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Electronic Supplementary Information

Visible-light driven oxygen evolution over $CoTiO_3$ perovskites *via* modified Pechini method: impact of humidity on its phase composition

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EXPERIMENTAL SECTION

Materials

Commercially available Titanium isopropoxide ($Ti(^iOPr)_4$) (Acros, 98+%), anhydrous ethanol (Pharmco-AAPER, ACS/USP grade), Citric acid monohydrate (Fischer Scientific), and cobalt nitrate hexahydrate (Acros, 99%) were used as received to prepare the $CoTiO_3$ photocatalysts.

Synthesis of $CoTiO_3$ materials

The $CoTiO_3$ materials were prepared by using modified Pechini method. In a typical synthesis, 3.37 g (0.016 mol) of citric acid (CA) was dissolved in 10 mL of ethanol. In a separate beaker, 1.2 mL of $Ti(^iOPr)_4$ (0.004 mol) was mixed with 3 mL of ethanol solution. This solution was added drop-wise to the citric acid solution. Finally, 1.1669 g of cobalt precursor ($Co(NO_3)_2.6H_2O$) in ethanol (0.004 mol) was added drop-wise to the above mixture to obtain a mixture with a citric acid: metal ion ratio ([CA:(Co^{2+}+Ti^{4+})]) of 2:1. All the mixing steps were carried out at room temperature in a humidity chamber (Cole Parmer) by controlling the relative humidity at 20, 40, 70, 90, and 100 % throughout the experiment. The thick gel obtained was kept in the humidity chamber for 30 min. Then, the materials were transferred to an oven for drying. The obtained pink colored crystals were ground and calcined by heating in static air at 800 ^oC for 6 h at heating rate of 3°C/min.

Materials Characterization

The powder X-ray diffraction patterns of the calcined $CoTiO_3$ materials were studied at room temperature using a Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.5408 Å). An accelerating voltage of 40 kV and emission current of 44 mA were used. The angle regions (2θ) scanned was from 10 to 80° with a step size of 0.02°. The crystallite sizes of the $CoTiO_3$ phase in all the materials were evaluated using the Halder-Wagner method and by choosing all peaks belonging to $CoTiO_3$. The crystallite sizes of $CoTiO_3$-H-20, $CoTiO_3$-H-40, $CoTiO_3$-H-70, $CoTiO_3$-H-90, and $CoTiO_3$-H-100 were estimated to be 218, 515, 611, 686, and 662 Å respectively. However, these values should be used with caution since the peaks are anisotropic in nature and thus deviate significantly from TEM measurements. The textural properties of the calcined cobalt titanate powders were obtained by using Quantachrome Nova 2200*e* Surface Area Analyzer. N_2 adsorption-desorption isotherms were obtained at 77 K. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation within the 0.05-0.30 range of relative pressure (P/P_0). The pore volume was obtained from the nitrogen amount adsorbed at the highest relative pressure (P/P_0) ≈ 0.99. All the materials resulted in H3 type hysteresis loop, which do not level off at relative pressures close to the saturation vapor pressure. H3 isotherms are typical of materials that have loose aggregates of particles with slit-like pores. The surface area of the materials were found to be generally below 4 m^2/g. The pure $CoTiO_3$ material showed a surface area of 3.51 m^2/g and the nitrogen isotherm of this material is illustrated in Fig. S8. In addition, all the materials show very broad pore size distribution, and the pore sizes of the materials lie between 15 and 42 Å (calculated by applying the BJH equation to the desorption isotherm). The structural properties of the materials prepared in this study are listed in the supplementary section in Table S7.

The synthesized $CoTiO_3$ materials were further characterized by diffuse reflectance spectra (DRS). The DR spectra of the materials were recorded in the range of 190-800 nm using a Carry 100 Bio UV-Vis spectrophotometer equipped with a Harrick DR praying mantis accessory.

Fourier Transform-Infrared (FT-IR) spectra were recorded using a Bruker instrument model ALPHA equipped with ATR platinum diamond module of spectral range capabilities in the range 50,000 – 50 cm^{-1}. The spectroscopy software OPUS 6.5 was used and optimal measurements were obtained at 24 scans and 4 cm^{-1} resolution in the wave number range of 400 – 4000 cm^{-1}. FT-IR spectra of materials prepared in this study are illustrated in Fig. S9. All the calcined materials show similar peak patterns, and the peak profile for a selected un-calcined material is illustrated as an inset in Fig. S9. The un-calcined material show a broad band at around 3200 cm^{-1} that is due to the stretching vibrations of –OH groups. The bands at 2976 and 2934 cm^{-1} are due to the C-H stretching frequency. The band around 1722 cm^{-1} is due to the stretching vibration of C=O. The bands at 1608 and 1367 cm^{-1} are accredited to COO^- vibrations of the mono-dentate ligand.[1,2] In addition, the band at 1328 cm^{-1} may be due to C-H bending frequency, and the band around 1187 cm^{-1} is from the bending vibration of the acetate group on citric acid. The bands at 1087 and 1024 cm^{-1} are due to the -OPr groups (Pr = propoxide) linked to Ti. The weak bands between 400 and 1000 cm^{-1} are due to the vibrations of Ti ions. The major peaks due to the carbonyl and C-H stretching frequencies were found to disappear after calcination. The Co-O-Ti stretching frequencies is observed at wavenumbers of 812 and 667 cm^{-1}. Finally, the band at 489 cm^{-1} is credited to the Co-O and Ti-O stretching frequencies.[3,4] Consequently, these results also support the formation of $CoTiO_3$ and other cobalt oxide species in the materials.

Photocatalytic water splitting

20 mg of $AgNO_3$, the electron scavenger, was dissolved in 20 mL of water in a glass cylindrical reactor. 40 mg of $CoTiO_3$ material was then added to the above solution. The resultant suspension was sonicated until a homogeneous suspension was obtained. Then, the solution was purged with argon for one hour. After degassing, the Xenon lamp (Newport 300 W) was initiated to provide irradiation through a Pyrex glass filter with a cut off wavelength of 420 nm. The reaction temperature was kept constant at 25 ± 2º C by routing water between the double walled reactor. These experimental conditions were maintained throughout the whole experiment (6 h). 0.5 mL of the gas head space was injected at various time periods, into a Gas Chromatograph (SRI 8610). The amount of oxygen evolved was determined from a calibration graph prepared previously.

Table S1. XRD Peak indexing for $CoTiO_3$-H-100

2 θ	***h***	***k***	***l***	**Phase name**
23.8	0	1	2	$CoTiO_3$
32.8	1	0	4	$CoTiO_3$
35.4	1	1	0	$CoTiO_3$
38.8	0	0	6	$CoTiO_3$
40.5	1	1	$\bar{3}$	$CoTiO_3$
41.6	0	2	1	$CoTiO_3$
43.2	2	0	2	$CoTiO_3$
49.1	0	2	4	$CoTiO_3$
50.3	1	0	7	$CoTiO_3$
53.5	1	1	$\bar{6}$	$CoTiO_3$
55.7	2	1	1	$CoTiO_3$
56.8	0	1	8	$CoTiO_3$
57.1	2	1	$\bar{2}$	$CoTiO_3$
61.9	1	2	$\bar{4}$	$CoTiO_3$
63.5	3	0	0	$CoTiO_3$
68.7	2	0	8	$CoTiO_3$
70.8	1	0	10	$CoTiO_3$
71.4	1	1	$\bar{9}$	$CoTiO_3$
74.9	2	2	0	$CoTiO_3$
77.0	3	0	6	$CoTiO_3$
78.2	2	2	$\bar{3}$	$CoTiO_3$
79.8	2	1	$\bar{8}$	$CoTiO_3$

Table S2. XRD Peak indexing for $CoTiO_3$-H-90

2 θ	***h***	***k***	***l***	**Phase name**
23.9	0	1	2	$CoTiO_3$
32.8	1	0	4	$CoTiO_3$
35.4	1	1	0	$CoTiO_3$
40.5	1	1	$\bar{3}$	$CoTiO_3$
44.7	4	0	0	Co_3O_4
49.0	0 3	2 3	4 1	$CoTiO_3$ Co_3O_4
53.5	1	1	$\bar{6}$	$CoTiO_3$
56.8	0	1	8	$CoTiO_3$
61.9	1	2	$\bar{4}$	$CoTiO_3$
63.5	3	0	0	$CoTiO_3$
68.8	2	0	8	$CoTiO_3$
70.9	1	1	10	$CoTiO_3$
74.9	2	2	0	$CoTiO_3$
76.9	3 5	0 3	6 3	$CoTiO_3$ Co_3O_4

Table S3. XRD Peak indexing for $CoTiO_3$-H-70

2 θ	h	k	l	Phase name
23.9	0	1	2	$CoTiO_3$
32.8	1	0	4	$CoTiO_3$
35.4	1	1	0	$CoTiO_3$
40.5	1	1	$\bar{3}$	$CoTiO_3$
49.0	0	2	4	$CoTiO_3$
	3	3	1	Co_3O_4
53.5	1	1	$\bar{6}$	$CoTiO_3$
56.8	0	1	8	$CoTiO_3$
61.9	1	2	$\bar{4}$	$CoTiO_3$
63.5	3	0	0	$CoTiO_3$
68.8	2	0	8	$CoTiO_3$
	5	3	1	Co_3O_4
70.9	1	1	10	$CoTiO_3$
74.9	2	2	0	$CoTiO_3$

Table S4. XRD Peak indexing for $CoTiO_3$-H-40

2 θ	***h***	***k***	***l***	**Phase name**
23.9	0	1	2	$CoTiO_3$
27.4	1	1	0	TiO_2 (Rutile)
32.8	1	0	4	$CoTiO_3$
35.4	1	1	0	$CoTiO_3$
	3	1	1	Co_2TiO_4
36.0	1	0	1	TiO_2 (Rutile)
40.5	1	1	$\bar{3}$	$CoTiO_3$
42.9	2	0	2	$CoTiO_3$
	4	0	0	Co_2TiO_4
49.0	0	2	4	$CoTiO_3$
	3	3	1	Co_3O_4
53.5	1	1	$\bar{6}$	$CoTiO_3$
54.3	2	1	1	TiO_2 (Rutile)
56.8	0	1	8	$CoTiO_3$
	2	2	0	TiO_2 (Rutile)
	5	1	1	Co_2TiO_4
61.9	1	2	$\bar{4}$	$CoTiO_3$
63.5	3	0	0	$CoTiO_3$
68.8	2	0	8	$CoTiO_3$
	5	3	1	Co_3O_4
	3	0	1	TiO_2 (Rutile)
70.9	1	0	10	$CoTiO_3$
71.3	1	1	$\bar{9}$	$CoTiO_3$
74.9	2	2	0	$CoTiO_3$
	6	2	0	Co_3O_4
	6	2	2	Co_2TiO_4

Table S5**.** XRD Peak indexing for $CoTiO_3$-H-20

2 θ	***h***	***k***	***l***	**Phase name**
23.9	0	1	2	$CoTiO_3$
30.0	2	2	0	Co_2TiO_4
32.8	1	0	4	$CoTiO_3$
35.4	1	1	0	$CoTiO_3$
	3	1	1	Co_2TiO_4
40.5	1	1	$\bar{3}$	$CoTiO_3$
42.9	4	0	0	Co_2TiO_4
49.0	0	2	4	$CoTiO_3$
	3	3	1	Co_3O_4
53.5	1	1	$\bar{6}$	$CoTiO_3$
	4	2	2	Co_2TiO_4
56.8	0	1	8	$CoTiO_3$
	5	1	1	Co_2TiO_4
61.9	1	2	$\bar{4}$	$CoTiO_3$
62.4	4	4	0	Co_2TiO_4
63.5	3	0	0	$CoTiO_3$
70.9	1	0	10	$CoTiO_3$
	6	2	0	Co_2TiO_4
74.9	2	2	0	$CoTiO_3$
	6	2	0	Co_3O_4
	6	2	2	Co_2TiO_4

Table S6. Lattice parameters of the materials

Sample	**Lattice Parameters (Å)**					
	$CoTiO_3$		**Co_3O_4**	**Co_2TiO_4**	**Rutile TiO_2**	
	a	**c**	**a=b=c**	**a=b=c**	**a=b**	**c**
$CoTiO_3$-H-20	5.0697	13.9321	8.0835	8.4088	NA	NA
$CoTiO_3$-H-40	5.0688	13.9398	8.0166	8.4244	4.5951	2.9622
$CoTiO_3$-H-70	5.0679	13.9409	8.0688	NA	NA	NA
$CoTiO_3$-H-90	5.0693	13.9412	8.1033	NA	NA	NA
$CoTiO_3$-H-100	5.0681	13.9424	NA	NA	NA	NA

NA refers to not applicable.

The lattice parameters were calculated by considering the phases $CoTiO_3$, Co_3O_4, Co_2TiO_4, Rutile TiO_2 separately. The angles are $\alpha = \beta = 90^o$; $\gamma = 120^o$ for $CoTiO_3$; $\alpha = \beta = \gamma = 90^o$ for Co_3O_4, Co_2TiO_4, and Rutile TiO_2.

Table S7. Textural Properties of the materials

Sample	**SA (m^2/g)**	**PV (cc/g)**	**PD (Å)**
$CoTiO_3$-H-20	1.81	0.0049	19
$CoTiO_3$-H-40	0.88	0.0034	42
$CoTiO_3$-H-70	1.87	0.0056	27
$CoTiO_3$-H-90	3.60	0.0098	24
$CoTiO_3$-H-100	3.51	0.0069	15

H-xx denotes relative humidity (in percentage). The xx (numbers) denote the relative humidity in %. SA, PV, and PD refer to specific surface area, pore volume, and BJH pore diameter, respectively.

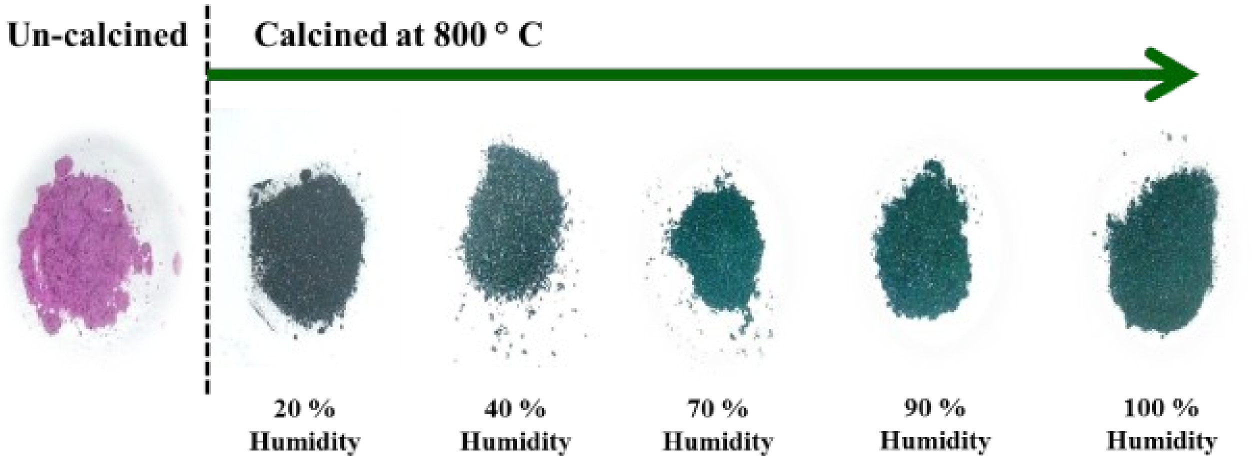


Fig. S1 The photograph of the $CoTiO_3$ materials prepared under different relative humidity, before (pink) and after calcination (green).

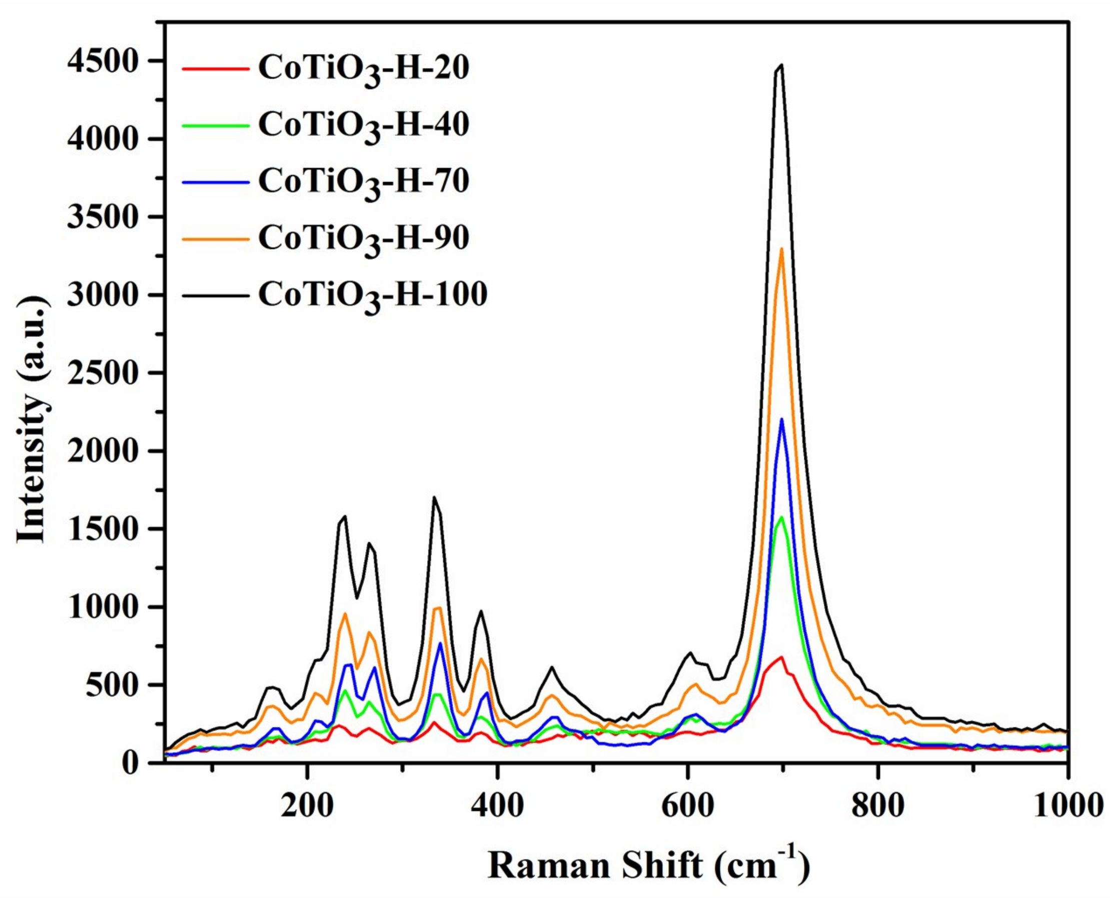


Fig. S2 Raman plots of CoTiO$_3$ materials prepared at different humidity conditions.

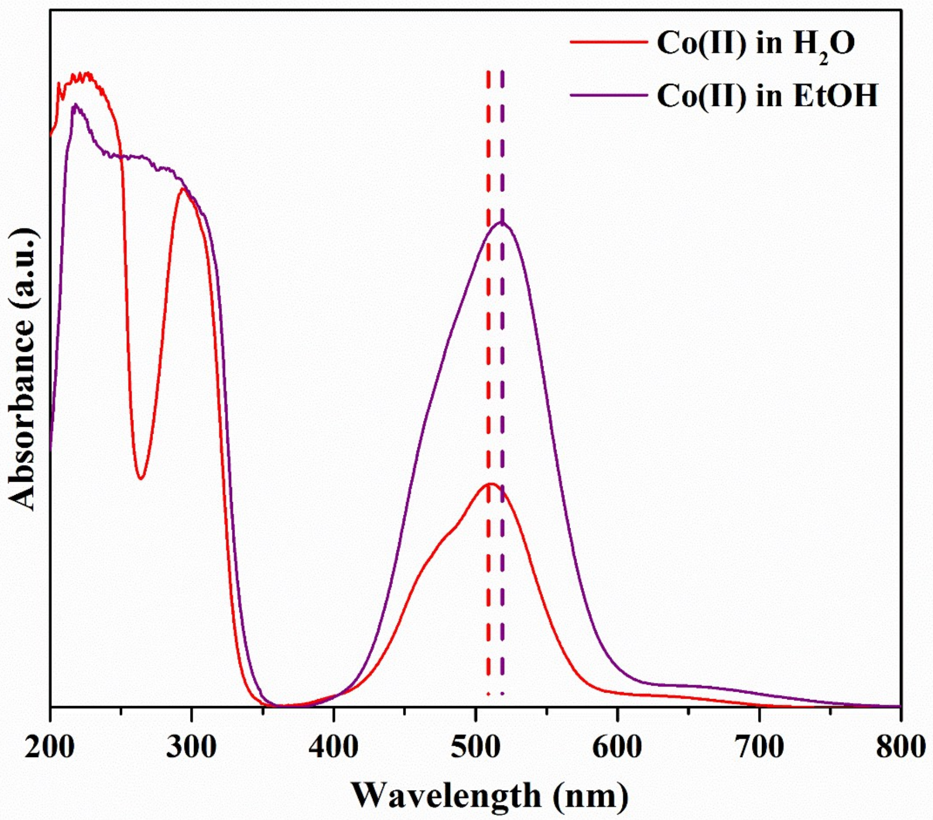
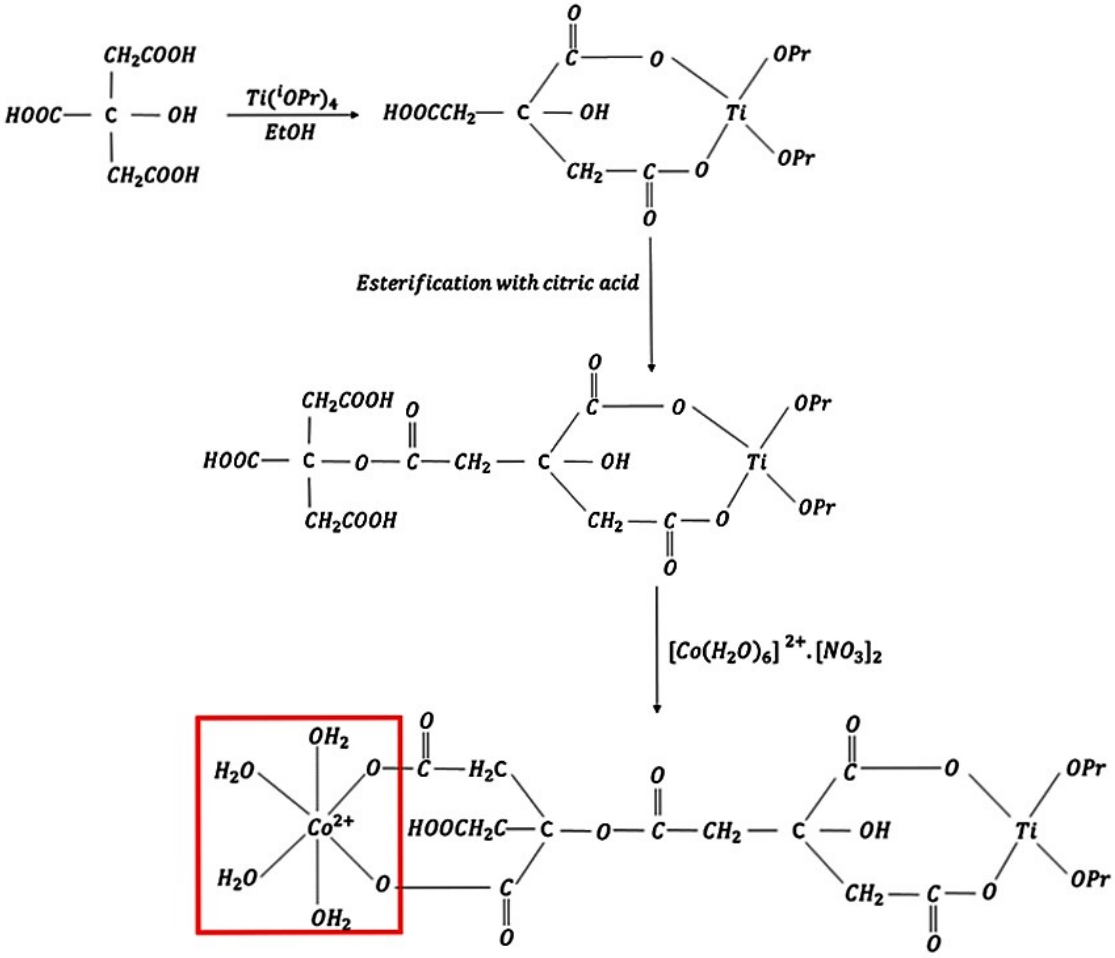


Fig. S3 UV-Vis spectra of cobalt (II) in ethanol and water.



Amorphous polymeric precursor.

Fig. S4 Scheme representing possible formation of amorphous polymeric precursor.

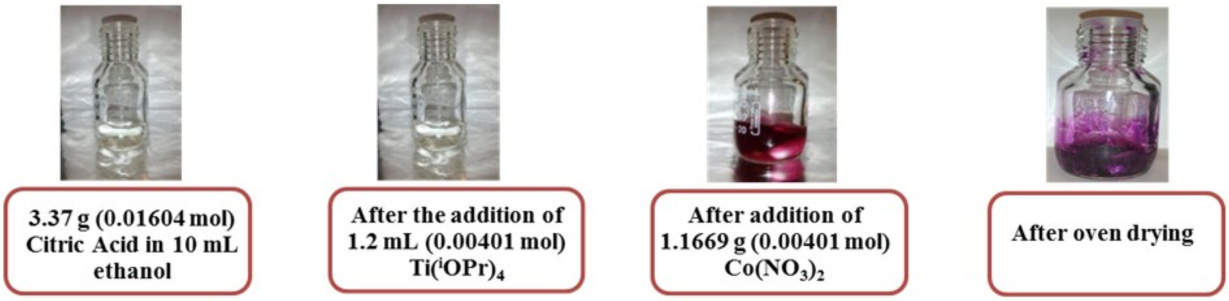


Fig. S5 Optical photographs of the reaction mixture during the synthesis procedure.

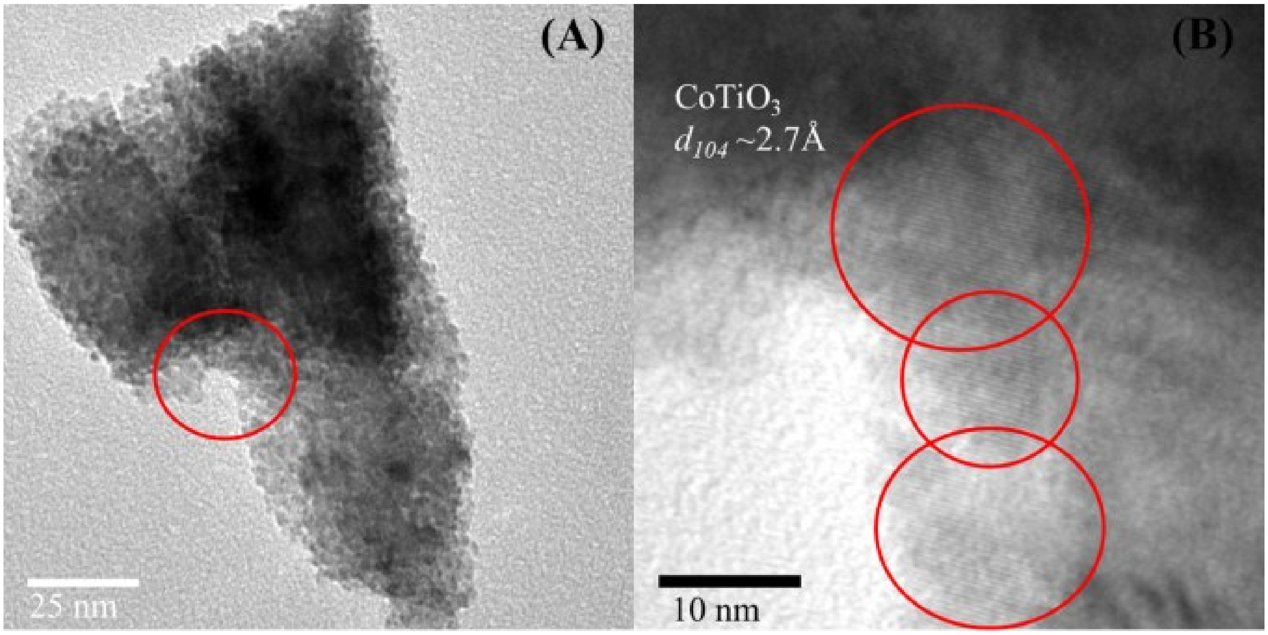


Fig. S6 TEM image of $CoTiO_3$-H-100 material prepared at the relative humidity of 100 %. (A) The zoomed out image with the scale bar of 25 nm and (B) The zoom in image with the scale bar of 10 nm. The dark portions in Fig. S6A indicate the agglomeration of the $CoTiO_3$ particles, and the image in S6B shows the magnified image, which indicates the crystalline nature of the materials.

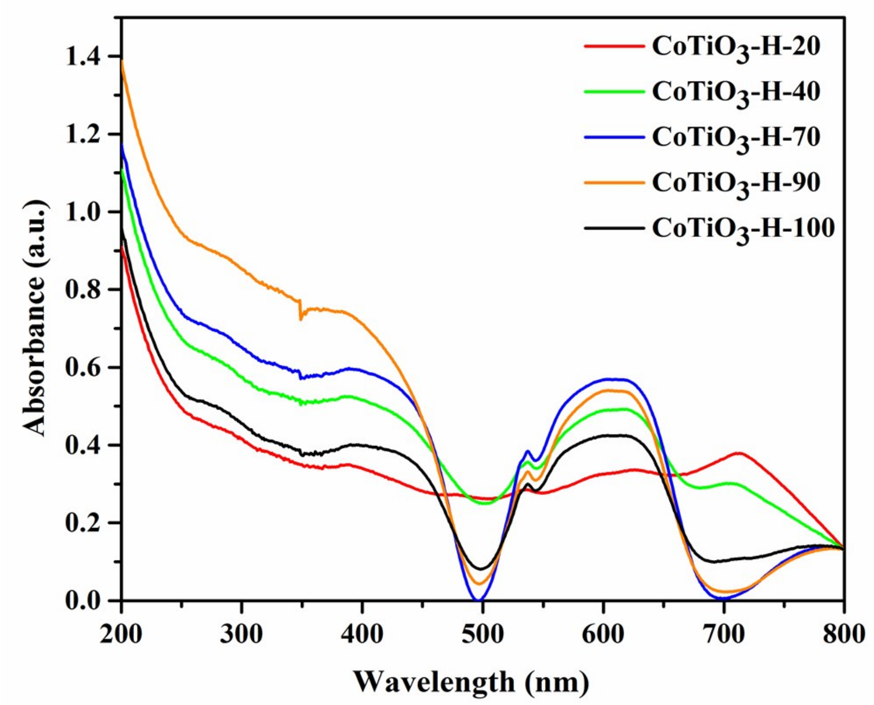


Fig. S7 DRS spectra of $CoTiO_3$ materials prepared under different relative humidity.

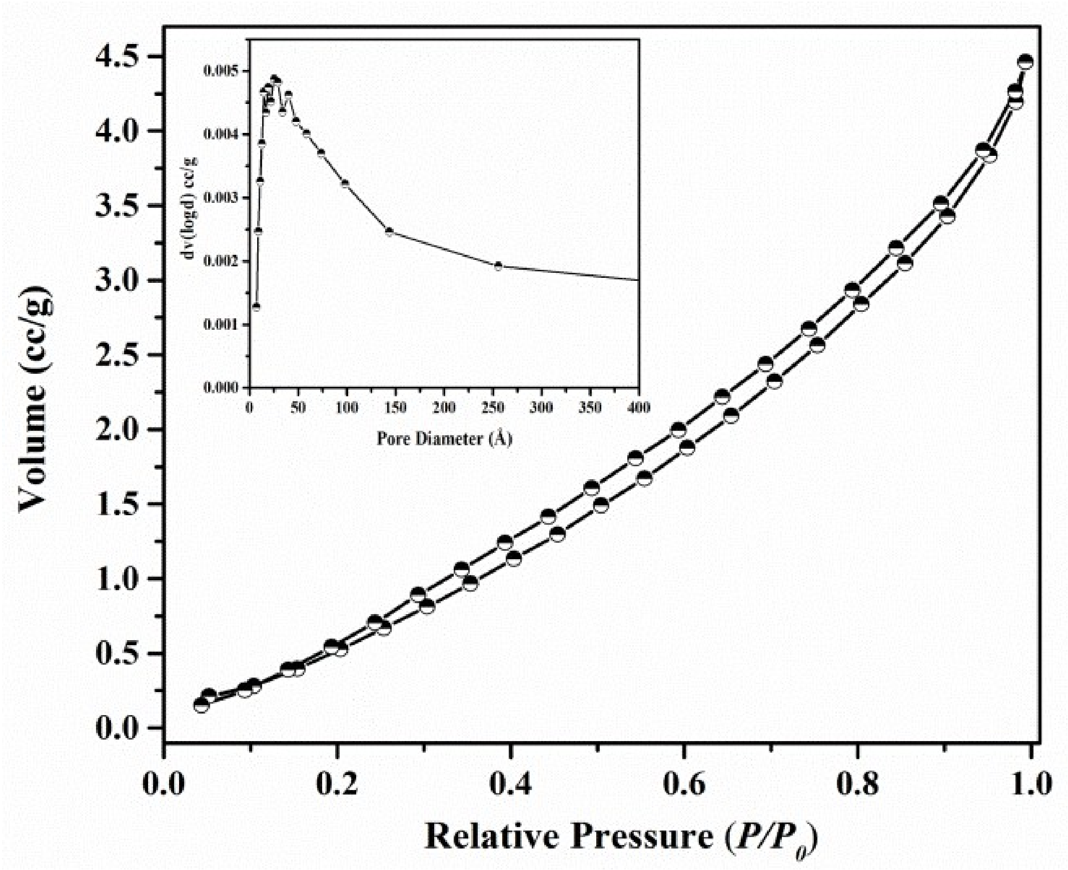


Fig. S8 N_2 physisorption isotherms of pure $CoTiO_3$ material prepared at the relative humidity of 100 %. The inset shows the corresponding pore size distribution plot.

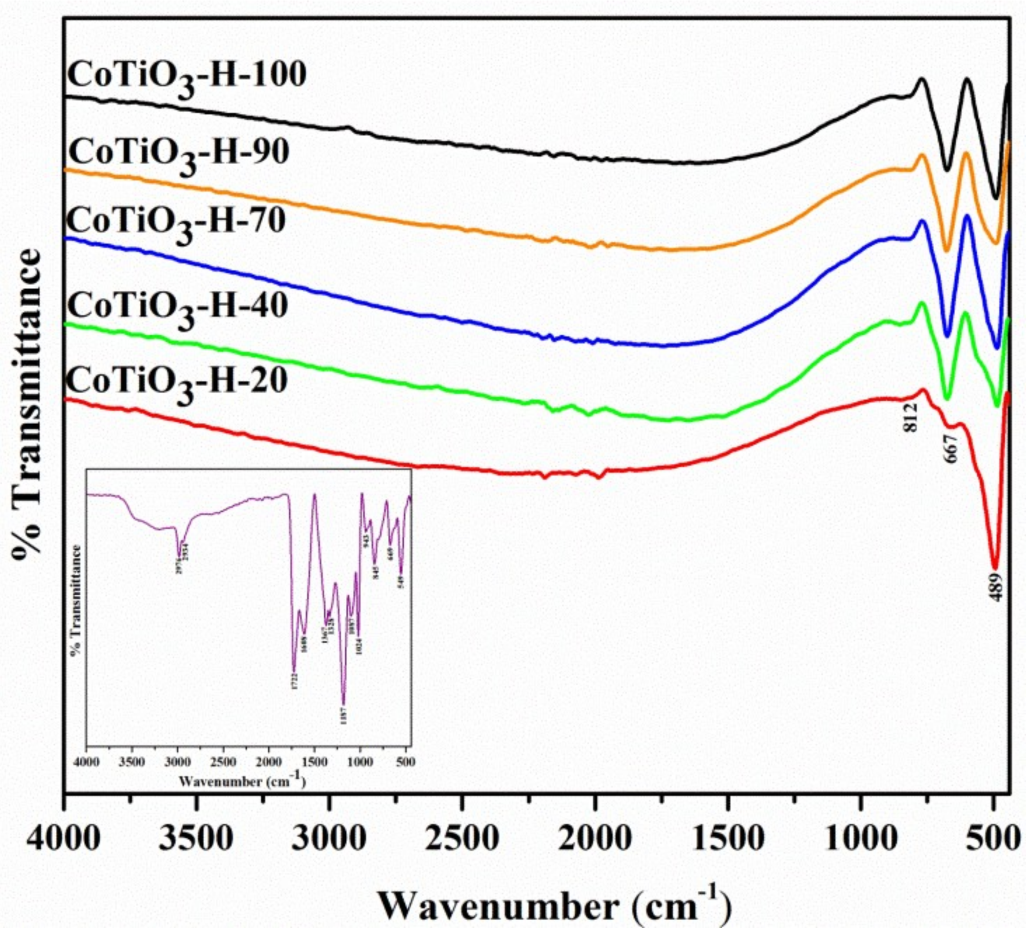


Fig. S9 FT-IR spectra of the materials prepared under different relative humidity conditions. Inset shows the FT-IR spectra of un-calcined material.

References

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