SUPPLEMENTARY INFORMATION

Optimisation of the electrochemical performance of $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$ cathode for solid oxide fuel cells via spray-pyrolysis deposition and decoration with Ag nanoparticles

Paula Rosendo Santos,[a] Domingo Pérez-Coll,[b] M. Teresa Azcondo,[a] Glenn C. Mather,[b] Álvaro Muñoz-Noval,[c,d] Eduardo Salas-Colera,[c,e] Ulises Amador,[a] Khalid Boulahya,[f] and Daniel Muñoz-Gil,[*,b,f]

[a] Universidad San Pablo-CEU, CEU Universities, Facultad de Farmacia, Departamento de Química y Bioquímica, Urbanización Montepríncipe, Boadilla del Monte, 28668, Madrid, Spain

[b] Instituto de Cerámica y Vidrio (ICV), CSIC, C/Kelsen, 5, 28049 Madrid, Spain

[c] SpLine Spanish CRG Beamline, ESRF, 6 Rue J. Horowitz, Grenoble, Isere/Rhone-Alpes, 38042, France.

[d] Departamento de Física de Materiales, Facultad de Físicas, Universidad Complutense de Madrid, 28040, Madrid, Spain.

[e] Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Sor Juana Inés de la Cruz, 3, 28049, Madrid, Spain

[f] Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040, Madrid, Spain

**Corresponding author*: dmunozgi@ucm.es

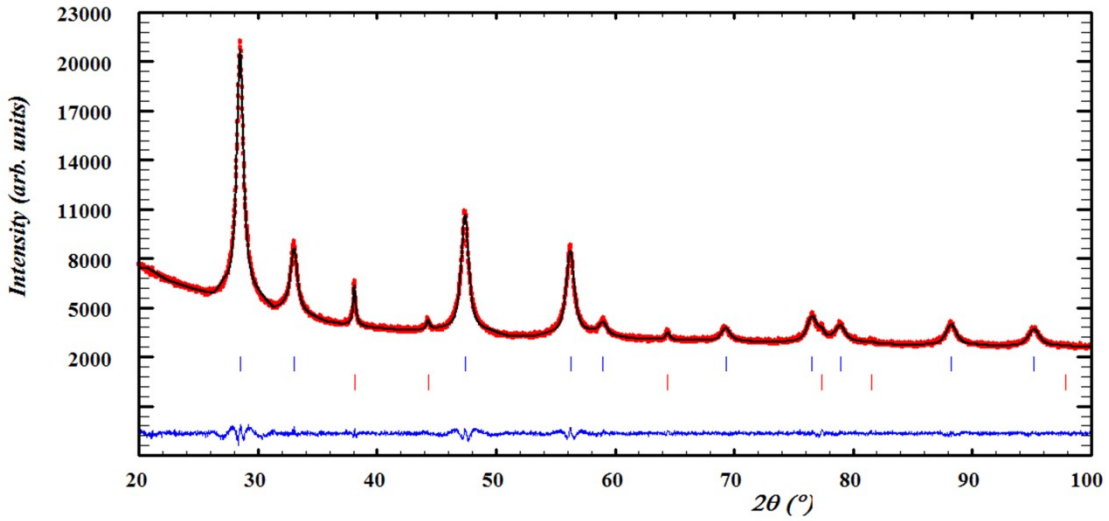

Figure S1: X-ray diffraction pattern of CGO:Ag nanocomposite with weight ratio 90:10. Red circles correspond to the observed pattern, the black solid line to the calculated pattern and their difference is shown as a blue line at the bottom. Positions of Bragg peaks are indicated by vertical bars for CGO (first row) and Ag (second row).

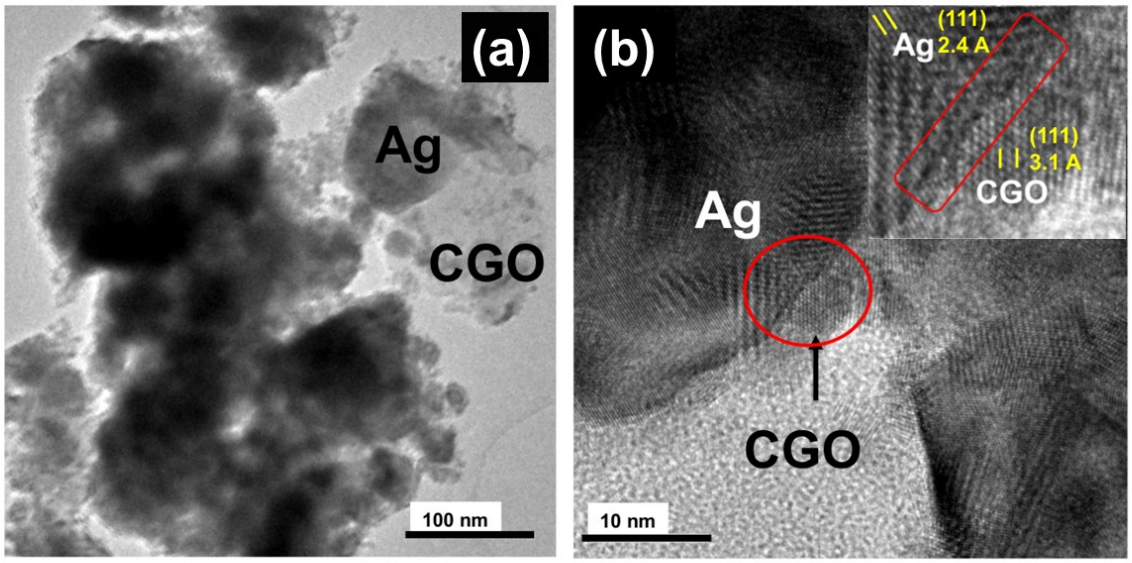

Figure S2: Low and high magnification TEM images ((a) and (b), respectively) of CGO:Ag nanocomposite with weight ratio 90:10. A zoomed view of the CGO/Ag interphase is shown in the inset of (b); relevant d-spacings of both phases are indicated.

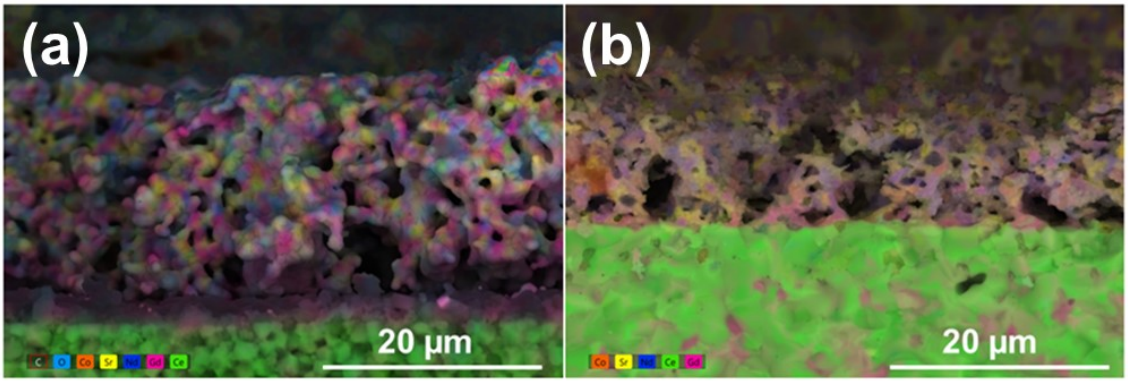

Figure S3: Elemental distribution determined by EDS in SEM for $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ electrodes obtained by (a) slurry coating and (b) spray-pyrolysis. The colour used for the identification of the elements: green-Ce; purple-Gd; blue-Nd; yellow-Sr and orange-Co.

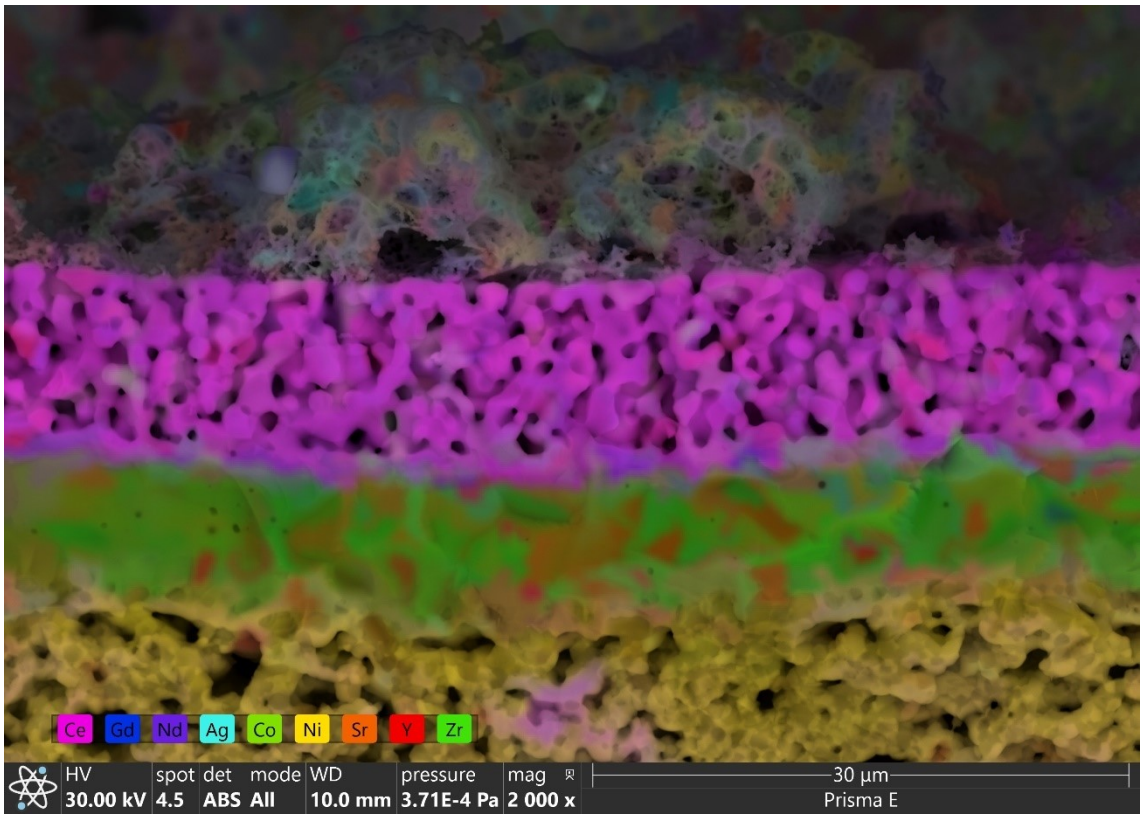

Figure S4. Elemental distribution determined by EDS in SEM for a single cell of NiO-CGO/YSZ/CGO/$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$:Ag after testing in SOFC mode. There is no evidence of microstructural deterioration attributable to grain coarsening or cracking of the layers.

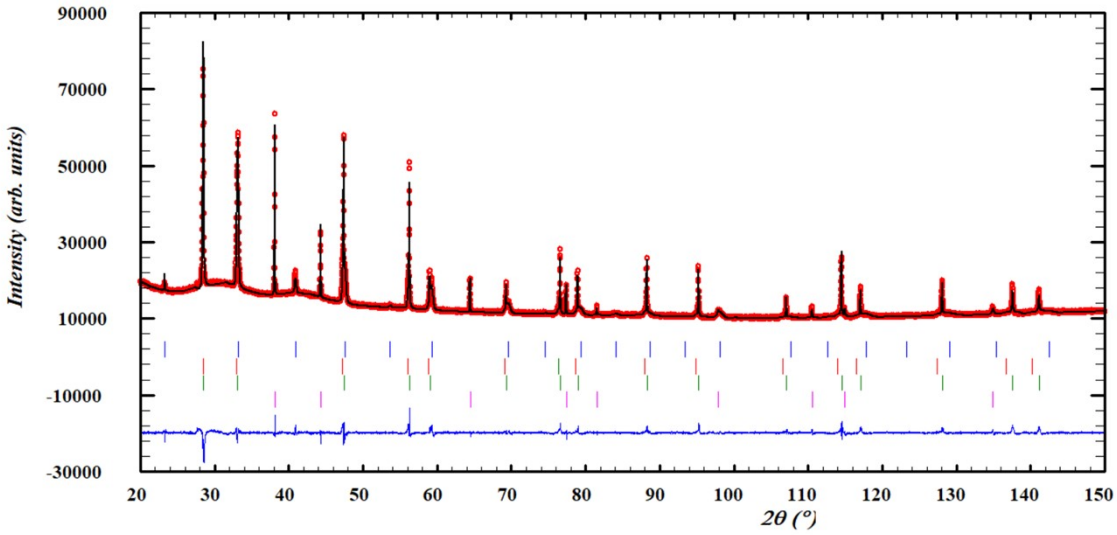

Figure S5. Experimental (red points), calculated (solid black line) and their difference (blue line at bottom) laboratory XRD patterns at room temperature of the cathode post-operation of a single SOFC with configuration Ni-CGO/YSZ/CGO/$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$:Ag. The X-ray beam penetrates just to the CGO buffer layer (the YSZ and the anode layers in Fig. S4 are not detected). The vertical bars indicate the positions of peaks corresponding to $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$ (blue), $Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ in the composite electrode (red), CGO in the buffer layer (green) and Ag in the composite (fuchsia).

Calculation of the shell thickness of the core-shell structure of AgNPs in the as-obtained composites

Nanoparticles have a large surface-to-volume ratio, which increases with decreasing particle radius, *r* (assuming spherical shape):

$$\frac{S}{V} = \frac{4\pi r^2}{4\pi r^3/3} = \frac{3}{r} \quad (1)$$

The volume of the oxide shell depends on the particle radius, where Δr is the shell radius:

$$V_{shell} = \frac{4}{3}\pi[(r+\Delta r)^3 - r^3] \quad (2)$$

The mass ratio between the phases present in the nanoparticles ($A=Ag_2O/Ag$) is given by:

$$\mathrm{A} = \frac{M_{shell}}{M_{core}} = \frac{\rho(Ag_2O)[(r+\Delta r)^3 - r^3]}{r^3\rho(Ag)} \quad (3)$$

which includes the densities of the two phases.

In Eq. 3 there are two unknown quantities: the radius of the metal particles, *r*, and the thickness of the oxide layer, Δr.

Using the densities of both phases (7.14 g/cm^3 for Ag_2O and 10.49 g/cm^3 for Ag), the particle size determined by XRD and HRTEM (r = 80 nm) and the mass ratio obtained from the fittings of the XANES spectrum (A= 15/85), we derive a cubic equation, with only one real solution for Δr as 0.54(5) nm. Thus, the outer particles shell consists of 1 unit cell of Ag_2O (whose unit cell parameter is 0.473 nm).[1]

References

1. P. Norby, R. Dinnebier, and A.N. Fitch, *Inorg. Chem.*, 2002. **41**(14), 3628-3637.

Table S1. Structural and microstructural parameters obtained from XRD data for $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ composite prepared by spray pyrolysis and deposited by slurry coating.

Sample	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ (SC)**		
Phase	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$** [a]		
Space Group	Pm-3m		
***a* (Å)**	3.81869 (3)		
Volume (Å^3)	55.686(1)		
A position	1b	**O1 position**	3d
Occ Sr/(Nd+Gd)	0.67(1)/0.33(1)	**Occ**	0.968(3)
U*100 (Å^2)	0.15(2)	**U*100 (Å^2)**	1.12(5)
B position	1a		
Occ Co	1		
U*100 (Å^2)	0.10(6)		
Crystallite size (nm)	71.89(5)		
Phase	**$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$** [b]		
Space Group	Fm-3m		
***a* (Å)**	5.43462(4)		
Volume (Å^3)	160.512(2)		
A position	4a	**O1 position**	8c
Occ Ce/(Gd+Nd)	0.90/0.10	**Occ**	0.976(3)
U*100 (Å^2)	0.06(1)	**U*100 (Å^2)**	0.32(4)
Crystallite size (nm)	51.23(2)		

[a] Pm-3m (#221): 1a (000), 1b (½ ½ ½), 3d (½ 0 0)
Composition: $(Nd,Gd)_{0.33(1)}Sr_{0.67(1)}CoO_{2.904(6)}$
R_B= 1.86%
[b] Fm-3m (#225): 4a (000), 8c (¼ ¼ ¼)
Composition: $Ce_{0.90}(Gd,Nd)_{0.10}O_{1.952(6)}$
R_B= 1.78%,

χ^2= 1.59, R_{wp}= 1.36%, R_{exp}= 1.08%,
Phase percentage (weight %): NSC 69(1) : CGO 31(1)

Table S2. Structural and microstructural parameters obtained from XRD data for $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ composite prepared and deposited by spray pyrolysis.

Sample	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$ (SP)**		
Phase	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$** [a]		
Space Group	Pm-3m		
***a* (Å)**	3.81736 (3)		
Volume (Å³)	55.627(1)		
A position	1b	**O1 position**	3d
Occ Sr/(Nd+Gd)	0.67(1)/0.33(1)	**Occ**	0.973(3)
U*100 (Å²)	0.05(1)	**U*100 (Å²)**	1.52(4)
B position	1a		
Occ Co	1		
U*100 (Å²)	0.10(6)		
Crystallite size (nm)	65.16(2)		
Phase	**$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$** [b] (composite)		
Space Group	Fm-3m		
***a* (Å)**	5.43162(8)		
Volume (Å³)	160.246(4)		
A position	4a	**O1 position**	8c
Occ Ce/(Gd+Nd)	0.90/0.10	**Occ**	0.971(3)
U*100 (Å²)	0.04(1)	**U*100 (Å²)**	0.41(4)
Crystallite size (nm)	66.50(5)		
Phase	**$Ce_{0.9}Gd_{0.1}O_{1.95}$** [c] (pellet)		
Space Group	Fm-3m		
***a* (Å)**	5.41993(5)		
Volume (Å³)	159.214(2)		
A position	4a	**O1 position**	8c
Occ Ce/Gd	0.90/0.10	**Occ**	0.973(3)
U*100 (Å²)	0.08(1)	**U*100 (Å²)**	0.36(4)
Crystallite size (nm)	N/A		

[a] Pm-3m (#221): 1a (000), 1b (½ ½ ½), 3d (½ 0 0)
Composition: $(Nd,Gd)_{0.33(1)}Sr_{0.67(1)}CoO_{2.919(6)}$
R_B= 1.53%
[b] Fm-3m (#225): 4a (000), 8c (¼ ¼ ¼)
Composition: $Ce_{0.90}(Gd,Nd)_{0.10}O_{1.942(6)}$
R_B= 1.70%,
[c] Fm-3m (#225): 4a (000), 8c (¼ ¼ ¼)
Composition: $Ce_{0.90}Gd_{0.10}O_{1.946(6)}$
R_B= 1.42%,

χ^2= 1.47, R_{wp}= 1.08%, R_{exp}= 0.89%,
Phase percentage in composite (weight %): NSC 70(1) : CGO 30(1)

Table S3. Structural and microstructural parameters obtained from XRD data for $(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$:Ag prepared and deposited by spray pyrolysis combustion method.

Sample	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$:$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$:Ag (SP_Ag)**		
Phase	**$(Nd,Gd)_{1/3}Sr_{2/3}CoO_{3-\delta}$** [a]		
Space Group	Pm-3m		
***a* (Å)**	3.82290 (5)		
Volume (Å³)	55.870(3)		
A position	1b	**O1 position**	3d
Occ Sr/(Nd+Gd)	0.66(1)/0.33(1)	**Occ**	0.967(3)
U*100 (Å²)	0.51(4)	**U*100 (Å²)**	1.48(4)
B position	1a		
Occ Co	1		
U*100 (Å²)	0.08(2)		
Crystallite size (nm)	27.73(2)		
Phase	**$Ce_{0.9}(Gd,Nd)_{0.1}O_{1.95}$** [b] (composite)		
Space Group	Fm-3m		
***a* (Å)**	5.4387(1)		
Volume (Å³)	160.877(6)		
A position	4a	**O1 position**	8c
Occ Ce/(Gd+Gd)	0.90/0.10	**Occ**	0.975(2)
U*100 (Å²)	0.14(2)	**U*100 (Å²)**	0.61(5)
Crystallite size (nm)	68.20(4)		
Phase	**Ag** [c]		
Space Group	Fm-3m		
***a* (Å)**	4.09168(6)		
Volume (Å³)	68.502(2)		
Ag position	4a		
U*100 (Å²)	1.31(4)		
Crystallite size (nm)	150.32(5)		
Phase	**$Ce_{0.9}Gd_{0.1}O_{1.95}$** [d] (pellet)		
Space Group	Fm-3m		
***a* (Å)**	5.42584(6)		
Volume (Å³)	159.735(3)		
A position	4a	**O1 position**	8c
Occ Ce/Gd	0.90/0.10	**Occ**	0.971(4)
U*100 (Å²)	0.26(2)	**U*100 (Å²)**	0.42(5)
Crystallite size (nm)	N/A		

[a] Pm-3m (#221): 1a (000), 1b (½ ½ ½), 3d (½ 0 0)
Composition: $(Nd,Gd)_{0.33(1)}Sr_{0.67(1)}CoO_{2.871(6)}$
R_B= 3.85%
[b] Fm-3m (#225): 4a (000), 8c (¼ ¼ ¼)
Composition: $Ce_{0.90}(Gd,Nd)_{0.10}O_{1.950(4)}$
R_B= 5.54%,
[c] Fm-3m (#225): 4a (000)
R_B= 4.14%,
[d] Fm-3m (#225): 4a (000), 8c (¼ ¼ ¼)
Composition: $Ce_{0.90}Gd_{0.10}O_{1.942(4)}$
R_B= 3.86%,

χ^2= 5.31, R_{wp}= 1.78%, R_{exp}= 0.77%,
Phase percentage in composite (weight %): NSC 66(2) : CGO 25(2) : Ag 9(2)

Table S4. EXAFS parameters obtained from the fitting of spectra: N is the mean number of neighbours in each atomic shell, R is the atomic shell radius (Å), σ^2 is the shell radius variance and ΔE0 is the non-structural parameter related to the shift of the edge energy set for the fitting. The r-factor and χ^2 are quality-criteria parameters

Parameter	**Bulk Ag**	**Ag in as-prepared composite (NPs)**
N(Ag-Ag)	12 (1)	8(1)
N(Ag-O)	---	1(1)
R(Ag-Ag)	2.873(5)	2.861(6)
R(Ag-O)	---	2.028(6)
σ^2(Ag-Ag)(Å^2)	0.0089 (5)	0.0075(7)
σ^2(Ag-O)(Å^2)	---	0.0111(10)
ΔE_0(eV)	5(1)	2 (2)
r-factor	0.001	0.002
χ^2	85	110