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In situ dynamic tracking of heterogeneous nanocatalytic processes by shell-isolated nanoparticle-enhanced Raman spectroscopy

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Surface molecular information acquired *in situ* from a catalytic process can greatly promote the rational design of highly efficient catalysts by revealing structure-activity relationships and reaction mechanisms. Raman spectroscopy can provide this rich structural information, but normal Raman is not sensitive enough to detect trace active species adsorbed on the surface of catalysts. Here we develop a general method for *in situ* monitoring of heterogeneous catalytic processes through shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) satellite nanocomposites (Au-core silica-shell nanocatalyst-satellite structures), which are stable and have extremely high surface Raman sensitivity. By combining operando SHINERS with density functional theory calculations, we identify the working mechanisms for CO oxidation over PtFe and Pd nanocatalysts, which are typical low- and high-temperature catalysts, respectively. Active species, such as surface oxides, superoxide/peroxide species and Pd–C/Pt–C bonds are directly observed during the reactions. We demonstrate that *in situ* SHINERS can provide a deep understanding of the fundamental concepts of catalysis.

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U de. a di g. c e-ac i i ela i hi a d eac i echa i i f ig i ca . i . a ce i . he a i al de ig f highl ef cie . ca al . [1 5]. Af e e i ee i g k del . e b b . h face a d . he e ical cie . i [6 16], ch g ha bee ade i . hi a ea. H e e , challe ge a cia ed i h . he e a i f del . e . i d . ial ca al e ai [8]. Th . he de el . f in situ face a al i . ech i . ha ca be ed . d eac i c cc i g e ac ical ca al i highl de i able. F e a le, e in situ . ech i cl di g i al . i elec ic c , high- e ca i g . eli g ic c (STM), a bie . e X- a h . elec ec c (XPS) a d X- a ab . i ec c ha e bee a lied . d a ca al a d e eal lec la i f a i ab . he ca al de ki g c di i , ch a face c i i , che ical . a e, h l gie a d c di a i i [17,18]. Tha e k ha e g eal l i ed de . a di g f ca al i .

O e f . he . idel ed face a al i . ech i i in situ i f a ed (IR) ec c , hich ca ide ich i f a i ab . e face . c e[19], ac i e i e[20] a d eac i echa i [21]. H e e , i i e dif c l f in situ IR . de ec i . e edia e i h ig al i . he l a e be egi f . he ec . I c . a , . he l a e be egi i acce ible b Ra a ec c [22]. Thi . ech i e ha bee ed . ide . if i . e edia e ecie ch a e al-C b d , ac i e ge ecie , h d l g a d face ide [23 25], b . i ge e al, al Ra a ec c i . ii e gh . i . ace a f face ecie e al ca al . S face-e ha ced Ra a ca . e i g (SERS) ha bee e l ed . ci c . hi li i a i , a i ffe . a . e d i e . i ii i (10[7] 10[10] . i) a d ca e be ed . de ec i gle lec la [26 29]. Ne e . hele , l a fe e al (i a il A , Ag a d C) i h a . c ed face ide a la ge SERS effec [30]. Th , i i g ca al . ic c a cc i g e . he e al e ai a g ea challe ge.

Rece . l , g i . ed a el . ech i e k a hell-i la ed a a . icle-e ha ced Ra a ec c 'SHINERS'[31], hich ha bee ega ded a a i e . ge e a i f ad a ced ec c [32]. I SHINERS, la ic A a a . icle (Ra a ig al a li e) a e c a ed i h i h le-f ee ilica hell . ha e e . he f i . e ac i g i h a al . ical . a ge . he che ical e i . The ilica hell a e . hi e gh (j . a c le f a e e) . ha . he e ha ced elec ag e ic eld ge e a ed a . he face f . he c e . e d be d . he face f . he hell. SHINERS ha b ke . he l g . a di g face a e ial a d h l g . ic i . ha e i . . adi i al SERS. I i ci le, . he SHINERS . ech e ca be a lied . a face f a a e ial a d a h l g . I ha bee idel ed i elec che i . [31,33 35], life cie ce[36], . he a e ial a d e ic d c i d . [31,37], la e g . age a d c e i [38,39], a d dail life[40].

I . hi k, e de el a i le . a eg . c . c A -c e ilica hell a ca al . a elli e a c i , hich e call SHINERS a elli e . c . Th ee-di e i al i e-diffe e ce . i e-d ai (3D-FDTD) i la i de . a e . ha Ra a ig al f che ical ecie . he a elli e . c a e g ea l a li ed b . he la ic ac i i f . he c e, aki g . hi a ideal a chi ec e f i i g he e ge e ca al . ic eac . i . Wi h . hi . a eg e ha e b ai ed di ec ec c ic e ide ce f . he f a i f e al-O a d e al-C b d , a ell a ac i e ge ecie , d i g CO ida i . Wi h . he aid f de i f c i al . he (DFT) calc la i , . he SHINERS- a elli e e h d ha e ealed e lec la i f a i ab . CO ida i .

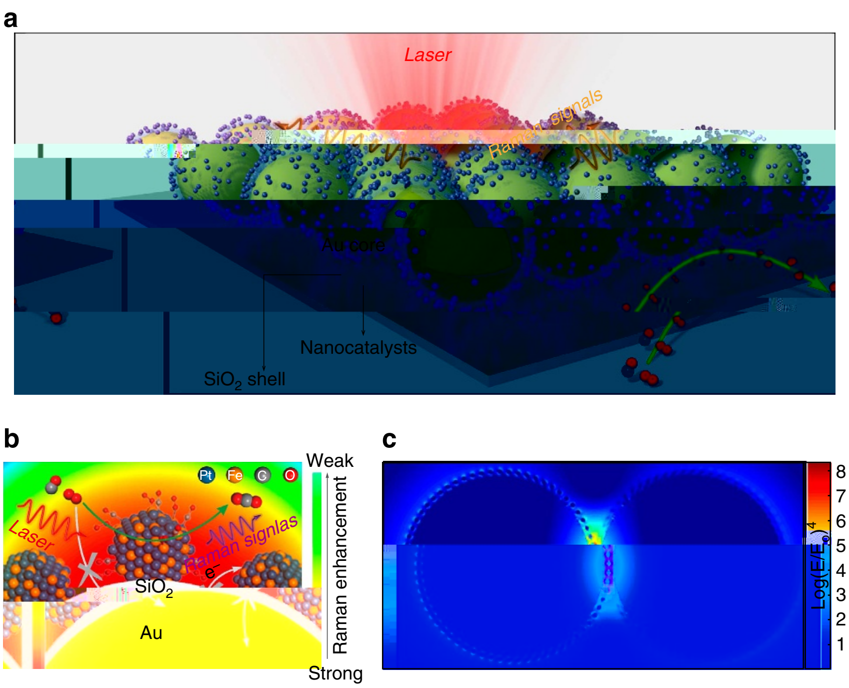


Figure 1 | Schematic illustration of a SHINERS-satellite study of a nanocatalytic process. (**a**) The Au-core silica-shell nanocatalyst-satellite architecture of SHIN-enhanced Raman spectroscopy (SHINERS)-satellite structures, and the mechanism for CO oxidation over PtFe bimetallic nanocatalysts revealed by our SHINERS-satellite method. The pinhole-free silica shell prevents the Raman signal amplifier from interfering with the system under study. (**b**) Schematic illustration of CO oxidation on PtFe. The blue, orange, grey and red spheres represent Pt, Fe, C and O atoms, respectively. (**c**) A 3D-FDTD simulation for a pair of Pt-on-shell isolated nanoparticle (SHIN) nanocomposite structures.

Results

Raman enhancement of SHINERS-satellite nanocomposites. SHINERS, ligh -i d ced l cali ed face la ield a ea f ha ced elec ag e ic eld . g h a .he face f .he A c e, a d .he elec ag e ic eld . g h deca e iall i h di .a ce f .he face f .he A c e de d g ea - eld cha ac e i .ic[31,41]. Th , e de ig ed a c e hell a elli e a c ie . c e i h .he a ca al .he ilica hell, j . a c le f a e e a a f .he c e. .hi a , Ra a ig al f eac i .e edia .he face f .he ca al ca be a li ed effec i el .

The A -c e ilica hell a ca al . a elli e a chi ec e i h i Fig. 1a. The SHINERS a elli e . c e i e a ed b c a i g a A a .icle i h a l a hi e i h le-f ee ilica hell, .h addi g .he a ca al . .he face f .he hell. The i h le-f ee ilica hell e . ad .i f lec la f .he che ical i . .he A c e, a d i al e . a i .e ac i be .he a ca al a d .he A c e (Fig. 1b). Th , i f a i ab . he e g e ca al .ic eac i ca ca be b.ai ed i h . i k f i .e fe ce b .he Ra a ig al a li e . T c .ha .hi . c e ill effec i el ha ce Ra a ig al f ecie .he a ca- .al , e delled elec ag e ic eld . g h i g a 3D-FDTD e h d i hich .he e fec l a ched la e b da c di i e e ada .ed . a id - h ical e ec i [42]. The . c e elec ed f delli g a a 120 A c e i h a 2 ilica hell .i g 2 P. a ca al . The dielec ic f c i f A a d P. e e .ake f a l i-c ef cie . .i g del ffe ed b L e ical S l .i . Fig e 1c h .ha a egi f e .a di a il high elec ag e ic eld . g h (a -called h .') cc .he a a .icle a a .icle j c i .he a ai f SHINERS a elli e . c a e ill i a ed i h a 633 la e (.he . al- eld ca.e ed- eld ce ac ed a a li ea l la i ed ligh al. .he ai). The 3D-FDTD i la i h .ha Ra a ca.e i g f lec la .he a ca al l ca ed i .he j c i be .he . hell-i la ed a .icl (SHIN) ld be ha ced b . 8 de f ag i de, hich i . g gh f l a ii e de ec i f face ecie[33].

Synthesis of SHINERS-satellite nanocomposites. The a ca- .al a elli a e added . .he face f .he SHIN b a elf- a e bl . The .ha i f SHIN i d c ibed i de ail el e he e[43]. Af e .ha i , .he SHIN face i ega i el cha ged d e . .he ce f ci a e (S le .a Fig. 1). The P. Fe bi e allic a ca al ., hich i idel ed f g ed c i eac i i f el cell[44] a d ca al .ic ida i [45], elec ed a a e .a i e ca al . i h hich e l e .he .ha i f SHINERS a elli e a . c . The .ha i a d cha ac e i a i f .he a ca al i de ailed i .he S le .a Me h d . The P. Fe a ca al e e di ed . c ea e a i i el cha ged face (S le .a Fig 1 3), a d i ed i h .he ega i el cha ged SHIN (S le .a Fig. 1) achie e .he elf-a e bl ca . Fig e 2a clea l h .ha .he l i g a .icl ha e a c e hell a elli e .ie ed a chi ec e. Thi . c e i f .he de . a ed b .he ele . a i Fig. 2b a d .he high- l .i . a i i elec ic c (HR-TEM) i age i S le .a Fig. 4. a c . l e e i ., di ed P. Fe a ca al e e added . a l f SHIN . The did . adhe e . .he ilica face, de . a i g .ha di ca i f .he P. Fe a ca al . c ea e a i i el cha ged face i c i ical f SHINERS a elli e .ha i (S le .a Fig. 5).

Th gh a .e a ic . d , e f d .ha .he . a eg e l ed he e f P. Fe a ca al ca be ed . a e ble a .he f a ca al . -SHIN . c (S le .a Fig. 6). Fig e 2c h HR-TEM i age f e allic P. a d Pd a ca al , bi e allic P. Pd a d P. Fe a ca al , A @P. Fe c e hell . c , PdFeC - c b , a d CeO_2 a d Fe_2O_3 e al ide SHIN . The i e a d h l g f .h e a ca al e e cha ged b .he elf- a e bl c , a d all f .he e e e l di . ib .ed .he face f .he SHIN . Th , i i fea ible . d . c e- ac i i ela i hi a d eac i echa i f he e g e ca al .ic c b SHINERS af e ca ef ll a i la i g .he c i i ,. c e, h l g a d i e f .he a ca al . a elli .

CO oxidation over PtFe bimetallic nanocatalysts. SHINERS- a elli e . c e e .h ed i e a d . di f CO ida i e P. -g a ca al . Thi c i f g ea i .a ce i f da .al ea ch, a d ha bee ec g i ed a a be ch a k .e f he e g e ca al i[46]. I i al i .a . f ac ical a lica i ch a i .al .ec i[47] a d .he d ci f l a e h d g [48]. The SHINERS a elli e e h d .a . ed . e a i e .he ela i hi be . c e a d ac i i f P. Fe a ca al . Rece . di ha e h .ha P. Fe bi e allic a ca al a e highl ac i e i .he ida i f CO (ef 45,49). DFT calc la i i dica e .he high ac i i l f ef cie . ac i a i f ga e O_2 lec la b .he c di a i el a a ed Fe c . i P. Fe (ef. 45). Di ec ec c ic e ide ce i ill eeded . e .hi echa i . The in situ SHINERS a elli e . a eg i . d ced ab e ca eal .he effec f .he fe c . .he e f a ce f CO ida i .

The al ce .a e f Fe i .he P. Fe a ca al . de e i ed b XPS (g da a i . i .he l e a . f Fig. 3a). F efe ce, XPS ec a f Fe i diffe . ida i .a e e b.ai ed b c . lli g .he a li g de .h A + . .e i g (bl e, ed a d black c i .he e a. f Fig. 3a). Fe f il e ed. .he a he e a idi ed hile .he b lk a e ial e ai ed i e allic f . The g ed da a i . i Fig. 3a h a Fe 2 $_{3/2}$ eak a ~710.4 eV. We e f ed a dec l .i f .he XPS ec . de e i e .he che ical .a f .he Fe ecie (l e a . f Fig. 3a) acc di g . .he li e a e[50] a d .he efe ce da a b.ai ed f Fe f il i h diffe . A + . .e i g . i . The . l h ha Fe^{2+} ecie , a ell a a e all a . f Fe^0 ecie , a e . i .he bi e allic ca al . I ca al be ed .ha .he bi di g e gie f .he e ecie a e ligh l highe .ha .h e i b lk Fe f il. Thi a be d e . .he l e Fe Fe c di a i a d highe Fe P. c di a i i .he bi e allic ca al ., hich ld lead . ced elec ic i .e ac i be Fe a d P. (ef 51,52). A hif f .he X- a diff ac i a.e f P. Fe c a ed . P. i dica a h i ki g f .he c al la .ice, ea i g .ha Fe f a all i h P. (S le .a Fig. 7). F .he e, ele . a d li e ca h ha Fe ecie l ca e e cl e . P. ecie (S le .a Fig. 8). The ef e, e belie e .he P. Fe bi e allic ca al . ha a all . c e i h fe ide i face.

Fig e 3b c a .he e f a ce f .he P. Fe bi e allic a ca al . a d a P. e allic a ca al . f CO ida i a diffe . .e e a . Clea l , .he P. Fe ca al . i ch eac i e .ha .he P. ca al . . CO i c le el e ed b P. Fe, e a .e e a e. The P. Fe a ca al . ca al be ed f efe .ial ida i f CO i .he ce f H_2, hich i f ig i ca . i .a ce f .he d ci f highl e H_2. A h i S le .a Fig. 9, .he P. Fe ca al . i highl ac i e a d able i .he efe .ial ida i f CO a .e e a e.

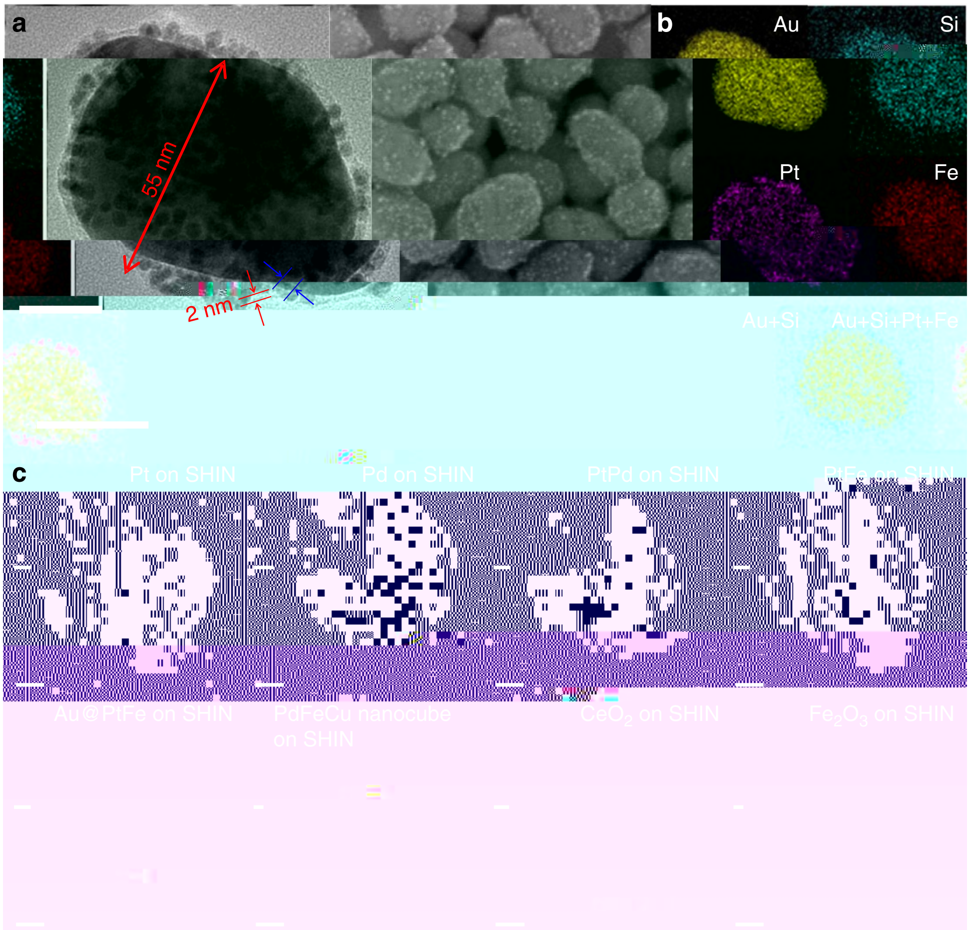
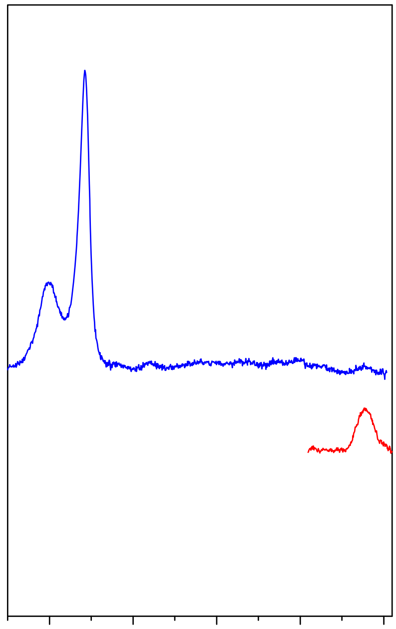


Figure 2 | The structure of various SHINERS-satellite nanocomposites. (**a**) TEM (inset) and scanning electron microscope images of PtFe-on-shell isolated nanoparticle (SHIN) core-shell-satellite nanocomposites. Scale bar, 100 nm. Scale bar for the inset, 20 nm. (**b**) Element maps of the single particle in the inset of (**a**). (**c**) TEM images of various nanocatalyst-on-SHIN structures. The insets in **c** are the zoomed-in image of the edge of the same particle as in main image. Scale bars, 20 nm. Scale bars for the insets, 5 nm.

T e eal he effec f he fe co , P Fe- -SHIN a d P - -SHIN a c i e e a ed f in situ SHINERS- a elli e die . Ac i i (S le a Fig. 9) a d XPS da a (S le a Fig. 10) h ha he ilica hell i la a he A c e ha i ha i ce he e io f he a ca al . F he e, he ca i g ago he ca al (ch a le la i e) e e ed d i g fab ica i f he SHINERS a elli e a c i a d he e a a i e ca ied bef e in situ SHINERS a elli e dia (S le a Fig. 11), ha ca al ic i e acce ible eac a . The black a d i k c a i Fig. 3c h ha Ra a ig al a e b e ed f P P Fe a ca al ilica d e he l i i i f al Ra a ec c . The g e c e h ha he e a e al Ra a ig al f SHIN i h a ca al a elli a d he ef e, he ig al b ai ed i he f ll i g e e i a be f ecie ad bed he ca al face. The bl e a d ed c a i Fig. 3c h ha g Ra a eak ca be b ai ed f he a e ca al ho he a e i c a ed i he SHINERS a elli e c a . The e a l de a e he le ha SHIN la i Ra a ig al a li ca i . We e ha he SHIN a elli e a c- a a e al ch e able ha A a elli e a c a high e e a a (S le a Fig. 12). The eak a 397 a d 485 c $^{-1}$ i he ec b ai ed f he P - -SHIN c a (bl e c e) ca be a ig ed he P C e chi g ib a i al de f b idge a d li ea ad bed CO a ec i el[53]. Thi ec (he bl e c e) i dica a ha l

CO a ad bed he face f he P , a d he ac i a i f O_2 a i hibi ed b he gl c e i i e ad i f CO. Thi ca al be de a ed b in situ SHINERS a elli e dia f P de e O_2 a d de CO ida i c di i a highe e e a a (S le a Fig. 13). The ec b ai ed f he P Fe- -SHIN c a (Fig. 3c ed c e) ha eak f O_2^{2-} a 870 a d 951 c $^{-1}$, a d a eak f O_2^- a 1,158 c $^{-1}$ (ef 23 25), i addi i he CO ad i eak a 389 a d 480 c $^{-1}$. The a ce f ac i e ge ecie he P Fe a all face a c ed b elec a a ag e ic a a ce (EPR) dia af e CO ida i (S le a Fig. 14). I ca be e ha he e i eak i he 500 700 c $^{-1}$ a ge, gge i g ha P ide i f ed a 30 °C. F he e, a ed hif f he P C e chi g ib a i cc f he P Fe a all c a ed he P e allic a ca al (Fig. 3c i e). Thi i lie ha Fe ecie eake he ad i f CO, a d hi a be a he ea f he high ac i i f he P Fe a all . The e l i dica e ha CO ida i he P Fe a all c ld ceed h gh a La g Hi hel d echa i , e a a e l e e a e, i hich he ad bed CO a d face ge ecie a e i l ed.

CO oxidation over Pd nanocatalysts. Pd ba ed a a icle i ca al ic c e e a e effec i e CO ida i ca al a d ed ce a ie e i i , h e e , he de l i g



echa i i . f ll de . d. Fig e 4a ida SHINERS- a e all eak a 490 c $^{-1}$, a d . eak i . he high
a elli e ec a f CO ida i e Pd a ca al . be e a e be egi a 1,935 a d 2,061 c $^{-1}$. The eak a 360
30 a d 150 °C. A l e e a a (∼30 50 °C), . he e i e a d 1,935 c $^{-1}$ ca be a ig ed . b idge ad bed CO Pd,
. g eak i . he l a e be egi a 360 c $^{-1}$ a ell a a d . he eak a 490 a d 2,061 c $^{-1}$ ca be a ig ed . li ea

ad bed CO Pd (ef. 54). A highe eac i .e e a .he i . i f .ha e ba d dec ea , i dica i g .ha CO . a . . da b f .he face. Wh .he .e e a e i i c ea ed ab e 70 °C, .he eak a ea i .he l a be egi . A h i S le .a Fig. 15, .he ecia ible f .he addi i al ba d a 860, 955 a d 1,165 c $^{-1}$ ca be eli i- a ed b e laci g O_2 i .he feed i h H_2, a d a e . ed b .he ei . d c i f O_2. The ef e, .ha e ba d . be ela ed . face g ecia . The e i . ce f face g ecia Pd a ca al . . a c ed b XPS (S le .a Fig. 16) a d EPR (S le .a Fig. 17). Acc di g. .he li e a e[23 25], .he ba d a 860 a d 955 c $^{-1}$ ca be a ig ed . e ide ecia hile .he ba d a 1,165 c $^{-1}$ ca be a ig ed . e ide ecia . Th e ba d ca al be a ig ed ia DFT calc la (S le .a Table 1), hich ill be di c ed i de ail la e . Wh .he .e e a e i f .he i c ea ed ab e 110 °C, . eak a ea a 433 a d 645 c $^{-1}$. Th e ba d ca be a . ib . ed . Pd O . e chi g ib a i [55]. Thei Ra a hif a e ligh l highe .ha .he Ra a hif b ai ed f b lk Pd O (S le .a Fig. 18), a d HR-TEM h .ha b lk PdO i f ed d i g Pd- -SHIN e e i . a 150 °C (S le .a Fig. 19). Th e l . i dica e .ha .he 433 a d 645 c $^{-1}$ eak a e d e . face ide a d . b lk PdO.

We al . died .he i ce .ha .he CO/O_2 ga a i ha face ecia d i g CO ida i (Fig. 4 a d S le .a Fig. 20). The SHINERS a e e ec a b ai ed i h diffe . CO/O_2 ga a i i .he feed a e e i ila , i dica i g .ha CO ida i ca Pd a ca al . de diffe . feed c di i a e i ila . A l e e a , l CO i ad bed .he ca al . . A eac i .e e a e i c ea , .he Ra a ig al i . . i i c ea f g ecia a d PdO hile .he the l a be egi . Wh c bi ed i h e adi i al cha ac e i a i ech i ch a TEM, XPS, X- a ab i ec c a d IR, a ell a DFT calc la i , he SHINERS a elli e a eg ca ide a dee de a di g f c e-ac i i ela i hi a d eac i echa i .

Thi a eg ca be ed ack face eci a d i e edia f he i d iall i a eac i , ba ida he del CO ida i eac i . F e a le, ad bed e h l e eci a e ea de ec ed b he SHINERS a elli e e h d (S le a Fig. 24), ha e ida i f e h l e ca be died in situ. A he i a ec f he SHINERS a elli e a eg i i abili f li id ha e eac i . O l Ra a ig al f eci l ca ed a fe a e a f he A c e a e ha ced, h Ra a ig al f l lec l a d he eci i he b lk l i hich d a ici a e i he eac i a e ha ced. The SHINERS a elli e e h d ca al be ed cha ac e i e he c i i a d elec ic e ia f a ca al face if be lec l a e (S le a Fig. 25). F he e, he Ra a ig al ha ce ca be i ed a ec a b i i g he a li e (f e a le, b i c ea i g he A c e i e cha gi g he A c a Ag e a h i S le a Fig. 26)[40,59] de ec eci i h alle Ra a ca e i g c ec i . Tha e i e e ia f he SHINERS a elli e a eg ake i a i e al a d i i e a ach f in situ d f a i eac i cc i g diffe a ca al .

T a i e, a i le, ge e al a d able a c i e a eg ha bee de el ed i he e ge ca al ic ca in situ i h e e el high face i i i i g A -c e ilica hell a a al a elli e c . 3D-FDTD i la i h ha Ra a ig al f eci he face f he a ca al ca be a li ed b 8 de f ag i de beca e f elec ag e ic eld ha ce b he A c . The ilica hell i la e he A c a d e he f i e ac i g i h he a ca al a d he che ical i hile i i g hei he al abili . U i g hi a eg , e died he ida i f CO P Fe a all a d Pd a ca al . F he P Fe e , e b ai ed di ec ec c ic e ide ce h i g ha he fe c e ca eak he P C b d a d ac i a e O_2 a e e a e. Thi lead CO ida i b he La g i Hi hel d echa i . F he Pd e , e c bi ed he SHINERS a elli e a eg i h DFT calc la i a d f d ha ac i e O_2 eci a e f ed il CO begi d b, ca i g he eac i f ll he Ele Rideal echa i . We ha e de a ed ha SHIN a be c bi ed i h a a ie f he a ca al a ell, ea i g ha a eg ca be de el ed a a da d cha ac e i a i e h d f in situ i i g f eac i i e edia a d el cida i g eac i echa i .

Methods

Synthesis of SHINs and nanocatalysts. SHIN i h 55 A c e ha i ed acc di g e i l e ed e h d[31]. I b ief, 55 A a a icle e e ha i ed acc di g F ' e h d[60] a d he A a a icle e e he c a ed i h a l a hi ilica hell a 90 °C i g 3-a i l i e h ila e a a c li g a d di ilica e a a ilic ce. SHIN i h 120 A c e e ha i ed b a i ila ced e, b 120 A a a icle e e a ed b a eed- edia ed g h e h d a d de ail f ha ha i ca be f d i he S le a I f a i . P ced f he e a a i f a ca al ch a P , Pd, P Pd, P Fe, A @P Fe, PdFeC a c b , CeO_2 a d Fe

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Additional information

Supplementary Information acc a ie .hi a e a h. :// a e.c / a ec ica i

Competing interests: The a .h decla e c e i g a cial i .e e .

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