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Supplementary Information

Efficient Co-Fe layered double hydroxide photocatalysts for water oxidation under visible light

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Experimental Section

The materials used in the synthesis process were obtained from Sigma Aldrich. The Co-Fe LDH was prepared by dissolving cobalt nitrate hexahydrate and iron nitrate nonahydrate in 1.25 M sodium carbonate in a 100 mL three-necked flask to yield 1.25 mM of the metal precursor (Co^{2+}:Fe^{3+}= 2:1, 3:1, 4:1). The solution, after purging with nitrogen gas, was annealed for 18 h at 80°C with continuous magnetic stirring. The resultant mixture was centrifuged several times at 7000 rpm for 20 min and washed with water. A brown powder was recovered after drying under vacuum at room temperature. Powder X-ray diffraction patterns were obtained with a Smartlab diffractometer (Rigaku, Japan) operated at 40 kV and 30 mA, using Cu Kα radiation. The scanning rate and step size were 0.5°/min and 0.02°, respectively. A JEM-ARM200F TEM (JEOL Ltd., Japan) was used to image the structure. XANES data were collected at the NSRRC (National Synchrotron Radiation Research Center) in Taiwan. FT-IR spectra were recorded using KBr pellets on a Bomem MB154 Fourier transform spectrometer (currently ABB Analytical Measurements, Switzerland). The band edge analysis was performed using a V-570 UV-vis spectrometer (Jasco, Japan) and a Sigma Probe (Thermo VG Scientific, England) with a He-I light source. The Kubelka-Munk transformation of reflectance was carried out using the following relation: $f(R) = (1 - R)^2/(2R)$. Experiments to measure the evolved oxygen were conducted in a 125 mL two-necked flask with 100 mL of the aqueous suspension. An inverted burette filled with water at atmospheric pressure was connected to the head space of the reactor to reduce leakage of the reacting gas. The powdered LDH (50 mg) was dispersed in 1 mmol silver nitrate solution, which acts as a sacrificial agent. Prior to light irradiation, the suspension was purged with argon gas for 30 min to remove all the air present in the reactor. The reactor was irradiated with a 300 W xenon lamp fitted with a UV and IR blocking filter, which allowed only visible light ($400 \text{ nm} < \lambda < 700 \text{ nm}$) to pass. A gas sample (0.5 mL) withdrawn from the reactor headspace was injected into a gas chromatographic column to measure the amount of evolved oxygen. A GC 7890A column (Agilent Technologies, United States) equipped with 5 Å molecular sieves was used along with a thermal conductivity detector. Argon was used as the carrier gas.

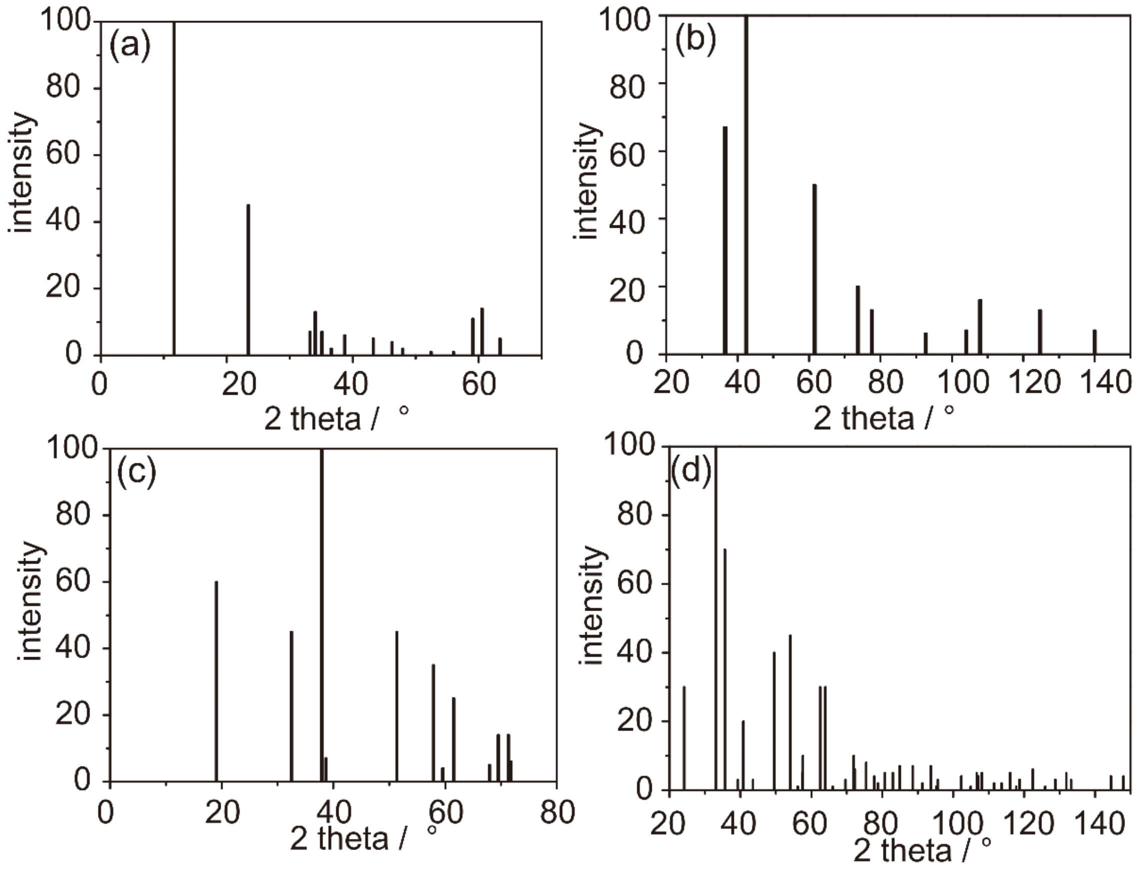

Figure S1. JCPDS reference XRD peaks of (a) Co-Fe LDH(PDF#50-0235), (b) CoO(PDF#43-1004), (c) $Co(OH)_2$(PDF#30-0443), (d) Fe_2O_3(PDF#33-0664) structures.

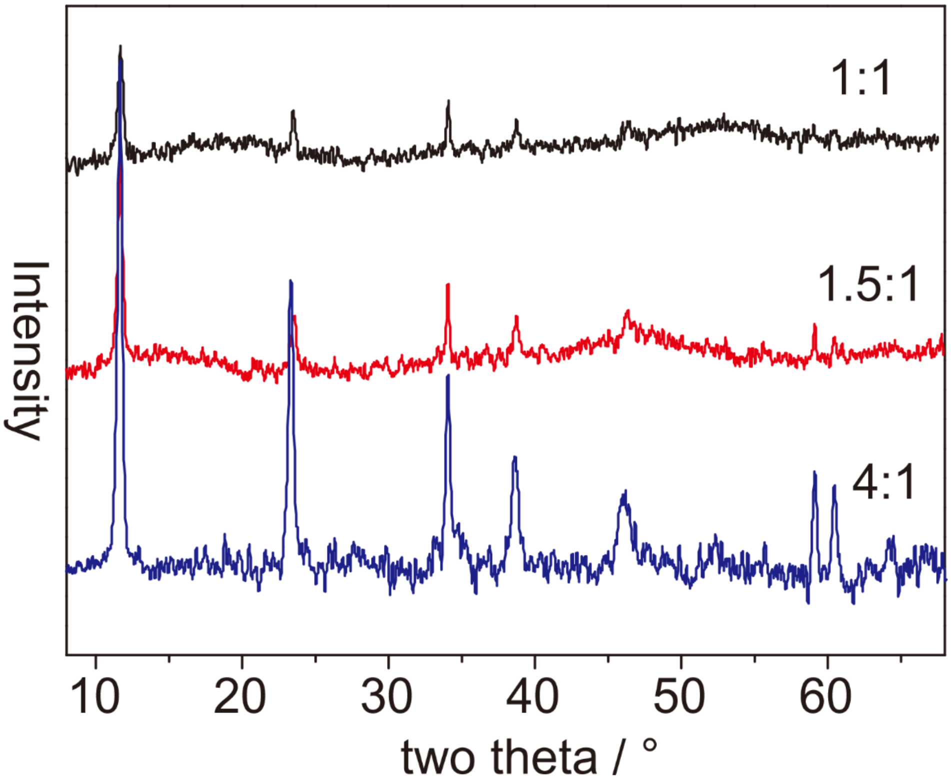

Figure S2. PXRD patterns of Co-Fe LDHs with cobalt and iron ratios of 1:1, 1.5:1, 4:1(CFL4), where LDHs having low ratios less than 2 were found to show bad crystallinity compared to even CFL4.

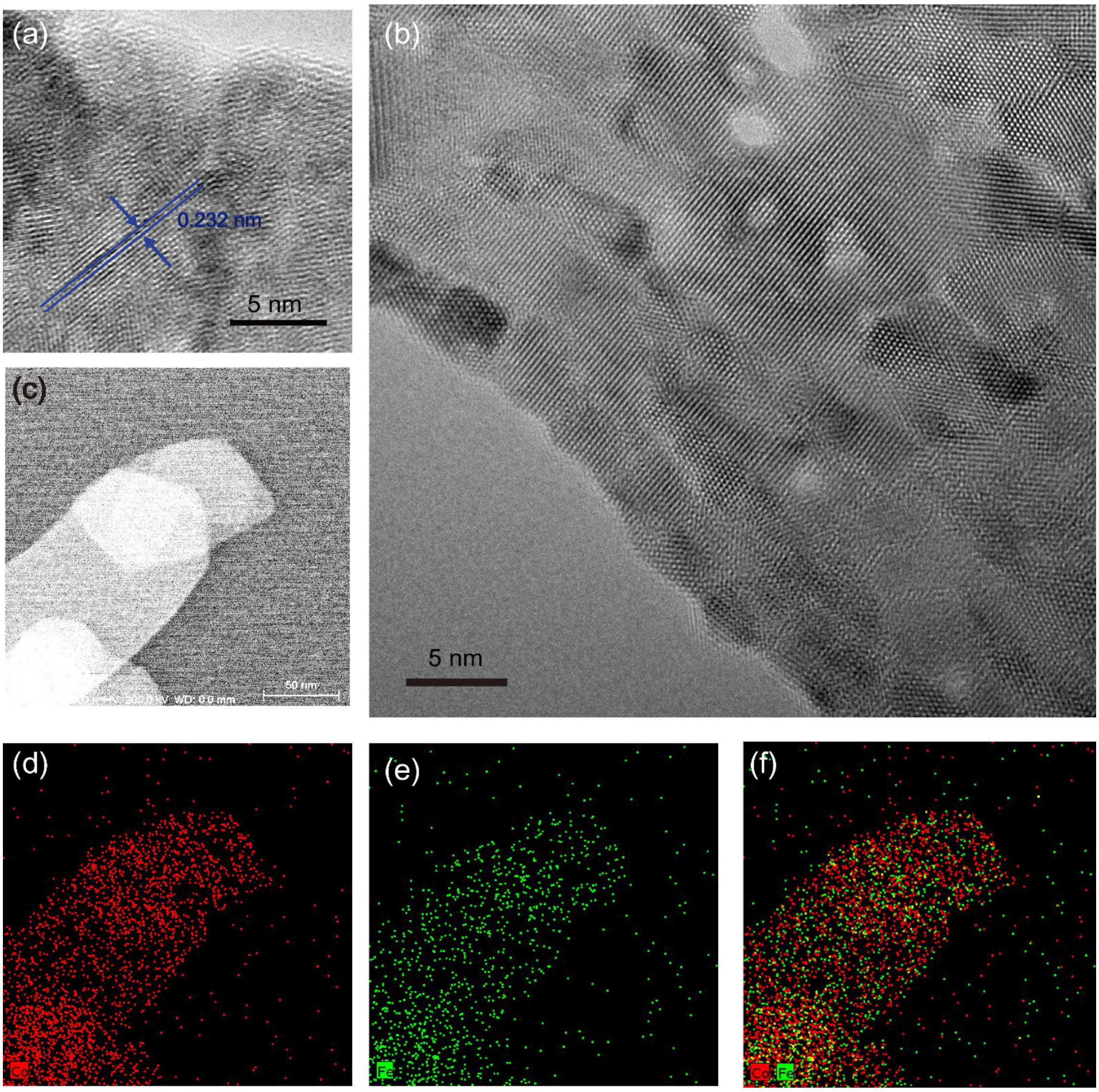

Figure S3. HR-TEM images for (a) a local area and (b) for a large area of a Co-Fe LDH (CFL3), (c) its STEM image, and EDAX images for (d) cobalt, (e) iron, (f) cobalt and iron of a Co-Fe LDH (CFL3)

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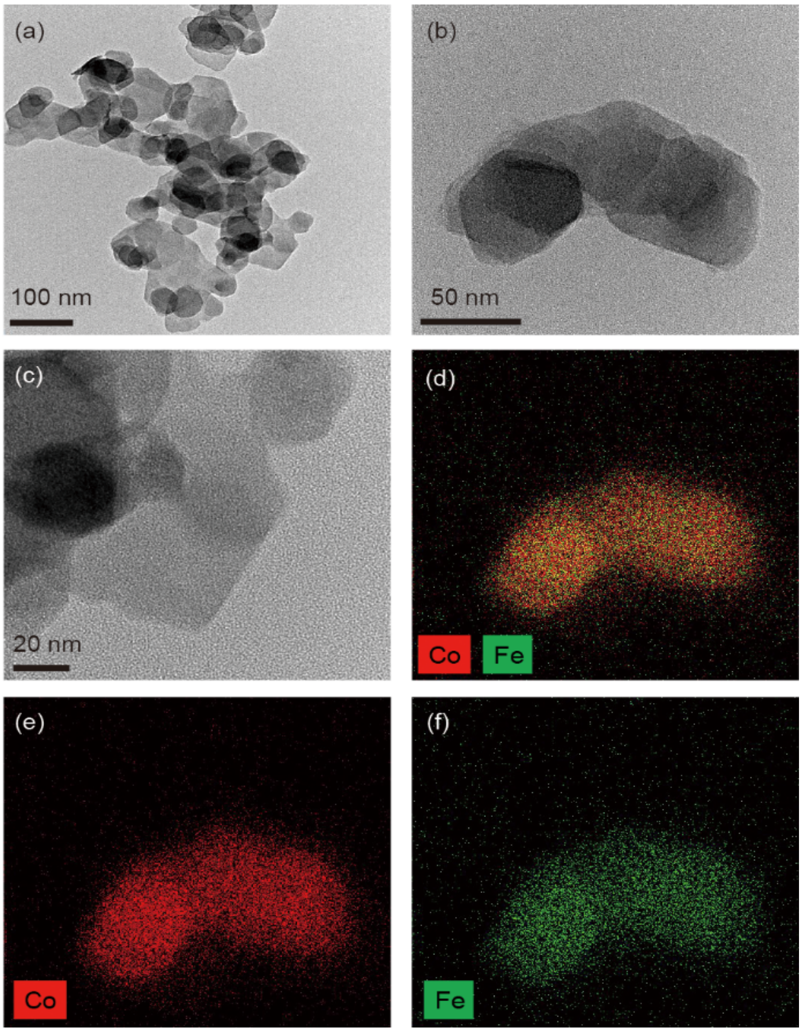

Figure S4. (a), (b),(c) HR-TEM images at different magnifications of a Co-Fe LDH(CFL4), and EDAX images for (d) cobalt and iron, (e) iron, (f) cobalt of a Co-Fe LDH(CFL4)

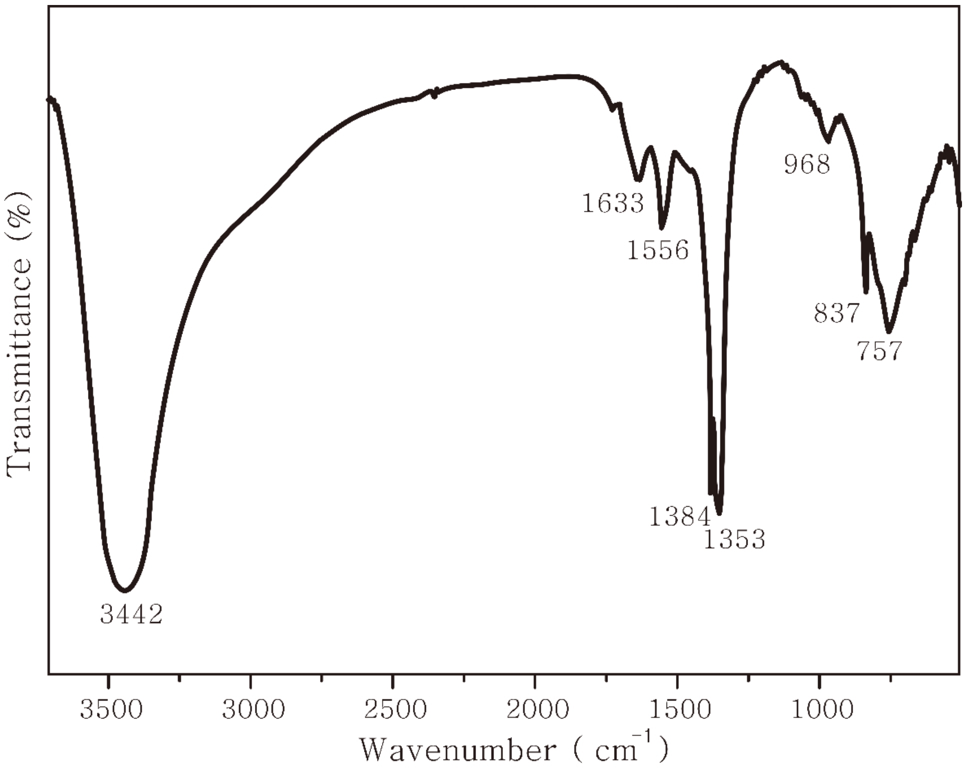

Figure S5. Fourier transform infrared (FT-IR) spectrum of Co-Fe LDH (CFL4).

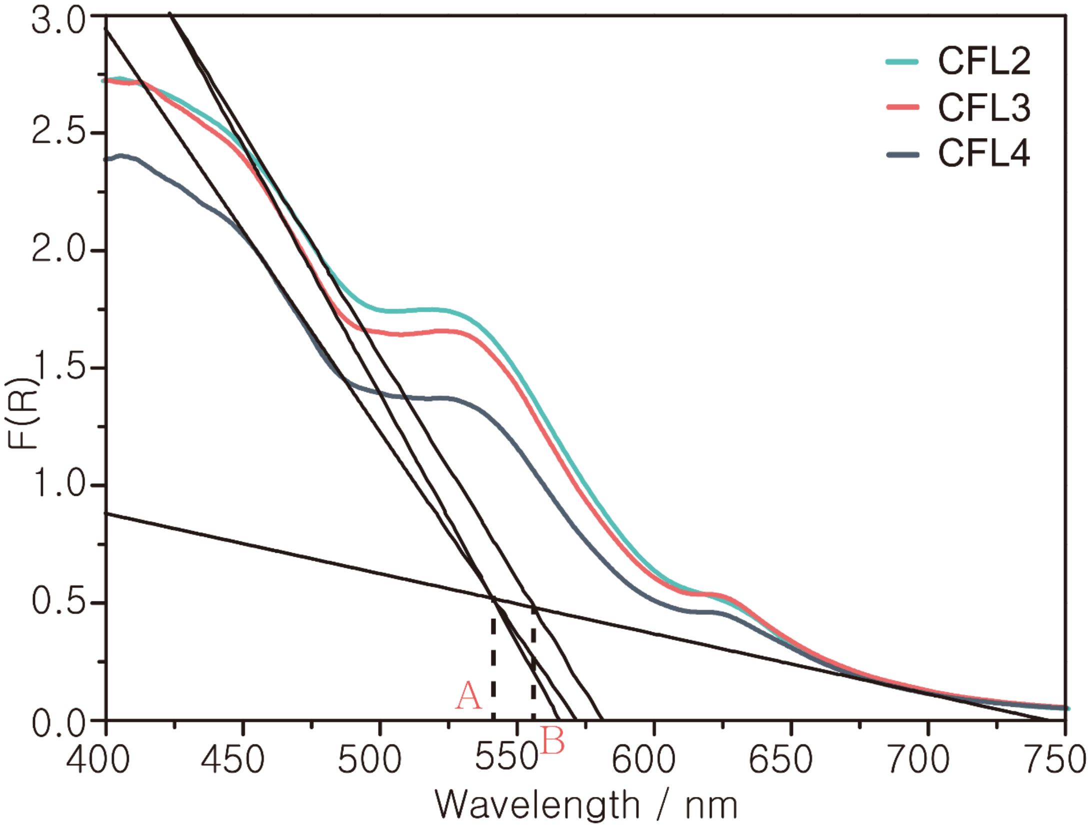

Figure S6. UV-Vis spectra and their calculated band gap energies. In general, the band gap can be estimated from a linear extrapolation to zero of energy vs. F(R) graph. However, the structures for CFL2, CFL3, and CFL4 did not show simple linear band edges.

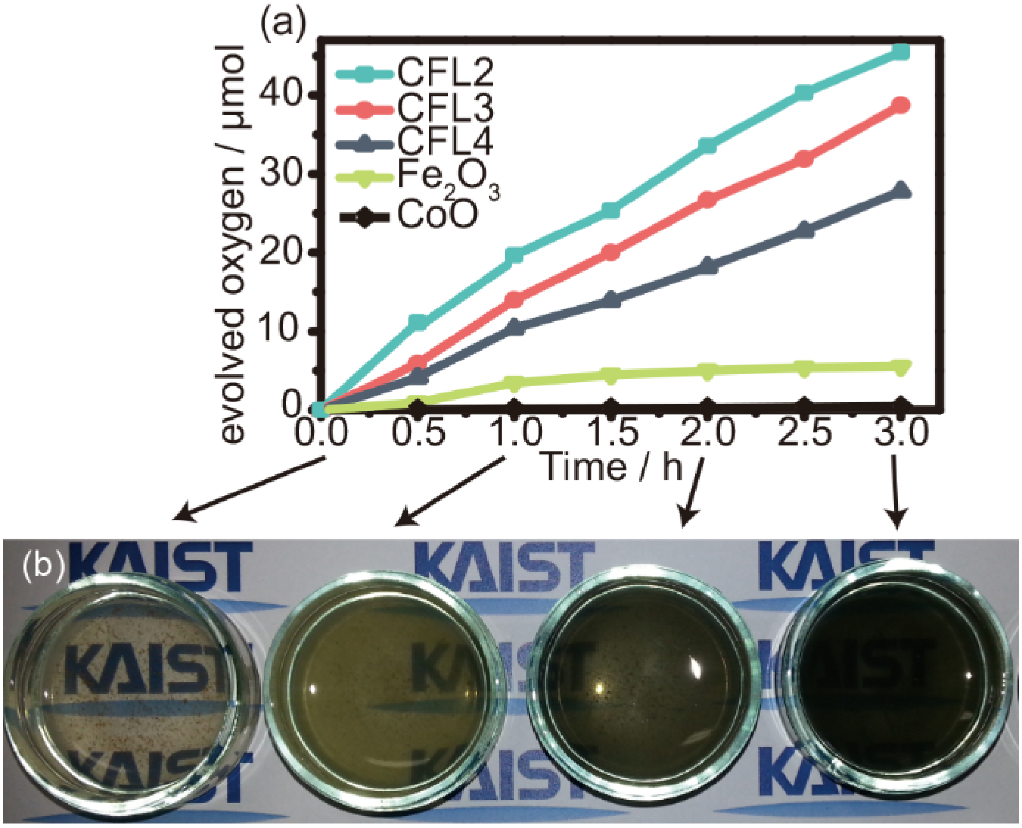

Figure S7. (a) Evolved oxygen on the Co-Fe LDH(CFL4) suspension versus the light irradiation time and (b) the color change on reduction of Ag^+ ions into Ag nanoparticles as the water oxidation reaction proceeds

Name	Co	Fe	ratio
CFL2	280359 ppm	125817 ppm	2.23:1
CFL3	361074 ppm	108369 ppm	3.33:1
CFL4	343157 ppm	82538 ppm	4.16:1

Table S1. Inductively coupled plasma mass spectroscopy analysis of Co-Fe LDHs treated using the nitric acid and hydrochloric acid(7:3).

Detail of XANES measurements

A series of XAS measurements of the synthesized samples were made using synchrotron radiation at room temperature. Measurements were made at the Fe K-edge and Co K-edge with the sample held and illuminated by the light of interest at room temperature. The experiments were conducted at the 01C1 beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan (http://140.110.203.42/EFD.php?num=230).