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SUPPORTING INFORMATION

Nanowires with Controlled Porosity for Hydrogen Production

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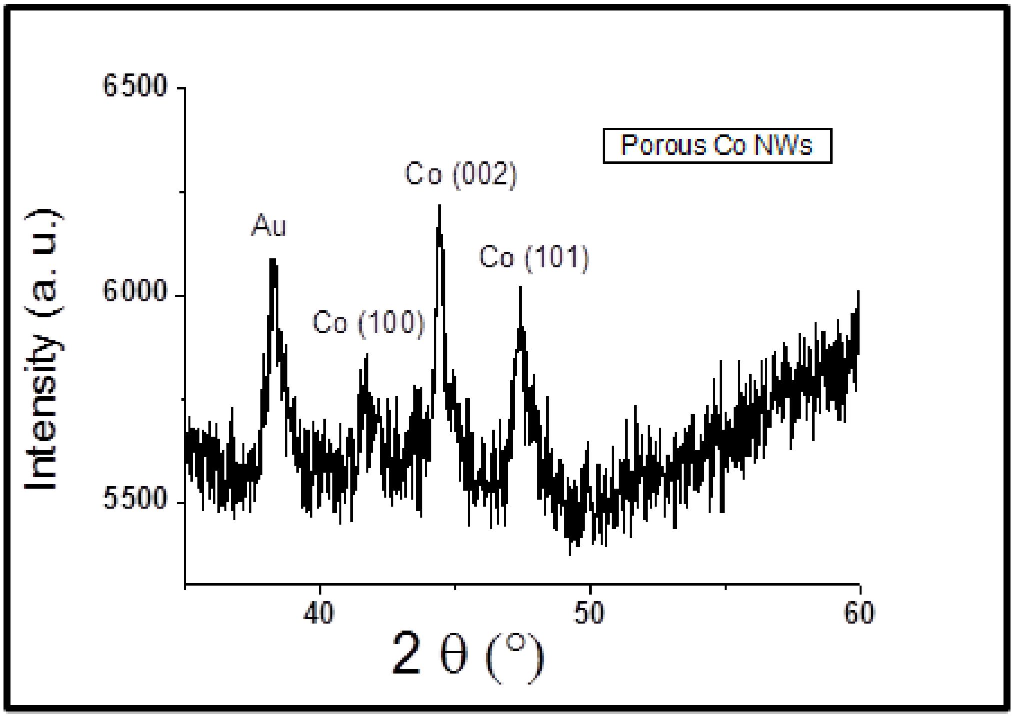
SI1. XRD measurement performed on Porous Nanowires

XRD diffraction was performed on the porous Co NWs. The diffraction peaks correspond to (100), (002) and (101) of the hexagonal phase of cobalt, asgenerally observed with the cobalt materials prepared by electrodeposition.



SI1. XRD pattern of porous Co NWs (r = 100 nm; R_1 = 35 nm). The gold is attributed to the metallic contact used during electrodeposition.

SI2. SPECIFIC SURFACE AREA OF NON-POROUS Co NWs

The specific surface area of non-porous NWs has been determined using the following equation where

$$S=\frac{s}{M}=\frac{2\pi rL+2\pi r^2}{\pi r^2 LD}=\frac{2L+2r}{rLD}=\frac{2}{D}(\frac{1}{r}+\frac{1}{L})$$

Where r is the NWs radius, L the NWs length and D the cobalt density.

SI3. SPECIFIC SURFACE AREA OF POROUS Co NWs with 1 size of PS spheres

For the Co p-NWs, we assume that the PS nanospheres arrange following the face-centered cubic (fcc) lattice. The face-centered cubic lattice has 4 nodes.

-8 nodes in the 8 summits are shared between 8 lattices

-6 nodes in the centers of the six cube faces and are each shared between two stitches.

In fcc, the lattice parameter is:

$$a\sqrt{2} = 4R_1$$

(R_1 is the radius of atom)

$$a = \frac{4\,R_1}{\sqrt{2}} = 2\,\sqrt{2}R_1$$

Assuming that PS spheres are organized in this way, the number N of lattice that may be confined into a cylinder with a radius r is:

$$N=\frac{Vcylinder}{Vcube}=\frac{\pi h r^2}{a^3}=\frac{\pi h r^2}{(2R\sqrt{2})^3}$$

The face-centered cubic lattice has 4 nodes → 4 PS spheres per lattice → the spheres number per cylinder is:

$$n=4(\frac{\pi h r^2}{(2R_1\sqrt{2})^3})$$

The total spheres (balls) area per cylinder is:

→A_{ball}=ball Area ×ball number per cylinder

$$=4(\frac{\pi h r^2}{(2R_1\sqrt{2})^3})\times 4\pi {R_1}^2 = \frac{\sqrt{2}}{2}\frac{\pi^2 r^2 h}{R_1}=\frac{\pi\sqrt{2}}{2R_1}\times V_{cylinder}$$

The volume occupied by the ball in each cylinder is:

→V_{ball}=ball number per cylinder × ball volume

$$=4(\frac{\pi h r^2}{(2R_1\sqrt{2})^3})\times \frac{4}{3}\pi {R_1}^3=\frac{\sqrt{2}}{6}\pi^2 r^2 h = \frac{\pi\sqrt{2}}{6}\times V_{cylinder}$$

The free volume per cylinder is:

Free Volume $=V_{cylinder}$-V_{ball}

$$=V_{cylinder}-\left(\frac{\pi\sqrt{2}}{6}\times V_{cylinder}\right)$$

$$=V_{cylinder}\left(1-\frac{\pi\sqrt{2}}{6}\right)$$

Free volume=deposit Volume

Deposit Weight= deposit Volume×volume density

$$= V_{cylinder}\left(1-\frac{\pi\sqrt{2}}{6}\right)\times D$$

The specific surface $(m^2/\text{g}) = \frac{A_{ball}}{Deposit\ Weight} = \frac{\frac{\pi\sqrt{2}}{2R_1}\times V_{cylinder}}{V_{cylinder}\left(1-\frac{\pi\sqrt{2}}{6}\right)\times D}$

$$=\frac{\frac{\pi\sqrt{2}}{2R_1}}{\left(1-\frac{\pi\sqrt{2}}{6}\right)\times D}$$

Than we should add to this value the specific area of non-porous Co NWs:

The specific surface $(m^2/\text{g}) = \frac{\frac{\pi\sqrt{2}}{2R_1}}{\left(1-\frac{\pi\sqrt{2}}{6}\right)\times D} + \frac{2}{D}\left(\frac{1}{r}+\frac{1}{L}\right)$

SI4. SPECIFIC SURFACE AREA OF POROUS Co NWs with 2 sizes of PS spheres

Assuming now that we use two kinds of balls, different sizes:R_1 and R_2($R_1 > R_2$)

The new specific surface is:

$$S = \frac{A_1 + A_2}{M_{depot}}$$

$$A_1 = \frac{\pi\sqrt{2}}{2R_1} \times V_{cylinder}$$

The available volume for the second size of ball is: $V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})$

The number N' of lattice that may be confined into this available volume is:

$$N' = \frac{Vavailable}{Vcube} = \frac{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3}$$

The ball number per available volume is:

$n=4(\frac{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3})$ (fcc 4 nodes per lattice)

The ball area in this available volume is:

A_{ball2}=ball Area ×ball number per available volume

$$=4\pi R_2^2 \times 4(\frac{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3})$$

$$= \frac{\pi\sqrt{2}}{2R_2} \times (1 - \frac{\pi\sqrt{2}}{6}) \times V_{cylinder}$$

The volume occupied by the ball in this available volume is:

$\rightarrow V_{ball2}$=ball number per thisavailable volume ×ball volume

$$= 4(\frac{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3}) \times \frac{4}{3}\pi R_2^3$$

The free volumein this available volume is:

Free Volume =$V_{cylinder}$-($V_{ball1} + V_{ball2}$)

$$= V_{cylinder} - V_{cylinder}(\frac{\pi\sqrt{2}}{6}) - 4(\frac{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3})\times\frac{4}{3}\pi R_2^3$$

$$= V_{cylinder}[\ (1\text{-}\frac{\pi\sqrt{2}}{6}) - 4(\frac{(1-\frac{\pi\sqrt{2}}{6})}{(2R_2\sqrt{2})^3})\times\frac{4}{3}\pi R_2^3]$$

$$= V_{cylinder}(1\text{-}\frac{\pi\sqrt{2}}{6})[1\text{-}(\frac{4}{(2R_2\sqrt{2})^3})\times\ \frac{4}{3}\pi R_2^3]$$

$$= V_{cylinder}(1 - \frac{\pi\sqrt{2}}{6})^2$$

Free volume=deposit Volume

Deposit Weight= deposit Volume×volume density

$$=V_{cylinder}(1 - \frac{\pi\sqrt{2}}{6})^2 \times D$$

The specific surface (m^2/g) =$\frac{A_1+A_2}{M_{depot}}$

$$=\frac{\frac{\pi\sqrt{2}}{2R_1}\times V_{cylinder} \quad +\frac{\pi\sqrt{2}}{2R_2}\times(1-\frac{\pi\sqrt{2}}{6})\times V_{cylinder}}{V_{cylinder}(1-\frac{\pi\sqrt{2}}{6})^2\times D}$$

$$=\frac{\frac{\pi\sqrt{2}}{2}\ [\frac{1}{R_1}\ +\frac{1}{R_2}\times\left(1-\frac{\pi\sqrt{2}}{6}\right)]}{(1-\frac{\pi\sqrt{2}}{6})^2\times D}$$

Than we should add to this value the specific area of non-porous Co NWs

→ The specific surface $(m^2/\mathrm{g}) = \frac{\frac{\pi\sqrt{2}}{2}\left[\frac{1}{R_1} + \frac{1}{R_2} \times \left(1 - \frac{\pi\sqrt{2}}{6}\right)\right]}{\left(1 - \frac{\pi\sqrt{2}}{6}\right)^2 \times D} + \frac{2}{D}\left(\frac{1}{r} + \frac{1}{L}\right)$

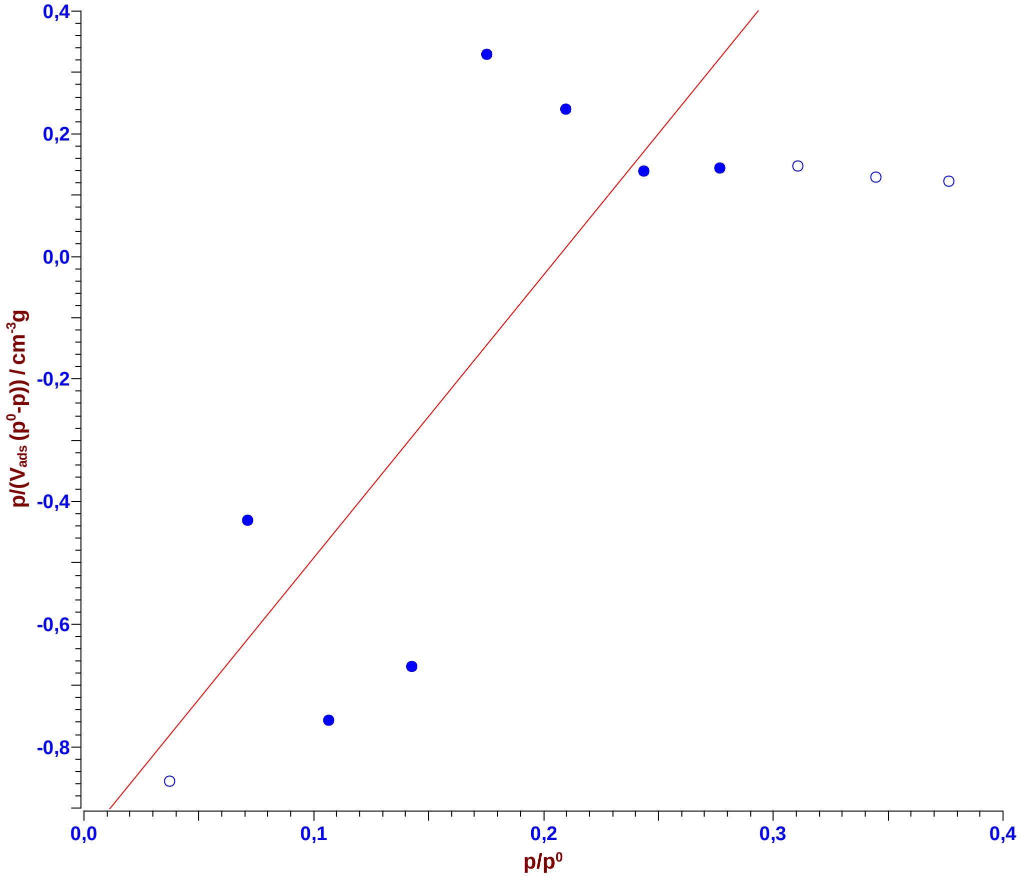
SI5. XPS measurements performed on porous and non-porous NWs

	Binding energies of B 1s	Binding energies of Co 2p/3
Non-Porous Co NWs (before hydrolysis)	192,3	781,3
	192,4	781,3
Porous Co NWs (before hydrolysis)	? [(a)]	782,1
	? [(a)]	781,6
Non-Porous Co NWs (after hydrolysis)	192,9	782,5
	192,7	782,5
Porous Co NWs (after hydrolysis)	192,5	781,9
	192,6	782,2

[(a)] Due to a charging effect, boron has not been detected.

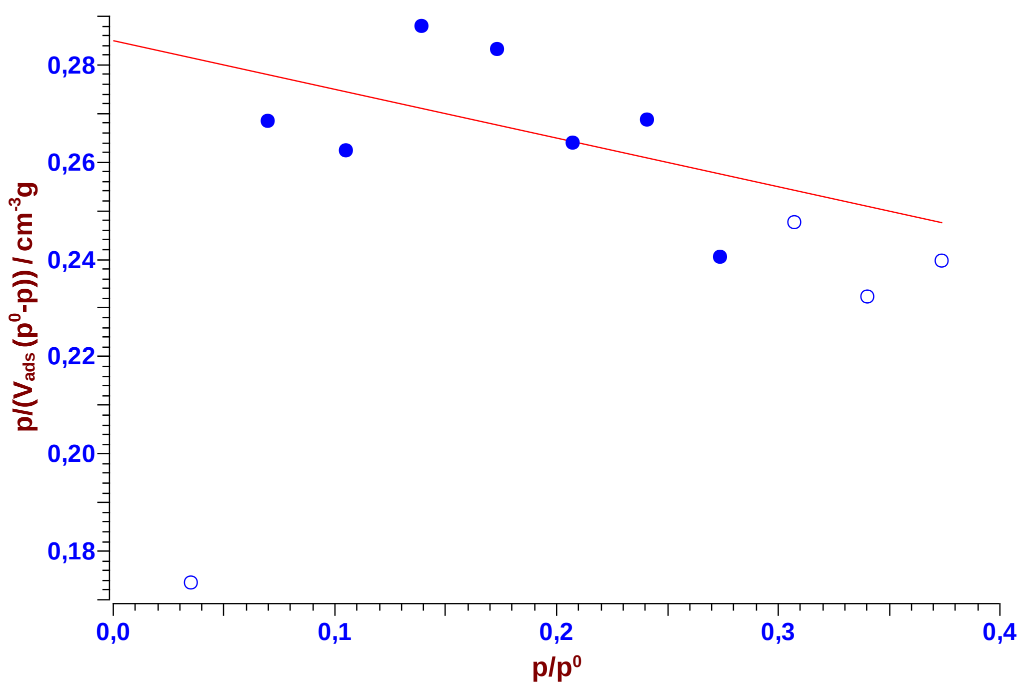
SI6. BET measurements

SI.6.a. BET measurement of non-porous Co NWs (r=100 nm)



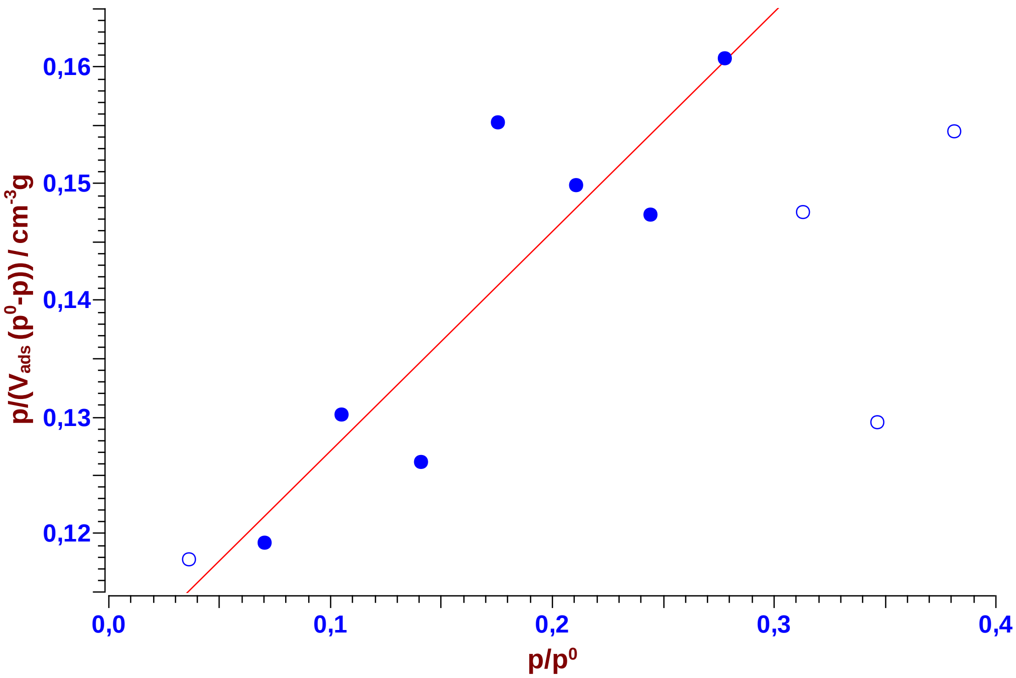
The surface area was: 1.1906 m^2g^{-1}

SI.6.b. BET measurement of porous Co NWs (r=500 nm, R_1=50nm)



The surface area was: 23.514 m^2g^{-1}

SI.6.c. BET measurement of porous Co NWs (r=500 nm, R_1=100nm)



The surface area was: 14.69 m^2g^{-1}