- J. Y. Rempel, M. G. Bawendi, K. F. Jensen, J. Am. Chem. Soc. 131, 4479–4489 (2009).
- R. García-Rodríguez, M. P. Hendricks, B. M. Cossairt, H. Liu, J. S. Owen, *Chem. Mater.* 25, 1233–1249 (2013).
- T. P. A. Ruberu *et al.*, *ACS Nano* 6, 5348–5359 (2012).
 Y. Guo, S. R. Alvarado, J. D. Barclay, J. Vela, *ACS Nano* 7, Young Youn
- 3616-3626 (2013).
- 12. I. Moreels et al., ACS Nano 3, 3023–3030 (2009).
- M. C. Weidman, M. E. Beck, R. S. Hoffman, F. Prins, W. A. Tisdale, ACS Nano 8, 6363–6371 (2014).
- C.-H. M. Chuang, P. R. Brown, V. Bulović, M. G. Bawendi, Nat. Mater. 13, 796–801 (2014).
- 15. C. D. Ritchie, W. F. Sager, Prog. Phys. Org. Chem. 2, 323–400 (1964).
- G. Marcotrigiano, G. Peyronel, R. Battistuzzi, J. Chem. Soc. Perkin Trans. 2 1972, 1539 (1972).
- 17. F. Wang, W. Buhro, J. Am. Chem. Soc. 134, 5369-5380 (2012).
- 18. G. G. Yordanov, C. D. Dushkin, E. Adachi, Colloids Surf.
- A Physicochem. Eng. Asp. 316, 37-45 (2008).

ELECTROCHEMISTRY

D. Zherebetskyy *et al.*, *Science* **344**, 1380–1384 (2014).
 N. C. Anderson, M. P. Hendricks, J. J. Choi, J. S. Owen,

J. Am. Chem. Soc. 135, 18536–18548 (2013).

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SUPPLEMENTARY MATERIALS

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High-performance transition metal-doped Pt₃Ni octahedra for oxygen reduction reaction

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Bimetallic platinum-nickel (Pt-Ni) nanostructures represent an emerging class of electrocatalysts for oxygen reduction reaction (ORR) in fuel cells, but practical applications have been limited by catalytic activity and durability. We surface-doped Pt_3Ni octahedra supported on carbon with transition metals, termed *M*-Pt_3Ni/C, where *M* is vanadium, chromium, manganese, iron, cobalt, molybdenum (Mo), tungsten, or rhenium. The Mo-Pt_3Ni/C showed the best ORR performance, with a specific activity of 10.3 mA/cm² and mass activity of 6.98 A/mg_{Pt}, which are 81- and 73-fold enhancements compared with the commercial Pt/C catalyst (0.127 mA/cm² and 0.096 A/mg_{Pt}). Theoretical calculations suggest that Mo prefers subsurface positions near the particle edges in vacuum and surface vertex/edge sites in oxidizing conditions, where it enhances both the performance and the stability of the Pt₃Ni catalyst.

roton-exchange membrane (PEM) fuel cells use reactions between the fuel (such as hydrogen or alcohols) at the anode and the oxidant (molecular oxygen) at the cathode (1-3). Both cathode and anode reactions need catalysts to lower their electrochemical overpotential for high-voltage output, and so far, platinum (Pt) has been the universal choice (4-6). To fully realize the commercial viability of fuel cells, the following challenges, which may not be strictly independent of one another, need to be simultaneously addressed: the high cost of Pt, the sluggish kinetics of the oxygen reduction reaction (ORR), and the low durability of the catalysts (7-11).

Alloying Pt with a secondary metal reduces the usage of scarce Pt metal while at the same time improving performance as compared with that of pure Pt on mass activity (*12–15*), which has led to the development of active and durable Pt-based electrocatalysts with a wide range of compositions (*16–20*). However, although studies

so far have led to a considerable increase in ORR activity, the champion activity as observed on bulk $Pt_3Ni(111)$ surface has not been matched in nanocatalyts (21–25), indicating room for further improvement. At the same time, one noted major limitation of Pt-Ni nanostructures is their low durability. The Ni element in these nanostructures leaches away gradually under detrimental corrosive ORR conditions, resulting in rapid performance losses (23–27). Thus, synthesizing Pt-based nanostructures with simultaneously high catalytic activity and durability remains an important open challenge (28).

Because surface and near-surface features of a catalyst have a strong influence on its catalytic performance, we adopted a surface engineering strategy to further explore and enhance the performance of $Pt_3Ni(111)$ nanocatalysts. We specifically focused our efforts on Pt_3Ni -based nanocatalysts because the bulk extended $Pt_3Ni(111)$ surface has been shown to be one of the most efficient catalytic surfaces for the ORR. On the basis of the

control over dopant incorporation of various transition metals onto the surface of dispersive and octahedral Pt₃Ni/C (termed as *M*-Pt₃Ni/C, where M = V, Cr, Mn, Fe, Co, Mo, W, or Re), we have developed ORR catalysts that exhibit both high activity and stability. In particular, our Mo-Pt₃Ni/C catalyst has high specific activity (10.3 mA/cm²), high mass activity (6.98 A/mg_{Pt}), and substantially improved stability for 8000 potential cycles.

We prepared highly dispersed Pt₃Ni octahedra on commercial carbon black by means of an efficient one-pot approach without using any bulky capping agents, which used platinum(II) acetylacetonate [Pt(acac)2] and nickel(II) acetylacetonate [Ni(acac)₂] as metal precursors, carbon black as support, N.N-dimethylformamide (DMF) as solvent and reducing agent, and benzoic acid as the structure-directing agent (fig. S1A). The surface doping for the Pt₃Ni/C catalyst was initiated by the addition of dopant precursors, $Mo(CO)_6$, together with Pt(acac)₂ and Ni(acac)₂ into a suspension of Pt_3Ni/C in DMF, and the subsequent reaction at 170°C for 48 hours (fig. S1B). The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images of the Pt₃Ni/C and Mo-Pt₃Ni/C catalysts (Fig. 1, A and B, and fig. S2) revealed highly dispersive octahedral nanocrystals (NCs) in both samples, which were substantially uniform in size, averaging 4.2 ± 0.2 nm in

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Fig. 1. Schematic illustration of the fabrication process and the structure analyses for the transition metal-doped Pt_3Ni/C catalysts. (A and B) Representative HAADF-STEM images of the (A) Pt_3Ni/C and (B) Mo- Pt_3Ni/C catalysts. (C and D) HRTEM images on individual octahedral (C) Pt_3Ni/C and (D) Mo- Pt_3Ni/C nanocrystals. (E and F) EDS line-scanning profile across individual (E) Pt_3Ni/C and (F) Mo- Pt_3Ni/C octahedral nanocrystals. (G) Pt, Ni, and Mo XPS spectra for the octahedral Mo- Pt_3Ni/C catalyst.

edge length. High-resolution TEM (HRTEM) images taken from individual octahedra showed a single-crystal structure with well-defined fringes (Fig. 1, C and D) and an edge lattice spacing of 0.22 nm, which is consistent with that expected for face-centered cubic (fcc) Pt_3Ni .

For Pt₃Ni, powder x-ray diffraction (PXRD) patterns of the colloidal products displayed typical peaks that could be indexed as those of fcc Pt₃Ni (fig. S3) (29, 30), and the Pt/Ni composition of 74/26 was confirmed by means of both inductively coupled plasma atomic emission spectroscopy (ICP-AES) and TEM energy-dispersive x-ray spectroscopy (TEM-EDS) (fig. S4 and table S1). Composition line-scan profiles across octahedra obtained by means of HAADF-STEM-EDS for Pt₃Ni/C (Fig. 1E) and Mo-Pt₃Ni/C (Fig. 1F) showed that all elements were distributed throughout the NCs (Fig. 1, E and F). For the doped NCs, x-ray photoelectron spectroscopy (XPS) shows the presence of Pt, Ni, and Mo in the catalyst (Fig. 1G). The Ni 2p and Pt 4f XPS spectra of the Mo-Pt₃Ni/C catalyst showed that the majority of the surface Ni was in the oxidized state and that the surface Pt was mainly in the metallic state, which were consistent with a recent Pt-Ni catalysts-based study (28). Mo exhibits mainly Mo^{6+} and Mo^{4+} states, which is in agreement with previous studies of PtMo nanoparticles (31). The overall molar ratio for Pt, Ni, and Mo obtained from ICP-AES was 73.4:25.0:1.6.

To assess ORR catalytic activity, we used cyclic voltammetry (CV) to evaluate the electrochemically active surface areas (ECSAs). Our catalysts were loaded (with the same Pt mass loading) onto



Fig. 2. Electrocatalytic properties of high-performance transition metal-doped octahedral Pt₃Ni/C catalysts and a commercial Pt/C catalyst. (A) Cyclic voltammograms of octahedral Mo-Pt₃Ni/C, octahedral Pt₃Ni/C, and commercial Pt/C catalysts recorded at room temperature in N₂-purged 0.1 M HClO₄ solution with a sweep rate of 100 mV/s. (B) ORR polarization curves of octahedral Mo-Pt₃Ni/C, octahedral Pt₃Ni/C, and commercial Pt/C catalysts recorded at room temperature in an O₂-saturated 0.1 M HClO₄ aqueous solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rotations per min (rpm). (C) The electrochemically active surface area (ECSA, top), specific activity (middle), and mass activity (bottom) at 0.9 V versus RHE for these transition metal-doped Pt₃Ni/C catalysts, which are given as kinetic current densities normalized to the ECSA and the loading amount of Pt, respectively. In (A) and (B), current densities were normalized in reference to the geometric area of the RDE (0.196 cm²).

glassy carbon electrodes. A commercial Pt/C catalyst [20 weight percent (wt %) Pt on carbon black; Pt particle size, 2 to 5 nm] obtained from Alfa-Aesar was used as a baseline catalyst for comparison (fig. S5). The CV curves on these different catalysts are compared in Fig. 2A. We calculated the ECSA by measuring the charge collected in the hydrogen adsorption/desorption region (between 0.05 and 0.35 V) after double-layer correction and assuming a value of 210 μ C/cm² for the adsorption of a hydrogen monolayer. The octahedral Pt₃Ni/C and Mo-Pt₃Ni/C catalysts display similar and high ECSAs of 66.6 and $67.5 \text{ m}^2/g_{Pt}$, respectively, which is comparable with that of the commercial Pt/C catalyst (75.6 m^2/g_{Pt}) (Fig. 2C, top).

The ORR polarization curves for the different catalysts, which were normalized by the area of the glassy carbon area (0.196 cm^2), are shown in Fig. 2B. The polarization curves display two distinguishable potential regions: the diffusionlimiting current region below 0.6 V and the mixed kinetic-diffusion control region between 0.6 and 1.1 V. We calculated the kinetic currents from the ORR polarization curves by considering the masstransport correction (32). In order to compare the activity for different catalysts, the kinetic currents were normalized with respect to both ECSA and the loading amount of metal Pt. As shown in Fig. 2C, the octahedral Mo-Pt₃Ni/C exhibits a specific activity of 10.3 mA/cm² at 0.9 V versus a reversible hydrogen electrode (RHE). In contrast, the specific activity of the undoped Pt₃Ni/C catalyst is ~2.7 mA/cm². On the basis of the mass loading of Pt, the mass activity of the Mo-Pt₃Ni/C catalyst was calculated to be 6.98 A/mgPt. The specific activity of the Mo-Pt₃Ni/C catalyst represents an improvement by a factor of 81 relative to the commercial Pt/C catalyst, whereas the mass activity of the Mo-Pt₃Ni/C catalyst achieved a 73-fold enhancement. To compare the activities of our catalysts with the state-of-the-art reported Pt-Ni catalysts, we also calculated the catalytic activities of our catalysts at 0.95 V and with the ECSA calculated with the CO stripping method. Whether we calculated at 0.90 or 0.95 V or used the ECSA based on Hupd and/or CO stripping, both the specific activity and the mass activity of the Mo-Pt₃Ni/C (fig. S6) are higher than those of the state-of-the-art Pt-Ni catalysts (21, 24), including the recently reported Pt-Ni nanoframes catalyst (Table 1 and table S2) (28).

Because Mo-Pt₃Ni/C exhibited an exceptional activity toward ORR, we further examined the doping effects for Pt₃Ni/C modified by other transition metals. Pt₃Ni/C catalysts doped with seven other transition metals—V, Cr, Mn, Fe, Co, W, or Re—were synthesized in a similar fashion with metal carbonyls (figs. S7 and S8 and table S1; details are available in the supplementary materials), and their catalytic activity toward the ORR was tested under the same conditions (Fig. 2C; individual sample measurements are available in fig. S9). The ECSAs of these transition metaldoped Pt₃Ni/C catalysts were all similar (Fig. 2C, top), but variable ORR activities were observed for differently doped Pt₃Ni/C catalysts. None of the other dopants resulted in a catalyst with activity as high as that of the Mo-Pt₃Ni/C (Fig. 2C, middle). The change of mass activities in various *M*-doped Pt₃Ni/C catalysts was also similar to that of the specific activities (Fig. 2C, bottom), with Mo-Pt₃Ni/C showing the highest activity. We further evaluated the electrochemical durability of the Mo-Pt₃Ni/C catalyst using the accelerated durability test (ADT) between 0.6 and 1.1 V (versus RHE, 4000 and 800 cycles) in O_2 -saturated 0.1 M HClO₄ at a scan rate of 50 mV/s. The Pt₃Ni/C catalyst was used as a baseline catalyst

Table 1. Performance of Mo-Pt₃Ni/C catalyst and several representative results with high performance from recent published works. NA, not availlable.

		Based on H _{upd}					Based on CO stripping		
	Catalyst EC: (m ⁻ g _P	ECSA	Specific activity A (mA/cm ²)		Mass activity (A/mg _{Pt})		ECSA	Specific activity (mA/cm ²)	
		(m 7 g _{Pt})	@ 0.9 V	@ 0.95 V	@ 0.9 V	@ 0.95 V	(m²/g _{Pt})	@ 0.9 V	@ 0.95 V
This work	Mo-Pt ₃ Ni/C	67.7	10.3	2.08	6.98	1.41	83.9	8.2	1.74
This work	Pt₃Ni/C	66.6	2.7	0.55	1.80	0.37	81.9	2.2	0.45
(53)	PtNi/C	50	3.14	NA	1.45	NA	NA	NA	NA
(24)	PtNi/C	48	3.8	NA	1.65	NA	NA	NA	NA
(21)	PtNi _{2.5} /C	21	NA	NA	3.3	NA	31	NA	NA
(28)	Pt ₃ Ni/C nanoframes	NA	NA	NA	5.7	0.97	NA	NA	1.48



Fig. 3. Electrochemical durability of the high-performance octahedral Mo-Pt₃NiCo/C catalyst and octahedral Pt₃Ni/C catalyst. (A and B) ORR polarization curves and (inset) corresponding cyclic voltammograms of (A) the octahedral Mo-Pt₃Ni/C catalyst and (B) the octahedral Pt₃Ni/C catalyst before, after 4000, and after 8000 potential cycles between 0.6 and 1.1 V versus RHE. (C) The changes of ECSAs (left), specific activities (middle), and mass activities (right) of the octahedral Mo-Pt₃Ni/C catalyst and octahedral Pt₃Ni/C catalyst before, after 4000, and after 8000 potential cycles between 0.6 and 1.1 V versus RHE. (C) The changes of ECSAs (left), specific activities (middle), and mass activities (right) of the octahedral Mo-Pt₃Ni/C catalyst and octahedral Pt₃Ni/C catalyst before, after 4000, and after 8000 potential cycles. The durability tests were carried out at room temperature in O_2 -saturated 0.1 M HClO₄ at a scan rate of 50 mV/s.

for comparison. After 4000 and 8000 potential cycles, the Mo-Pt₃Ni/C catalyst largely retained its ECSA and activity (Fig. 3A), exhibiting only 1and 3-mV shifts for its half-wave potential, respectively. And after 8000 cycles, the activity of the Mo-Pt₃Ni/C catalyst was still as high as 9.7 mA/cm² and 6.6 A/mgPt (Fig. 3C), showing only 6.2 and 5.5% decreases from the initial specific activity and mass activity, respectively. On the other hand, the undoped Pt₃Ni/C catalyst was unstable under the same reaction conditions. Its polarization curve showed a 33-mV negative shift after durability tests (Fig. 3B), and the Pt₃Ni/C retained only 33 and 41% of the initial specific activity and mass activity, respectively, after 8000 cycles (Fig. 3C). The morphology and the composition of the electrocatalysts after the durability change were further examined. As shown in fig. S4, although the size of the Pt₃Ni/C octahedra were largely maintained, their morphologies became more spherical. This change of the morphology likely resulted from the Ni loss after the potential cycles, as confirmed by means of EDS and XPS analyses (the Pt/Ni composition ratio changed from 74.3/25.7 to 88.1/11.9) (figs. S4 and S10). In contrast, the corresponding morphology of the Mo-Pt₃Ni/C catalyst largely maintained the octahedral shape, and the composition change was negligible (from 73.4/25.0/1.6 to 74.5/24.0/1.5).

To investigate the cause of the enhanced durability of the Mo-Pt $_3$ Ni/C catalysts, cluster expan-

sions of Pt-Ni-Mo NCs were used in Monte Carlo simulations (33-35) to identify low-energy NC and (111) surface structures for computational analysis (details of our calculations are provided in the supplementary materials). In vacuum, the equilibrium structures predicted by the cluster expansion have a Pt skin, with Mo atoms preferring sites in the second atomic layer along the edges connecting two different (111) facets (Fig. 4, A and B, and fig. S11). Density functional theory (DFT) (36) calculations indicate that in vacuum, the subsurface site is preferable to the lowest-energy neighboring surface site, but in the presence of adsorbed oxygen, there is a strong driving force for Mo to segregate to the surface, where it was found to be most stable on a vertex site. This suggests the formation of surface Mo-oxide species, which is consistent with our XPS measurements. Our calculations indicate that the formation of surface Mo-oxide species may contribute to improved stability by "crowding out" surface Ni. Our computational prediction that Mo favors sites near the particle edges and vertices is consistent with the dopant distributions for Fe shown in our STEM electron energy loss spectroscopy (EELS) line scan results (fig. S12).

Our calculations suggest that doping the NCs with Mo directly stabilizes both Ni and Pt atoms against dissolution and may inhibit diffusion through the formation of relatively strong Mo-Pt and Mo-Ni bonds. Calculations on a representative



Fig. 4. Computational results. (**A** and **B**) The average site occupancies of the second layer of (A) the Ni₁₁₇₅Pt₃₃₉₈ NC and (B) the Mo₇₃Ni₁₁₄₃Pt₃₃₅₇ NC at 170°C as determined by means of a Monte Carlo simulation. Occupancies are indicated by the color triangle on the right. Small spheres represent the atoms in the outer layer. (**C**) The calculated binding energies for a single oxygen atom on all fcc and hcp sites on the (111) facet of the Mo₆Ni₄₁Pt₁₇₈ NC, relative to the lowest binding energy. Gray spheres represent Pt, and colored spheres represent oxygen sites. Three binding energies are provided for reference: the calculated binding energy on the fcc site of a pure Pt (111) surface, the binding energy corresponding to the peak of the Sabatier volcano (37), and the binding energy on a Pt₃Ni(111) surface. (**D**) The change in binding energies when a Ni₄₇Pt₁₇₈ NC is transformed to a Mo₆Ni₄₁Pt₁₇₈ NC by the substitution of Mo on its energetically favored sites in the second layer below the vertices.

nanoparticle with dimensions and composition comparable with those observed experimentally (fig. S13) indicate that a Mo on an edge or vertex site increases the energy required to remove a Pt atom from a neighboring edge or vertex site by an average of 362 meV, with values ranging from 346 to 444 meV, and to remove a Ni atom by an average of 201 meV, with values ranging from 160 to 214 meV. These predictions are consistent with our ADT results (fig. S14). The evidence that Mo may have a stabilizing effect on undercoordinated sites suggests that Mo atoms may also pin step edges on the surface, inhibiting the dissolution process.

Although the exact mechanisms by which the surface-doped Pt₃Ni shows exceptional catalytic performance demand more detailed studies, local changes in oxygen binding energies provide a possible explanation for some of the observed increase in specific activity. A Sabatier volcano of ORR catalysts predicts that ORR activity will be maximized when the oxygen binding energy is ~0.2 eV less than the binding energy on Pt(111) (37). Our calculations indicate that sites near the particle edge bind oxygenated species too strongly, such as in Pt(111), and sites near the facets of the particles bind oxygenated species too weakly, such as in Pt₃Ni(111) (Fig. 4C). However, compared with the undoped NC, the oxygen binding energies in the doped NC near the Mo atoms are decreased by up to 154 meV, and binding energies at sites closer to the center of the (111) facet are increased by up to 102 meV (Fig. 4D). Thus, if Mo migrates to the thermodynamically favored sites near the particle edges, it may shift the oxygen binding energies at these sites closer to the peak of the volcano plot. Similarly, Mo doping may increase the oxygen binding energies at sites closer to the center of the (111) facet that bind oxygen too weakly. As a result of these shifts, some sites may become highly active for catalysis. Together, our studies demonstrate that by engineering the surface structure of the octahedral Pt₃Ni nanocrystal, it is possible to fine-tune the chemical and electronic properties of the surface layer and hence modulate its catalytic activity.

REFERENCES AND NOTES

- Y. Bing, H. Liu, L. Zhang, D. Ghosh, J. Zhang, *Chem. Soc. Rev.* 39, 2184–2202 (2010).
- D. S. Su, G. Sun, Angew. Chem. Int. Ed. Engl. 50, 11570–11572 (2011).
- Z. W. Chen, D. Higgins, A. P. Yu, L. Zhang, J. J. Zhang, *Energy Environ. Sci.* 4, 3167–3192 (2011).
- J. Y. Chen, B. Lim, E. P. Lee, Y. N. Xia, Nano Today 4, 81–95 (2009).
- J. Wu, H. Yang, Acc. Chem. Res. 46, 1848–1857 (2013).
- N. S. Porter, H. Wu, Z. Quan, J. Fang, Acc. Chem. Res. 46, 1867–1877 (2013).
- H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Appl. Catal. B* 56, 9–35 (2005).
- F. A. de Bruijn, V. A. T. Dam, G. J. M. Janssen, *Fuel Cells* 8, 3–22 (2008).
- 9. J. Greeley et al., Nat. Chem. 1, 552-556 (2009)
- H. A. Gasteiger, N. M. Marković, Science 324, 48–49 (2009).
- J. K. Nørskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, *Nat. Chem.* 1, 37–46 (2009).
- 12. V. R. Stamenkovic et al., Nat. Mater. 6, 241-247
- (2007). 13. V. R. Stamenkovic *et al.*, *Science* **315**, 493–497 (2007).
- 10. T. A. Stamonkovic et al., Science 313, 433-437 (2007).

- 14. A. S. Aricò, P. Bruce, B. Scrosati, J. M. Tarascon,
- W. van Schalkwijk, Nat. Mater. 4, 366–377 (2005).
 15. S. Guo, S. Zhang, S. Sun, Angew. Chem. Int. Ed. Engl. 52,
- 8526-8544 (2013). 16. J. Wu, A. Gross, H. Yang, *Nano Lett.* **11**, 798-802
- (2011). 17. J. Zhang, J. Fang, J. Am. Chem. Soc. **131**, 18543–18547
- (2009). 18. Y. Kang, C. B. Murray, *J. Am. Chem.* Soc. **132**, 7568–7569
- (2010).
 19. Y. Wu, S. Cai, D. Wang, W. He, Y. Li, J. Am. Chem. Soc. 134, 8975–8981 (2012).
- 20. D. Wang et al., Nat. Mater. 12, 81–87 (2013).
- S. I. Choi et al., Nano Lett. 13, 3420–3425 (2013).
- J. Zhang, H. Yang, J. Fang, S. Zou, Nano Lett. 10, 638–644 (2010).
- X. Huang et al., Adv. Mater. 25, 2974–2979 (2013).
- C. Cui, L. Gan, M. Heggen, S. Rudi, P. Strasser, *Nat. Mater.* 12, 765–771 (2013).
- M. K. Carpenter, T. E. Moylan, R. S. Kukreja, M. H. Atwan, M. M. Tessema, J. Am. Chem. Soc. 134, 8535–8542 (2012).
- J. Snyder, I. McCue, K. Livi, J. Erlebacher, J. Am. Chem. Soc. 134, 8633–8645 (2012).
- H. Zhu, S. Zhang, S. Guo, D. Su, S. Sun, J. Am. Chem. Soc. 135, 7130–7133 (2013).
- 28. C. Chen et al., Science 343, 1339-1343 (2014).
- K. Ahrenstorf et al., Small 3, 271–274 (2007).
 Y. Wu et al., Angew. Chem. Int. Ed. Engl. 51, 12524–12528 (2012)
- Z. Liu et al., J. Am. Chem. Soc. 131, 6924–6925 (2009).
- 32. B. Lim et al., Science **324**, 1302–1305 (2009).
- J. M. Sanchez, F. Ducastelle, D. Gratias, *Physica A* 128, 334–350 (1984).
- N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, J. Chem. Phys. 21, 1087–1092 (1953).
- 35. T. Mueller, G. Ceder, *Phys. Rev. B* **80**, 024103 (2009).
- W. Kohn, L. J. Sham, *Phys. Rev.* **140** (4A), A1133–A1138 (1965).
- J. Rossmeisl, G. S. Karlberg, T. Jaramillo, J. K. Nørskov, Faraday Discuss. 140, 337–346 (2009).
- 38. K. Momma, F. Izumi, J. Appl. Cryst. **41**, 653–658 (2008).

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SUPPLEMENTARY MATERIALS

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SOLAR CELLS

High-performance photovoltaic perovskite layers fabricated through intramolecular exchange

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The band gap of formamidinium lead iodide (FAPbI₃) perovskites allows broader absorption of the solar spectrum relative to conventional methylammonium lead iodide (MAPbI₃). Because the optoelectronic properties of perovskite films are closely related to film quality, deposition of dense and uniform films is crucial for fabricating high-performance perovskite solar cells (PSCs). We report an approach for depositing high-quality FAPbI₃ films, involving FAPbI₃ crystallization by the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI₂ with formamidinium iodide. This process produces FAPbI₃ films with (111)-preferred crystallographic orientation, large-grained dense microstructures, and flat surfaces without residual PbI₂. Using films prepared by this technique, we fabricated FAPbI₃-based PSCs with maximum power conversion efficiency greater than 20%.

he tremendous improvements in device architecture (1-3), high-quality film formation methodologies (4-6), and compositional engineering of perovskite materials (7-9) over the past 3 years have led to rapid improvements in the power conversion efficiency (PCE) of perovskite solar cells (PSCs). Although solarto-electric PCEs of up to 18% have been reported for PSCs (10), developing technologies further to achieve PCEs near theoretical values (>30%) continues to be an important challenge in making the solar cell industry economically competitive.

Formamidinium lead iodide (FAPbI₃) is a perovskite material that can potentially provide better performance than methylammonium lead iodide (MAPbI₃) because of its broad absorption of the solar spectrum. In addition, FAPbI₃ with the n-i-p architecture (the n-side is illuminated with solar radiation) exhibits negligible hysteresis with sweep direction during current-voltage measurements (*8–13*). However, it is more difficult to form stable perovskite phases and highquality films with FAPbI₃ than with MAPbI₃.

¹Division of Advanced Materials, Korea Research Institute of Chemical Technology, 141 Gajeong-Ro, Yuseong-Gu, Daejeon 305-600, Korea. ²Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea. *These authors contributed equally to this work. **†Corresponding author. E-mail: seoksi@krict.re.kr** Various methodologies such as sequential deposition (4), solvent engineering (5), vapor-assisted deposition (14), additive-assisted deposition (15, 16), and vacuum evaporation (6) can now produce high-quality films of MAPbI₃ with flat surfaces and complete surface coverage by controlling its rapid crystallization behavior and have led to substantial improvements in the PCE of MAPbI₃based PSCs.

Among these methodologies, two-step sequential deposition and solvent engineering are representative wet processes that can yield perovskite films for high-performance PSCs. In the sequential deposition process, a thin layer of PbI₂ is deposited on the substrate; methylammonium iodide (MAI) or formamidinium iodide (FAI) is then applied to the predeposited PbI₂ to enable conversion to the perovskite phase. This process involves crystal nucleation and growth of the perovskite phase because of solution-phase or solidstate reaction between PbI2 and an organic iodide such as MAI or FAI (4, 13, 17, 18). However, the sequential reaction of organic iodides with PbI₂ that occurs from the surface to the inner crystalline regions of PbI₂ has been ineffective in producing high-performance perovskite films that are >500 nm in thickness because of incomplete conversion of PbI₂, peeling off of the perovskite film in solution, and uncontrolled surface roughness. In contrast, the solvent-engineering process uses the formation of intermediate phases to

Table 1. Comparison of layer thickness before and after FAPbl₃ phase is formed by conventional and intramolecular exchange process (IEP). The thin Pbl₂ and Pbl₂(DMSO) layers were deposited on a fused quartz glass, and their layer thickness was measured by alpha-step IQ surface profiler.

Method	Before	After
Conventional process (Pbl ₂)	290 nm	570 nm
IEP [Pbl ₂ (DMSO)]	510 nm	560 nm



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