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Communication

Functional Monolayers on a Superatomic Pegboard

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Cite This: J. Am. Chem. Soc. 2023, 145, 8314–8318
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ABSTRACT: We advance the chemistry of apical chlorine substitution in the 2D superatomic semiconductor $Re_6Se_8Cl_2$ to build functional and atomically precise monolayers on the surface of the 2D superatomic Re_6Se_8 substrate. We create a functional monolayer by installing surface (2,2′-bipyridine)-4-sulfide (Sbpy) groups that chelate to catalytically active metal complexes. Through this reaction chemistry, we can create monolayers where we can control the distribution of catalytic sites. As a demonstration, we create highly active electrocatalysts for the oxygen evolution reaction using monolayers of cobalt(acetylacetonate)$_2$bipyridine. We can further produce a series of catalysts by incorporating organic spacers in the functional monolayers. The structure and flexibility of the surface linkers can affect the catalytic performance, possibly by tuning the coupling between the functional monolayer and the superatomic substrate. These studies establish that the Re_6Se_8 sheet behaves as a chemical pegboard: a surface amenable to geometrically and chemically well-defined modification to yield functional monolayers, in this case catalytically active, that are atomically precise. This is an effective method to generate diverse families of functional nanomaterials.

This Communication describes a new methodology for creating functional monolayers on the surface of the two-dimensional (2D) superatomic semiconductor Re_6Se_8. 2D solids, essential building blocks of modern materials science,[1−6] are difficult to functionalize in a predetermined way. Chemical processes intended to modify these 2D solids may not only fail but even irreversibly damage the original material by disrupting in-plane connectivity and introducing defects, and the chemical modifications may not be as predictable as expected from molecular reaction chemistry.[7−10] Compared to traditional atomic 2D materials, the superatomic structure of $Re_6Se_8Cl_2$ is unique: it is composed of clusters of Re_6 octahedra with Se atoms residing on their faces (Figure 1A). The Re_6Se_8 clusters are covalently bonded along the *a* and *b* crystallographic directions to form a 2D pseudo-square lattice. The *trans*-Re sites in the 2D sheets are capped by apical Cls,[11] establishing an ordered array of chemically replaceable sites, which result in superatomic sheets that can be used as chemical pegboards for functionalization. Here we advance our previously reported surface functionalization approach to impart catalytic activity to this pegboard.[12] The sequence of Li intercalation, exfoliation, surface group attachment, and ultimate metalation results in the precise positioning of an atomically precise and functional monolayer of catalytic sites on the pegboard. The unique structure of $Re_6Se_8Cl_2$ allows for site-selective functionalization during which the apical Cl atoms are replaced with one-electron reagents such as organosulfides while preserving the in-plane Re_6Se_8 connectivity.[12,13]

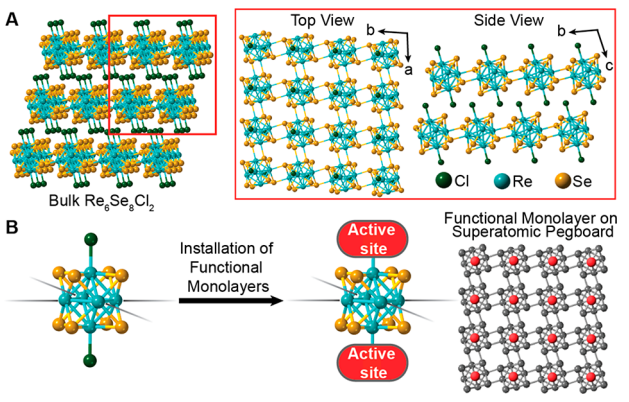

Figure 1. (A) $Re_6Se_8Cl_2$ crystal structure. (B) Functionalization of $Re_6Se_8Cl_2$ to form a functional monolayer of active sites on the 2D superatomic Re_6Se_8 pegboard. Top view of a functional monolayer (red) on a 2D superatomic pegboard (gray) is shown on the right.

$Re_6Se_8Cl_2$ is a promising platform because it shows an uncommon electronic coupling intermediate between the weak coupling of molecular crystals and the strong coupling of atomic solids.[14] The hierarchical electronic structure of $Re_6Se_8Cl_2$ and its strong electron−phonon coupling result in the formation of acoustic exciton-polarons that are shielded from lattice scattering, resulting in wavelike and ballistic room-temperature exciton transport.[15] This combination of visible bandgap and ballistic exciton transport offers opportunities for unexplored applications, such as (photo)electrocatalysis. To exploit these properties we develop a new synthetic strategy (Figure 1B), appending to the Re_6Se_8 pegboard a functional monolayer that is terminated with 2,2′-bipyridines to which we

Received: February 13, 2023
Published: April 6, 2023

https://doi.org/10.1021/jacs.3c01622
J. Am. Chem. Soc. 2023, 145, 8314−8318

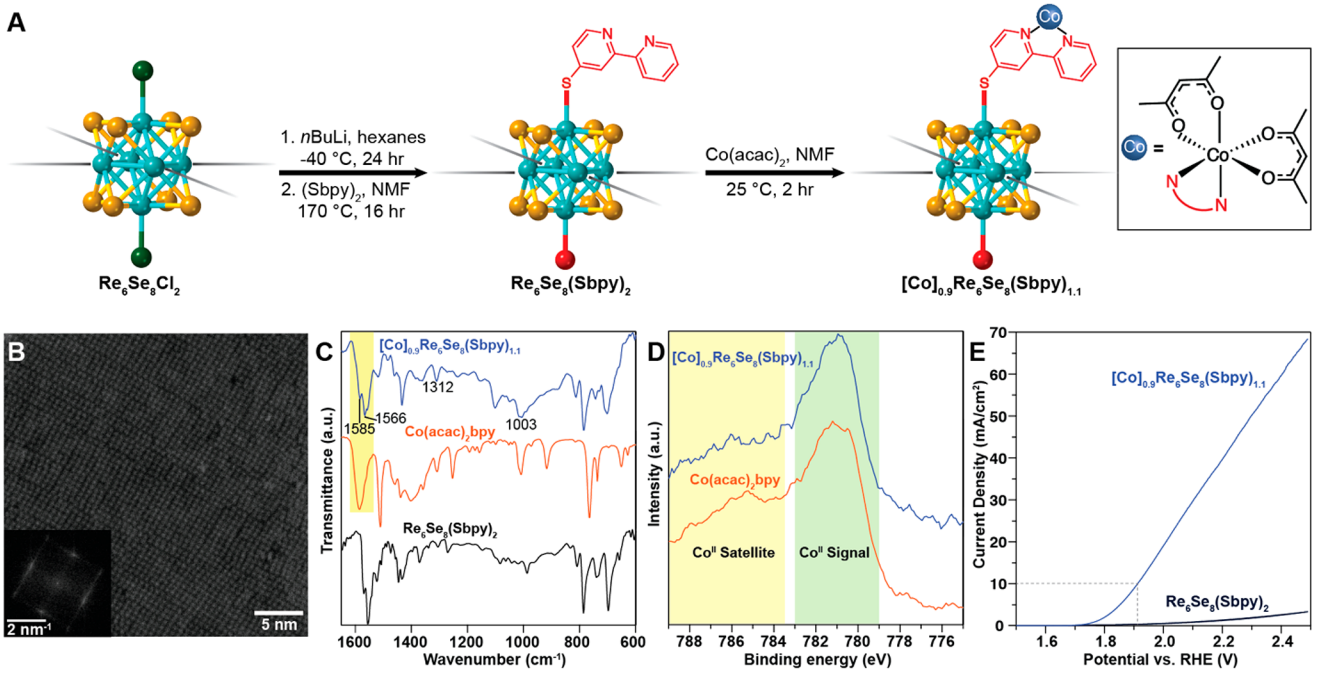

Figure 2. (A) Reaction scheme for creating functional monolayers by installing [Co] active sites on the surface of the Re_6Se_8 pegboard. (B) HR-STEM image of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$, with fast Fourier transform pattern in the inset. (C) FT-IR spectra of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$, $Re_6Se_8(Sbpy)_2$, and $Co(acac)_2bpy$. (D) XPS spectra showing the Co $2p_{3/2}$ region. (E) Linear sweep voltammograms of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ and $Re_6Se_8(Sbpy)_2$ collected in 0.1 M KOH(aq) electrolyte with 0.1 V/s scan rate; LSVs were subjected to *iR* correction.

attach cobalt complexes that are active in the oxygen evolution reaction (OER).[16,17] Surface characterization studies indicate that this method provides synthetic control over the surface catalytic site density, and electrochemical studies establish that the surface cobalt sites impart the otherwise inert 2D superatomic semiconductor with robust electrocatalytic activity. We further demonstrate that we can modulate the activity of these functional materials by incorporating organic spacers in the monolayers, revealing that the connectivity between the 2D superatomic pegboard and the functional monolayer affects the catalytic activity.

In order to exfoliate and functionalize the chemical pegboard we stoichiometrically replace Cl in $Re_6Se_8Cl_2$ with (2,2′-bipyridine)-4-sulfide (Sbpy), where the sulfide groups coordinate to apical Re sites on the clusters.[12] We first intercalate Li into the layered $Re_6Se_8Cl_2$ by soaking the powder in *n*-butyllithium solution. We then suspend $Li_2Re_6Se_8Cl_2$ in a solution of di(2,2′-bipyridine)-4-disulfide ($(Sbpy)_2$) in *N*-methylformamide (NMF) at 170 °C for 16 h. The intercalated material exfoliates, disperses in solution, and reacts with the disulfide to yield a stable suspension of $Re_6Se_8(Sbpy)_2$ nanosheets. The substitution of Cl with Sbpy is quantitative based on energy-dispersive X-ray spectroscopy (EDX) analysis. The superatomic pegboard positions the Sbpy groups in a periodic array to form the bottom portion of the functional monolayers. We metalate the surface-bound bipyridines with $Co(acac)_2$ (acac = acetylacetonate) by adding the suspension of $Re_6Se_8(Sbpy)_2$ nanosheets dropwise to a solution of $Co(acac)_2$ in NMF (Figure 2A). After stirring the mixture at room temperature for ∼2 h, we precipitate the Co-metalated $Re_6Se_8(Sbpy)_2$ by adding toluene. The resulting solid is washed thoroughly with toluene to remove the excess $Co(acac)_2$.

EDX analysis reveals that 45% of the surface Sbpy ligands are metalated in this process. We label this compound $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$, where [Co] = $Co(acac)_2(Sbpy)$. High-resolution scanning transmission electron microscopy (HR-STEM) and powder X-ray diffraction (PXRD) confirm the structural integrity of the Re_6Se_8 pegboard (Figures 2B and S1). Fourier-transform infrared spectroscopy (FT-IR) confirms the metalation of the bpy. The IR spectrum of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ shows peaks that are attributable to both $Co(acac)_2bpy$ and $Re_6Se_8(Sbpy)_2$. In particular, new peaks appear at 1003, 1312, and 1585 cm^{-1} after Co-metalation; these correspond to the IR spectrum of $Co(acac)_2bpy$ (Figure 2C). Furthermore, the 1535−1615 cm^{-1} band (stretching of pyridyl rings; highlighted in yellow in Figure 2C) in $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ matches the broad band in $Co(acac)_2bpy$.[18] This spectroscopic evidence confirms that a fraction of the surface Sbpy groups have been metalated with cobalt ions in $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$. We employ X-ray photoelectron spectroscopy (XPS) to probe the oxidation state and the local coordination environment of the Co sites. Figure 2D presents the Co $2p_{3/2}$ XPS spectra of $Co(acac)_2bpy$ and $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$. The two spectra closely match, with a Co $2p_{3/2}$ signal at 781 eV and a satellite shoulder characteristic of Co^{II} (Figure 2D). These results verify that the local chemical environment of the Co ions in $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ closely resembles that of $Co(acac)_2bpy$. Our surface metalation method is general: we can install Fe^{II}, Ni^{II}, and Ir^{III} by reacting the $Re_6Se_8(Sbpy)_2$ nanosheets with $FeCl_2$, $NiCl_2$, and $[IrCp^*Cl_2]_2$ (Cp* = pentamethylcyclopentadienyl), respectively. We will investigate the electrocatalytic properties of these materials in future studies. For all of the new functional materials synthesized, we confirm the structural integrity of the Re_6Se_8 pegboard using HR-STEM and PXRD (Figures S1−S5); we further confirm the fidelity of the chemistry using EDX, FT-IR, and XPS (Tables S1−S7 and Figures S6−S17).

To assess the OER performance of the functional monolayers, we prepare anodes by spincasting a thin film of

https://doi.org/10.1021/jacs.3c01622
J. Am. Chem. Soc. 2023, 145, 8314−8318

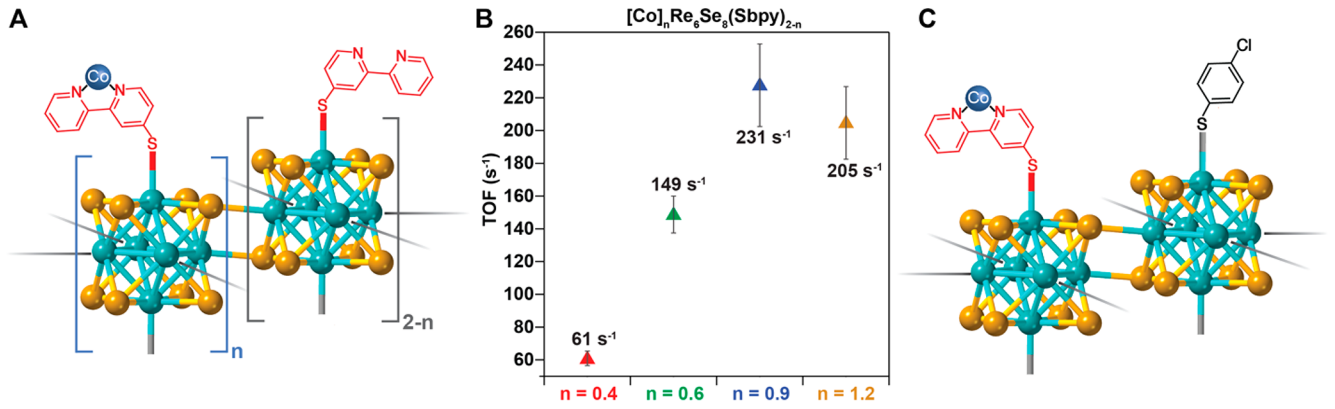

Figure 3. (A) $[Co]_nRe_6Se_8(Sbpy)_{2-n}$ with different surface Co site densities. (B) TOFs at 2.5 V vs RHE of $[Co]_nRe_6Se_8(Sbpy)_{2-n}$ for OER. (C) Co-functionalization of 2D Re_6Se_8 pegboard with Sbpy and 4-ClPhS.

$[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ onto a 1 cm^2 area of a fluorine-doped tin oxide (FTO) electrode. All electrochemical studies were performed in 0.1 M KOH aqueous solution. The linear sweep voltammogram (LSV) of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ displays a current onset at 1.7 V vs the reversible hydrogen electrode (RHE) potential and reaches a current density of 70 mA/cm^2 at 2.5 V vs RHE (Figure 2E). The LSV and the formation of bubbles at the surface of the electrode point to OER, and this was confirmed by analyzing the composition of the headspace above the solution by gas chromatography (Table S8). By contrast, we see no bubble formation on the $Re_6Se_8(Sbpy)_2$ electrode, and the LSV shows only a modest current increase as the voltage is increased to 2.5 V vs RHE (Figure 2E). Furthermore, $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ is ∼7 times more active than the molecular complex $Co(acac)_2bpy$ at 2.5 V vs RHE (Figure S18). We determine the overpotential at 10 mA/cm^2 for $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ to be ∼0.67 V. To put these results in context, we compare the electrocatalytic performance of $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ to those of other cobalt-containing heterogeneous catalysts (Table S9) and find that the OER activity of our material without any optimization is approaching those of other material systems. Given that molecular catalysts such as polypyridyl-ruthenium complexes can have even lower overpotentials of ∼0.20 V at 10 mA/cm^2,[19] our method will allow us to append these complexes to form new functional monolayers on the surface of the 2D Re_6Se_8 pegboard.

We estimate the turnover frequency (TOF) from the current at 2.5 V vs RHE, which describes the quantity of oxygen formed per unit time normalized to the amount of Co sites. $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ exhibits a current density of 70 mA/cm^2 with a low Co loading of 0.05 ± 0.01 $\mu g/cm^2$, resulting in a TOF of 231 ± 25 s^{-1} at 2.5 V vs RHE. These results clearly establish that the surface modification of the Re_6Se_8 pegboard yields a catalytic monolayer, suggesting that a diverse family of new functional materials may be generated using this method.

To demonstrate the tunability of our approach, we vary the surface density of Co catalytic sites in the functional monolayers (Figure 3A) and compare the catalytic activities of the resulting materials. We prepare $[Co]_nRe_6Se_8(Sbpy)_{2-n}$ nanosheets with low Co loading (n = 0.4 and 0.6) by controlling the relative stoichiometry of $Co(acac)_2$ used for the metalation reaction. Higher [Co] loading (n = 1.2) is achieved by carrying out the metalation reaction at 100 °C for 48 h (Table S2). We first prepare electrodes by spincasting solutions with the same molarity of the [Co] complex; these resulting electrodes are [Co]-normalized. The TOF increases as n is increased from 0.4 to 0.9, and then remains mostly unchanged when increasing from n = 0.9 to 1.2 (Figure 3B). When we normalize to the Re_6Se_8 pegboard by spincasting solutions with the same Re_6Se_8 molarity, we observe that the measured current increases linearly with the surface density of Co sites while the TOF remains constant (Table S10 and Figure S19). These results indicate that all the surface cobalt sites are active and similarly behaved when a certain threshold of cobalt coverage is reached. This further implies that cooperativity between adjacent cobalt sites does not significantly contribute to the observed catalytic behavior.

The well-defined surface of the 2D Re_6Se_8 pegboard allows us to tune the catalytic site density not only by varying the $Co(acac)_2$ stoichiometry and but also by co-functionalizing with other groups (*e.g.* 4-chlorophenylsulfide, 4-ClPhS, displayed in Figure 3C) (Tables S4 and S11). This will facilitate the design of the next generation of 2D superatomic pegboard-based catalysts with a functional monolayer of both active and auxiliary sites. We note that the functionalized materials are stable under catalytic conditions: we detect no Co in the electrolyte solution down to the ppb level ([Co] < 0.001 μg) after a 20 min bulk electrolysis, as determined by inductively coupled plasma mass spectrometry (ICP-MS) (Table S12). This is important as a previous study has demonstrated that the close association between the electrode surface and the catalytic sites through covalent attachment favors the efficient charge transfer from the electrode through the tethered catalyst to the reactant.[20]

We next turn to investigating how the anchoring of the molecular catalyst onto the 2D superatomic pegboard controls its OER activity. To this end, we incorporate phenyl (SPhbpy) and ethylene (SC_2H_4bpy) spacers between the Re_6Se_8 pegboard and surface-chelated cobalt complexes to modify the length and flexibility of the linkers (Figure 4A). We assess the OER electrocatalytic behavior of materials with comparable surface Co densities: $[Co]_{0.8}Re_6Se_8(SC_2H_4bpy)_{1.2}$, $[Co]_{0.8}Re_6Se_8(SPhbpy)_{1.2}$, and $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$. While all three materials are active toward electrocatalytic OER, there are quantitative differences. Their LSVs all feature sharp current onsets at ∼1.7 V vs RHE, signifying the start of OER (Figure 4B). We find that $[Co]_{0.8}Re_6Se_8(SC_2H_4bpy)_{1.2}$ and $[Co]_{0.9}Re_6Se_8(Sbpy)_{1.1}$ exhibit very similar TOFs, indicating that the addition of an ethylene spacer does not significantly affect the OER performance. In contrast, the addition of a phenyl spacer decreases the TOF by ∼40% (Figure 4). These studies show

https://doi.org/10.1021/jacs.3c01622
J. Am. Chem. Soc. 2023, 145, 8314−8318

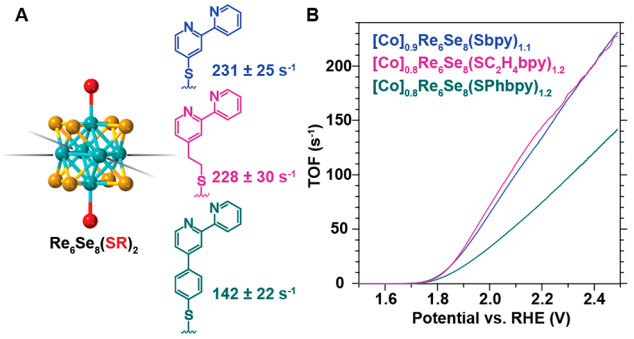

Figure 4. (A) $Re_6Se_8(SR)_2$, where R = bpy, C_2H_4bpy, or Phbpy. TOFs at 2.5 V vs RHE are shown next to the surface functionalities. (B) TOF vs potential plots of Co-metalated materials with different surface functionalities.

that we can produce a series of catalytic materials by building functional monolayers on the 2D superatomic Re_6Se_8 pegboard. The differences in the catalytic performance of the material with surface linkers of varying lengths and flexibility may arise from a combination of mechanisms, including surface cooperativity between the catalytic sites and Re_6Se_8 pegboard, differences in charge transfer between the surface and the catalytic site, and changes of the electronic structure of the Co complex through an inductive effect. We note that the Re−S bond in the functional monolayer is tilted relative to the Re_6Se_8 pegboard surface; this may have an effect in tuning the surface cooperativity between the catalytic Co complexes and the superatomic pegboard.

We have built atomically defined and functional monolayers on the surface of a 2D superatomic Re_6Se_8 pegboard by replacing the apical Cl in the semiconductor $Re_6Se_8Cl_2$ with Sbpy groups, which can then bind to $Co(acac)_2$ for electrocatalytic OER. The well-defined surface of the 2D superatomic pegboard allows us to synthetically control the catalytic site density in the functional monolayers. We further demonstrate the creation of a series of OER-active materials by inserting organic spacers into the functional monolayer. This changes the catalytic performance of the materials, which may be due to the differences in interactions between the functional monolayer and 2D superatomic pegboard that are modulated by the surface linkers. Our work serves as a platform for combining the synthesis of functional monolayers with the ballistic transport of excitons in the 2D Re_6Se_8 pegboard for applications in photocatalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c01622.

Materials, experimental methods, and characterization, including EDX, XPS, ICP, PXRD, HR-STEM, FT-IR, and electrochemistry measurements (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Research into the surface functionalization of 2D materials was supported by the NSF CAREER award DMR-1751949 (X.R.). Work on superatomic materials was supported by the NSF through the Columbia University Materials Research Science and Engineering Center (MRSEC) on Precision-Assembled Quantum Materials DMR-2011738 and the Air Force Office of Scientific Research award FA9550-22-1-0389 (X.R., C.N., M.L.S.). C.N. thanks Sheldon and Dorothea Buckler for their generous support. S.H. is a Postgraduate Scholar-Doctoral (PGS-D) supported by the National Sciences and Engineering Research Council of Canada (NSERC). N.M.O. thanks the Columbia Nano Initiative at Columbia University for postdoctoral fellowship support. The authors thank Prof. Milan Delor from the Department of Chemistry at Columbia University for his scientific contribution, and the authors thank Tai-De Li from the City University of New York for conducting the XPS measurements. The authors acknowledge the use of facilities and instrumentation supported by NSF through the Columbia University MRSEC DMR-2011738. The authors acknowledge the Columbia University Shared Materials Characterization Lab and the Electron Microscopy Lab.

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