Prelithiation Activates $Li(Ni_{0.5}Mn_{0.3}$

F he mo e, he an i ion me al elemen Ni, Co, o Mn in
b lk NMC ill al o e e ience an i e e ible lo d e o he
ide eac ion i h elec ol e, f om hich a of he od c
fo m face de o i ion in he fi cha ging oce , and lead

ho n in S ⁄ ⁄ o ing Info ma ion Fig e S1. The NMC532 ⁄ a icle con i ed of 5−10 μm ⁄ he ical econda ⁄ a icle agg ega ed in o bmic on- i ed ⁄ ima ⁄ a icle i h a na o di ib ion in he ange of 300−500 nm. The f ee- anding, binde -f ee NMC532/CNT com⁄ o i e ca hode a

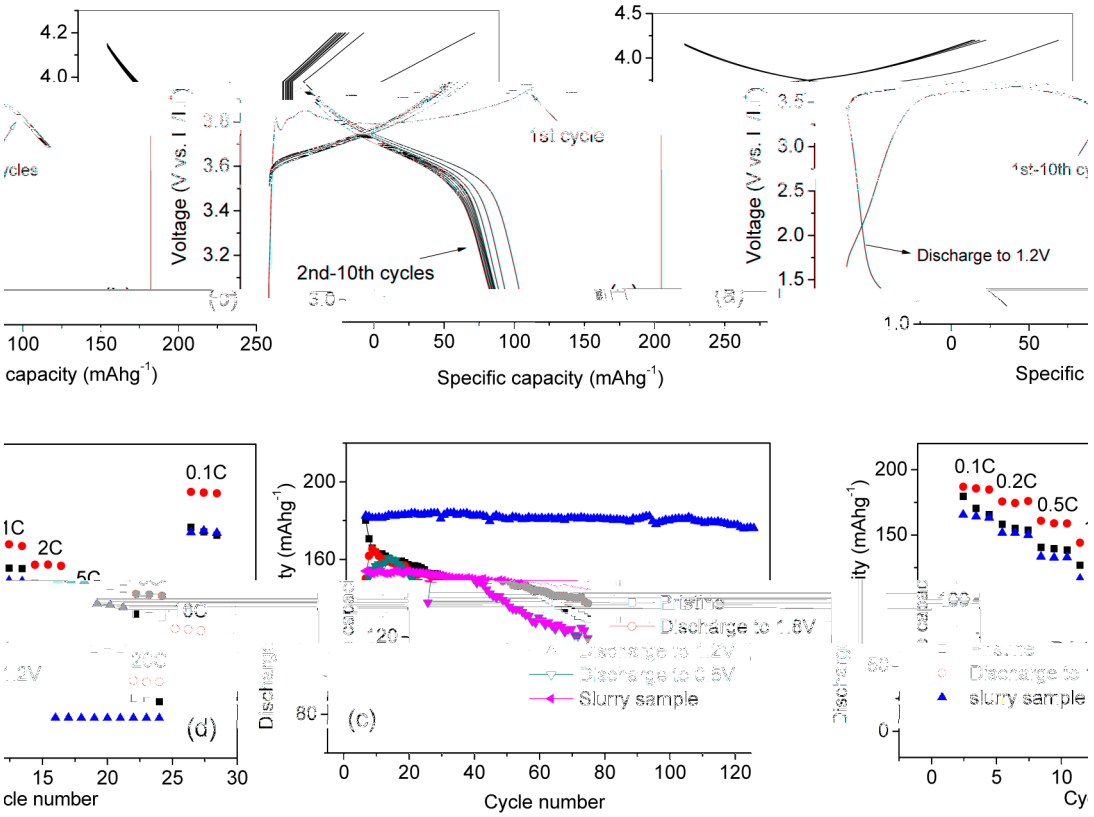

Figure 3. Elec ochemical ¸e fo mance of a io NMC532/CNT com¸o i e ca hode : The ol age ¸ ofile in he fi 10 cha ge/di cha ge c cle fo he am¸le i ho ¸ eli hia ion (a) and he am¸le ¸ eli hia ed o 1.2 V (b), and he c cling abili (c) and a e ¸e fo mance (d) of a io am¸le . All of he e e e o¸e a ed be een 3.0 and 4.2 V ing Li a bo h co n e and efe ence elec ode . Fo com¸a i on, he c cling and a e ¸e fo mance of he l am¸le e e al o ho n in c and d.

Fig e 3a,b. The on e o ida ion of he ¸ i ine am¸le a f om 3.8 V in he fi c cle, hich i m ch highe han ha of he la e c cle (abo 3.6 V), i h a lo Co lombic efficienc d e o i e e ible eac ion . Al ho gh i ini ial ca¸ aci i a high a com¸ ed fo he de¸ola i ed c e e¸o ed ¸ e io l ,[6] i failed o be main ained in b e en fi e c cling , imila o ha e¸o ed b o he g o ¸ .[22,23] In ha ¸ con a , fo he NMC532 ha e ¸e ienced ¸ eli hia ion, he on e o ida ion eac ion in he e fi cha ge c cle occ a 3.6 V, hich emain con an in all he follo ing c cle . Thi la e fea e migh gge ha NMC532 ca hode ma ha e been c all an fo med b he ¸ eli hia ion. Al ho gh he fi cha ging ca¸ aci a¸ ¸ ea o be e ce i el la ge, i i in fac clo e o he fi di cha ge ca¸ aci if he ca¸ aci co e ¸onding o ¸ eli hia ion i b ac ed. Th , he de fac o Co lombic efficienc fo he ini ial c cle ho ld be 91.2%, m ch highe han ho e i ho being ¸ eli hia ed, gge ing ha he ¸a a i ic eac ion be een NMC ac i e ing edien and elec ol e m ha e been effec i el ¸¸ e ed. The SEI fo med d ing ¸ eli hia ion demon a ed e cellen ¸ o ec i e na e, a e idenced b he 185 mAh/g ca¸ aci , hich i clo e o heo e ical al e and ell-main ained in he e ended c cling a ho n in Fig e 3c, in ong com¸a i on again he ignifican ca¸ aci fading ob e ed in he fi 50 c cle fo all o he NMC am¸le ha did no e ¸e ience ¸ eli hia ion. Al ho gh he NMC532 ¸ e¸a ed ia con en ional l me hod ho a good c cling ¸e fo mance, he ili ed ca¸ aci i m ch lo e han he de¸ola i ed NMC am¸le ¸ e¸a ed b fil a ion me hod. Com¸a ed i h he am¸le made b l me hod, all fil a ion am¸le ho good a e ¸e fo mance d e o he de¸ola i a ion effec of CNT ne o k a ho n in he Fig e 3d; na all , he mo con ¸ic o im¸ o emen e e achie ed in he fil a ion NMC am¸le ha e ¸e ienced ¸ eli hia ion.

In o de o e eal he mechani m of ho ¸ eli hia ion affec he ca¸ aci and c cling abili of NMC532, c clic ol ammo- g am (CV) a ed o clea l diffe en ia e he co e ¸onding elec ochemical ¸ oce e , a ho n in S ¸¸ o ing Info ma ion, Fig e S6 and S7, and Fig e 4. D ing he fi li hia ion be een 3.0 and 0.5 V, h ee main ¸eak a¸ ¸ ea (Fig e S6) a abo 1.2, 0.8, and 0.5 V (o lo e han 0.5 V), e ¸ec i el . The a e loca ed a abo 1.2, 0.8, and 0.5 V (o lo e han 0.5 V), e ¸ec i el . The 1.2 V ¸ oce i likel ela ed o he ed c i e eac ion of elec ol e and elec ode, beca e i in en i ignifican l dec ea e af e he fi c cle and he ¸o en ial ag ee i h ha kno n fo SEI fo ma ion on anode face . The ¸eak a 0.5 V con i en l a¸ ¸ ea in each c cle i h he in en i inc ea ing i h he c cle n mbe . Acco ding o Fig e S6b, i migh a i e f om he colla¸ e of NMC532 la ice and ma be e ¸on ible fo he ¸oo elec ochemical ¸e fo mance of he am¸le ¸ edi cha ged o lo e han 1.2 V. The malle ¸eak ha a¸ ¸ ea ed a 0.8 V onl in he fi ¸ eli hia ion ¸ oce ma belong o a hi he o nkno n elec ochemical ¸ oce of ¸ hing e a Li in o NMC la ice. In e e ingl , fo all NMC532 ha bjec o di ec c cling be een 3.0 and 4.2 V, ei he ¸ e¸a ed h o gh l o fil a ion me hod, an in en e o ida ion c en occ ed in he fi cha ging c cle a abo 4.2 V on he ¸ i ine am¸le (Fig e 4a), hen an ob io hif o lo ol age ha¸ ¸ en immedia el follo ing he fi di cha ging (Fig e 4a), he e

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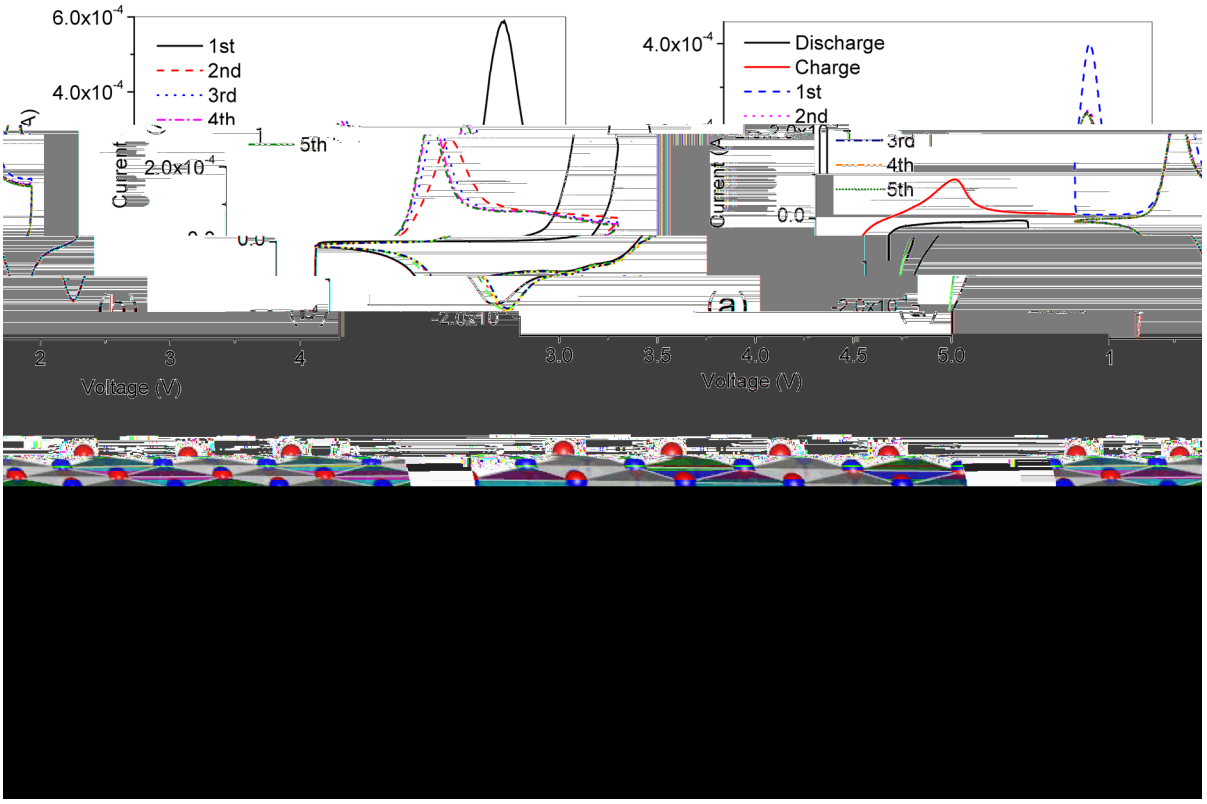

Figure 4. C clic ol ammog am (CV) of a io NMC532/CNT com o i e ca hode : (a) A - e a ed am le, (b) am le eli hia ed o 1.2 V, (c) chema ic c e of NMC532 a icle face i ho eli hia ion, and (d) chema ic c e of NMC532 a icle face af e eli hia ion.

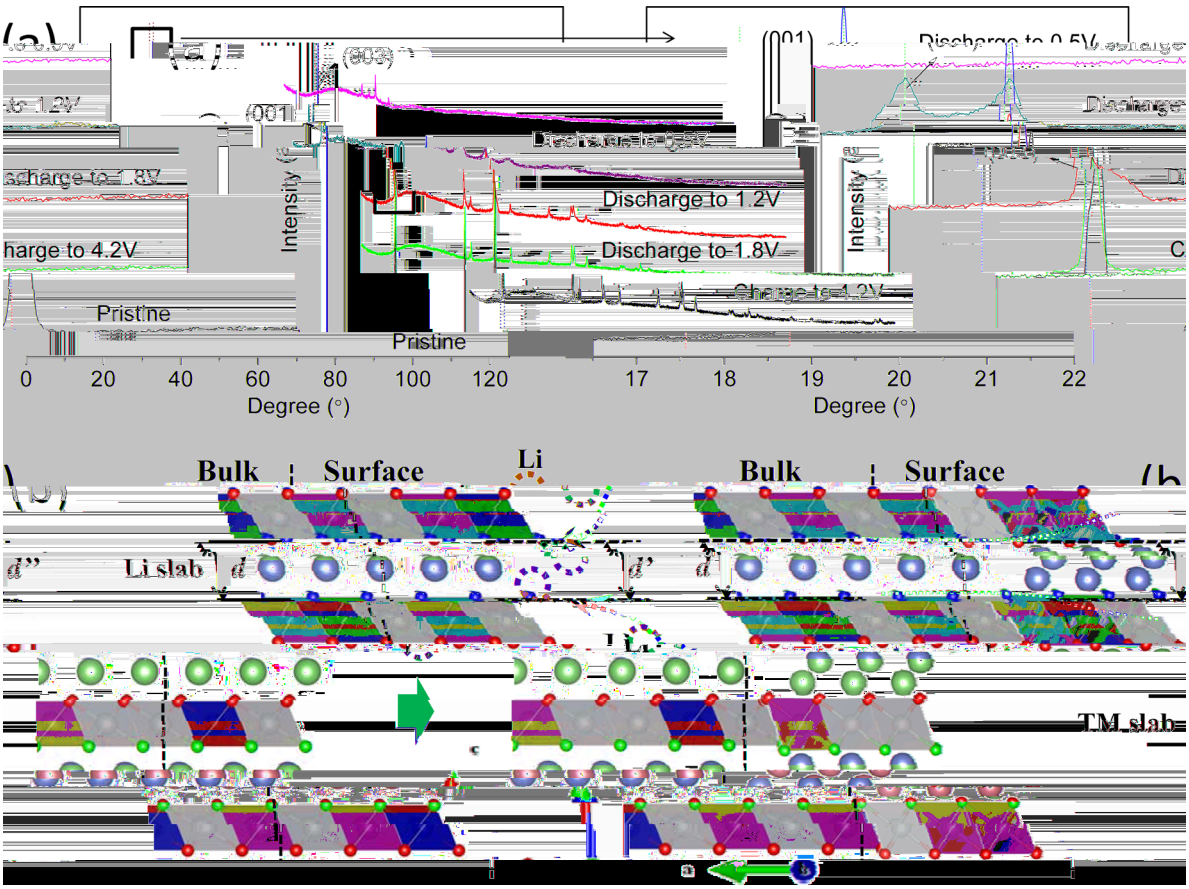

Figure 5. XRD of a io NMC532/CNT com o i e ca hode (a) and he chema ic mechani m of i ac i a ion in he eli hia ion oce (b).

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he edo eac ion i a e a he ame o en ial i h he eli hia ed NMC532 am le (Fig e 4b). The abo e co ela ion be een he ini ial o ida ion o en ial and he e ence o ab ence of li hia ion ma ha e eflec ed he c al an fo ma ion ha a ca ed b he la e , and e belie e ha i ho ld be a ib ed o a oce of NMC532 la e ed c e being li hia ed b e ce amo n of Li (Fig e 4c and d).

XRD anal i a cond c ed on a io NMC532/CNT com o i e ha ha e been eli hia ed o a ing o en ial , and Fig e 5a ho he co e onding c e e ol ion . Com a ed i h he i ine NMC532, no ob io change a ob e ed in he am le ha en h o gh con en ional c cling ; ho e e , i h he dec ea ing eli hia ion ol age, he NMC fea e become eake and ide . When he eli hia ion ol age i 1.2 V, a ne eak NMC (001) clo ed o NMC (003) a ea , hich a al o ob e ed in e io o k fo he la e ed ca hode ma e ial i h e ce Li ha a chemicall li hia ed.[24] The a ea ance of hi NMC (001) confi m ha e ce i e Li ion a e indeed in e ed in o he la e ed la ice of NMC d ing he eli hia ion oce and fo m a do ble Li la e ed c e a ho n in Fig e 5b, e ha im l aneo l i h he fo ma ion of SEI. Once he eli hia ion ol age i lo e han 1.2 V (a o nd 0.8 V), he am le ho an amo ho cha ac e i ic, hich indica e ha he NMC532 la ice colla ed beca e of he e ce i e in e ion of Li.

U ing ab ini io calc la ion , he e e e en ed a im lified model fo he e ce i e Li o age in Fig e S8, hich ho he o imi ed c e fo he no mal one la e Li o age cena io ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$) and he e ce i e o-la e Li o age cena io ($Li_2Ni_{0.5}Mn_{0.3}Co_{0.2}O_2$) be een o an i ion me al lab . In he fo me ca e, he o gen ion a e a anged in a he agonall clo e-acked (hc) a a , hile he an i ion me al ion a e loca ed a all of he oc ahed al i e , i h he ingle la e of Li oc ahed all coo dina ed b o gen. In he la e ca e, he coo dina ion of an i ion me al ion and o gen ion emain nchanged, b he Li ion no a e loca ed in all he e ahed al i e of adjacen la e . Com a ed i h he no mal $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$, he la ice a ame e (a,b,c) of $Li_2Ni_{0.5}Mn_{0.3}Co_{0.2}O_2$ a e inc ea ed f om 14.178 Å, 11.357 Å, and 13.948 Å o 14.76 Å, 11.813 Å, and 15.802 Å, e ec i el , in hich he la e di ance along -a i a inc ea ed b abo 1.9 Å. Thi i al o ell con i en i h he XRD de ec ion of a ne eak NMC (001) clo e o he (003) eak (Fig e 5a) and he co e onding inc ea e of -a i o 1.85 Å acco ding o $\lambda = 2 \sin\theta$. The o en ial fo he e ce Li o age a hen calc la ed, and he al e of 2.27 V a ob ained, acco ding o he follo ing e a ion:[25]

$$V = -\left\{\frac{E(\mathrm{Li}_{x+\Delta x}R) - E(\mathrm{Li}_{x}R)}{dx} - E(\mathrm{Li})\right\} \quad (1)$$

he e (Li) and (Li +) and fo he o al ene g befo e and af e li hi m ion i emo ed f om Li com o nd e fo m la ni , and (Li) i he o al ene g of li hi m me al. The di cha ge ol age o in e he e ce Li in o he la e ca hode de i ed f om hi calc la ed o en ial fo he e ce Li o age i 1.33 V (3.6 − 2.27 = 1.33 V), e clo e o he e e imen al al e of 1.2 V.

Rega ding he hif of eak o en ial a ho n in he CV d ing he on e o ida ion of he diffe en am le ha did no e e ience eli hia ion, he e ma be o fac o e on ible: he fi one i he o ec i e SEI fo med in he eli hia ion, hich o he i e e ible eac ion ha ind ce he hif in he fi cha ging oce d e o highe im edance, b mo e likel i he econd fac o a ib ed o he alence e ol ion of Ni. I i ell-kno n ha Ni in he NMC532 e i in o alence , Ni^{2+} and Ni^{3+}. Acco ding o XPS da a in Fig e 2a, a no iceable hif of he Ni $2p_{3/2}$ eak o lo e binding ene g a ob e ed i h inc ea ing e ching de h, hich indica e ha Ni^{3+} i iche han Ni^{2+} on he face of NMC532 a icle . Acco ding o of X- a ab o ion ec o co in Fig e S9, Ni^{4+} and Ni^{3+} e i on he face of NMC532 a icle . In o he o d , an inhomogeneo c e of he NMC532 a icle co ld ha e been made d e o he e a a ion oce . In o e io o k, e ill a ed he o- age deli hia ion mechani m in NMC532 ma e ial , he fi one being Ni^{2+}/Ni^{3+} loca ed a abo 3.8 V, and he o he one being Ni^{3+}/Ni^{4+} eaked a 4.0 V o e en highe . To he i ine NMC532 a icle , Ni^{3+} a he face ill ha e o e e ience he fi o ida ion o Ni^{4+}, follo ed b he Ni^{2+}/Ni^{3+} oce dee e in he NMC a icle ha co e ond o a m ch la ge eak a e ealed in he lef of Fig e 4a. Af e he fi cha ging and hen di cha ging oce , all NMC532 a icle ill be "nified" o a nifo m Ni- alence, and con e en l , he on e o en ial fo o ida ion eac ion d o o 3.8 V and emain con an in he follo ing c cle . Fo he eli hia ed am le, ho e e , all face Ni^{4+} and Ni^{3+} ill be ed ced o Ni^{2+} d ing he li hia ion oce , hile he Li la e i e en all loaded i h o lab of Li-ion . In hi i a ion, he on e o ida ion o en ial fo all eli hia ed am le o ld a ea a 3.8 V and emain con an he eaf e , a ho n in he igh of Fig e 4b. Fo all he NMC532 am le ha bjec o di ec c cling, he e a e mo e Ni^{3+} and Ni^{4+} a and nea he am le face (Fig e 4c), he Li-ion diff ion ac o he face need o o e come la ge ac i a ion ba ie ,[26] h leading o an o e o en ial in he fi deli hia ion oce . Thi o e o en ial o ld become malle and finall ani h af e e e al c cle , beca e mo e Li-ion o ld be in e ed a and nea he face o ed ce he Ni^{3+} and Ni^{4+} con en a and nea he am le face d ing he li hia ion oce . B con a , fo he eli hia ed NMC532 am le , he e a e o la e of Li-ion o age a and nea he am le face (Fig e 4d), and he ol age fo he e Li-ion deli hia ion i lo e han ha fo he no mal one la e Li-ion deli hia ion. Thi al o acco n fo he o ida ion eak a 2.1 V in he fi cha ge oce (Fig e 4b), con i en i h o follo ing ab ini io calc la ion of 2.27 V. D e o he la ge Li lab ace a and nea he am le face ca ed b he e ce amo n of Li, he e i no o en ial fo he one la e Li-ion deli hia ion (Fig e 4b).

In concl ion, e o o e a eli hia ion oce o im o e bo h he ca aci and c cling abili of NMC532 ma e ial. Thi oce b o gh ac i e ma e ial o lo ol age befo e con en ion cha ge/di cha ge c cle , o ha a de i ed olid elec ol e in e face (SEI) co ld be fo med. Thi no el SEI, mainl fo med a o nd NMC532/CNT b elec ol e ed c ion a he hickne of abo 40 nm, i chemicall imila o SEI fo nd onl on anode face i ho he a ici a ion of an i ion me al and co e he hole face of NMC532 a icle , in ha con a o he in e ha e fo med hen di ec l cha ged o 4.2 V. T o majo benefi a o e f om hi no el SEI incl de he o ec ion of NMC a icle f om Mn(II)-di ol ion and he ac i a ion of NMC fo e a Li o age. The NMC532/CNT com o i e ca hode h e a ed no onl main ain he de ola i ed c e in od ced b

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fil a ion me hod and a high ca aci con i en i h he heo e ic calc la ion a e o ed e io l , b al o e cellen c cling e fo mance. Thi com o nded echni e of de ola- i a ion ia nano i ing along i h eli hia ion can be e ended o all ca hode ma e ial ba ed on he la e ed- c e of NMC de i a i e , lending f he in i a ion o he de ign and o imi a ion of ne com o i e ma e ial fo he ne gene a ion li hi m ba e ie .

■ ASSOCIATED CONTENT

Supporting Information

De ail of he me hod ec ion, he mo holog , XRD a e n , e i ance, elec ochemical e fo mance of he e a ed am le and he e CNT am le , he TEM and of X- a da a of he in e face la e , la e ed c al c e im la ed b he fi inci le me hod. The S o ing Info ma ion i a ailable f ee of cha ge on he ACS P blica ion eb i e a DOI: 10.1021/ac .nanole .5b02246.

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Author Contributions

Z.W., S.J., and J.Z. con ib ed e all .

Author Contributions

Thi o k a ini iali ed b Z.W., S.J., and F.P. The e e imen and elec ochemical da a a e fo med b Z.W., S.J., S.X., Q.L., and Z.Z. The da a anal i a e fo med b Z.W., S.J., F.P., Y.L., and W.Y. The calc la ion a done b Z.H., Y.W., and J. Z. The man c i a i en b Z.W., F.P., K.X., and K.A.

Notes

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