

A unique method to disperse Au nanoparticles at ultra-high loading *via* LDH intercalation chemistry

Yi Du*, Bradley Wooler, Brian Weiss, Chris Kliever, Sabato Miseo, and Stuart Soled*

Corporate Strategic Research, ExxonMobil Research and Engineering Company, 1545 US22, Annandale, NJ

Synthesis of Mg₂Al-NO₃ LDH: A mixture (Solution 1) of 18.749 g (0.05 mol) Al(NO₃)₃•9H₂O and 28.210 g (0.11 mol) Mg(NO₃)₂•6H₂O in 130 mL D.I. water was stirred until it formed a clear, colorless solution. pH of this solution 1 is 2.39. Separately, a mixture (Solution 2) of 24g 50wt% NaOH and 18g NaNO₃ were dissolved in 30 ml D.I. water. Solution 2 was added dropwise to the Solution 1 with stirring, resulting in the formation of white precipitate. The pH of the mixture was adjusted to ~9.5-10 using 50wt% NaOH. The mixture was then refluxed for 20 hours with stirring at 85 °C. After cooling to room temperature, the final solution has a pH of 12. The mixture was filtered using a ceramic Büchner funnel with filter paper, then washed thoroughly with water (~100mL x 3) and acetone (~50mL). The product was then dried overnight at 100°C, yielding ~12.46g of white product. Elemental analysis: Carbon = 0.55%, Hydrogen = 3.49%, Nitrogen = 4.12%; Heavy metal analysis (excluding light elements): Mg = 34.45wt%, Al = 21.71 wt%. The heavy elements' weight percentage need to be readjusted based on CNH analysis. Since this is the base case, we will assume the extra charge on Al is charged balance by NO₃⁻ and CO₃²⁻ combined. Keeping these assumptions in place, and keeping the ratio from each type of analysis a constant, we can derive the Mg₂Al LDH formula to be Mg_{1.76}Al_{1.00}(OH)_{5.52}(NO₃)_{0.77}(CO₃)_{0.12}•1.8H₂O and Mw is 250.36. [26688-37A]

Synthesis of TA/LDH by anion exchange from Mg₂Al-NO₃ LDH: 6.026 g Mg₂Al-NO₃-LDH was stirred with 6.645 g terephthalic acid and 6.041 g 50wt% NaOH solution in 30 ml D.I. water. pH of the final solution is around 9-10. The mixture was heated in oil bath to 87 °C for 14 hours with stirring. After cooling to room temperature, the mixture was filtered using a ceramic Büchner funnel with filter paper, then washed thoroughly with water (~100mL x 3) and acetone (~50mL). The product was then dried overnight at 100°C, yielding ~32g of white product. The as made TA- Mg₂Al LDH was added to 100mL of water, and the mixture was adjusted to pH 4.5 using 1N HCl. After mixing at room temperature for 2 hours, the mixture was filtered using a ceramic Büchner funnel with filter paper, then washed thoroughly with water (~20mL x 3) and acetone (~20mL). Elemental analysis: Carbon = 13.0%, Hydrogen = 4.00%, Nitrogen <0.10%; Heavy metal analysis (excluding light elements): Mg = 33.17 wt%, Al = 22.67 wt%. The lower Mg content indicates some dissolution of Mg at such a low pH. We assume the amount of C from CO₃²⁻ is very similar to the Mg₂Al-NO₃ LDH above. Mg₂Al LDH formula is estimated to be Mg_{1.63}Al_{1.00}(OH)_{5.25}(C₈H₄O₄)_{0.38}(CO₃)_{0.12}•2.4H₂O and Mw is 268.3. [26688-51A]

Direct synthesis TA/LDH. A mixture (Solution 1) of 37.498g (0.1 mol) Al(NO₃)₃•9H₂O and 56.418g (0.22 mol) Mg(NO₃)₂•6H₂O in 250mL water was stirred until it formed a clear, colorless solution. Separately, a mixture (Solution 2) of 80.00g 50wt% NaOH and 33.2g terephthalic acid (C₈H₆O₄) in 400mL water was stirred until it formed a clear, colorless solution. Solution 2 was added dropwise to the Solution 1 with stirring, resulting in the formation of white precipitate. The pH of the mixture was adjusted to ~9.5-10 using 50wt% NaOH. The mixture was then refluxed for 16 hours with stirring. After cooling to room

temperature, the mixture was filtered using a ceramic Büchner funnel with filter paper, then washed thoroughly with water (~100mL x 3) and acetone (~50mL). The product was then dried overnight at 100°C, yielding ~32g of white product. The as made TA- Mg₂Al LDH was added to 100mL of water, and the mixture was adjusted to pH 4.5 using 1N HCl. After mixing at room temperature for 2 hours, the mixture was filtered using a ceramic Büchner funnel with filter paper, then washed thoroughly with water (~20mL x 3) and acetone (~20mL). Elemental analysis: Carbon = 13.0%, Hydrogen = 4.52%, Nitrogen <0.10%; Heavy metal analysis (excluding light elements): Mg = 29.77 wt%, Al = 26.27 wt%. The lower Mg content indicates some dissolution of Mg at such a low pH. We assume the amount of C from CO₃²⁻ is very similar to the Mg₂Al-NO₃ LDH above. Mg₂Al LDH formula is estimated to be Mg_{1.26}Al_{1.0}(OH)_{4.52}(C₈H₄O₄)_{0.38}(CO₃)_{0.12}-3.526H₂O and Mw is 264.9. [This is the TA/LDH throughout the paper]. [26688-51]

Anion exchange with Au in TA/LDH.

Au:Al ratio = 0.001 (≈ 1wt% Au/LDH if all adsorbed) 0.02g HAuCl₄ (HAuCl₄-3H₂O, >99.9%, Aldrich) are dissolved in 100 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 1g of TA/LDH (0.0061mol) were added to the mixture and stirred at 80 °C for 1.5hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour [26688-37N] and then 250 C for 3hrs. The powder color was purple after 80C and become slightly darker purple after 250C. Elemental analysis: Mg = 29.1 wt%, Al = 25.73 wt%, Au = 1.149%. [26688-37N, 250C] Note: another attempt [26688-74B1] was carried out at 10 times the concentration and the Au results in a much more aggregated form.

Au:Al ratio = 0.01 (≈ 1wt% Au/LDH if all adsorbed) 0.02 g HAuCl₄ (HAuCl₄-3H₂O, >99.9%, Aldrich) are dissolved in 100 ml D.I. water and just diluted NaOH solution to adjust the pH to 10. 1g of TA/LDH (0.0061mol) were added to the mixture and stirred at 80 °C for 1.5hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour [26688-37L] and then 250 C for 3hrs. The powder color was purple after 80C and become slightly darker purple after 250C. Elemental analysis: Mg = 29.45 wt%, Al = 25.5 wt%, Au = 1.11%. [26688-37L, 250C] Note: another attempt [26688-74B2] was carried out at 10 times the concentration and the Au results in a much more aggregated form.

Au:Al ratio = 0.10 (≈ 1:10) 0.15g HAuCl₄ (0.0004mol) (HAuCl₄-3H₂O, >99.9%, Aldrich) are dissolved in 100 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 1g of TA/LDH (0.0037 mol) were added to the mixture and stirred at 80 °C for 14hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour. We will further analyze the filtrate (bright yellow) and the powder (orange/brown) to get an accurate Au loading. [26688-51C]

Au:Al ratio = 0.15 (≈ 1:6) 0.25g HAuCl₄ (0.0006mol) (HAuCl₄-3H₂O, >99.9%, Aldrich) are dissolved in 100 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 1g of TA/LDH (0.0037mol) were added to the mixture and stirred at 80 °C for 14hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour. We will further analyze the filtrate (bright yellow) and the powder (orange/brown) to get an accurate Au loading. [26688-51B]

Au:Al ratio = 0.56 (≈ 1:2) 0.17g HAuCl₄ (0.0004mol) (HAuCl₄-3H₂O, >99.9%, Aldrich) are dissolved in 50 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 0.2g of TA/LDH (0.0007mol) were added to the mixture and stirred at 80 °C for 14hrs. Cool the solution to room temperature, filtered

and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour. We will further analyze the filtrate (clear/colorless) and the powder (orange/brown) to get an accurate Au loading. Elemental analysis: Mg = 9.425 wt%, Al = 10.31 wt%, Oxygen = 15.55 wt%, Au = 62.8%. The lower Mg content indicates some dissolution of Mg at such a low pH. B.E.T. surface area of this sample is 103.4 m²/g. [26688-51F]

Au:Al ratio = 1.19 (≈ 1:1) 0.35g H₂AuCl₄ (0.0009 mol) (H₂AuCl₄·3H₂O, >99.9%, Aldrich) are dissolved in 50 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 0.2g of TA/LDH (0.0007mol) were added to the mixture and stirred at 80 °C for 14hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour. We will further analyze the filtrate (yellow) and the powder (orange/brown) to get an accurate Au loading. [26688-51E]

Au:Al ratio = 1.82 (≈ 2:1) 0.5g H₂AuCl₄ (0.0013 mol) (H₂AuCl₄·3H₂O, >99.9%, Aldrich) are dissolved in 50 ml D.I. water and just diluted NaOH solution to adjust the pH to 4.5. 0.2g of TA/LDH (0.0007mol) were added to the mixture and stirred at 80 °C for 14hrs. Cool the solution to room temperature, filtered and washed with abundance D.I. water and acetone. The powders are dried at 80 °C in air for an hour. We will further analyze the filtrate (bright yellow) and the powder (orange/brown) to get an accurate Au loading. B.E.T. surface area of this sample is 120.3 m²/g. [26688-51D]

X-ray Diffraction (EXRD). XRD patterns were recorded on a PANalytical X'Pert Pro instrument in reflection mode with Cu KR radiation ($\lambda = 1.54178 \text{ \AA}$). The accelerating voltage was set at 45 kV with 40 mA current. The diffractometer was equipped with X'Celerator detector. Scan rates were typically 0.06° s⁻¹ (continuous scan, step size 0.0167°, time per step 35 s). Scans at 1.0° to 75.0° typically take 10 minutes. Antiscatter slit, receiving slit, and divergent slit were all fixed to be 1/2''.

Transmission Electron Microscope (TEM). The catalyst powder was prepared for characterization in the TEM by crushing it into small pieces (<100 nm thick) using an agate mortar and pestle. The fines were dusted onto a 200 mesh, holey-carbon-coated, copper TEM grid. The grid was examined in the bright field (BF) TEM imaging mode of a Philips CM200F electron microscope that was operated at an accelerating voltage of 200 kV. Digital images were collected from randomly selected areas using a Gatan CCD camera and Digital Micrograph v. 2.5.4 software. Metal particles were visually identified in the images, and the diameters of more than 250 of these features were measured “by hand” using the “line” tool in Digital Micrograph. The particle diameter measurement data was stored in the Digital Micrograph Results file and then transferred into KaleidaGraph v.3.0 software in order to generate a particle size distribution (PSD) histogram and the statistical data. A surface-volume-averaged diameter, $D_{(sv)}$, was also calculated using the following equation:

$$D_{sv} = (N_i D_i^3) / (N_i D_i^2)$$

where N represents the number of particles of a given measured diameter and D is the diameter that is measured from the digital TEM image.

CO oxidation testing. CO oxidation reactions were measured in a fixed bed reactor with heat input from an electric furnace. Catalyst (0.10 g) was pressed and sieved to form 0.25 – 0.43 mm pellets. The catalyst was diluted with quartz pellets of the same size to obtain 5 cm³ total volume and loaded in a stainless steel tube with 3/8 in. outer diameter. The reactor was set in a 2.0 kg brass block to improve temperature control. The electric furnace controlled catalyst temperature based on a thermocouple in the brass block. The reactor was confirmed to be gas tight by a pressure test. Mass flow controllers (Brooks instruments) established a flow comprising 0.45 vol % carbon monoxide, 2.8 vol % oxygen, and balance nitrogen (99.99% purity) to the catalyst at 0.1 std. L/min. and ambient pressure. The temperature was then stepped at 10 °C/min. to 65 °C, 110 °C, 170 °C, and 230 °C. A gas

chromatograph (Agilent 7890) detected all species using Q and 5A mol sieve columns and thermal conductivity detectors

Results and discussions (SI)

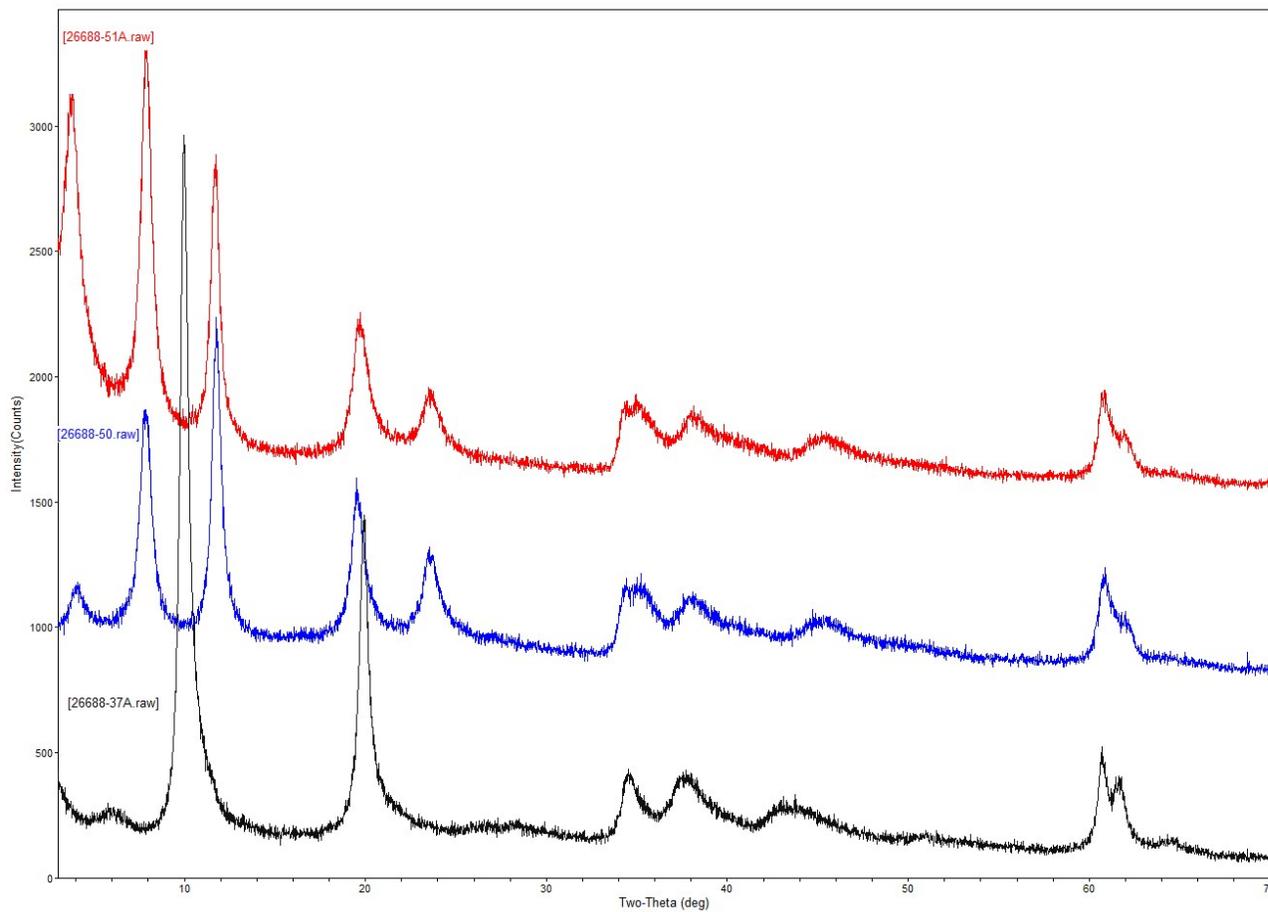


Figure S1. XRD for the as made $Mg_2Al(NO_3)_6 \cdot 6H_2O$ LDH and its anion exchange once product(26688-50) and the acid treated product with clean 23.1 Å interlayer distance (26688-51A).

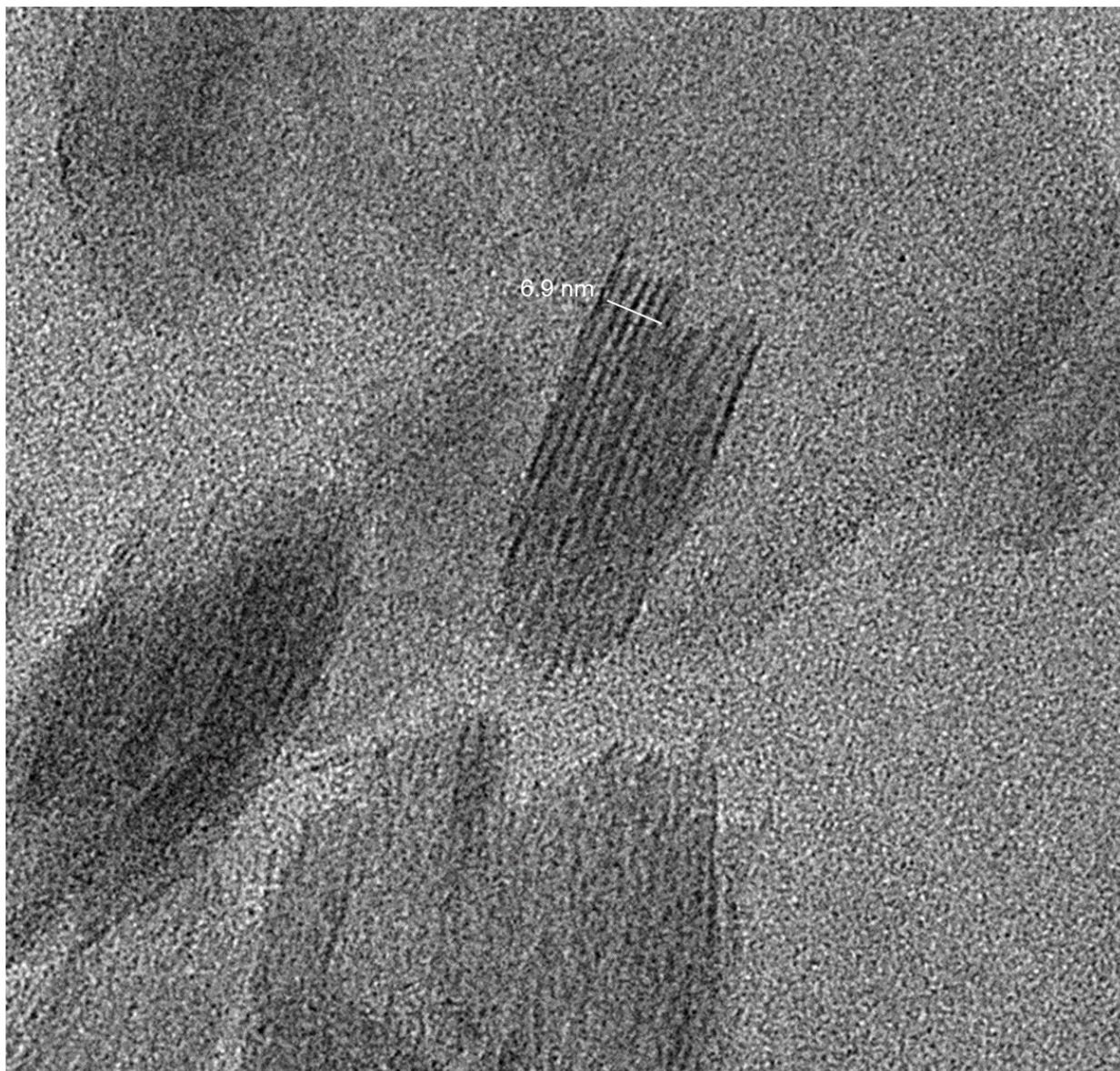


Figure S2. TEM confirmations of the 23.1 Å interlayer distance TA/LDH (26688-51A).

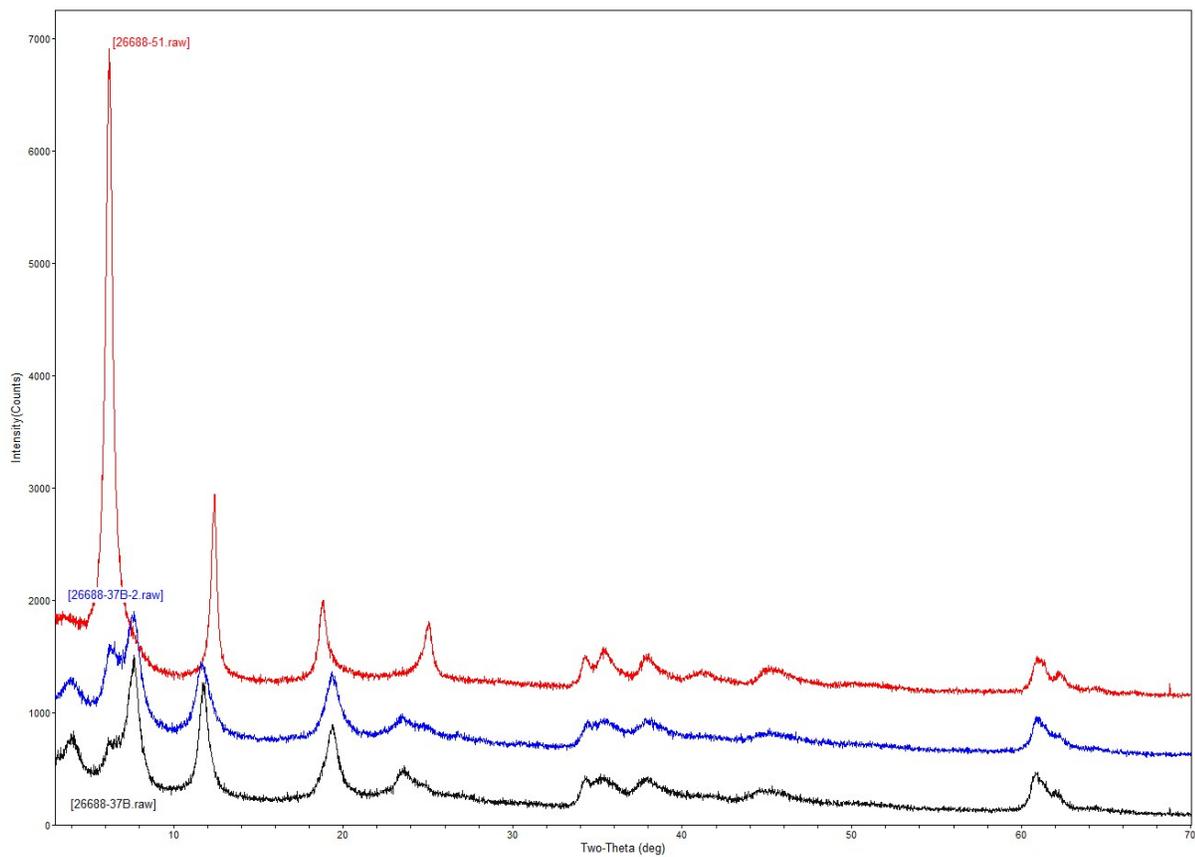


Figure S3. XRD for direct synthesis of TA/LDH (26688/-37B) and its anion exchange once (26688-37B₂) product at pH 9-10. It indicates TA is exchanged in but the pattern is not a clean phase of TA/LDH. Only after acid treatment at pH 4.5 that we obtained a clean 14.4 Å interlayer distance TA/LDH (26688-51).

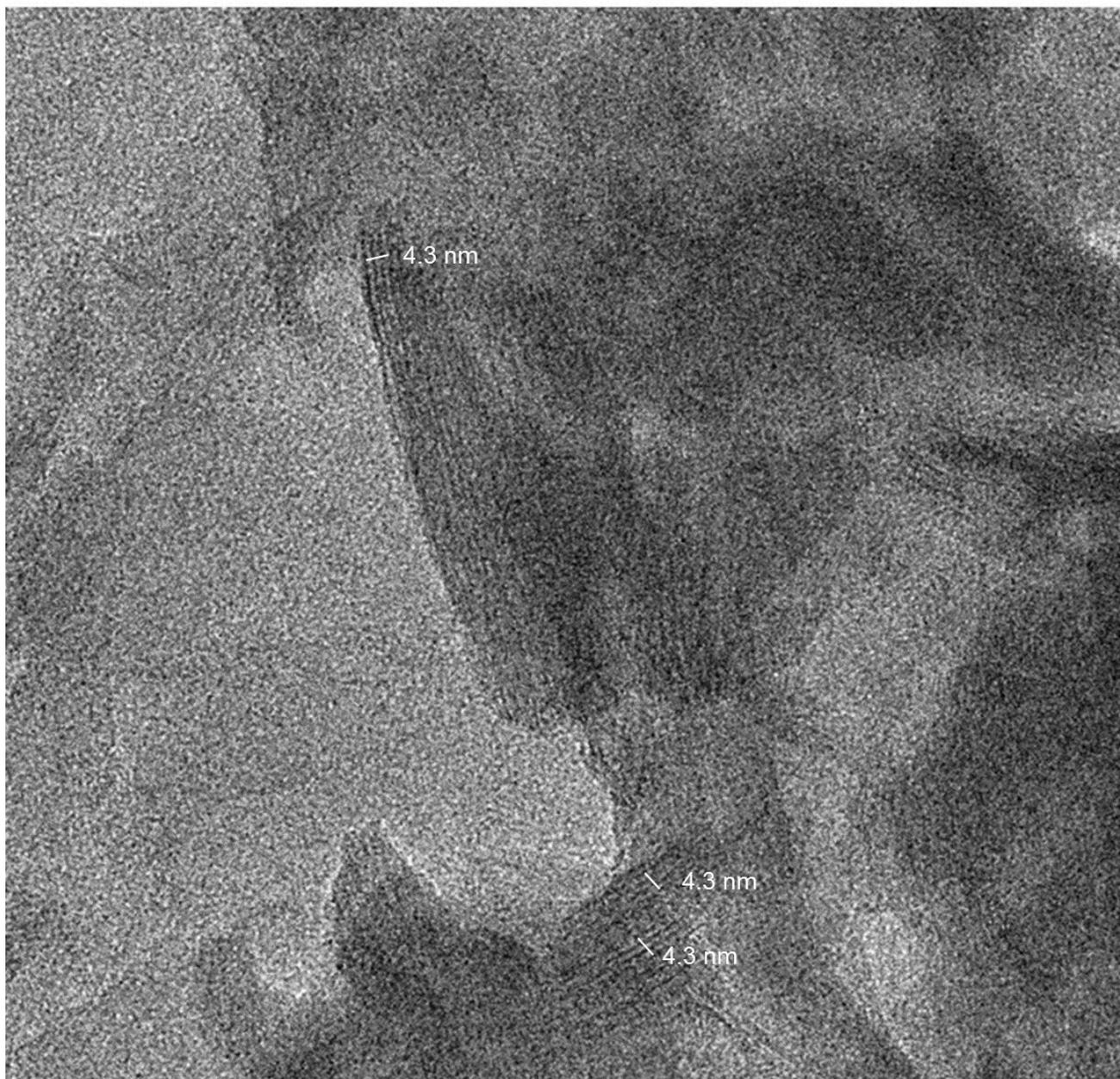


Figure S4. TEM confirmations of the 14.4 Å interlayer distance TA/LDH (26688-51).

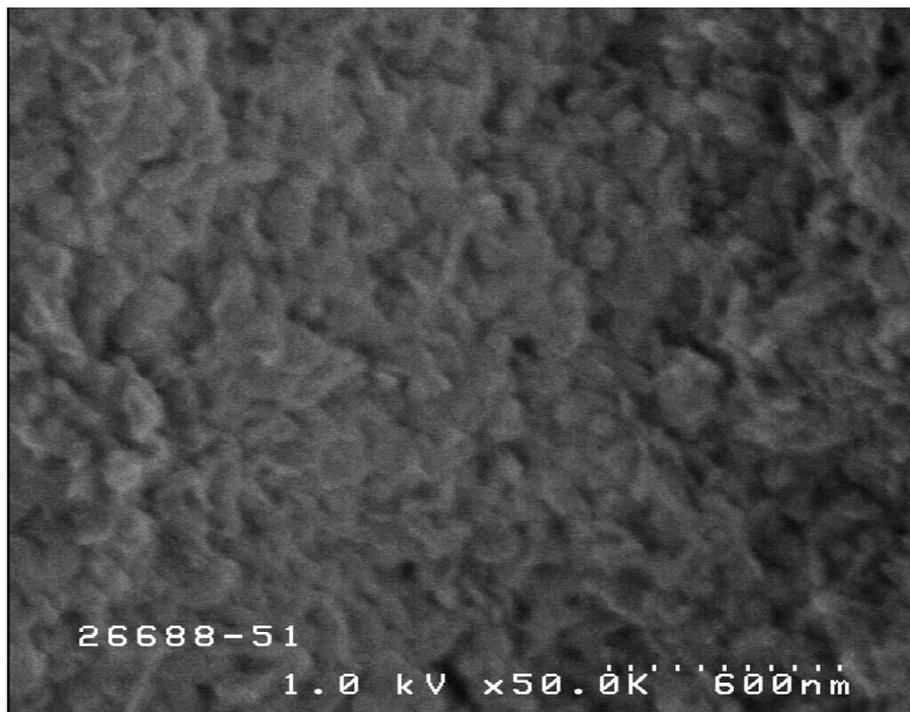


Figure S5. SEM image TA/LDH after acid treatment [26688-51]. This is the starting LDH material for all subsequent Au anion exchange.

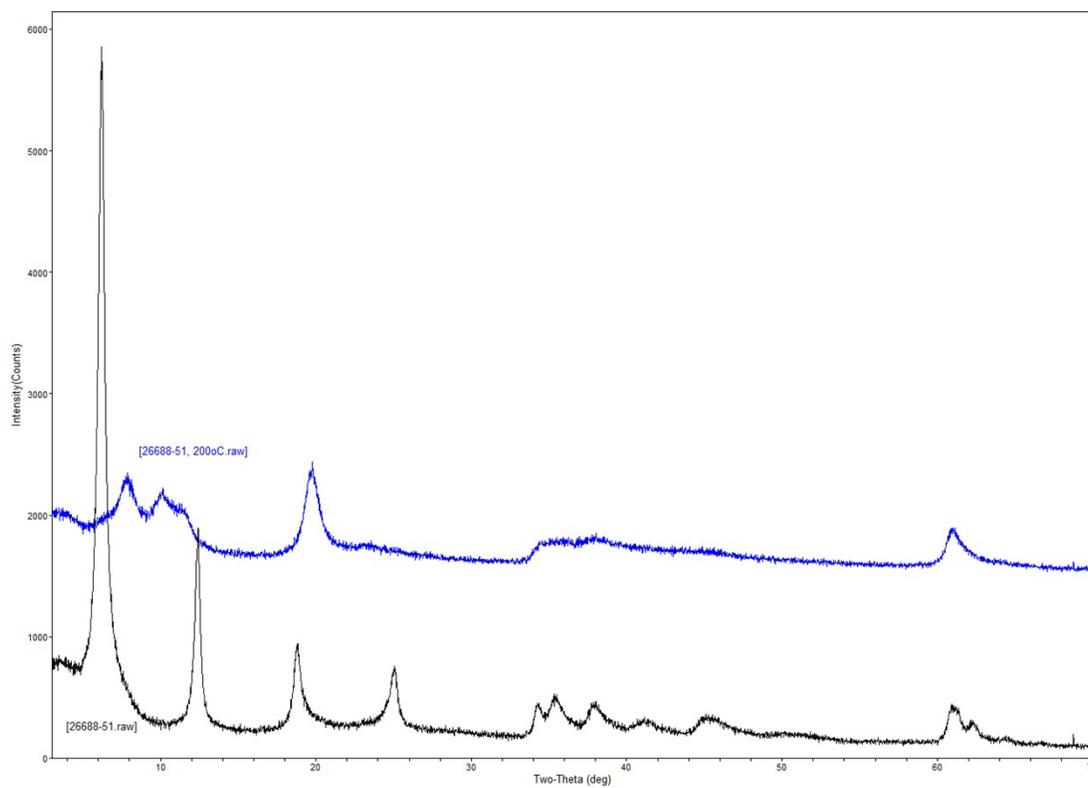


Figure S6. XRD of the calcination product of the acide treated TA/LDH [26688-51-200C].

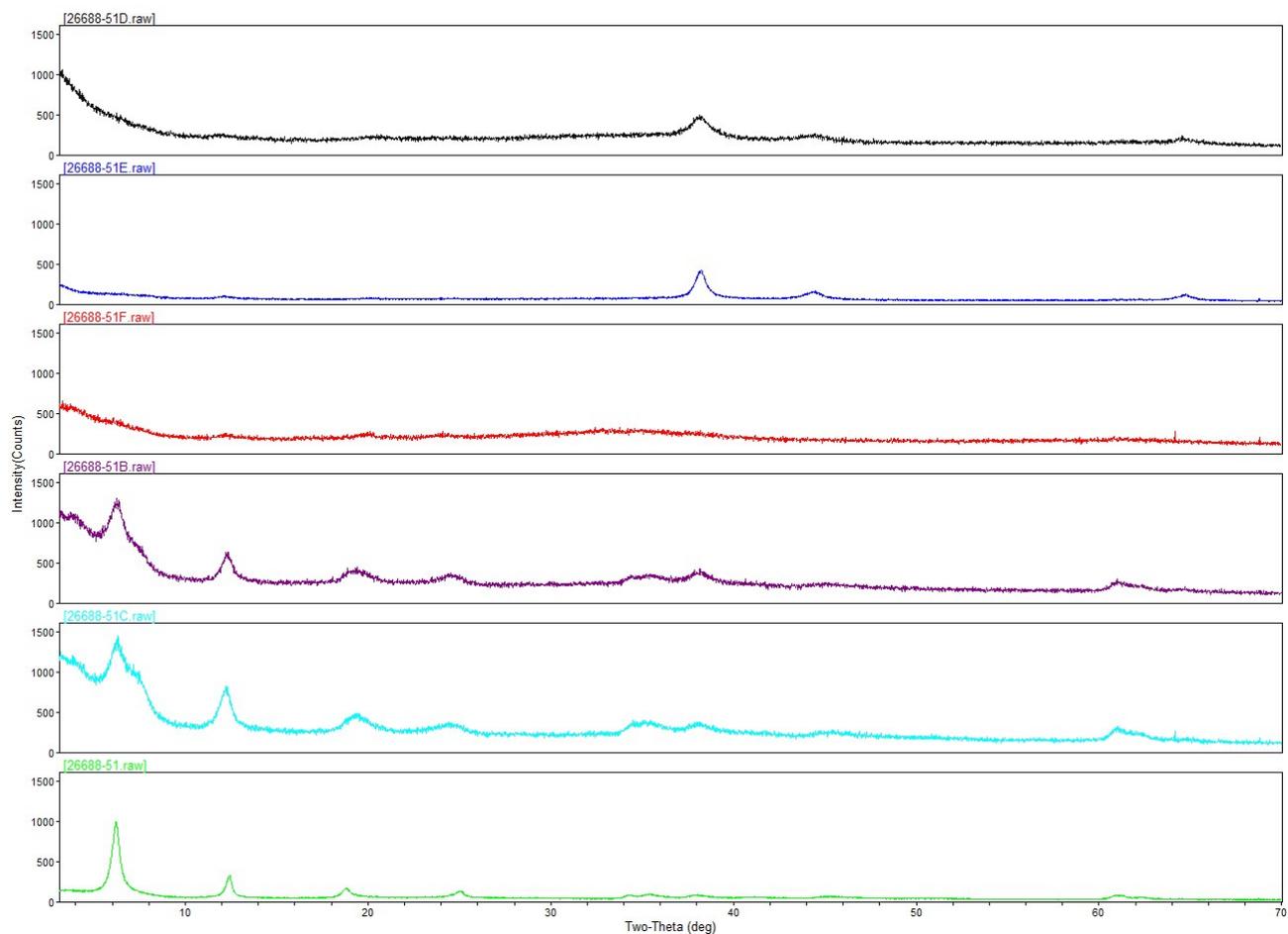


Figure S7. XRD patterns for the as made TA/LDH [Green; 26688-51], Au and TA/LDH exchange product at Au:Al ratio of 0.008 [Aqua; 26688-51C], 0.013 [Purple; 26688-51B], 0.06 [Red; 26688-51F], 0.13 [Blue; 26688-51E], and 0.20 [Black; 26688-51D]. The diffraction peaks from sample 26688-51D and 51F are from Au [PDF 97-004-4362]. Sample 51F is further analyzed by XRF and confirmed the Au composition to be 62.8%.

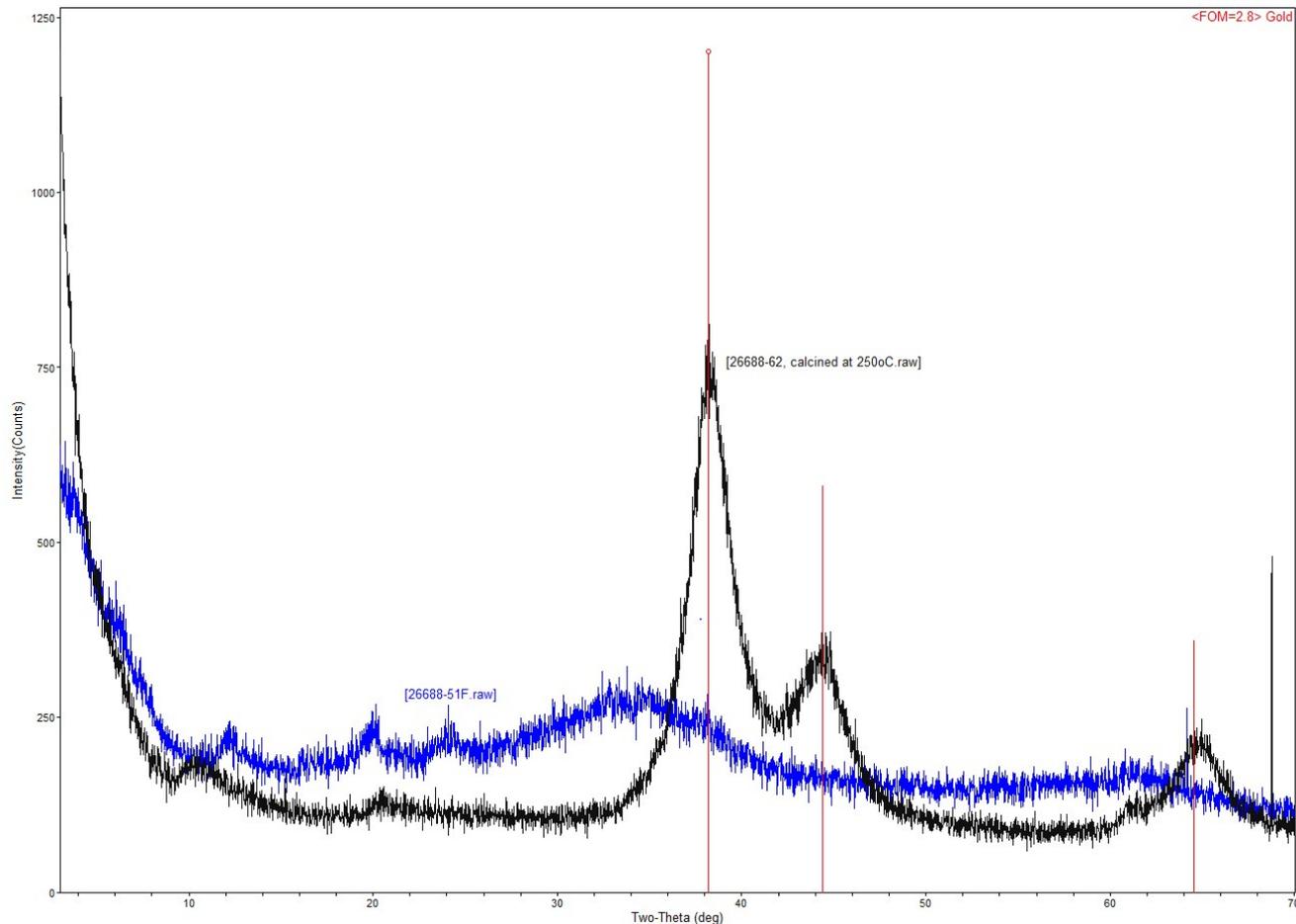


Figure S8. XRD pattern of calcination product of sample 26688-51F with 62.8% Au loading will result in severe Au aggregation. By having Au intercalating in between LDH layers was successful in stopping its sintering at 80 °C which was the synthesis and reduction temperature but it is insufficient to keep it from aggregation at 250 C. [26688-62]

At lower Au loading, it is however possible to avoid Au aggregation at 250C by tuning the pH to 10 during the Au anion exchange reaction. We have conducted an experiment starting from TA/LDH. We prepare 200ml of Au solution that has 0.0799g HAuCl₄ solid, we adjust the PH to 10 using 0.5M NaOH. We took 50ml of the above Au solution and then add 1g TA/LDH to the above solution and dilute this with another 50ml water. We stirred the solution at 80C in air for an hour, yielded product 26688-37L, and we then calcine this same sample to 250C and yielded sample 26688-37L, 250C. Their XRD and TEM images are below indicating that the LDH structure in this case is retained and no obvious Au growth is seen. We had further calcined this sample to 400C and started to see a little particle growth but still not severe aggregation. This is due to a much lower Au loading (1-2wt%) and a much higher pH during anion exchange.

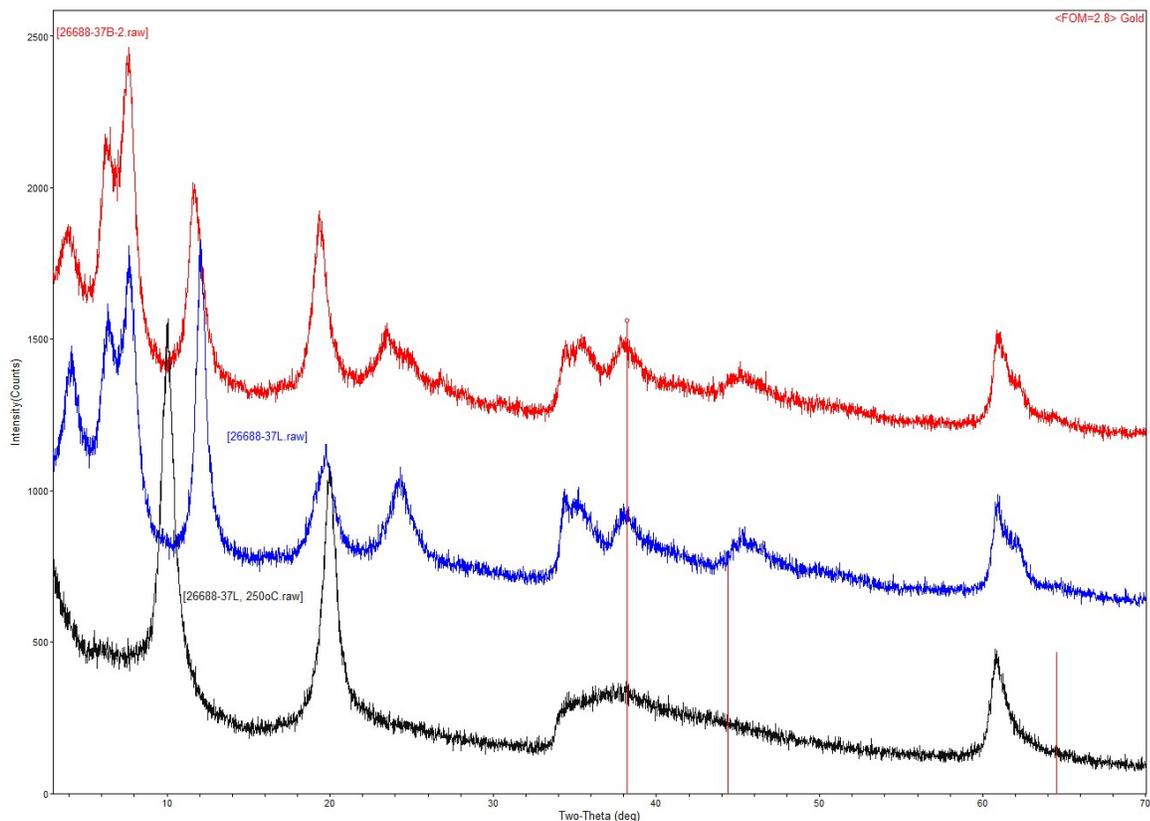
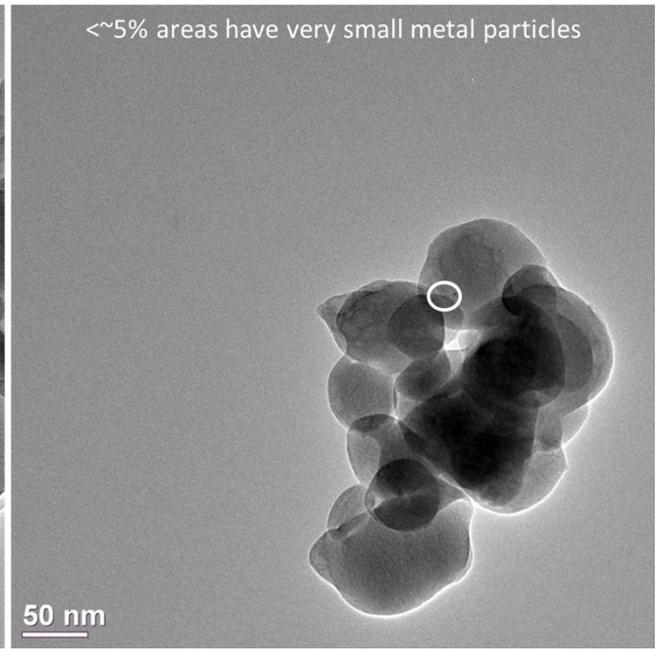
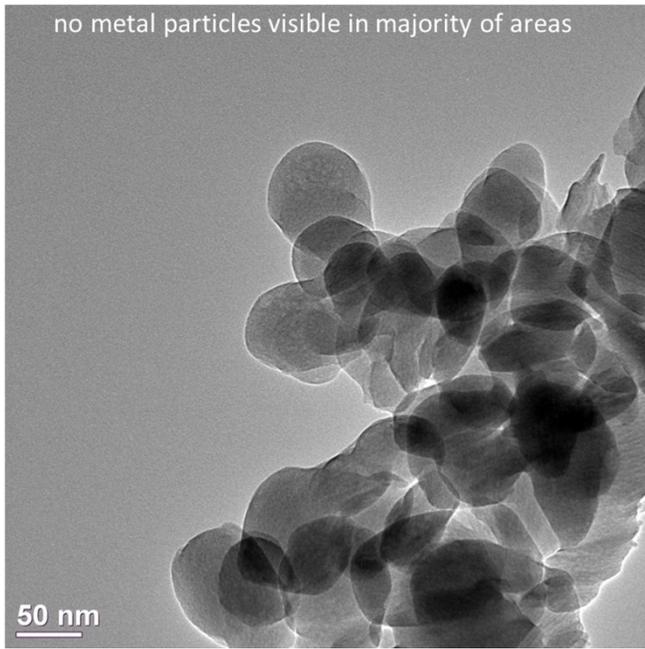


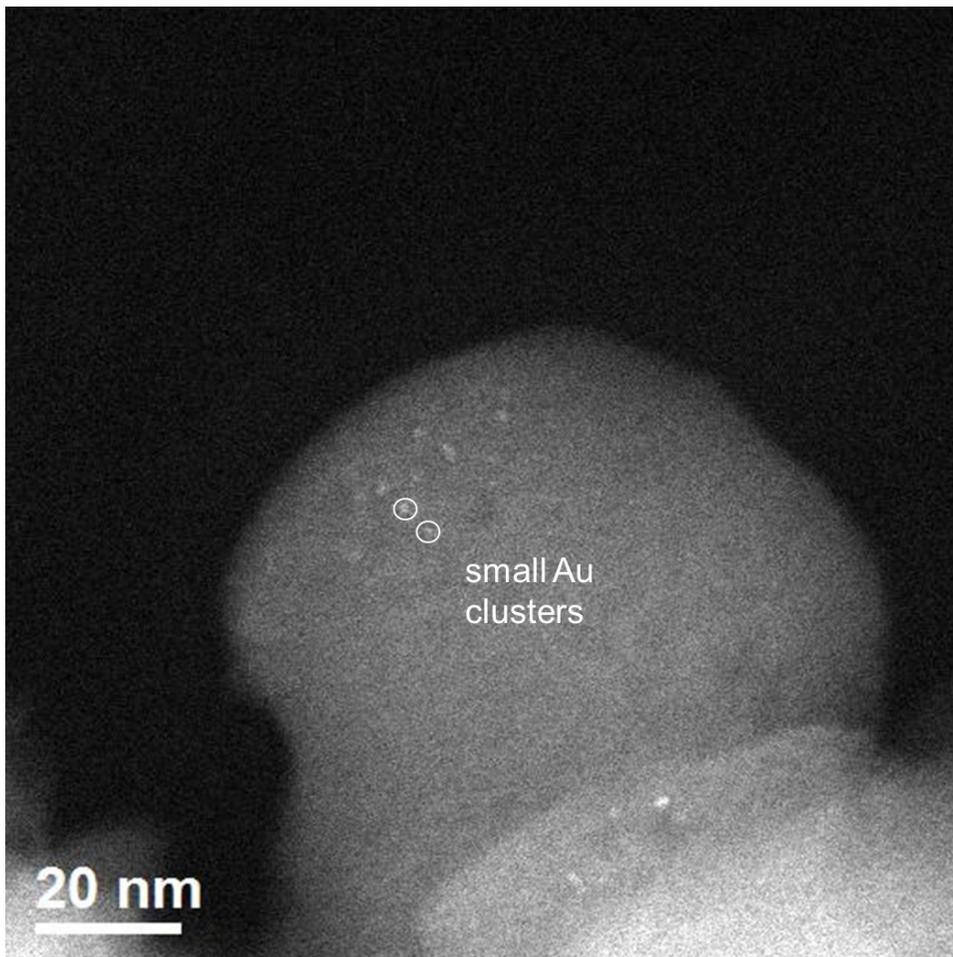
Figure S9. XRD patterns to evaluate different calcination temperature and its impact in Au particle size growth. Up to 250C [26688-37L] there is no observable Au aggregation.

The sample was also white in color after 80C drying and remains white after 250C. If there is sintering of Au, even at this low loading, we should have seen some Au peak from XRD or some color change as an indication. The presence of Au in this 26688-37L sample is further confirmed by TEM below in S8. As a contrary, we have performed a similar experiment at pH 10 but starting from Mg_2Al-NO_3 LDH (26688-37A), where the interlayer distance is not big enough to exchange Au precursor and the resulting product is unlikely to remain thermally stably. In this case, the sample color turn from white at 80C drying to purple at 250C. The corresponding TEM images in Figure S10 below serve another evidence of how small and thermally stable these Au particles are.

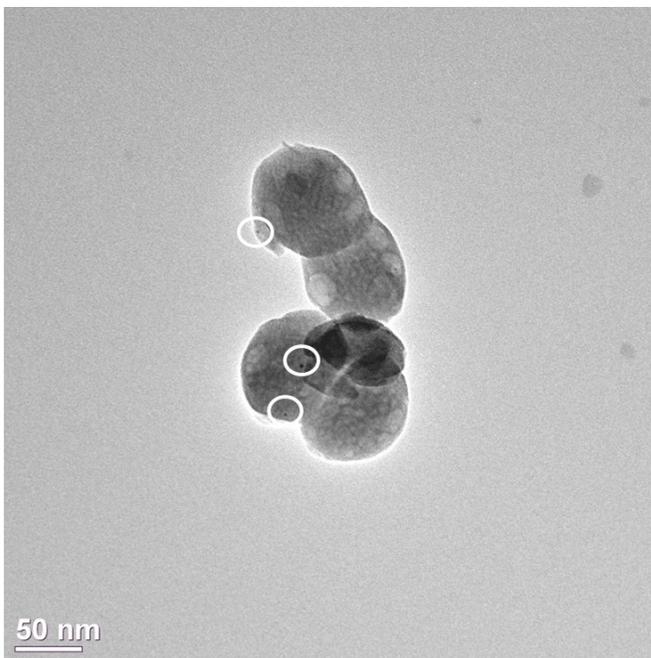
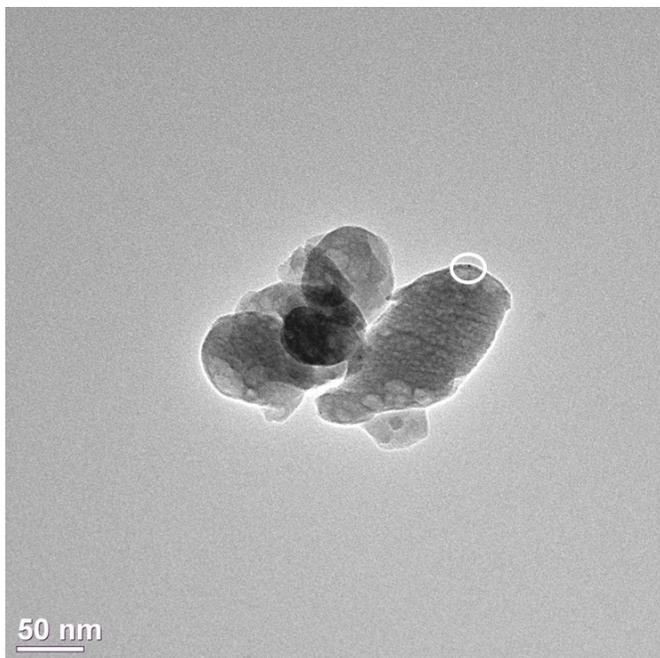
After 80C drying



Only under AC TEM the Au particles are visible



After 250C drying, still very small Au particles throughout



After 400C drying, some Au sintering is observed

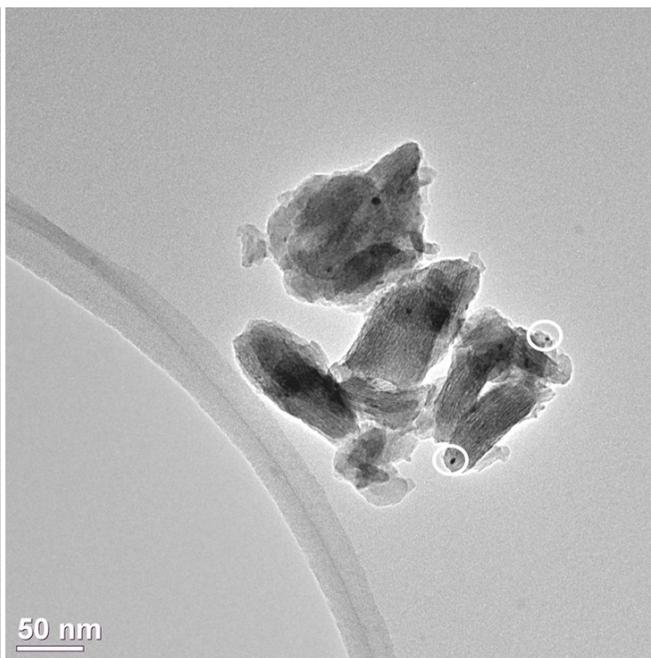
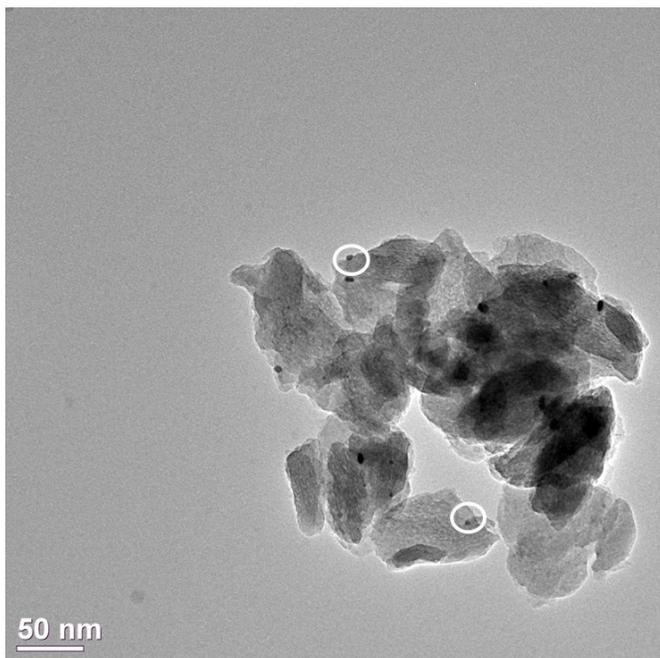
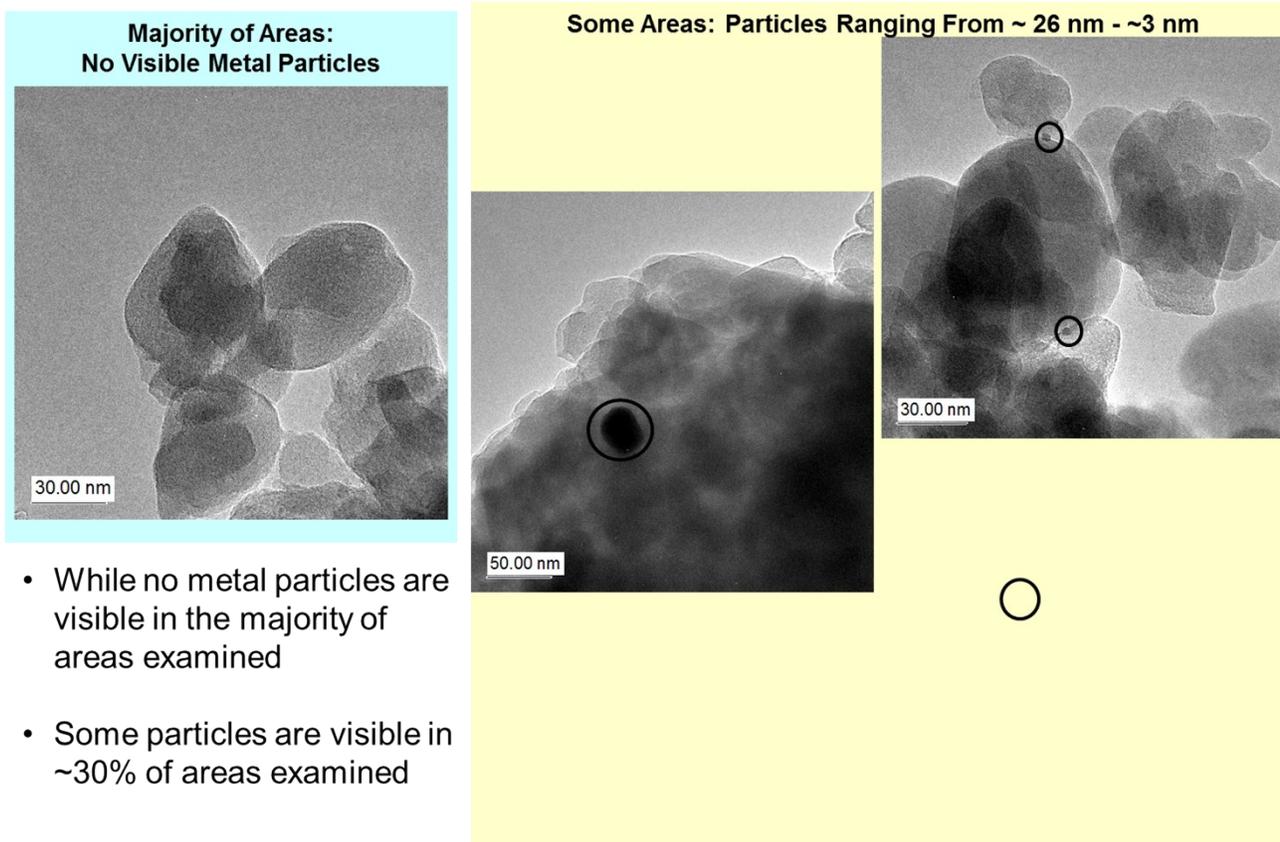


Figure S10. TEM images of (26688-37L). It was made by anion exchange of TA/LDH (26688-37B2) with Au at pH 10. This sample's color remain white even after 250C calcination indication.

When we increased the concentration from 26688-37L by 10 times [26688-74B1], we notice a significant growth in particle size after 250C calcination.



- While no metal particles are visible in the majority of areas examined
- Some particles are visible in ~30% of areas examined

Figure S11. TEM images of (26688-74B1). It was made by anion exchange of TA/LDH (26688-37B2) with Au at pH 10. This sample has however 10 times concentration during the anion exchange and the resulting particles are aggregated more significantly than the diluted version.

When we performed the Au anion exchange series with different Au: Al ratio, when Au:Al ratio (initial ratio in the solution) is at 2.0 (26688-51D), Au was severely aggregated as shown in Figure S5 and the TEM below (Figure S10). When Au:Al ratio is only at 0.06 (26688-51F), Au did not aggregate to form a bulk Au peak from XRD and TEM also confirmed to have well dispersed 1-3nm particle throughout (Figure S11).

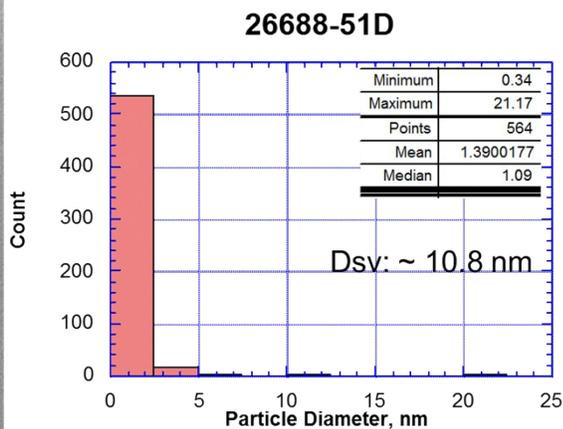
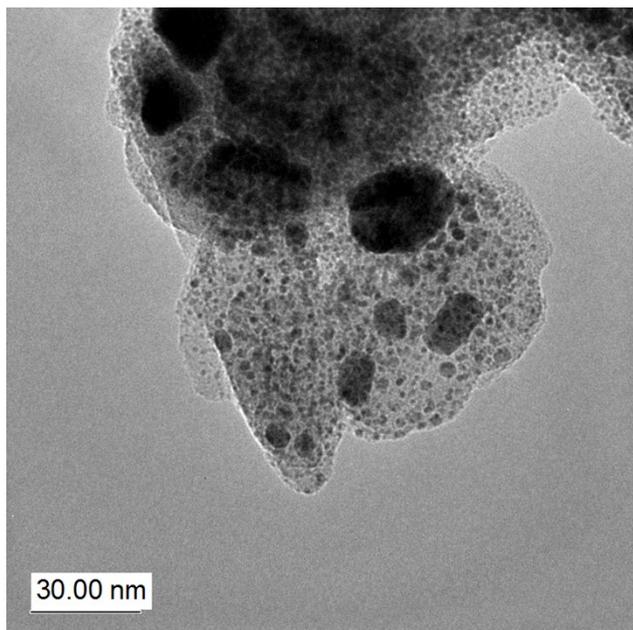
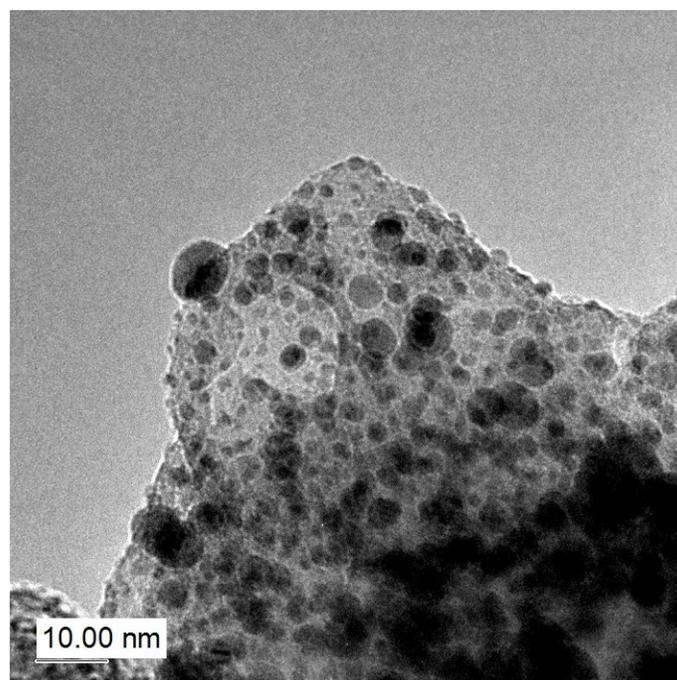
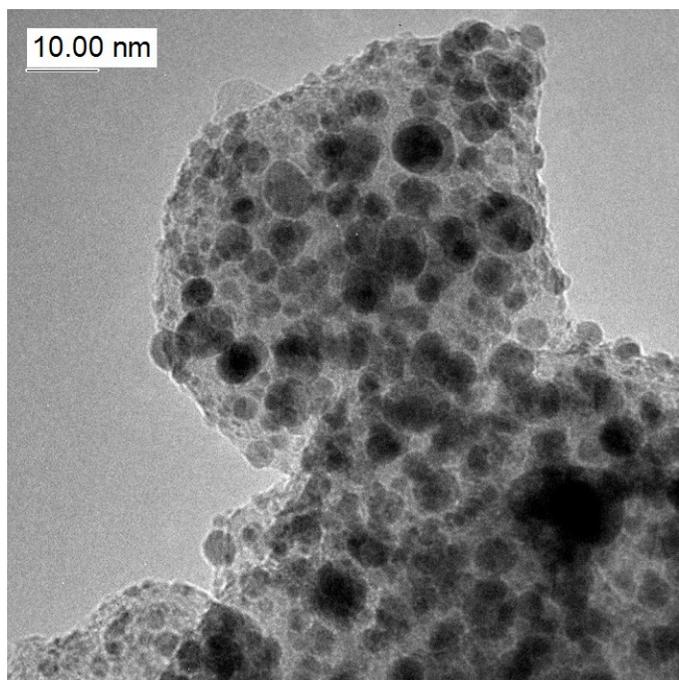


Figure S12. TEM images of (26688-51D) Au/TA, LDH sample when Au and Al ratio was at 0.20 during the initial anion exchange.



26688-51F

- Very high concentration of metal particles observed throughout the catalyst
- Metal particle mean: ~1.7 nm
median: ~1.4 nm
Dsv: ~ 3.2 nm

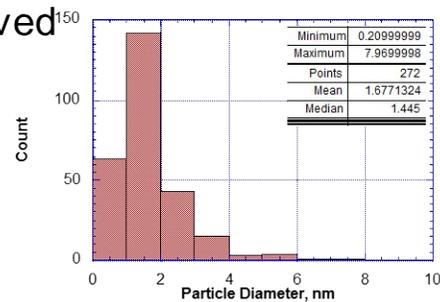


Figure S13. TEM images of (26688-51F) Au/TA, LDH sample when Au and Al ratio was at 0.06 during the initial anion exchange. (this sample is also thoroughly discussed in the main manuscript).

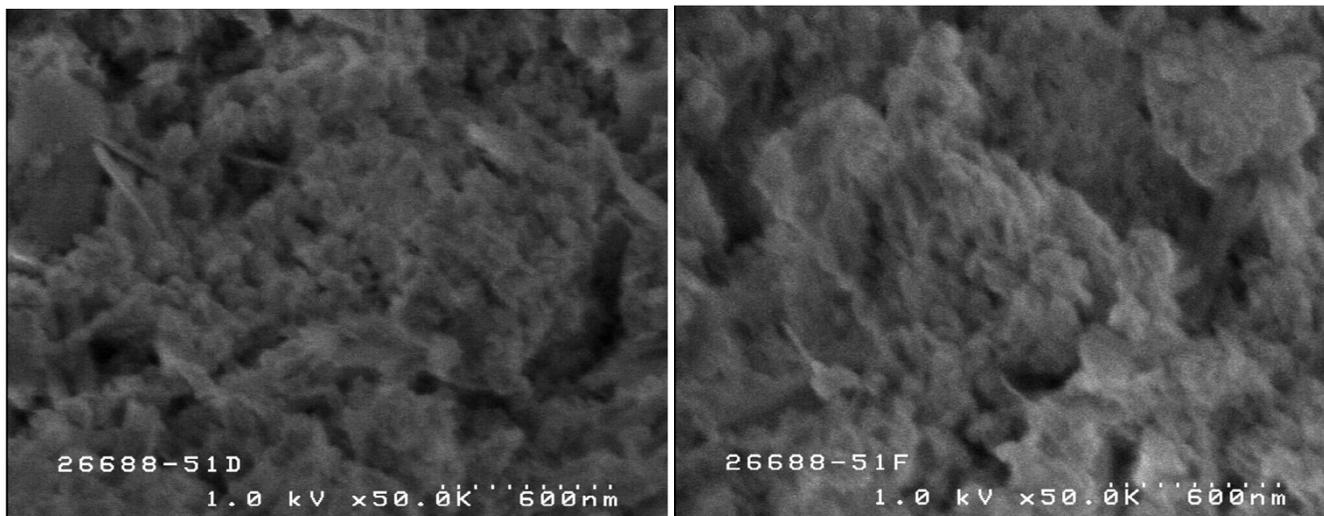


Figure S14. SEM images of the same samples above: 26688-51D and 26688-51F.

Some other control experiments to prove the uniqueness of this reported TA/LDH as Au exchange precursors (SI)

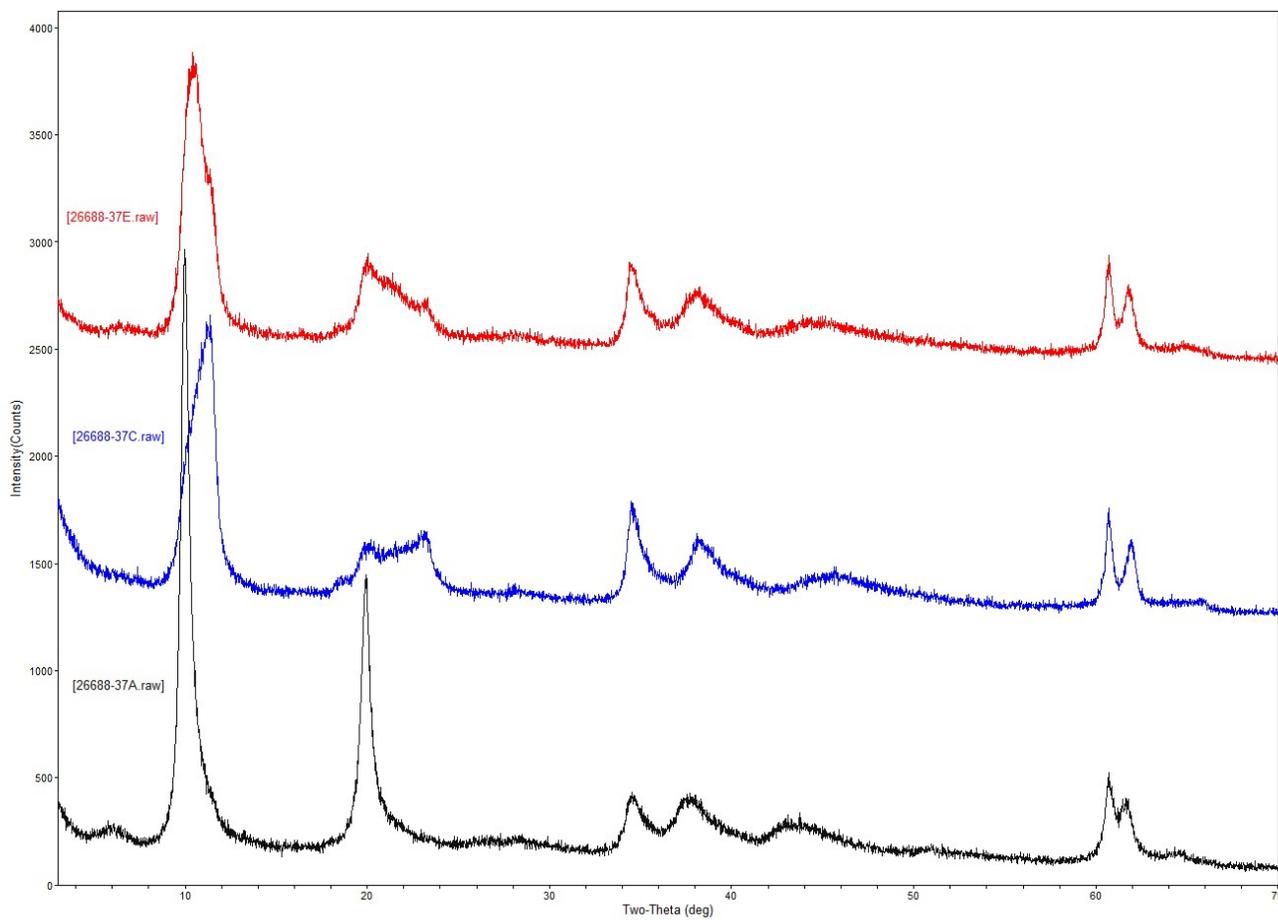


Figure S15. Two sets of initial anion exchange experiments were carried out on $\text{Mg}_2\text{Al-NO}_3$ LDH (26688-37A) at pH 4.5 and at pH 10, resulting in corresponding samples of 26688-37C at pH 4.5, and sample 26688-37 E at pH 10. The exchange was carried out with 0.08 g $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ and 1g corresponding LDH precursor and pH was adjusted by diluted NaOH to reach the targeted pH. Yield at pH 4.5 is 70.47wt% and yield at pH 10 is at 64.7wt% indicating this LDH sample is slightly more unstable at higher pH. 26688-37C is a dark purple powder and 26688-37E is also dark purple color powder. 26688-37C's XRF solid analysis shows Au loading to be 2.14%, correspondingly the filtrate analysis show Au content to be less than 4ppm indicating most Au is grafting onto LDH surface.

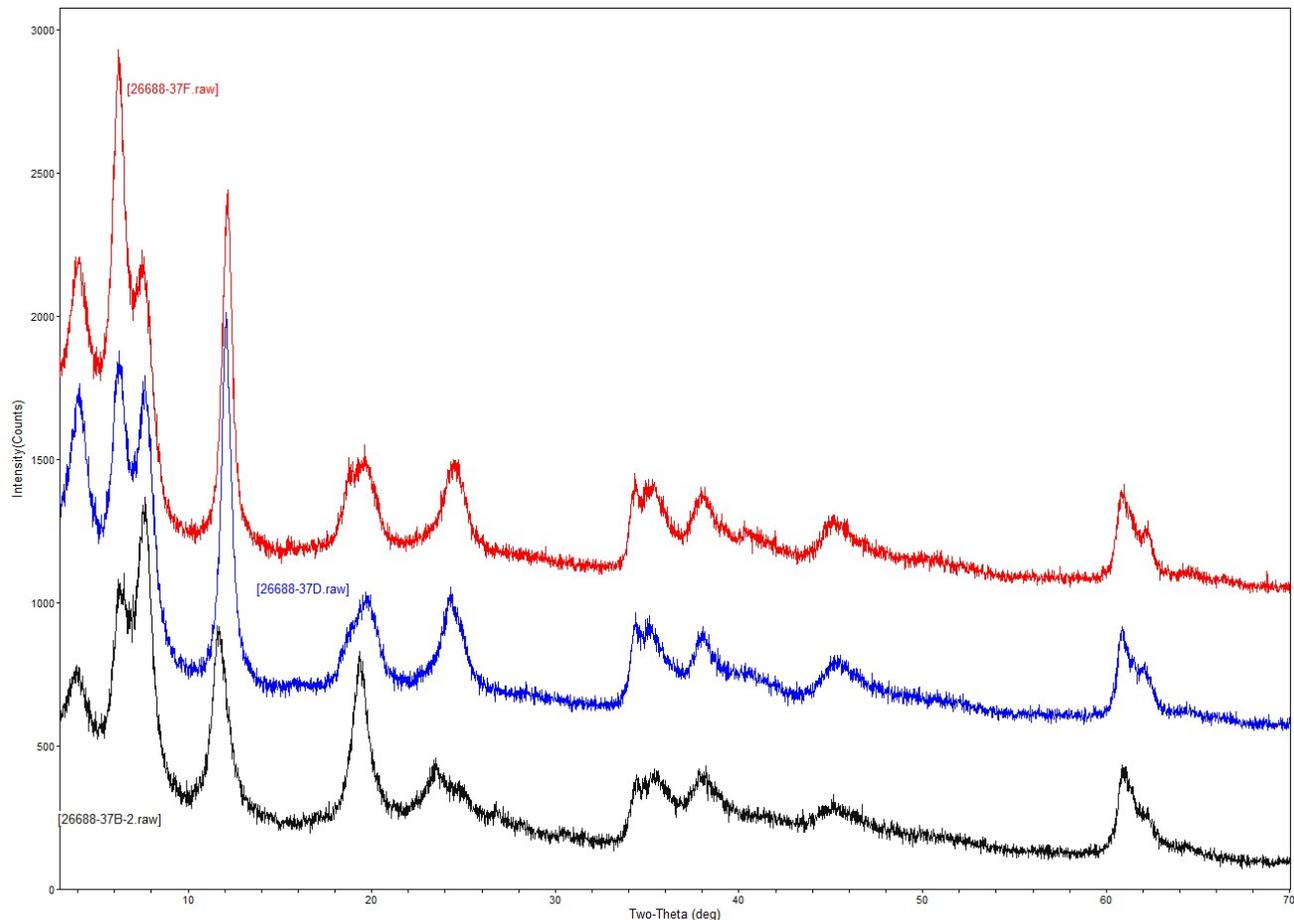


Figure S16. Two sets of initial anion exchange experiments were carried out on twice exchange $\text{Mg}_2\text{Al-TA}$ LDH (26688-37B2) at pH 4.5 and at pH 10, resulting in corresponding samples of 26688-37D at pH 4.5, and sample 26688-37 F at pH 10. The exchange was carried out with 0.02 g $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ and 1g corresponding LDH precursor and pH was adjusted by diluted NaOH to reach the targeted pH. Yield at pH 4.5 is 78.0wt% and yield at pH 10 is at 88.1wt% indicating this LDH sample is slightly more unstable at higher pH. 26688-37D is a pink and light purple powder and 26688-37F is also pink and light color powder. 26688-37D solid XRF analysis shows Au loading to be 1.02% and filtrate analysis shows Au content to be less than 44ppm. We lost around 50% of Au into the filtrate.

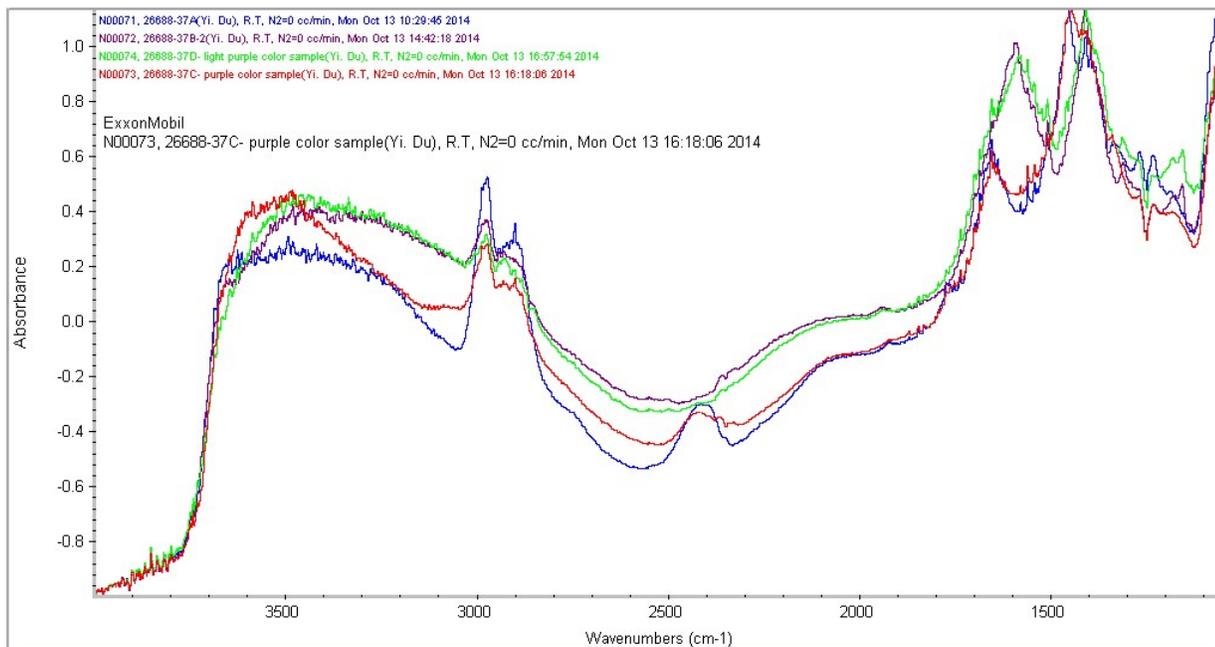
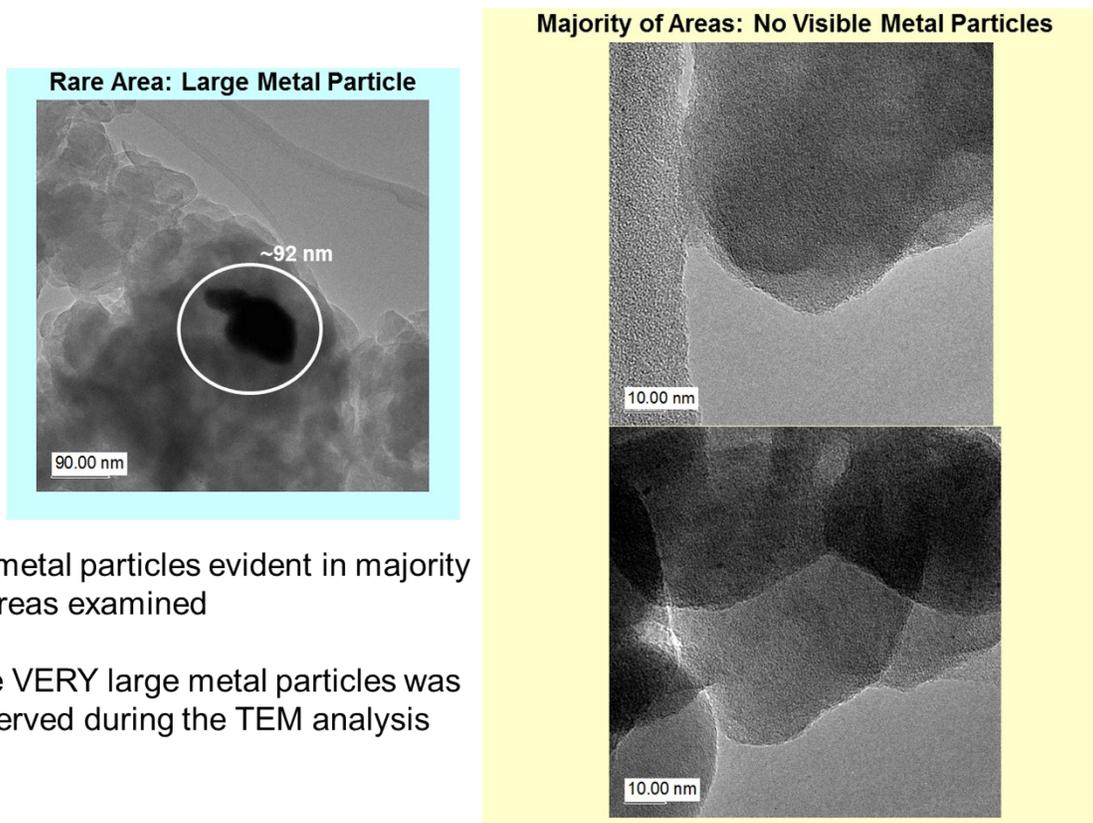


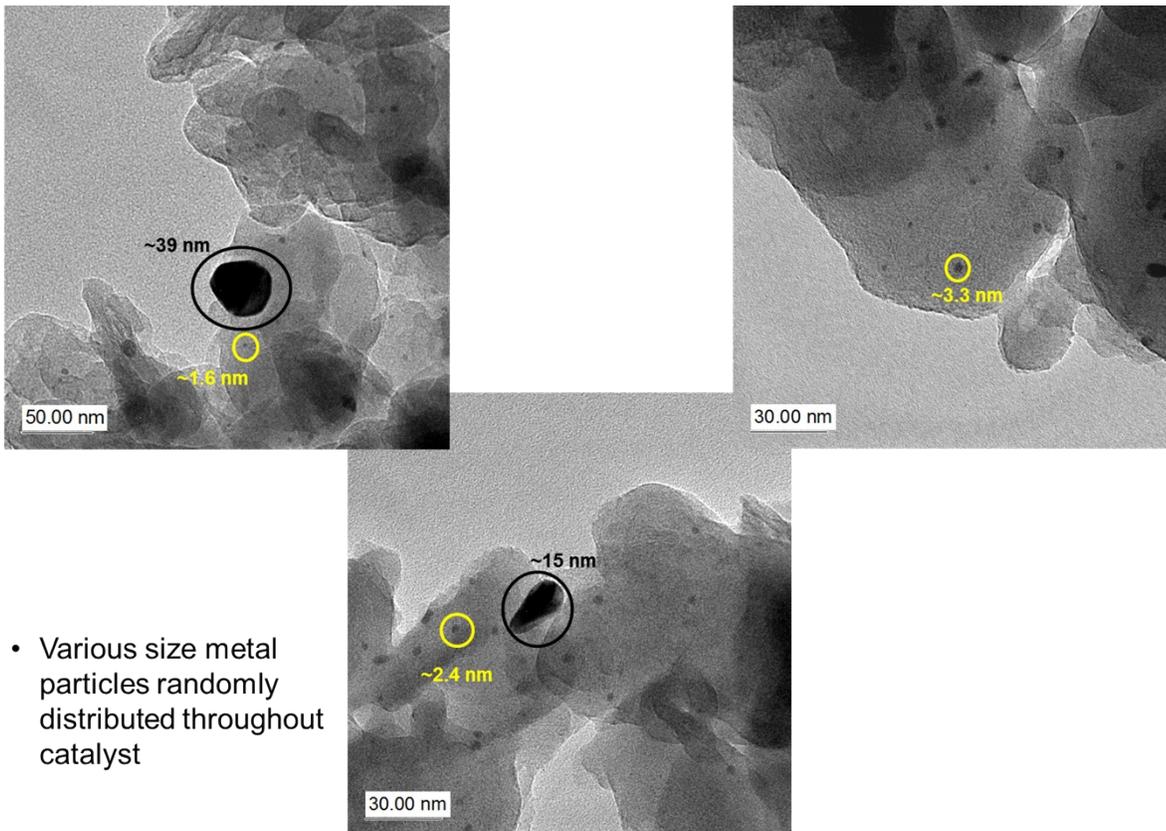
Figure S17. IR of the above sample sets, indicating no significant information can be revealed by IR to identify the presence of TA. IR does prove no obvious CO_3^{2-} present in the sample even though the sample was prepared in air when CO_2 is present.

We've also attempted some incipient method to produce the LDH starting from TA/LDH or the calcined version of TA/LDH. Both resulted in highly aggregated Au particles even at the initial loading of 1wt%.



- No metal particles evident in majority of areas examined
- One VERY large metal particles was observed during the TEM analysis

Figure S18. TEM of sample 26688-74B3. This sample starts from TA/LDH followed by incipient wetness of Au with the goal to make 1wt% loading. Resulting TEM images indicate that a highly aggregated Au - 92nm occur.



- Various size metal particles randomly distributed throughout catalyst

Figure S19. TEM of sample 26688-74C2. This sample starts from TA/LDH followed by 400C calcination to make LDO , which is followed by incipient wetness of Au with the goal to make 1wt% loading. Resulting TEM images indicate that a highly aggregated Au - 39 -15 nm occur. Note that anion exchange from Mg₂Al-NO₃ or Mg₂Al-CO₃ LDH were also attempted. Even though 1wt% Au was aimed, only less than 0.06wt% Au was actually grafted. Once again, expanding the interlayer d spacing is essential to obtain well disperse Au precursor and hence well disperse Au particles after reduction at elevated temperatures.

Table S1. CO oxidation TOF (Au% is based on XRF analysis) calculation

Take Sample 26688-51F with 62.8% Au loading as an example. We load the reactor 0.10 g of the pelletized catalyst, at a XRF analysis confirmed weight loading of 62.8%, we have $0.1/0.628/197 \times 10^6 = 318.782$ micromolar Au in the reactor system.

For all CO oxidation measurements, a flow comprising 0.45 vol % carbon monoxide, 2.8 vol % oxygen, and balance nitrogen (99.99% purity) was established to the catalyst at 0.1 std. L/min. and at ambient pressure. That means the flow rate of CO in micromolar/second is $0.1/60/22.4 \times 0.0045 \times 10^6 = 0.335$ micromolar/second.

The reactor temperature was stabilized at room temperature and set to run to 110, 170, and 230C. In this particular case, the actual temperature reading in each step is 23C, 118C, 165C and 222C correspondingly. At each temperature, the total conversion of CO was measured by GC (Agilent 7890) and it is at 0%, 27.2%, 77.0% and 100% at each temperature in this example. As a result the reaction rate is calculated to be total "CO flow rate at micromolar/second" x Conversion percentage / per gram of Au in micromolar. So at 165C, 77% conversion, we have $0.335 \times 0.77/318.782 = 0.000808$

We applied the same methods to 26688-117B series and obtained all calculated numbers below in Table S1.

26688-51F	Au/HT	Unit	Temp	Conv	Rate
Wt. cat	0.100	g	23.000	0.000	0.000000
Au loading	0.628		118.000	0.272	0.000286
Au loading	318.782	umol Au	165.000	0.770	0.000808
CO flow rate	0.335	umol CO/s	222.000	1.000	0.001050

26688- 117B-1	Au/HT		Temp	Conv	Rate
80 C calcine			23.000	0.012	0.001600
Wt. cat	0.100	g	71.000	0.015	0.001989
Au loading	0.005		123.000	0.033	0.004346
Au loading	2.284	umol Au	186.000	0.225	0.029749
CO flow rate	0.335	umol CO/s	248.000	1.000	0.132184
26688-117B-1	Au/HT		Temp	Conv	Rate
250 C calcine			23.000	0.005	0.000612
Wt. cat	0.100	g	71.000	0.005	0.000672
Au loading	0.005		123.000	0.020	0.002580
Au loading	2.284	umol Au	186.000	0.218	0.028881
CO flow rate	0.335	umol CO/s	248.000	1.000	0.132184
26688-117B-1	Au/HT		Temp	Conv	Rate
400 C calcine			23.000	0.004	0.000532
Wt. cat	0.100	g	71.000	0.008	0.001017
Au loading	0.005		123.000	0.032	0.004201
Au loading	2.284	umol Au	186.000	0.152	0.020099
CO flow rate	0.335	umol CO/s	248.000	1.000	0.132184

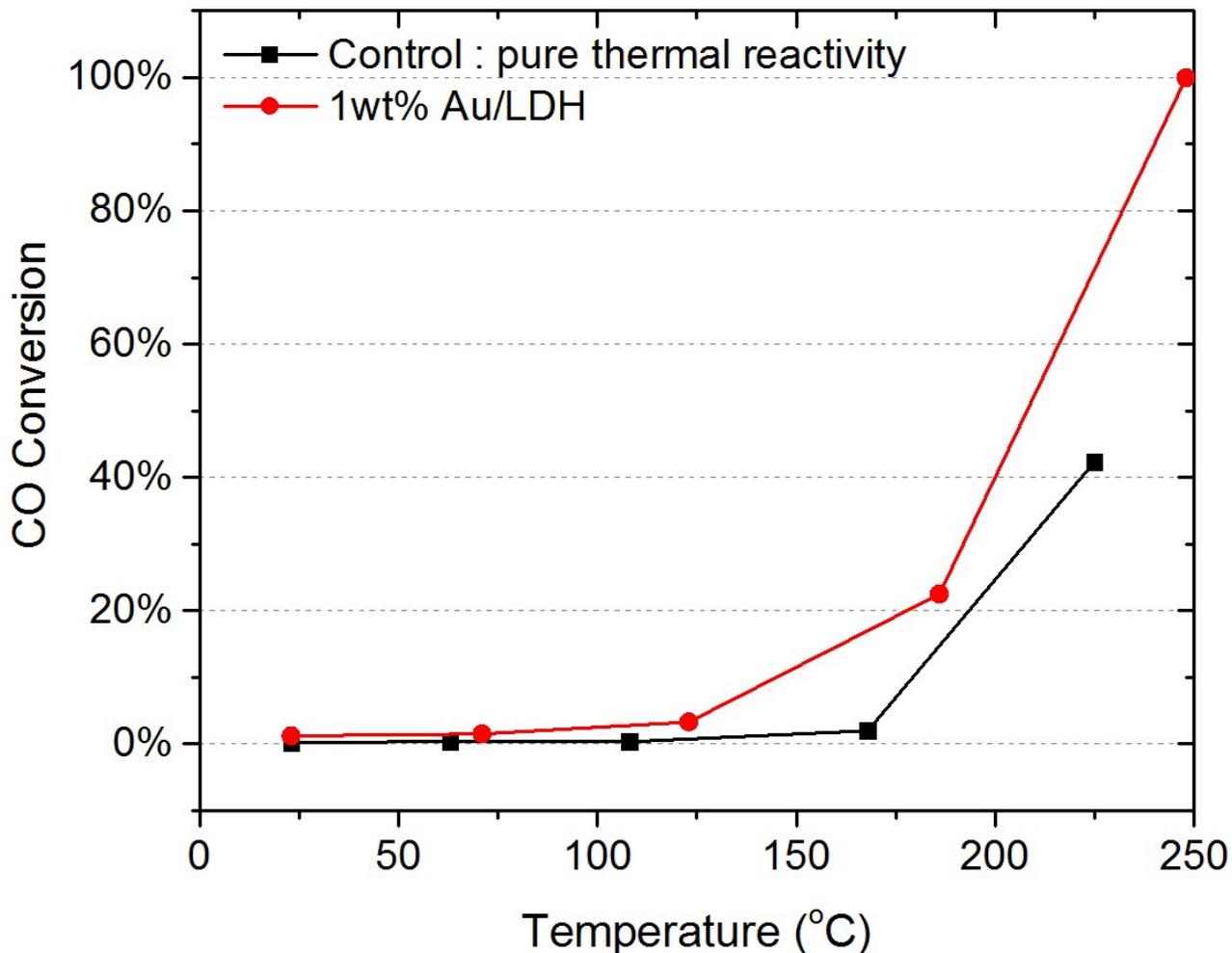


Figure S20. CO conversion as a function of temperature for the 1wt% loading Au/LDH sample.

If we plot the turnover frequency as a function of temperature, we obtain a similar curve like this below for the three ~1% sample (XRF and liquid supernatant elemental analysis confirmed the Au content is actually between 0.39% to 0.61%). As expected, at low conversion level (lower temperature), the TOF remains from 0.0006 to 0.0019/sec with the 80°C sample having the highest TOF. This is consistent with our TEM results which indicates the 80°C sample has the most well disperse Au nanoparticles, see Figure S10. Also the color of the 80°C samples remains white, while 250°C and 400°C sample starts to appear to be greyish indicating particle growth again.

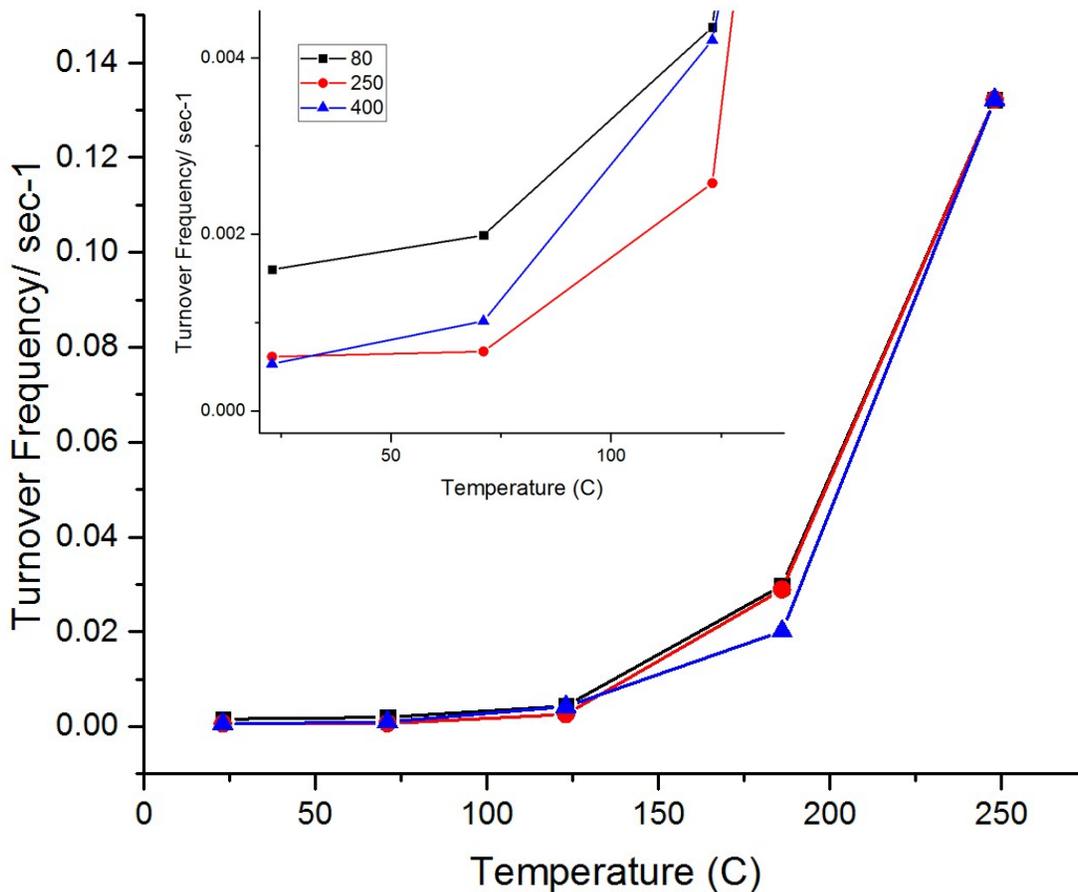


Figure S21. CO conversion TOF as a function of temperature for the 1wt% loading Au/LDH sample.

It is challenging to compare TOF for different samples that has a dramatically difference in its conversion at a given temperature as well as a different dispersion in supported heterogeneous catalysis.

At the same temperature around 120 C, our 62.8% Au/LDH sample achieve a CO conversion around 27.2% versus the 1%Au/LDH sample is only at 3%. This data indicates our high loading Au is a more active catalyst by total sample weight. Considering the volume is set by the support, we anticipated an even higher activity by sample volume.

To directly compare TOF, even if we assume the particle size are exactly the same, it will require us to keep it at the same temperature, and vary the CO flow rate to achieve the same conversion for the two catalyst. Unfortunately, this detail studies was not done. It was a conscious choice because in addition to the conversation being different, we are also talking about two drastically different Au loading as well as their particle size distribution. Hence we chose to factually report the particle size differences among the two catalyst and their TOF, conversion respectively, without directly comparing them in the main manuscript.

Majority of Areas: Relatively Small Metal Particles

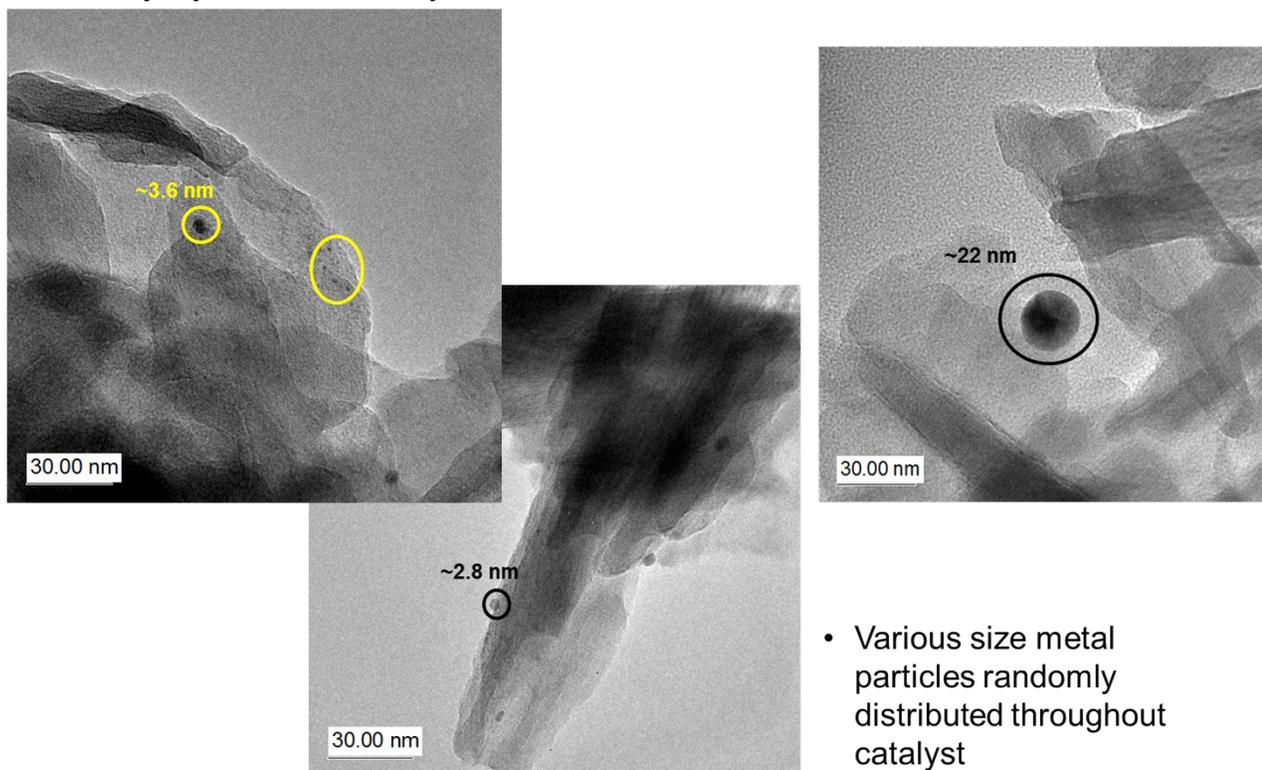


Figure S22. TEM of sample 26688-74C3. This sample starts from CO₃/LDH followed by incipient wetness of Au with the goal to make 2.1wt% loading. Resulting TEM images indicate that a highly bimodal distribution of Au <3nm or >22 nm occur.