 0.0058 |  |  |  |
| PVB               | 0.0025 |  |  |  |
| DMSO              | 0.0085 |  |  |  |

Table 1. Prices for chemicals in the Cu-aqueous and Ag-DMSO electrolyte.

#### **Building energy-saving calculation**

The HVAC energy consumption of buildings in different U.S. areas is calculated by *EnergyPlus* version 9.4. Fifteen cities are selected to represent 15 climate zones in the U.S.(*71*) The new-2004 midrise apartment model from the U.S. Department of Energy is utilized for simulation. The building area is  $3135 \text{ m}^2$  and has 4 stories and 42 windows. The cooling and heating load are calculated hourly all yearround. For the building installed with the electrochromic mid-IR device, the emissivity of the out-layer materials is set to 0.07 and 0.92 for heating and cooling mode. We used normal buildings (the default building model with emissivity equal to 0.9) to represent the baseline. By running the model for building under cooling mode, the cooling and heating load under heating and cooling mode (emissivity = 0.92).  $P_{\text{cool, c}}$  and  $P_{\text{heat, c}}$  represent the cooling and heating load under the heating model (emissivity = 0.07). The energy consumption for the building per hour is calculated as below:

$$E = 3600 \cdot MAX(P_{cool}, P_{heat})$$

Thus, the energy consumption for heating and cooling mode can be calculated as  $E_h$  and  $E_c$ . Considering the dynamic tuning ability of the device, the building can vary its emissivity in response to the demand. Therefore, the building can use the minimal energy cost among the heating and cooling modes and can be calculated as:

$$E_d = MIN(E_h, E_c)$$

The total energy cost all year round is obtained by summing up the hourly energy cost.

#### **DFT calculation**

To model the adsorption mechanism on graphene and Pt surface, self-consistent DFT calculations are carried out using the Bayesian error estimation function with van der Waals correlation (BEEF-vdW) exchange-correlation functional owing to its accuracy for describing adsorption energies and van der Waals interaction between graphene layers, as implemented in the open-source package GPAW.(75-77) All simulations are carried out with the help of a python package BASIC developed by Jiankun Pu. Calculator setting convergence tests are conducted on bulk Pt, Cu, and pristine monolayer graphene. Real-space grid and k-point are considered converged when the difference of energies is within 0.015 eV/atom. The calculator settings are listed in the *Supplementary Information* (Table S2). To set up the slab for adsorption energy, BASIC is used to create, manipulate, visualize and analyze the slab structures. The bottom two layers on the z-axis of the Pt slab are held fixed. Periodic boundary conditions are used for the x and y directions. Dipole correction is turned on, and a vacuum of 10 Å is added along the z-axis on both sides of the slab. The minimum number of layers needed for the slab is tested for convergence against the surface energy using BASIC. The convergence criterium is set to be 0.015eV/atom. Lastly, to carry out the adsorption and interaction simulation, AutoCat (GitHub repo: <u>https://github.com/aceddifferentiate/auto\_cat/tree/master</u>) was used to generate all the possible adsorption sites on a slab. Then, BASIC handles the calculation automatically and selects the most stable adsorption energy. All simulations were considered converged for forces <0.01 eV/Å.

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#### **Author Contributions:**

P.C.H. and C.S. conceived the idea. C.S. performed all the experiments, optical fitting, building energy simulation and their corresponding data analysis. T.C. helped with the heat transfer measurement. V.V. and J.P. performed the DFT calculation. Y.L., Y.R. and J.L. helped with the transparent electrode fabrication. X.L. helped with the energy saving calculation. C.S., J.P., and P.C.H. wrote the manuscript with input from all co-authors.

#### **Competing interests:**

The authors declare no competing financial interests.

#### Data and materials availability:

All data needed to support the conclusions in the paper are present in the manuscript and/or the

Supplementary Materials. Additional data related to this paper may be requested from the

corresponding author upon request.

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Supplementary Information for

# Aqueous mid-infrared electrically switchable opaque building envelopes for all-season radiative thermoregulation

Sui et al.

# **Supplementary Figures**



Figure S1. The emissivity of the electrochromic device can be varied at different values by tuning the deposition charge density. ( $\lambda = 10 \ \mu m$ ) The bottom part of this panel is the corresponding voltage profile for this demonstration.



Figure S2. Cyclic voltammetry test of the electrochromic 3-electrode system. The reference electrode is Ag/AgCl.



Figure S3. Cyclic voltammetry test of the electrochromic 2-electrode system. The reference electrode is Cu foil, which is also the counter electrode.

## Pt modification



Figure S4. Schematic of deposited Cu morphology on the transparent electrode without and with Pt modification.



Figure S5. XPS of the sputtered thin Pt layer.



Figure S6. TEM image of the Pt layer and its density estimation. The scale bar is 50 nm.

## Flexible applicability

The mechanical flexibility of an electrochromic device is indispensable for the radiative thermal management of objects with various shapes of surfaces. Here, we use a porous nylon film as the separator to prevent the contact between the working electrode (ultra-wideband transparent electrode) and the counter electrode (Cu foil). The  $2 \text{ cm} \times 2 \text{ cm}$  device can switch between cooling and heating modes when bent to different shapes, making it suitable for human skin thermal management (Figure S7). The 6 cm  $\times$  6 cm large-scale flexible device (Figure S8) is attached to the human knees (Figure S7c). The thermal camera images elucidate that the apparent temperature can be uniformly tuned with nearly 10 °C contrast, proving the Cu-aqueous electrochromism applicable to flexible and large-scale thermal management.

To make the flexible device for objects with complex surfaces, the transparent conductive electrode, porous nylon film, and Cu foil are sandwiched together with the double-sided acrylic tapes (3M, ~0.25mm). The nylon film serves as the separator to insulate the transparent electrode and Cu foil when the device is bent. For the 6 cm  $\times$  6 cm large-scale device, Cu tape is used on the four edges of the graphene to reduce the potential drop of the transparent electrode.



Figure S7. Flexible device for thermal management. (a) Scheme for flexible electrochromic mid-IR modulation device and its thermal management application. (b) Thermal camera images for the flexibility test. The device still switches between cooling and heating modes after being bent. The scale bar is 2 cm. (c) Thermal camera images for the 6 cm  $\times$  6 cm flexible device. The device is attached to the human's knee and can switch between cooling and heating modes when supplied by bias. The scale bar is 5 cm.



Figure S8. The optical image of the 6 cm  $\times$  6 cm large-scale flexible electrochromic mid-IR modulation device.

## Heat transfer measurement



Figure S9. Heat transfer measurement setup.

# Building envelope year-round energy saving calculation



Figure S10. Climate zones of the U.S.



Figure S11. Building operational HVAC energy saving and saving percentage of 15 climate zones with different types of building envelopes. The baseline is the normal midrise apartment's annual HVAC energy consumption.



Figure S12. Embodied carbon of thermal insulation materials and the carbon footprint during their end-of-life cycle. The carbon footprint data for different common-used thermal insulation materials are extracted from the previous study.(1)



Figure S13. The HVAC energy saving and saving percentage of the buildings with different thicknesses of the insulation layer. We considered three types of building envelopes (high-E, low-E, and electrochromic dynamic tuning envelopes).

| Strategy                                       | Working principle | Switch materials     | Operating  | Emissivity   | Emissivity |
|--|-------------------|----------------------|------------|--------------|------------|
|  |                   |                      | voltage    | Tunable      | Tunable    |
|  |                   |                      |            | range        | contrast   |
| $VO_2$ (ref(2))                                | Thermal phase     | VO <sub>2</sub>      | -          | 0.21 to 0.61 | 0.4        |
|  | change            |                      |            | (2.5 to 25   |            |
|  |                   |                      |            | μm)          |            |
| W <sub>x</sub> V <sub>1-x</sub> O <sub>2</sub> | Thermal phase     | $W_x V_{1-x} O_2$    | -          | 0.2 to 0.9   | 0.7        |
| (ref(3))                                       | change            |                      |            | (8-13 µm)    |            |
| Hydrogel                                       | Thermal phase     | poly(N-              | -          | 0.352 to     | 0.571      |
| (ref(4))                                       | change            | isopropylacrylamide) |            | 0.923        |            |
|  |                   | and silver nanowires |            | (2.5–16      |            |
|  |                   |                      |            | μm)          |            |
| Graphene #1                                    | Electrical ion    | Graphene             | 0 V for    | 0.25 to 0.7  | 0.45       |
| (ref(5))                                       | intercalation     |                      | high-e &   | (10 µm)      |            |
|  |                   |                      | 3.6 V for  |              |            |
|  |                   |                      | low-e      |              |            |
| Graphene #2                                    | Electrical ion    | Graphene             | 0 V for    | 0.33 to 0.76 | 0.43       |
| (ref(6))                                       | intercalation     |                      | high-e &   | (10 µm)      |            |
|  |                   |                      | 3.8 V for  |              |            |
|  |                   |                      | low-e      |              |            |
| Conductive                                     | Electrochromic    | Poly (aniline co-    | -1 V for   | 0.237 to     | 0.514      |
| polymer #1                                     |                   | diphenyl amine)      | low-e &    | 0.751        |            |
| (ref(7))                                       |                   |                      | 0.5 V for  | (2.5–45      |            |
|  |                   |                      | high-e     | μm)          |            |
| Electrodeposit                                 | Electrodeposition | Ag                   | -1.5 V for | 0.08 to 0.79 | 0.71       |
| Ag (ref(8))                                    |                   |                      | low-e &    | (7.5 to 13   |            |
|  |                   |                      | 0.3 V for  | μm)          |            |
|  |                   |                      | high-e     |              |            |
| This work                                      | Electrodeposition | Cu                   | -0.7 V for | 0.07 to 0.92 | 0.85       |
|  |                   |                      | low-e &    | (7.5 to 13   |            |
|  |                   |                      | 1 V for    | μm)          |            |
|  |                   |                      | high-e     |              |            |

| Materials | Exchange correlation functional | Grid spacing | k-point grid | Smearing algorithm |
|-----------|---------------------------------|--------------|--------------|--------------------|
| Bulk Cu   | BEEF-vdW                        | 0.16         | (6, 6, 6)    | Fermi-Dirac (0.01) |
| Slab Pt   | BEEF-vdW                        | 0.16         | (8, 8, 1)    | Fermi-Dirac (0.01) |
| Bulk Pt   | BEEF-vdW                        | 0.16         | (8, 8, 8)    | Fermi-Dirac (0.01) |
| Graphene  | BEEF-vdW                        | 0.14         | (12, 12, 1)  | Fermi-Dirac (0.01) |

Table S1. Comparison of different IR emissivity tuning strategies, corresponding to Figure 1e.

Table S2. Density function theory calculation details.

## Supplementary note 1: Device switch electricity intensity calculation

The electricity intensity for switching the device is calculated by multiplying the overall charge density (Q) by the deposition voltage (V), which is described as the below equation:

$$E_{device} = Q \times V$$

To calculate the averaged electricity intensity per unit floor of the buildings installed with the electrochromic building envelopes, the total electricity consumption should be calculated first by multiplying the  $E_{device}$  and the total envelope's area (roof and wall). Then, the total electricity consumption is divided by the number of floors (4 stories) and the unit floor space area (3135 m<sup>2</sup>) to get the averaged electricity intensity per unit floor, which can be described as the equation below:

$$E_{unit} = \frac{E_{device} \times S_{roof+wall}}{4 \ stories \times S_{floor}}$$

In the end, we conservatively assume the building needs 3 times switching. The daily electricity intensity of the electrochromic device would be  $3 \times E_{unit}$ . Then, the annual electricity intensity is calculated by  $365 \times 3 \times E_{unit}$ . The charge density corresponding to emissivity is shown in Figure S1.



Figure S14. Midrise apartment model in *EnergyPlus*.

### Supplementary note 2: Embodied carbon calculation

The embodied carbon of thermal insulation layer can be calculated by the total mass of the thermal insulation materials multiplied by its carbon footprint per mass, 0.062 kg CO<sub>2</sub> –eq./kg (can be found in the literature (1), Wood fibre wool–low density). To calculate the mass of the thermal insulation materials, the volume should be first calculated. We assume the insulation materials is inserted in all walls and roofs. Therefore, the volume of the insulation materials can be calculated as below:

$$V = (S_{wall} + S_{roof}) \times t$$

where  $S_{wall}$  and  $S_{roof}$  are the areas of the wall and roof, and t is the thickness of the insulation layer. Then, the total mass of the insulation materials is calculated as:

$$m = \rho \times V$$

where  $\rho$  is the density of the insulation materials (wood fibre wool-low density (1)). Finally, the embodied carbon of an apartment can be calculated by mutiliplying the mass of the thermal insulation materials and its carbon footprint per mass, 0.062 kg CO<sub>2</sub> –eq./kg:

$$Carbon = m \times 0.062$$

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