

Platinum Alloy Tailored All-Weather Solar Cells for Energy Harvesting from Sun and Rain

Qunwei Tang,* Yanyan Duan, Benlin He, and Haiyan Chen

Abstract: Solar cells that can harvest energy in all weathers are promising in solving the energy crisis and environmental problems. The power outputs are nearly zero under dark conditions for state-of-the-art solar cells. To address this issue, we present herein a class of platinum alloy (PtM_x , $M = \text{Ni, Fe, Co, Cu, Mo}$) tailored all-weather solar cells that can harvest energy from rain and realize photoelectric conversion under sun illumination. By tuning the stoichiometric Pt/M ratio and M species, the optimized solar cell yields a photoelectric conversion efficiency of 10.38 % under simulated sunlight irradiation (AM1.5 , 100 mW cm^{-2}) as well as current of $3.90 \mu\text{A}$ and voltage of $115.52 \mu\text{V}$ under simulated raindrops. Moreover, the electric signals are highly dependent on the dripping velocity and the concentration of simulated raindrops along with concentrations of cation and anion.

Solar cells are energy-harvesting devices that can convert solar energy into electricity under sunlight irradiation.^[1–3] Till now, the maximal power conversion efficiencies of over 25 % for single-junction crystalline silicon solar cells,^[4] over 40 % for multi-junction silicon solar cells,^[5] over 14 % for dye-sensitized solar cells,^[6] over 11 % for quantum dot-sensitized solar cells,^[7] and over 22 % for perovskite solar cells^[8] have been recorded by developing advanced cell materials and technologies. However, the power outputs are nearly zero at dark conditions including rainy, foggy, snowy, cloudy days and night.^[9] The sunshine time is around 3000 hours/year in China, indicating that the solar cells can generate electricity in 65.8 % of the total time and this percentage is higher in European and Southeast Asian countries. A solution to this impasse is to create all-weather solar cells that can be actuated by other stimuli except for photons from sunlight. However, it is still a great challenge for solar cells to harvest energy beyond sunny days. To address this significant scientific issue, we herein develop a class of all-weather solar cells by combining platinum-alloy electrodes with traditional solar cells for power generation on sunny and rainy days.

Recent work from our group demonstrates that it is a feasible strategy by hot-pressing reduced graphene oxide (rGO) film onto the rear side of a flexible solar cell,^[10] yielding a photoelectric conversion efficiency of 6.53 % under a solar simulator (AM1.5 Global spectrum with

100 mW cm^{-2} intensity and spectral mismatch correction) as well as maximal current of approximately $0.50 \mu\text{A}$ and voltage of around $150 \mu\text{V}$ for each droplet. Limited by the hot-press technique for the flexible indium tin oxide/polyethylene terephthalate (ITO/PET) plastic substrate, the power conversion efficiency is relatively low in comparison with state-of-the-art solar cells on fluorine-doped tin oxide (FTO) glass. Moreover, the route of fabricating the graphene tailored film is not applicable to FTO glass based solar cells because of their frangible and uncohesive nature, therefore we have recently designed a graphene assisted bifunctional solar cell on a FTO glass substrate by an electrophoresis deposition method,^[11] creating a solar cell efficiency of 9.14 % along with current of $4.9 \mu\text{A}$ and voltage of $62.0 \mu\text{V}$. A remaining problem of these two approaches is the challenging film-forming of graphene for large-scale applications. More recently, a conducting composite coating from electron-conducting graphene/carbon black incorporated polytetrafluoroethylene (PTFE) has been developed to reduce the graphene dosage and to increase the film-forming ability,^[9] in which carbon black acts as binders for compatibility between graphene and PTFE, while graphene can form percolating pathways for electron migration.

The mechanism behind the electric signal outputs arises from gigantic delocalized π -electron systems for graphene as well as interfacial interactions between rainwater and graphene tailored films. Graphene is made out of carbon atoms arranged on hexagon honeycomb structure. The sp^2 hybridization between one s-orbital and two p-orbitals leads to a trigonal-planar structure with the formation of an σ -bond between carbon atoms, and therefore a half-filled π -band. Rainwater, always contains gigantic charged ions, can split into cation (e.g. NH_4^+ , H^+ , Ca^{2+} , Na^+) and anion (e.g. NO_3^- , Cl^- , SO_4^{2-}) species. When rainwater drops on to the graphene tailored film, the positive charged ions can be adsorbed by π -electrons from graphene to form electron/cation electric double-layer (EDL) pseudocapacitance.^[12,13] During the expanding and shrinking process of raindrop on graphene film, the EDL pseudocapacitors are charged and discharged, yielding periodic current and voltage outputs.

Apart from graphene, we have recently found that bimetallic alloys from precious Pt and transition-metals, such as Fe, Co, Ni, Cu, Mo, are also applicable for generating electricity when incorporated into such all-weather solar cells. To reveal how a transition-metal influences the electronic structure of Pt, we compare the electronegativities of transition metals, they are 1.83, 1.88, 1.92, 1.90, and 2.16 for Fe, Co, Ni, Cu, and Mo, respectively, which are lower than 2.28 for metallic Pt. In this fashion, electrons can deviate from the transition metal to Pt during alloying process, making an

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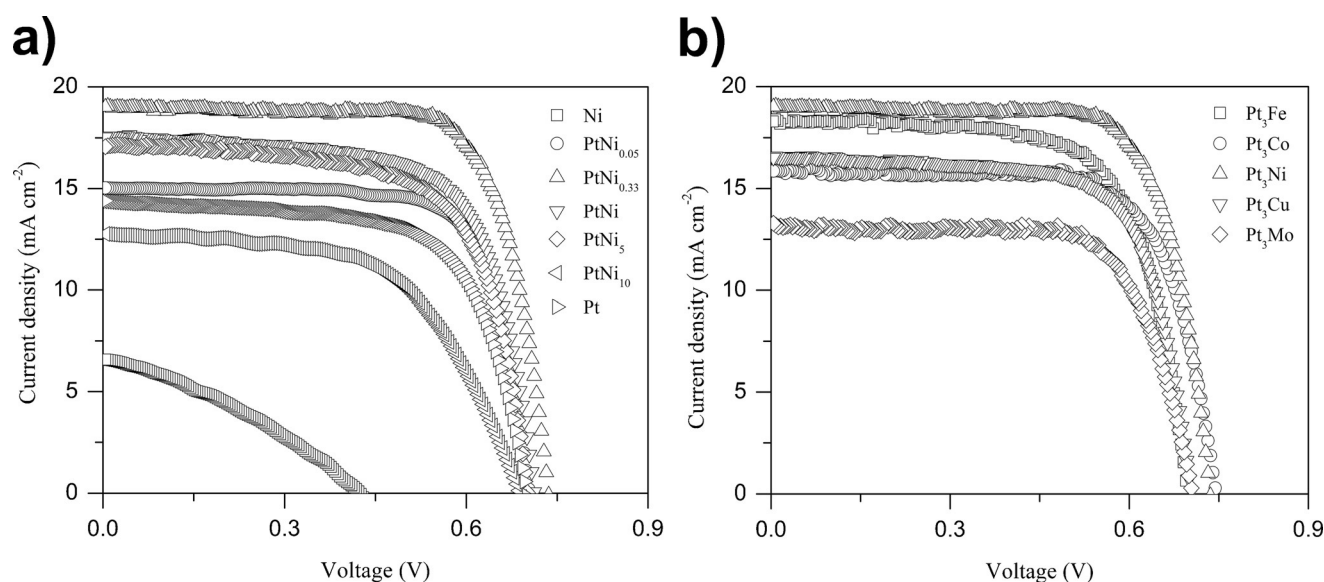


Figure 1. The J - V characteristics of all-weather solar cells with a) bilayer PtNi_x and b) $\text{Pt}_3\text{M} | \text{PtM}_5$ alloy electrodes.

electron-enriched Pt surface in comparison with pristine Pt.^[14] We present herein platinum-alloy (PtM , $\text{M} = \text{Fe}$, Co , Ni , Cu , Mo) tailored all-weather solar cells that can harvest energy from sun and rain.

The solar-cell structure and mechanisms of photovoltaic conversion are shown in Figure S1 of the Supporting Information. Figure 1a shows photo J - V curves of all-weather solar cells with bilayer PtNi_x counter electrodes (CEs) by tuning the stoichiometric Ni/Pt ratio of from 0 to 10. As references, pristine Pt and Ni electrodes are also fabricated using a method similar to that reported for the alloys and the corresponding photovoltaic parameters are summarized in Table 1. A maximal η of 10.38 % is determined on the solar cell ($J_{\text{sc}} = 19.04 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.735 \text{ V}$, $FF = 74.2\%$) with $\text{PtNi}_{0.33}$ (Pt_3Ni) CE in comparison with 6.75 % and 0.93 % for Pt and Ni based solar-cell devices, respectively. The markedly elevated solar-cell efficiency is attributable to the increased catalytic activity and charge-transfer ability (Figure S2 and Table S1), arising from matching the work function of the alloy CE to redox potential of I^-/I_3^- couple,^[15] gigantic

catalytic sites for I_3^- adsorption and electron-enriched surface. Using the similar alloying mechanism, other platinum alloys, such as Pt_3Fe , Pt_3Co , Pt_3Cu , and Pt_3Mo are also applicable as CE materials, as shown in Figure 1b, yielding cell efficiencies of 8.83 %, 8.47 %, 8.22 % and 6.69 % in their all-weather solar cells, respectively.

The PtNi_x alloy electrode is also sensitive to rain droplets, as shown in Figure 2a and summarized in Table S2, the current output is 0 by raining simulated raindrops (0.6 M NaCl aqueous solution) to pristine Ni electrode at an injection velocity of 100 mL h^{-1} . Interestingly, there are periodical current peaks during the repeated spreading and shrinking of the rain drops. The peak current is gradually increased to $1.13 \mu\text{A}$ for the PtNi_5 alloy electrode in comparison with $0.11 \mu\text{A}$ for the pure Pt electrode. According to our previous studies,^[9,10] the electron/cation EDL is a prerequisite for realizing power generation, this conclusion can also be supported with the horizontal line obtained by raining deionized water onto the PtNi_5 alloy electrode, as shown in Figure S4. From the unchanged ohmic resistances measured with and without simulated rain, as shown in Figure S5, we can conclude that the induced current fluctuation originates from real electricity output. When used as CE materials, the PtNi_x CE should integrate matching work function, active site, and electron-enriched surface into a single alloy electrode, while the rain-enabled PtNi_x electrodes only require maximized electron exposure. The enhanced EDL pseudocapacitance is cross-checked by our Hall measurements, showing that the surface electron concentrations of metallic Ni and Pt are 1.33×10^{12} and $3.53 \times 10^{16} \text{ cm}^{-2}$ (Table S2), respectively. By alloying Pt with Ni, the surface electron concentration is maximized to be $5.62 \times 10^{16} \text{ cm}^{-2}$ for the PtNi_5 electrode. The nanoporous platinum alloy electrodes also provide gigantic contact interfaces as active sites for adsorbing cations to generate EDL (Figure S6). Apart from the nature of the alloy species, rainfall intensity also influences the current signals. By tuning the injection velocity of raindrops from 20 to

Table 1: The photovoltaic parameters of all-weather solar cells.

Electrodes	V_{oc} [V]	J_{sc} [mA cm^{-2}]	η [%]	FF
Ni	0.423	6.58	0.93	33.4
$\text{PtNi}_{0.05}$	0.706	15.05	7.86	74.0
$\text{PtNi}_{0.33}$ (Pt_3Ni)	0.735	19.04	10.38	74.2
PtNi	0.714	17.58	8.56	68.2
PtNi_5	0.704	17.14	8.01	66.4
PtNi_{10}	0.687	12.76	5.08	58.0
Pt	0.702	14.37	6.75	66.9
Pt_3Fe	0.695	18.36	8.83	69.2
Pt_3Co	0.744	15.88	8.47	71.7
Pt_3Cu	0.707	16.53	8.22	70.3
Pt_3Mo	0.704	13.25	6.69	71.7

[a] V_{oc} : open-circuit voltage; J_{sc} : short-circuit current density; η : power conversion efficiency; FF: fill factor.

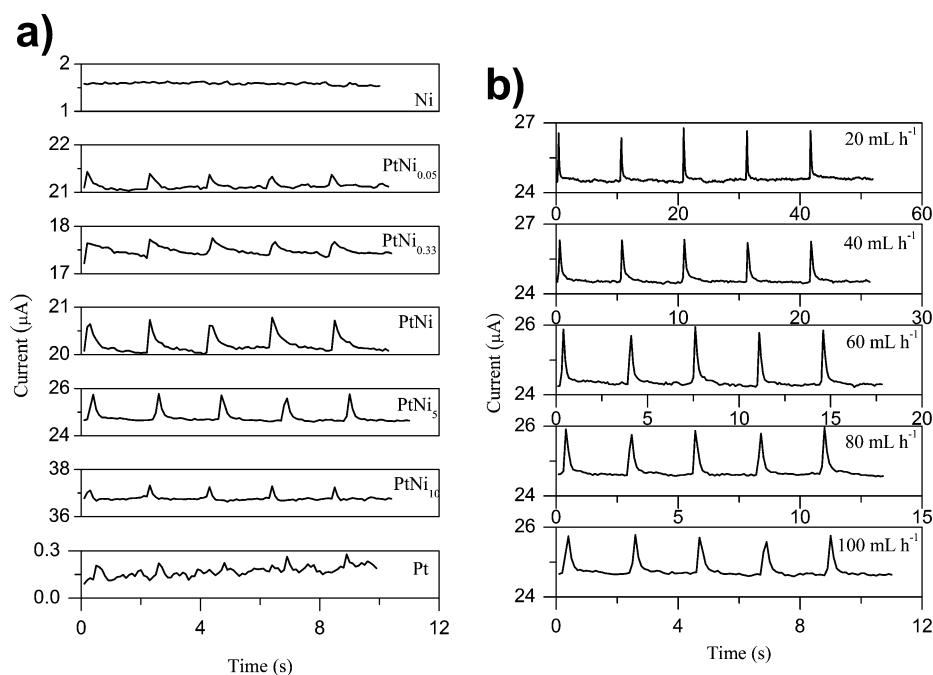


Figure 2. a) Current signals produced by dropping simulated raindrops (0.6 M NaCl aqueous solution) on PtNi_x alloy electrodes of all-weather solar cells. The injection velocity was 100 mL h⁻¹. b) Current signals produced by dropping simulated rain droplets (0.6 M NaCl aqueous solution) on PtNi₅ alloy electrodes of the all-weather solar cells. The injection velocity ranged from 20 to 100 mL h⁻¹.

100 mL h⁻¹, one can simulate different levels of rainfall: high injection velocity means heavy rain and low injection velocity simulates light rain. According to Figure 2b and Table S3, the average peak current is inversely proportional to rainfall intensity. A potential mechanism behind this is the incomplete recovery of the outspread of the raindrop at platinum alloy surface and therefore reduced charging/discharging capacity for electricity output.

The rain-enabled electricity stems from electron/cation EDL pseudocapacitance, therefore the cation concentration has a profound influence on current signals. To address this issue, we have tuned the concentration of simulated rainwater (NaCl aqueous solution) within 0.01 approximately 5 M and the stacking current signals at an injection velocity of 20 mL h⁻¹ are shown in Figure 3a. Notably, the current is only 0.34 μA for 0.01 M rainwater, as summarized in Table S4, while it rises to 1.83 μA by increasing the cation concentration to 1 M. At high cation concentration, more cations can be adsorbed by electron-enriched PtNi₅ alloy electro-

des to give high-capacity pseudocapacitance. Therefore, the all-weather solar cells are expected to generate most electricity under light rain with a high ionic concentration.

In addition, the cationic charge and radius are also crucial in impacting electricity-generating capacity, which can be found by raining 0.6 M chloride aqueous solutions on PtNi₅ alloy electrodes at an injection velocity of 100 mL h⁻¹ (Figure 3b). As summarized in Table S5, the peak current data follows an order of H⁺ > Li⁺ > Na⁺ > K⁺ > NH₄⁺ because of ionic radius of H⁺ (32 pm) < Li⁺ (60 pm) < Na⁺ (95 pm) < K⁺ (122 pm) < NH₄⁺ (133 pm). The mechanisms behind this evolution rule can be attributable two reasons: 1) According to Coulomb's law, the electrostatic adsorption force between electrons and cations increases with decreasing cationic radius, allowing for elevated electron/cation EDL pseudocapacitance; 2) The diffusion of the cations with large ionic radius is limited during rain spreading stage, leading to reduced pseudocapacitance in charging stage. This hypothesis is also applicable to explain increased

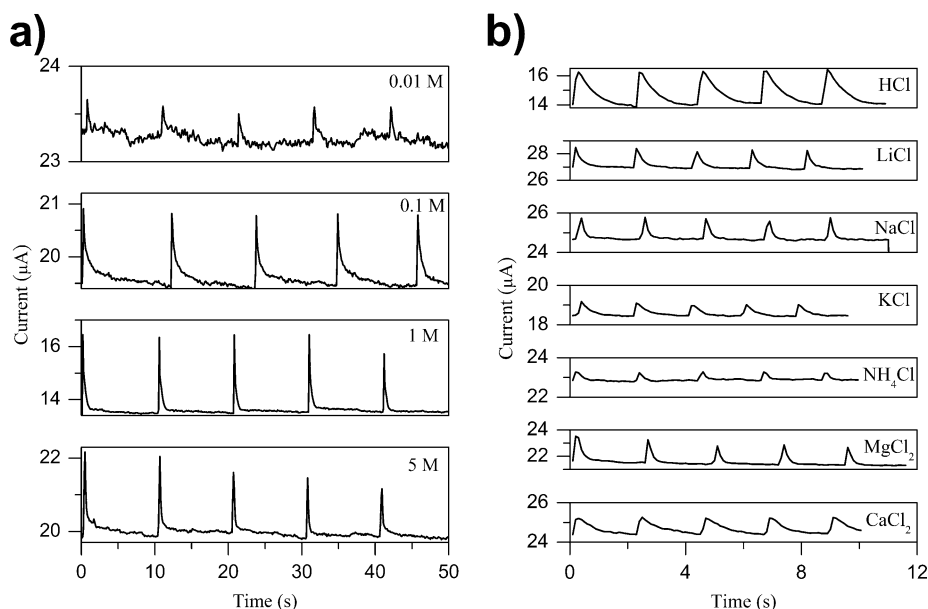


Figure 3. a) Current signals produced by dropping simulated raindrops (NaCl aqueous solutions at different concentrations) on PtNi₅ alloy electrodes of all-weather solar cells. The injection velocity was 20 mL h⁻¹. b) Current signals produced by dropping simulated rain droplets (0.6 M chloride aqueous solutions) on PtNi₅ alloy electrodes of the all-weather solar cells. The injection velocity was 100 mL h⁻¹.

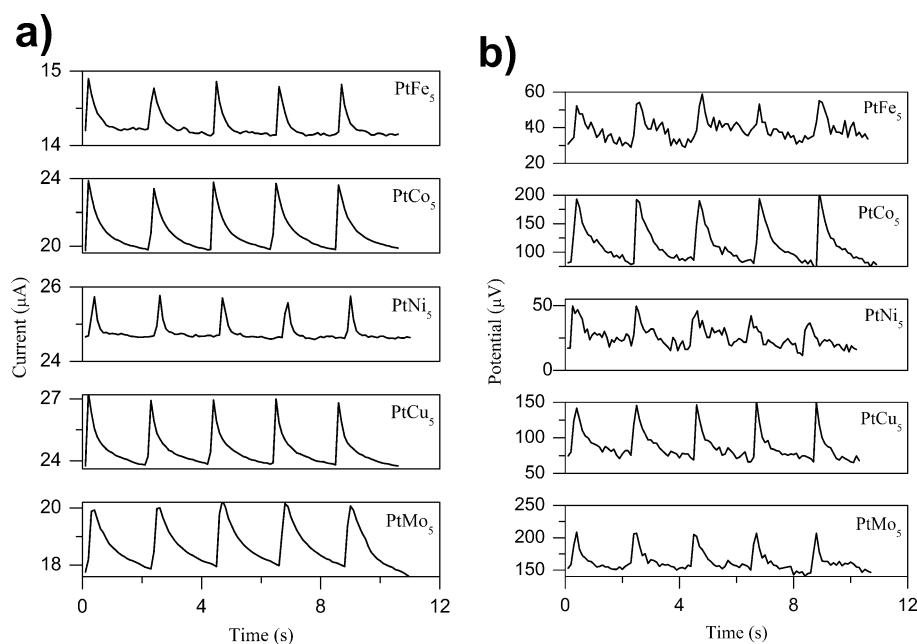


Figure 4. a) Current and b) voltage signals produced by dropping simulated raindrops (0.6 M NaCl aqueous solution) on PtM₅ electrodes of all-weather solar cells. The injection velocity was 100 mL h⁻¹.

current values for Mg²⁺ and Ca²⁺ in comparison with Na⁺ and K⁺, respectively.

The fundamental principle for generating electricity by rainfall onto a platinum alloy electrode is to create electron/cation EDL pseudocapacitances, and the maximal capacity for these pseudocapacitors decides the final energy harvest. By alloying Pt with other transition metals, as summarized in Table S6, the surface electron concentrations are 5.20×10^{16} , 8.19×10^{16} , 5.62×10^{16} , 6.75×10^{16} , and 5.65×10^{16} cm⁻² for PtFe₅, PtCo₅, PtNi₅, PtCu₅, and PtMo₅, respectively. The increased charge density arising from electron transfer from the transition metal to Pt is also expected to yield higher current and voltage signals. As shown in Figure 4 and Table S6, the electric signals for PtCo₅, PtCu₅, and PtMo₅ alloy electrodes are all enhanced in comparison to the PtNi₅ electrode, and the highest current of 3.90 μA and voltage of 115.52 μV is achieved by raining simulated rainwater onto the PtCo₅ alloy electrode, enhancements of 245.1 % and 316.1 % compared with PtNi₅ electrode.

The persistent power generation of a platinum alloy electrode is equally important for its practical application for sun and rain enabled all-weather solar cells. To address this issue, we have subjected the all-weather solar cell with a PtNi₅ alloy electrode to continuous rain at an injection velocity of 60 mL h⁻¹, as shown in Figure S8. There is a significant reduction within the first 100 s, subsequently, current remains relatively stable over 1200 s. The high photoelectric conversion efficiency under sun illumination and increased electric signals on rainy days as well as the long-term stability indicate that the all-weather solar cells have promising application prospects for advanced energy harvest.

In summary, all-weather solar cells that can realize photovoltaic conversion on sunny days and electricity outputs

on rainy days have been successfully fabricated by integrating platinum alloy electrodes with a traditional solar cell. The optimal all-weather solar cell can yield a photoelectric conversion efficiency as high as 10.38 % under simulated sun irradiation (100 mW cm⁻², AM1.5), and a maximized current of 3.90 μA and voltage of 115.52 μV by tuning the alloy electrode species. Further investigations demonstrate that the electrical output signals are highly dependent on the stoichiometric Pt/Ni ratio, time interval of adjacent raindrops, and cation concentration, species and charge number. Although the current work is still far from optimization, it represents a significant step forward for solar cells, as it guides us to explore energy harvesting beyond sunny days.

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Keywords: alloy electrode · all-weather solar cell · charge transfer · energy conversion

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