APENDIX A

Experimental Data

A.1 Catalyst Preparation

PVA Protection Method

Example of 20% Au of Au/C catalyst preparation was discussed below;

Catalysts 100 mg contain → 20 mg of Au
→ 80 mg of carbon

	Au	0.5	mg	was obtained from	$HAuCl_4$	1	mg
Thus,	Au	20	mg	was obtained from	$HAuCl_4$	40	mg

40 mg of $HAuCl_4$ was weighed out and dissolved in 181.8 ml of water to obtain 110 µg/ml .

Next, 100 mg of PVA was weighed out and dissolved in 5 ml of water, and then about 0.2 ml was dropped into $HAuCl_4$ solution (2 %wt of PVA).

$NaBH_4$ were used with the mole ratio of $NaBH_4$:Au (4:1);$NaBH_4$ 0.1M was prepared by weighed out 0.0189 g and then dissolved in 5 ml of water. After that 4.7 ml of $NaBH_4$ was added dropwise in $HAuCl_4$ solution. The amounts of every component for preparing 20, 30 and 40 wt% Au/C were summarized in Table A.1, A.2 and A.3, respectively.

Table A.1 The amount of substances used in preparing 20 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	40	181.8	-
2. Carbon	80	-	-
3. PVA	100	5	0.2
4. $NaBH_4$	0.0189	5	4.7

Table A.2 The amount of substances used in preparing 30 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	60	272.7	-
2. Carbon	70	-	-
3. PVA	100	5	0.3
4. $NaBH_4$	0.0378	10	7.05

Table A.3 The amount of substances used in preparing 40 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	80	363.6	-
2. Carbon	60	-	-
3. PVA	100	5	0.4
4. $NaBH_4$	0.0378	10	9.4

Citrate Protection Method

Table A.4 The amount of substances used in preparing 20 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	40	381	-
2. Carbon	80	-	-
3. tri-potassium citrate	44	4	4
4. tri-potassium citrate $NaBH_4$	0.0189 44	5	4.7

Table A.5 The amount of substances used in preparing 30 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	60	571.43	-
2. Carbon	70	-	-
3. tri-potassium citrate	66	6	6
4. tri-potassium citrate $NaBH_4$	0.0378 132	10	7.05

Table A.6 The amount of substances used in preparing 40 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	80	762	-
2. Carbon	60	-	-
3. tri-potassium citrate	88	8	8
4. tri-potassium citrate $NaBH_4$	0.0378 176	10	9.4

A.2 Results of Atomic Absorption Spectroscopy

Table A.7 Results of AAS and calculation of Au deposition on carbon support

Catalyst	AAS_{result} (mg/L)	filtrate volume (ml)	Au_{Total} (g)	Au_s (g)	Support (g)	$\%Au_{deposited}$
PVA method						
20% Au/untreated C	n.d.	197	0.02	0.0200	0.08	20.00
20% Au/treated C	n.d.	186	0.02	0.0200	0.08	20.00
30% Au/treated C	11	280	0.030	0.0270	0.07	27.81
40% Au/treated C	48.2	408	0.042	0.0226	0.06	27.35
Citrate method						
20% Au/untreated C	n.d.	387	0.02	0.0200	0.08	20.00
20% Au/treated C	n.d.	407	0.02	0.0200	0.08	20.00
30% Au/treated C	0.47	575	0.03	0.0296	0.0698	29.80
40% Au/treated C	5.9	780	0.04	0.0354	0.06	37.11

A.3 Transmission Electron Microscopy (TEM) image

There are many TEM images of each catalyst captured by National Metal and Materials Technology Center (MTEC). TEM images of each catalyst were taken at three magnifications, 40,000x, 100,00x and 200,000x.

PVA protection method

1. 20% Au/ untreated Carbon

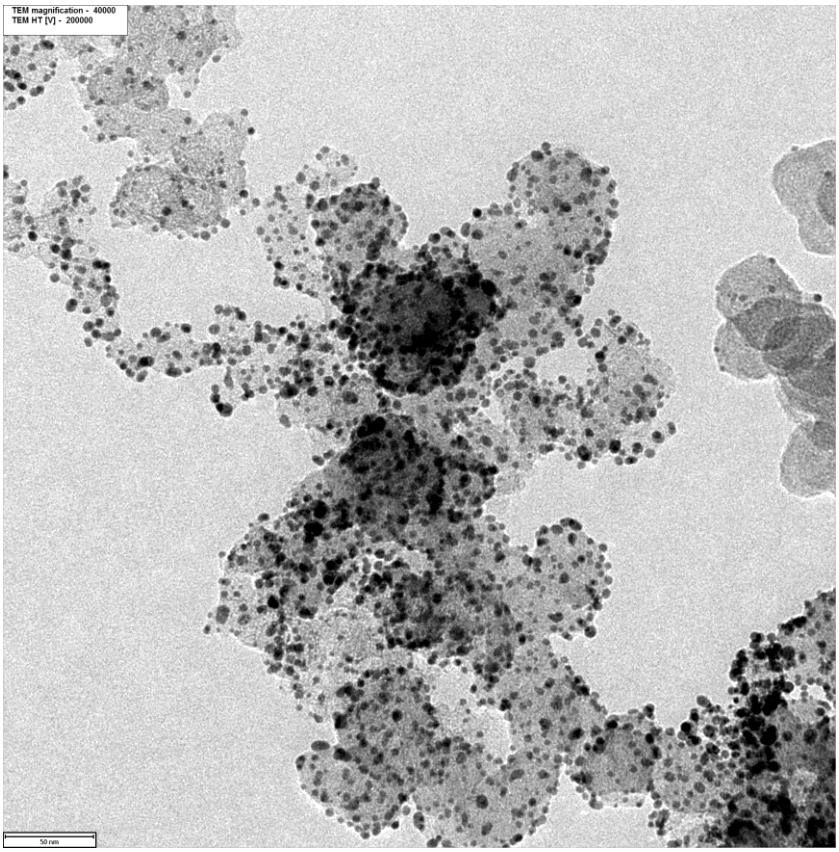
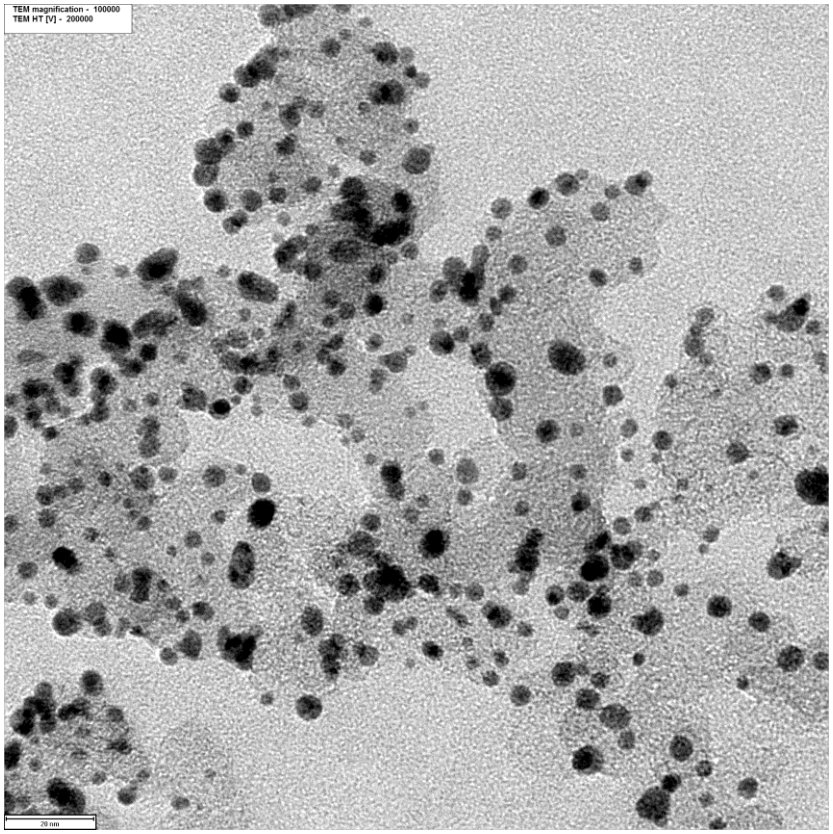
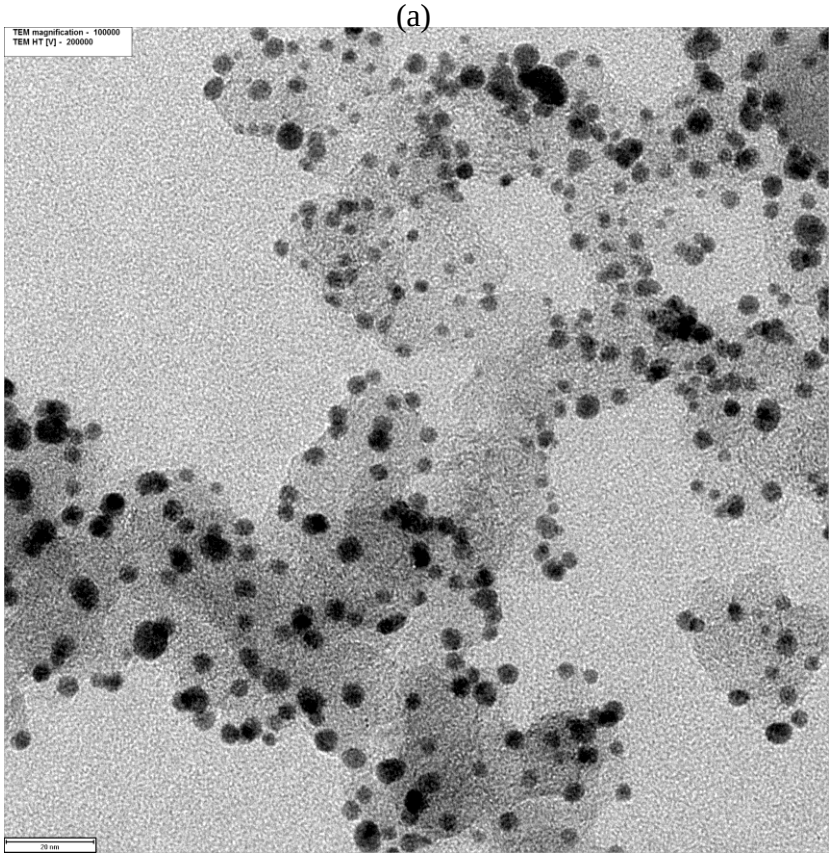


Figure A.1 TEM image at magnification of 40,000x. of 20 wt% Au on untreated carbon

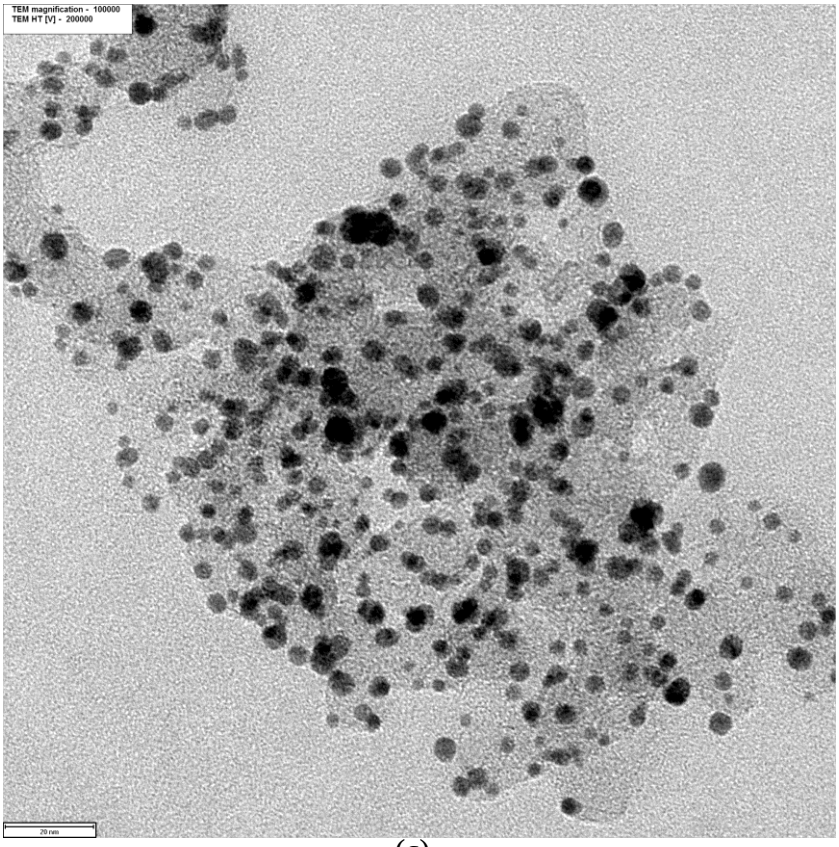


(a)

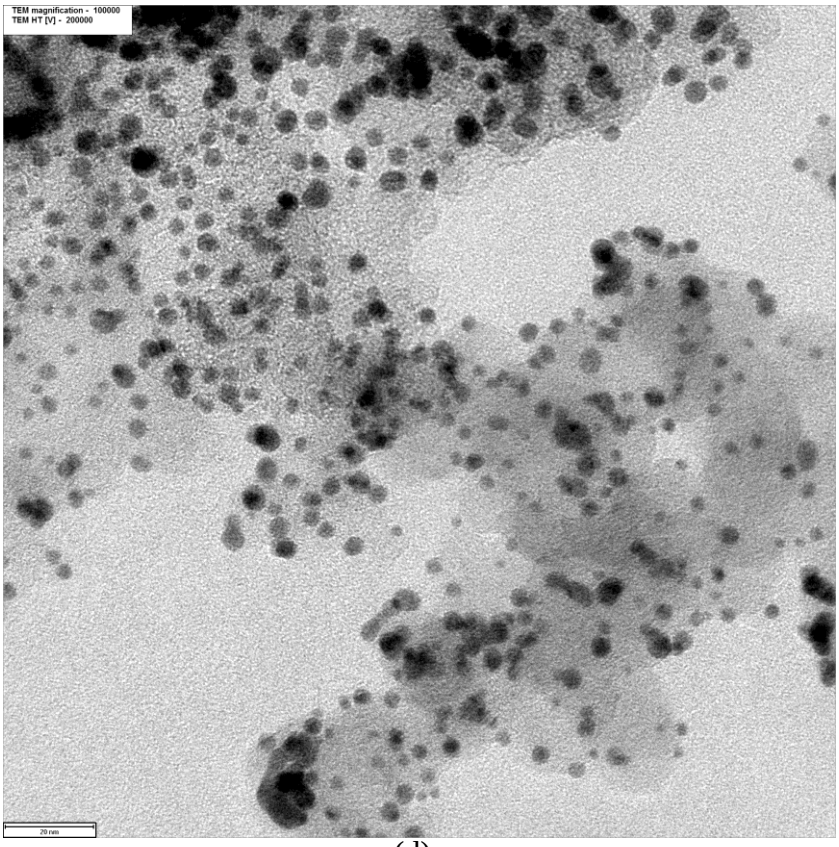


(b)

Figure A.2 (a)-(d) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon



(c)



(d)

Figure A.2 (a)-(d) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)

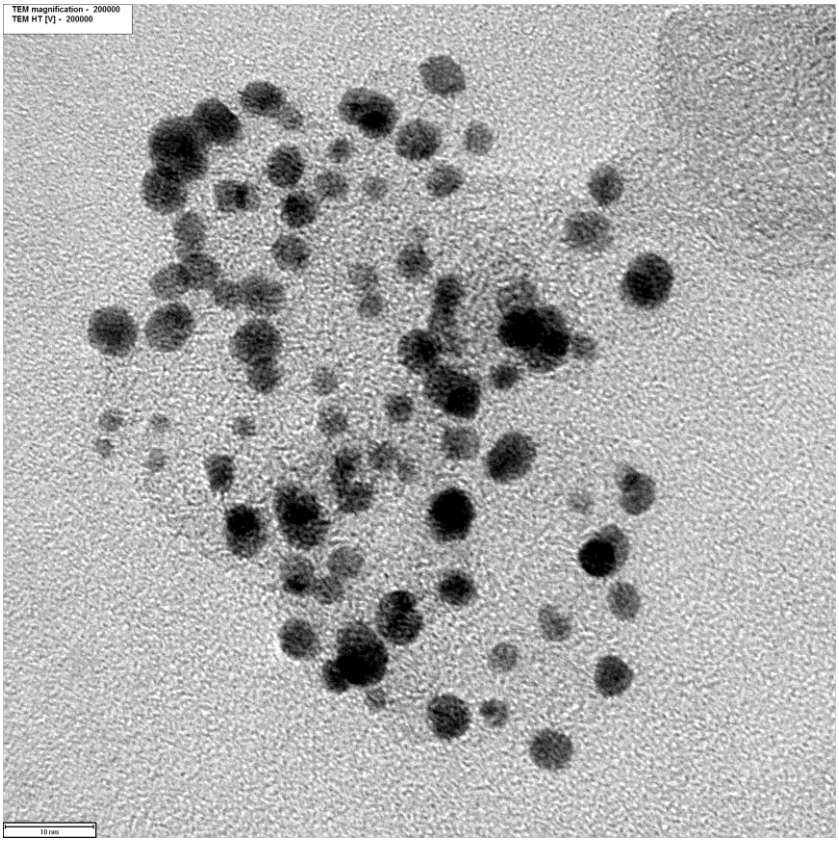
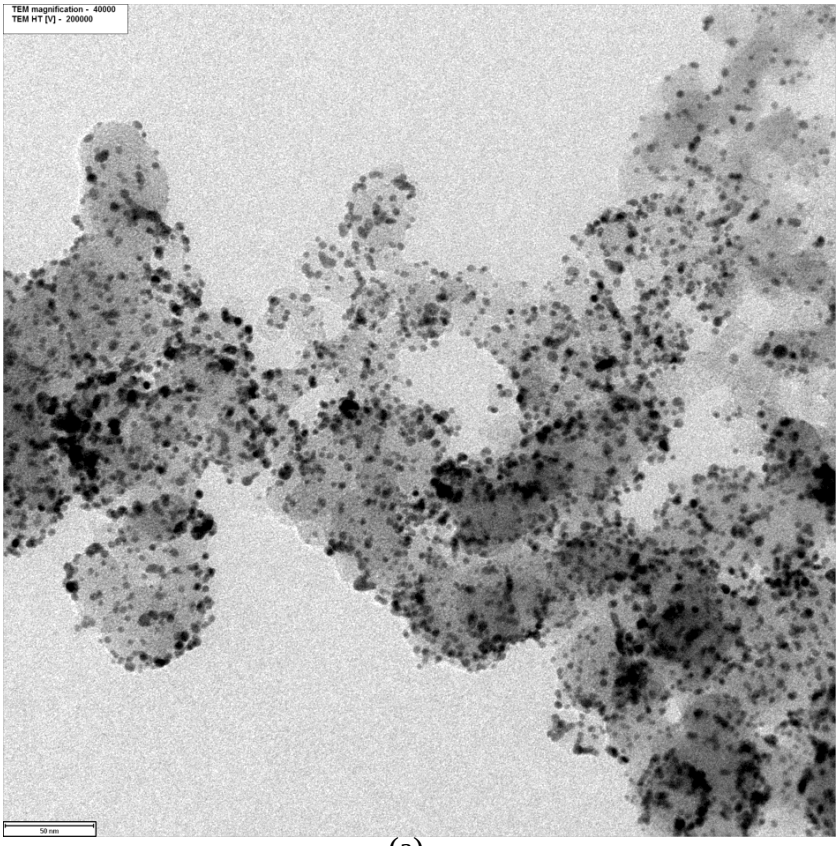
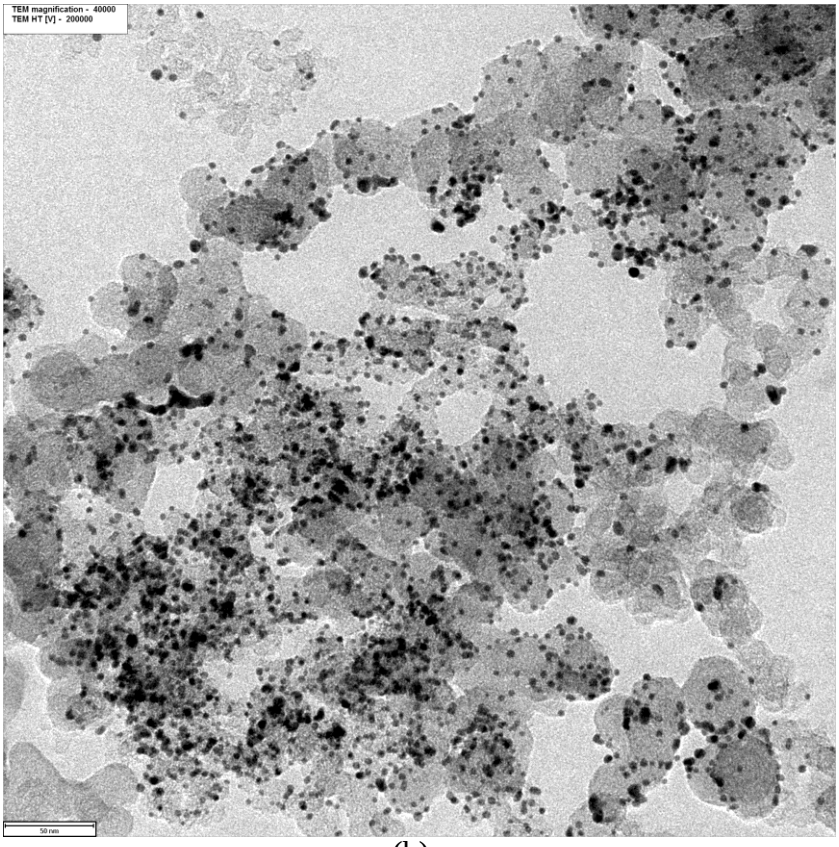


Figure A.3 TEM image at magnification of 200,000x. of 20 wt% Au on untreated carbon

2. 20% Au/ treated Carbon

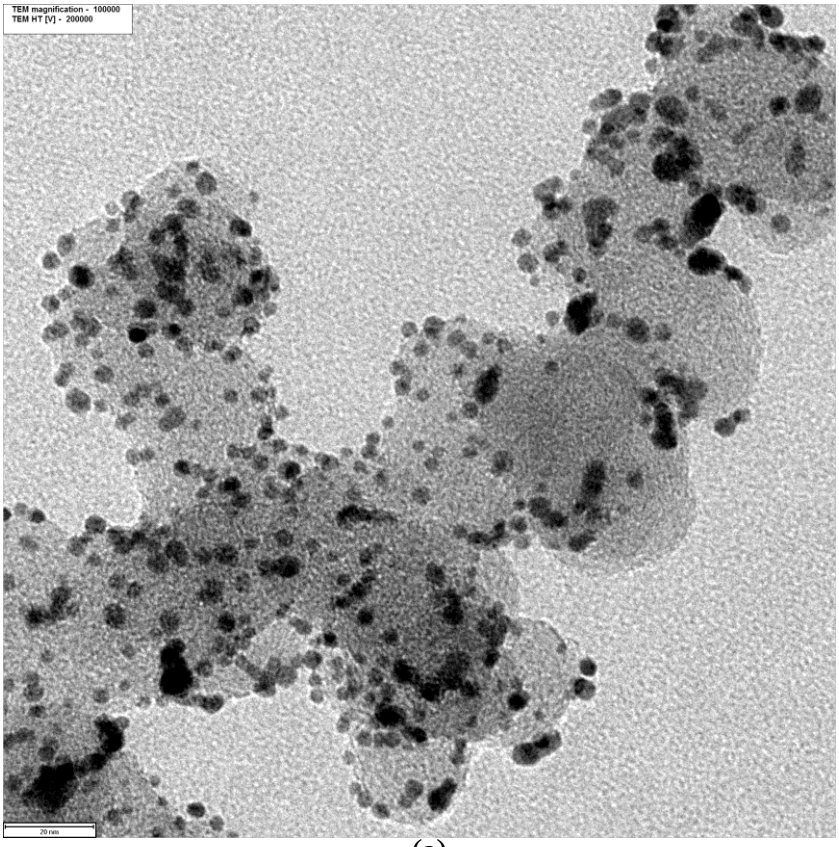


(a)

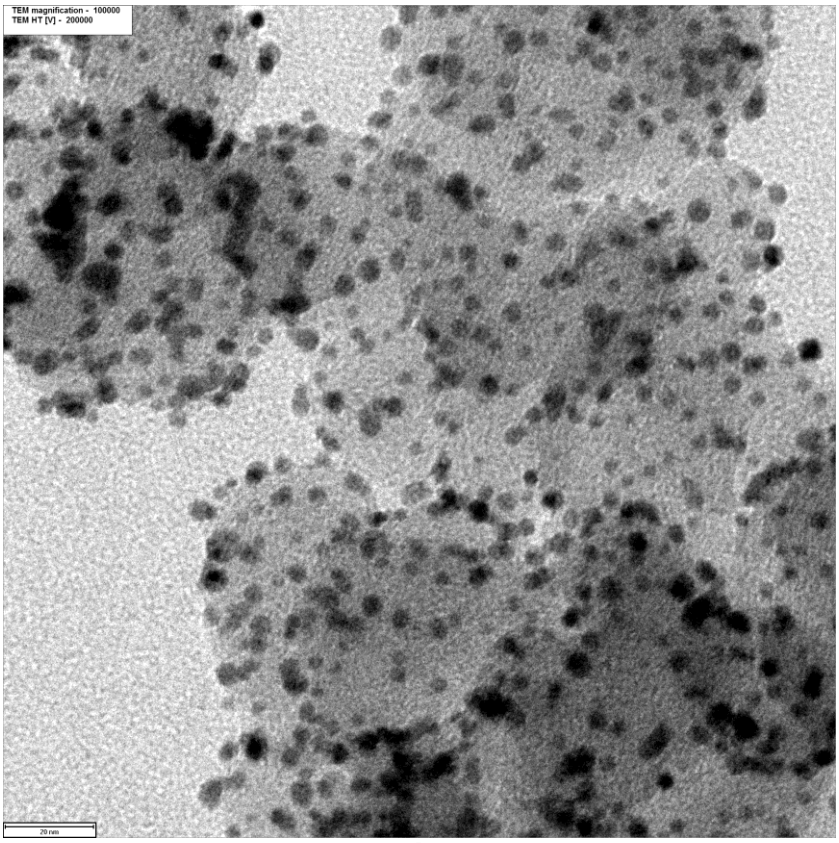


(b)

Figure A.4 (a)-(b) TEM image at magnification of 40,000x. of 20 wt% Au on treated carbon

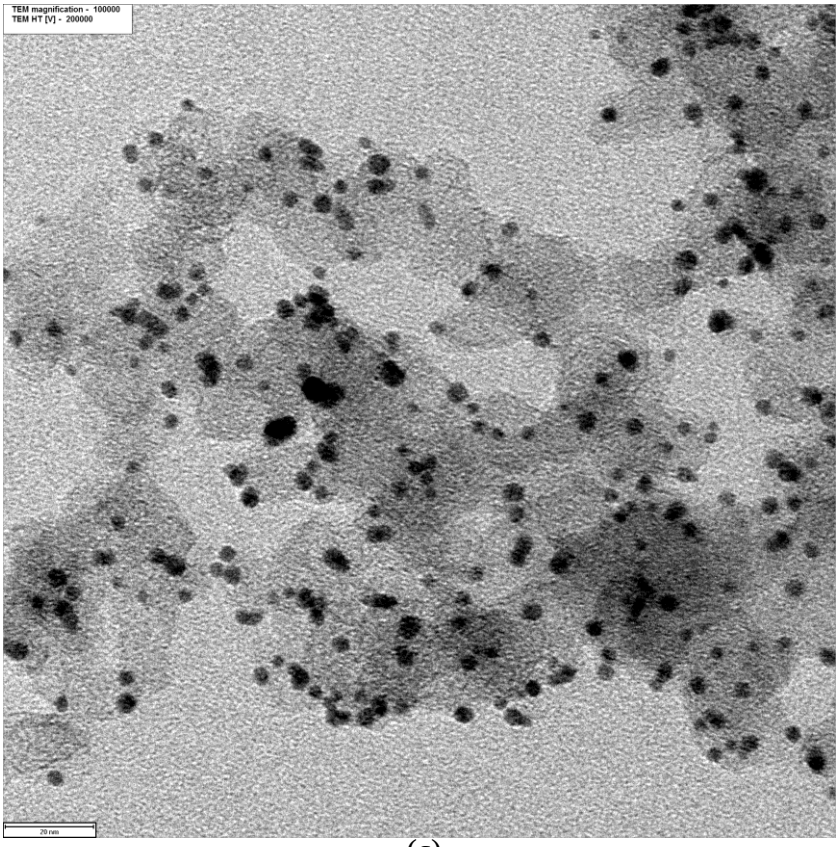


(a)

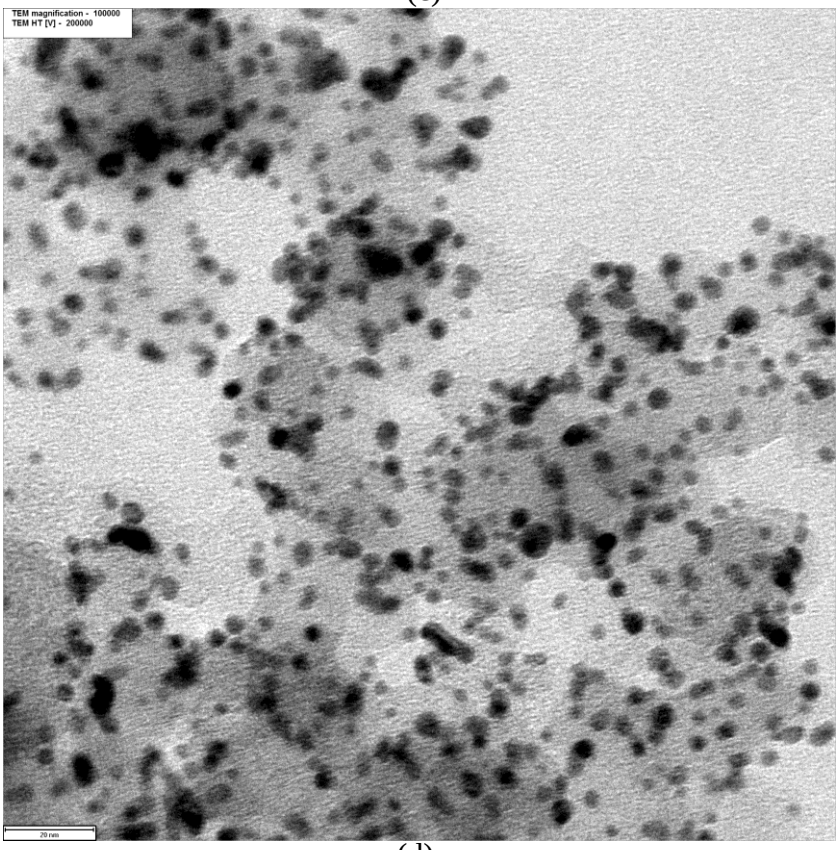


(b)

Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon

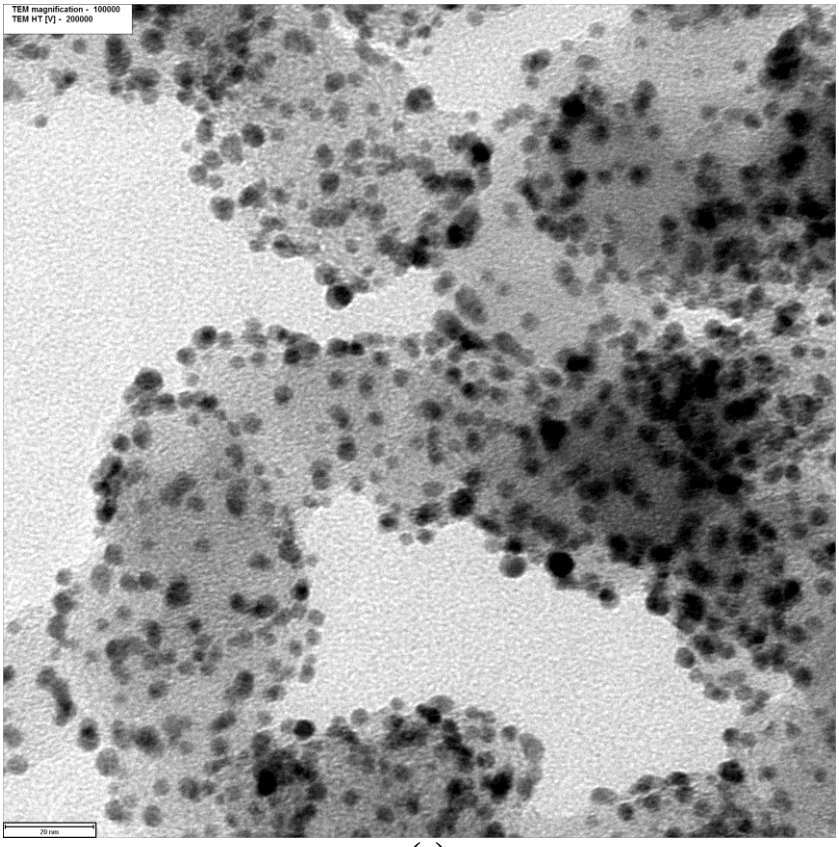


(c)



(d)

Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon (continue)



(e)

Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon (continue)

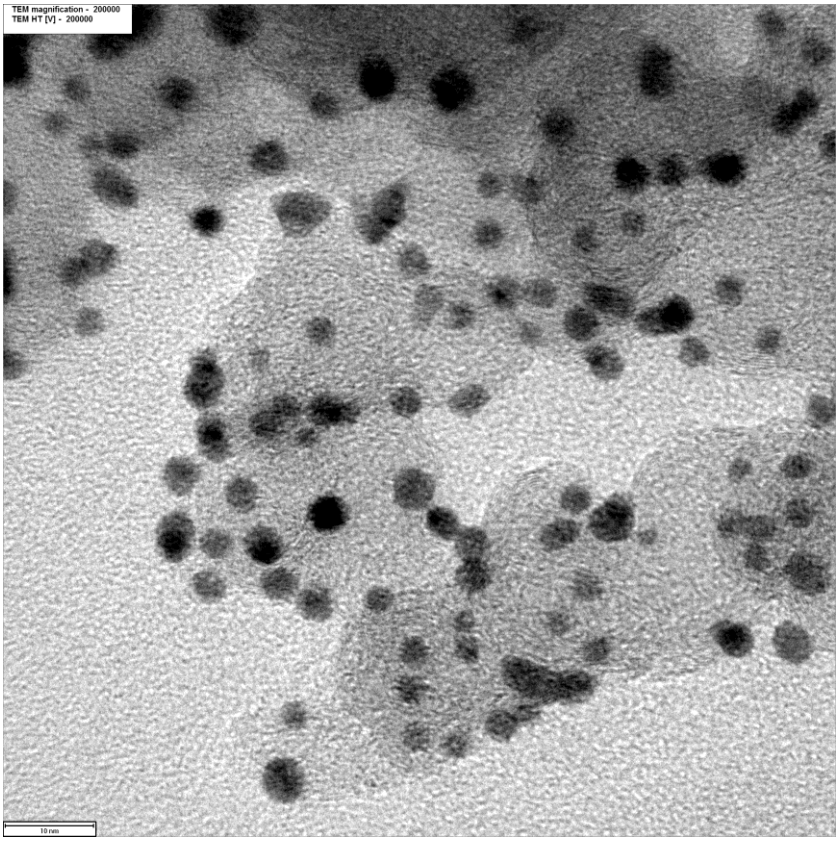
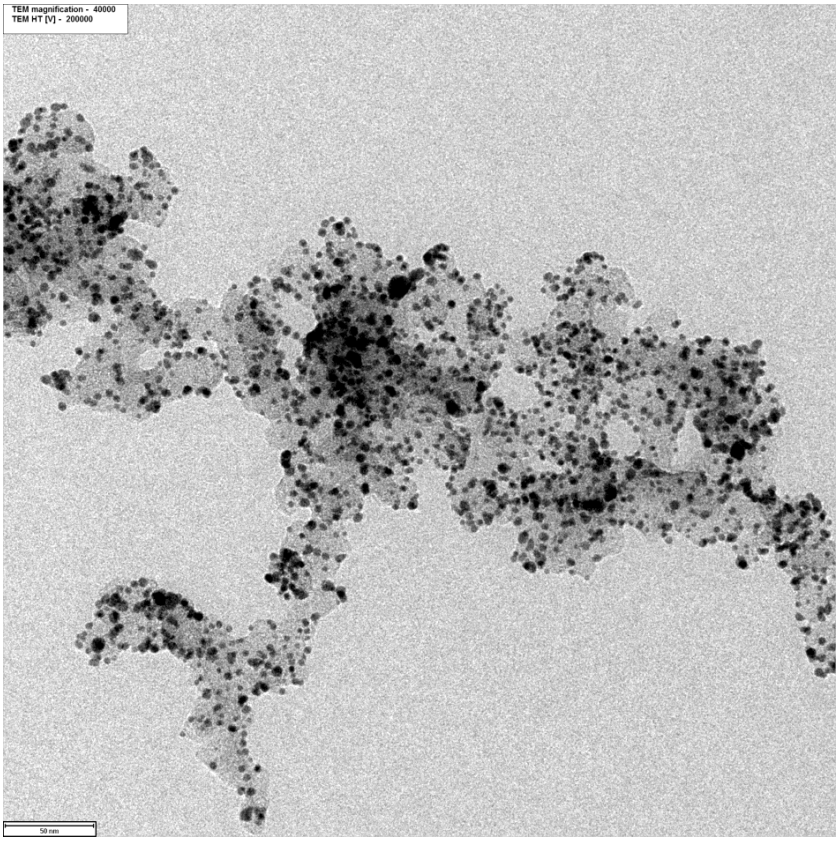
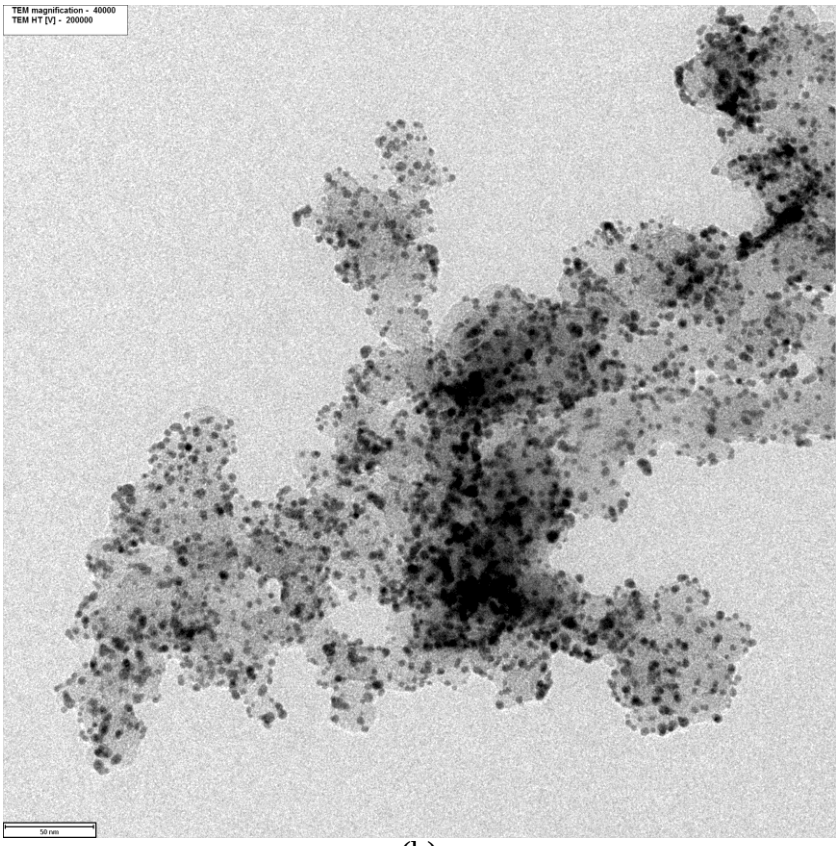


Figure A.6 TEM image at magnification of 200,000x. of 20 wt% Au on treated carbon

3. 30% Au/ treated Carbon

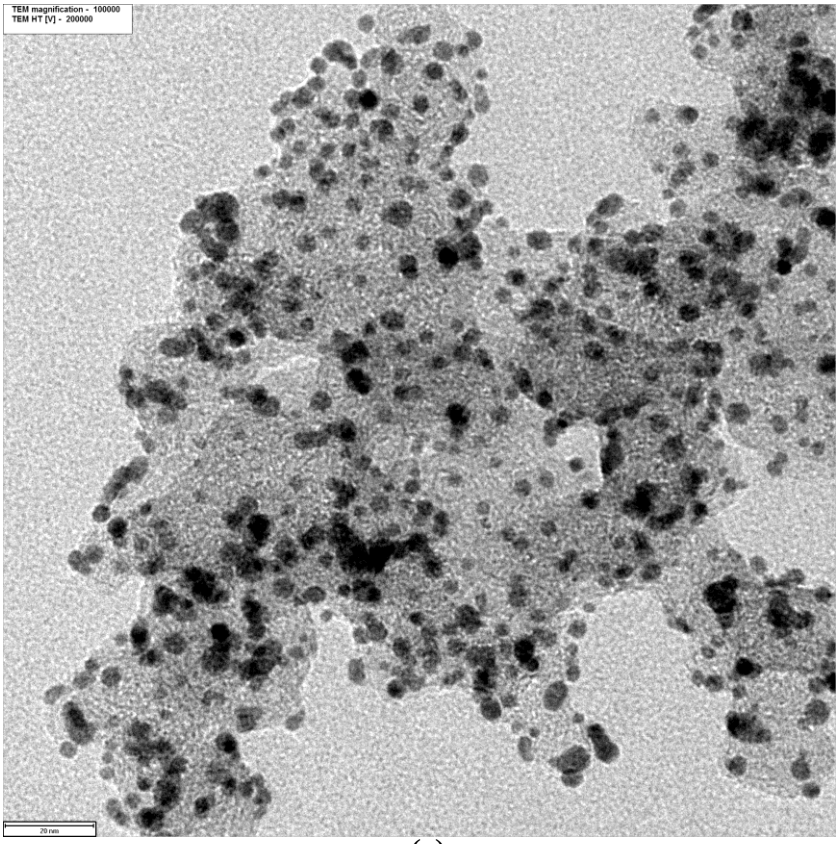


(a)

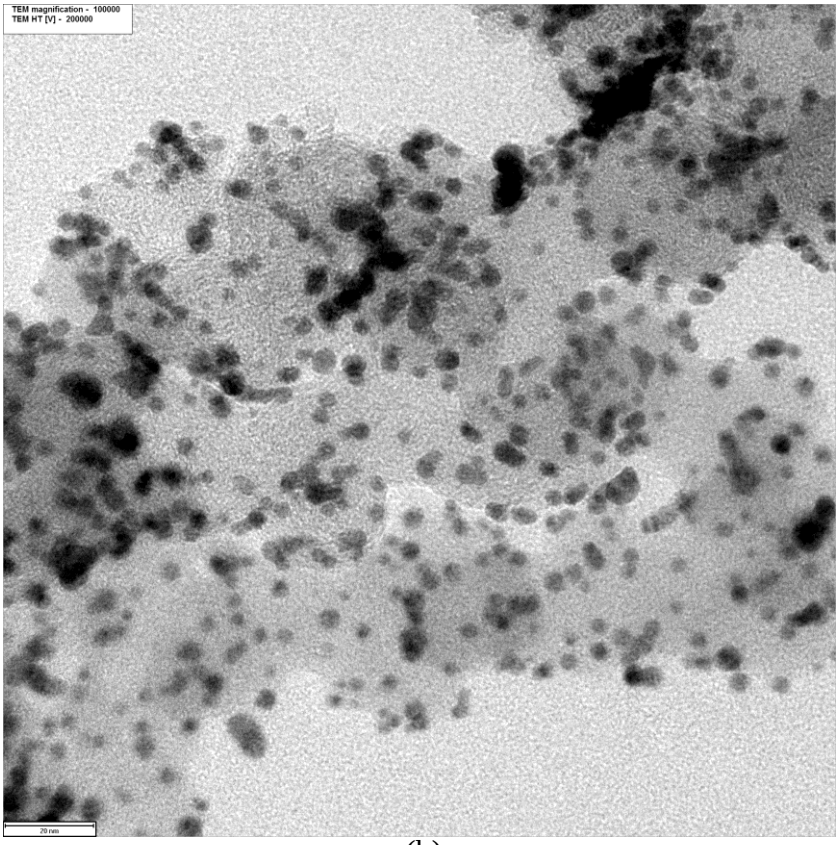


(b)

Figure A.7 (a)-(b) TEM image at magnification of 40,000x. of 30 %wt Au on treated carbon

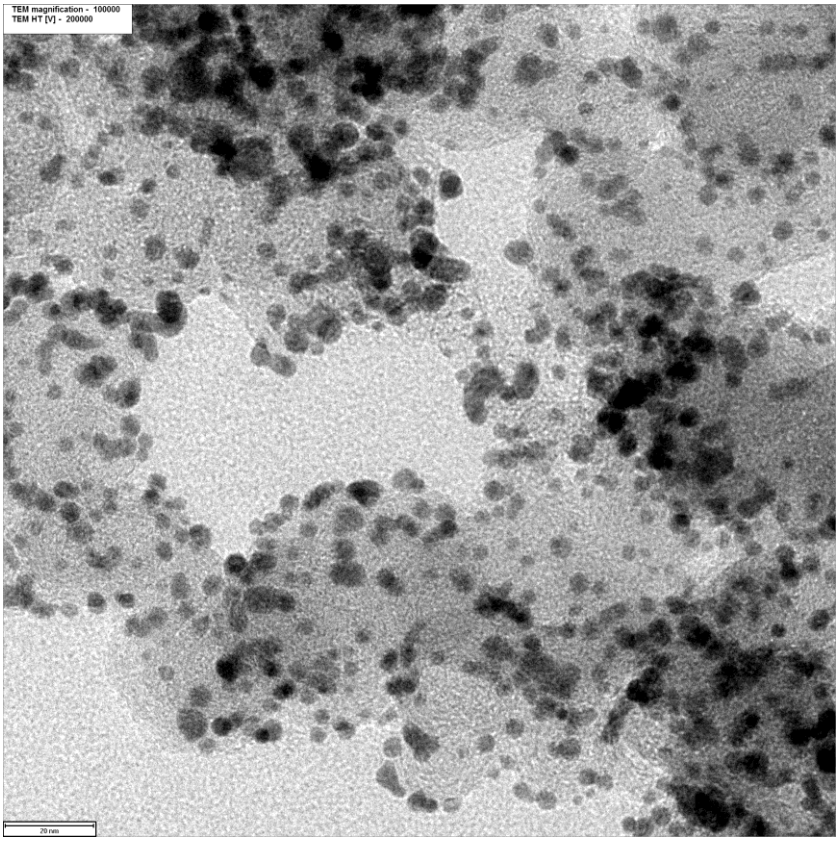


(a)

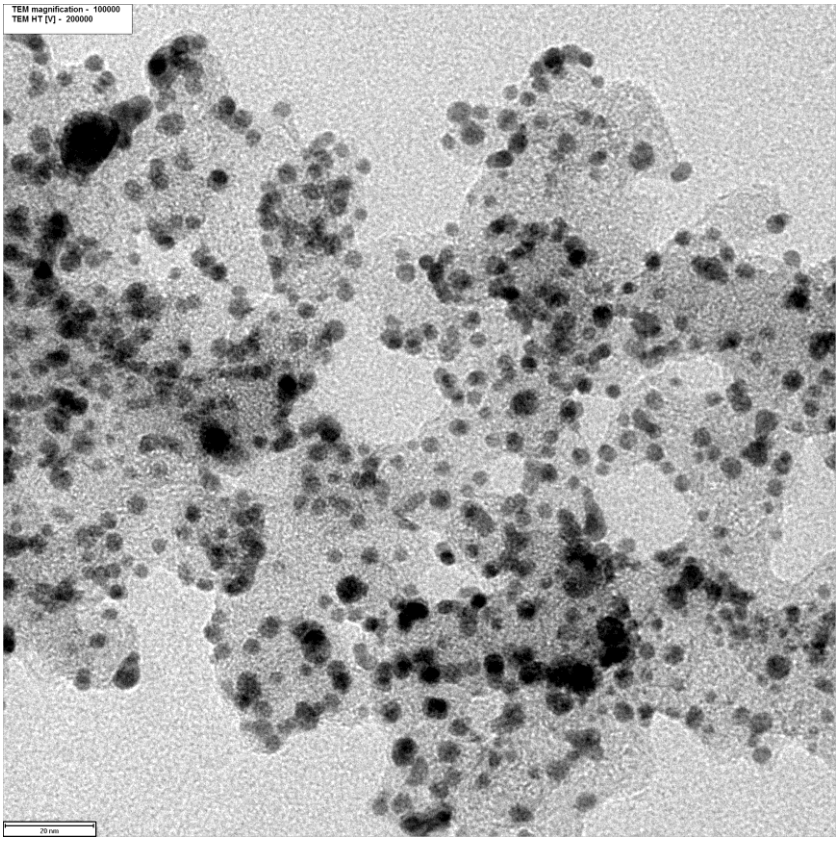


(b)

Figure A.8 (a)-(d) TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon

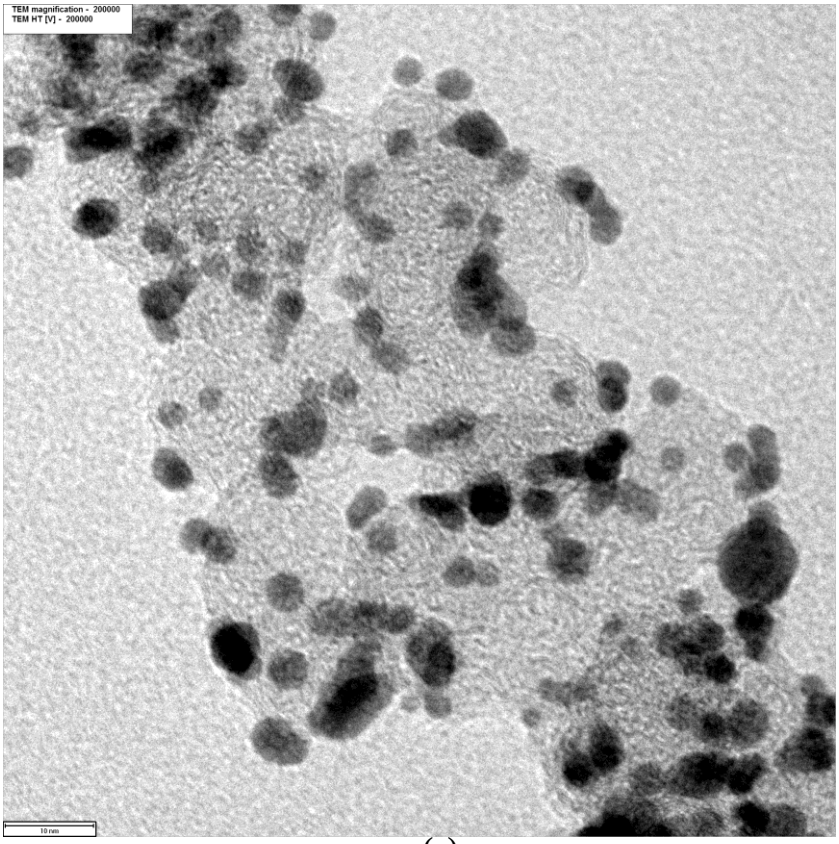


(c)

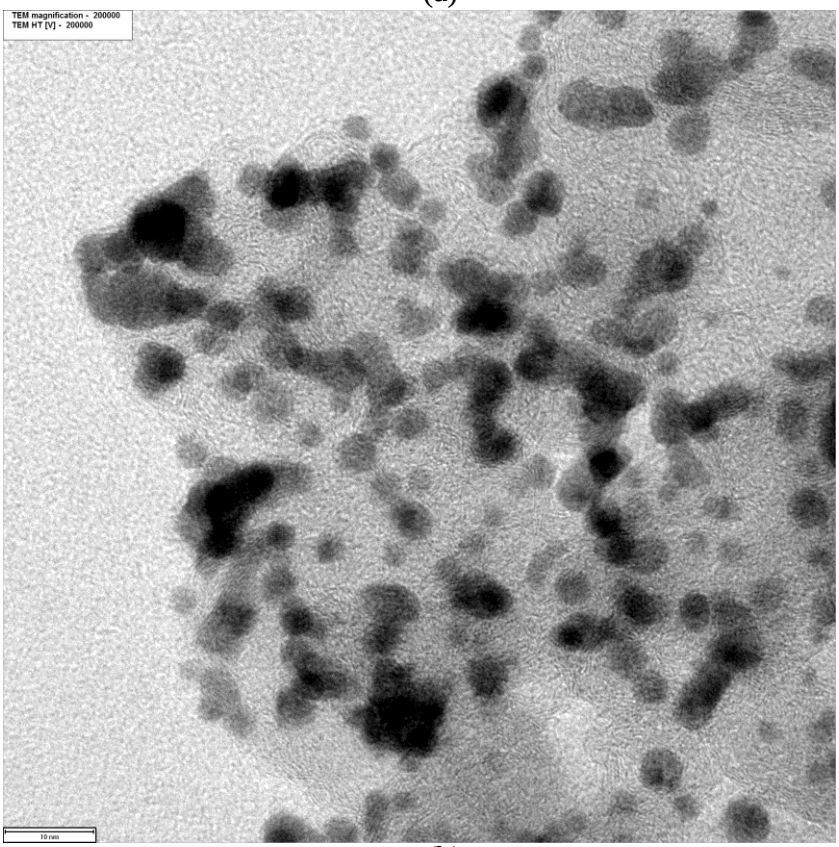


(d)

Figure A.8 (a)-(d) TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)



(a)



(b)

Figure A.9 (a)-(b) TEM image at magnification of 200,000x. of 30 wt% Au on treated carbon

4. 40% Au/ treated Carbon

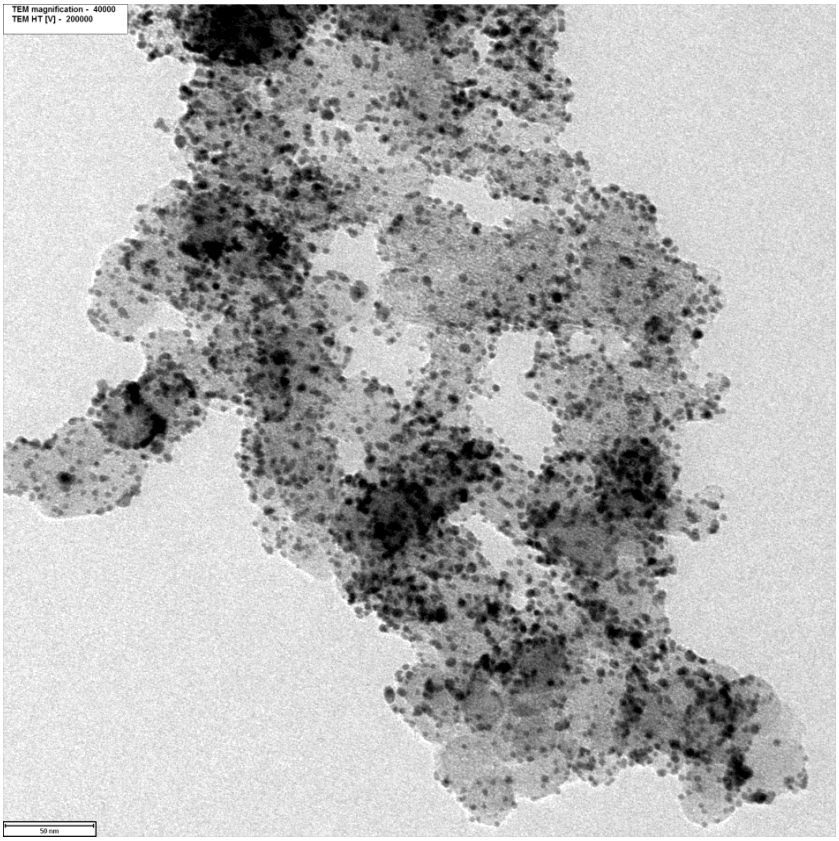
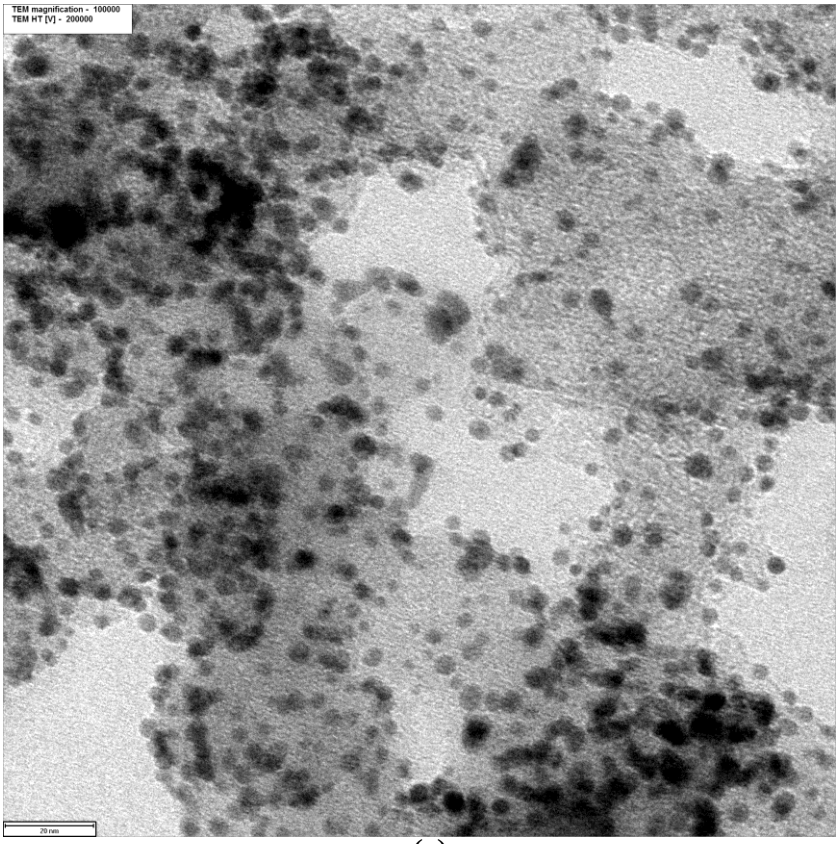
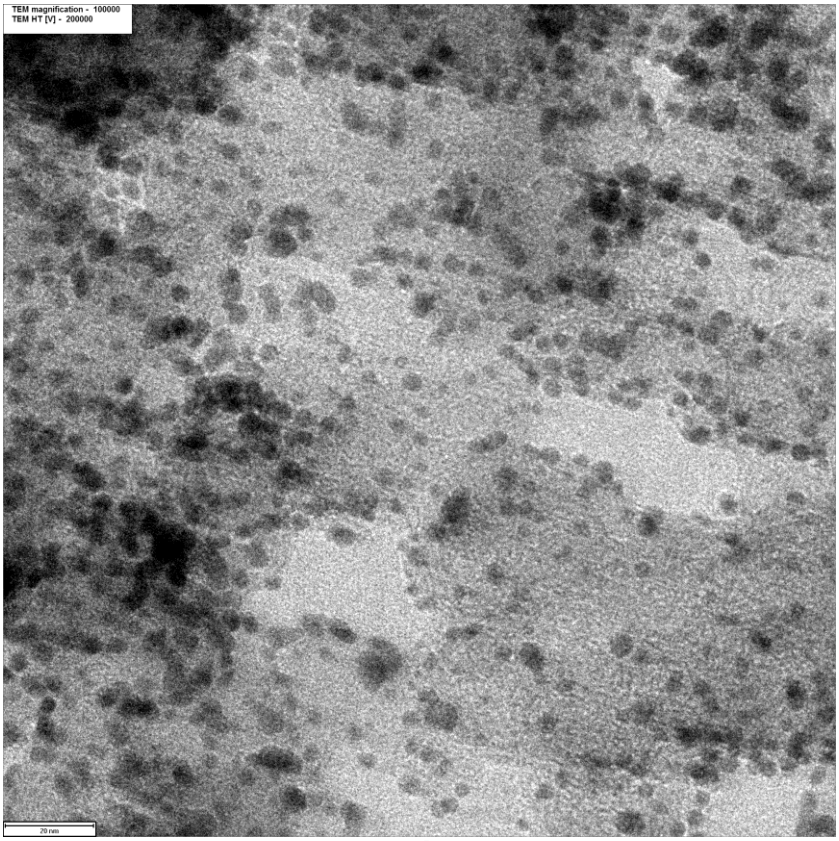


Figure A.10 TEM image at magnification of 40,000x. of 40 %wt Au on treated carbon

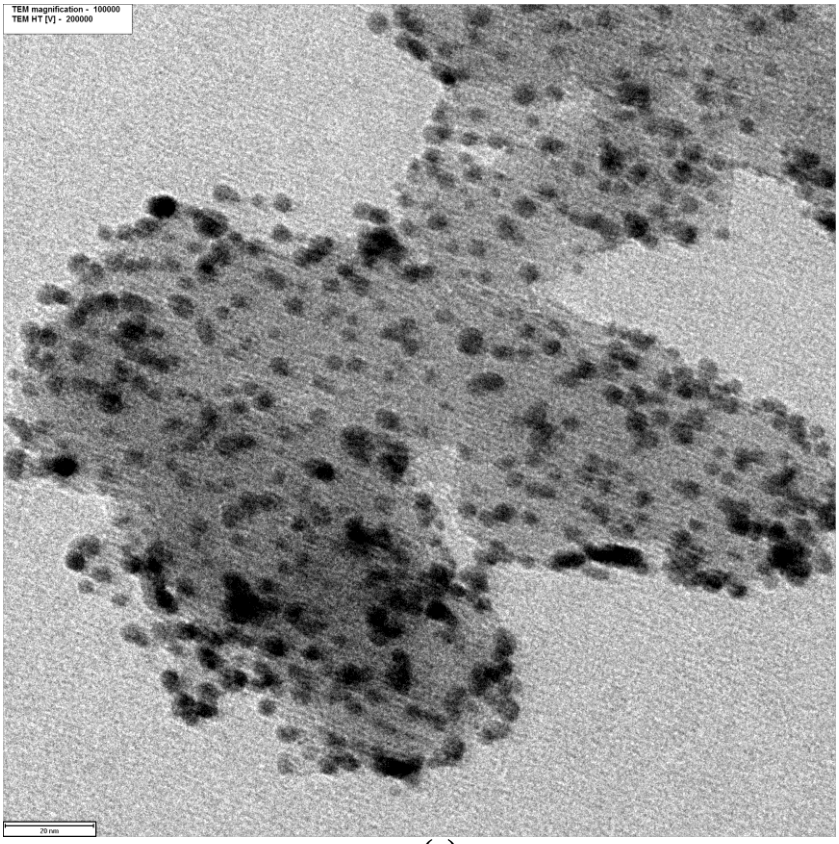


(a)

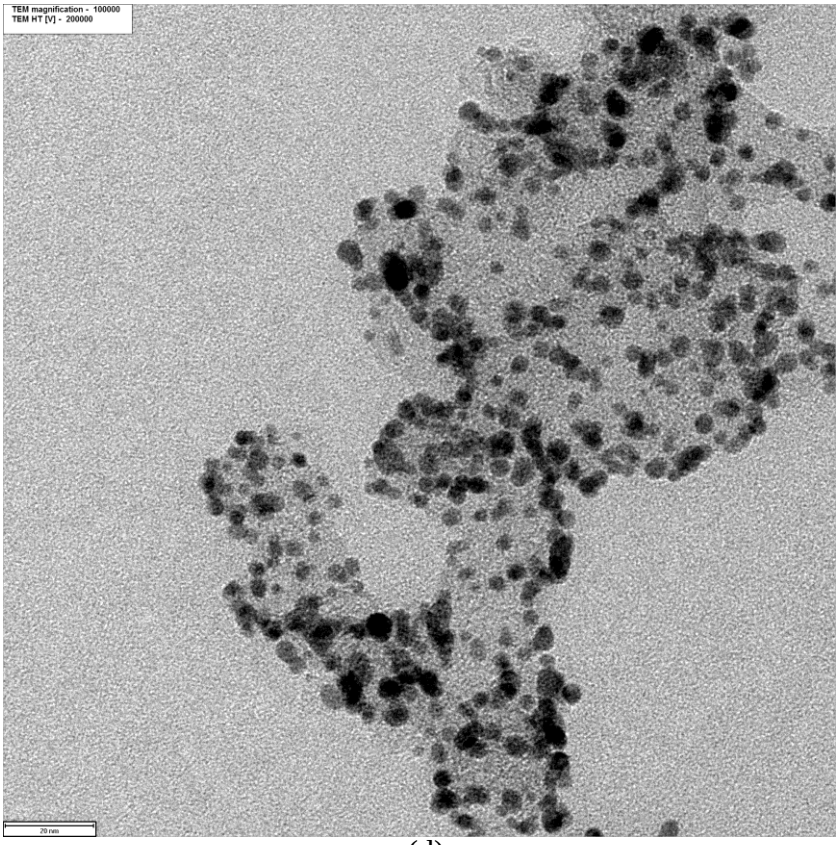


(b)

Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon

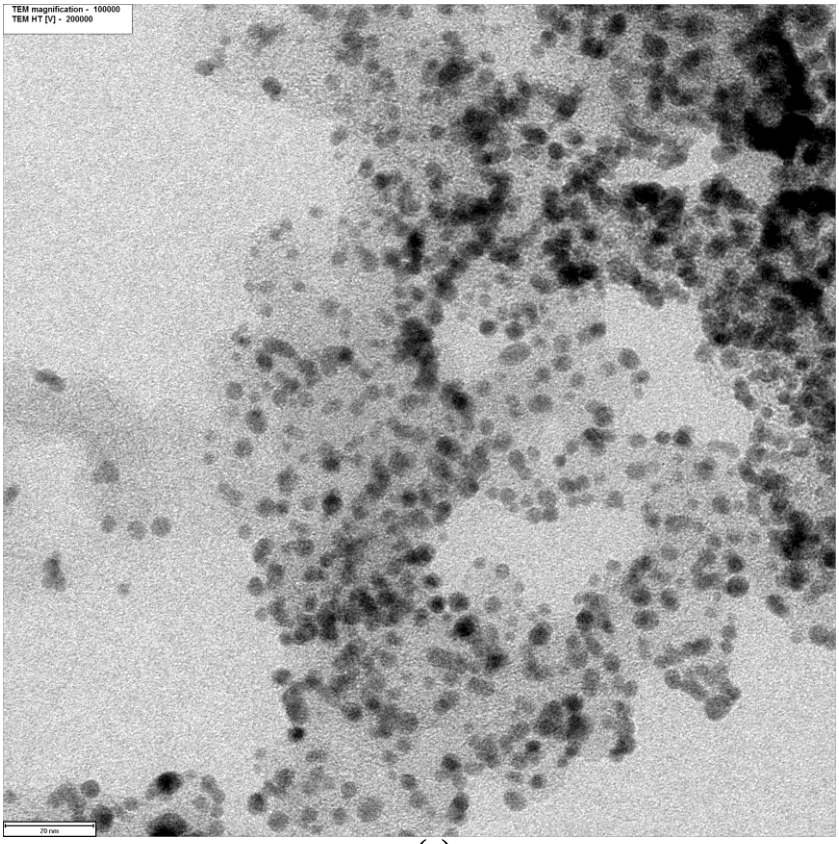


(c)

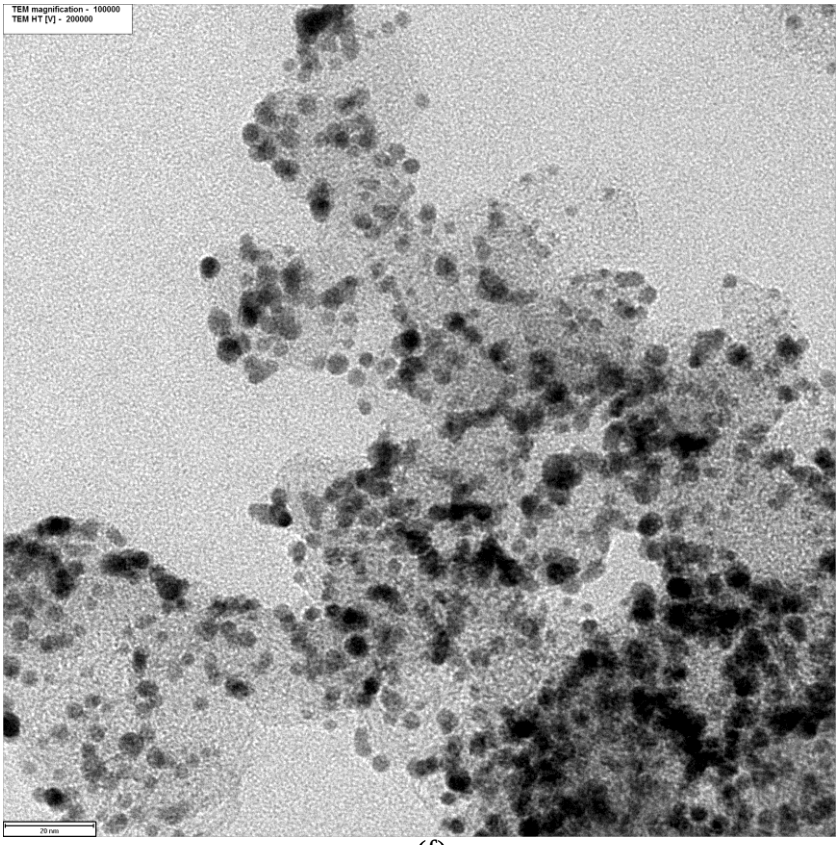


(d)

Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)



(e)



(f)

Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)

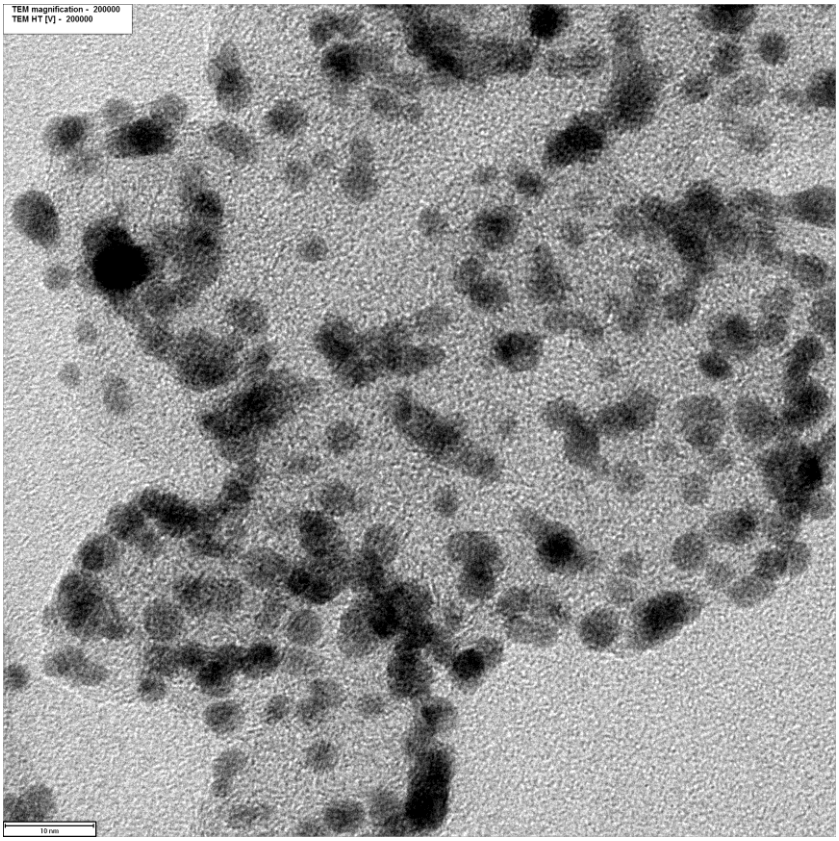


Figure A.12 TEM image at magnification of 200,000x. of 40 wt% Au on treated carbon

Citrate protection method

1. 20% Au/ untreated Carbon

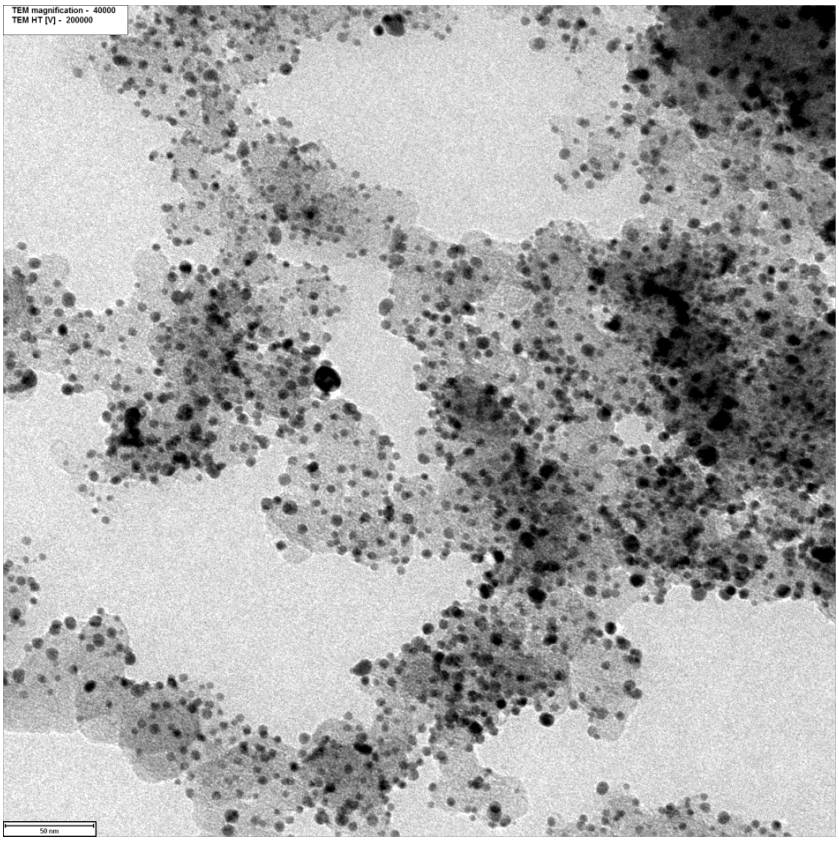
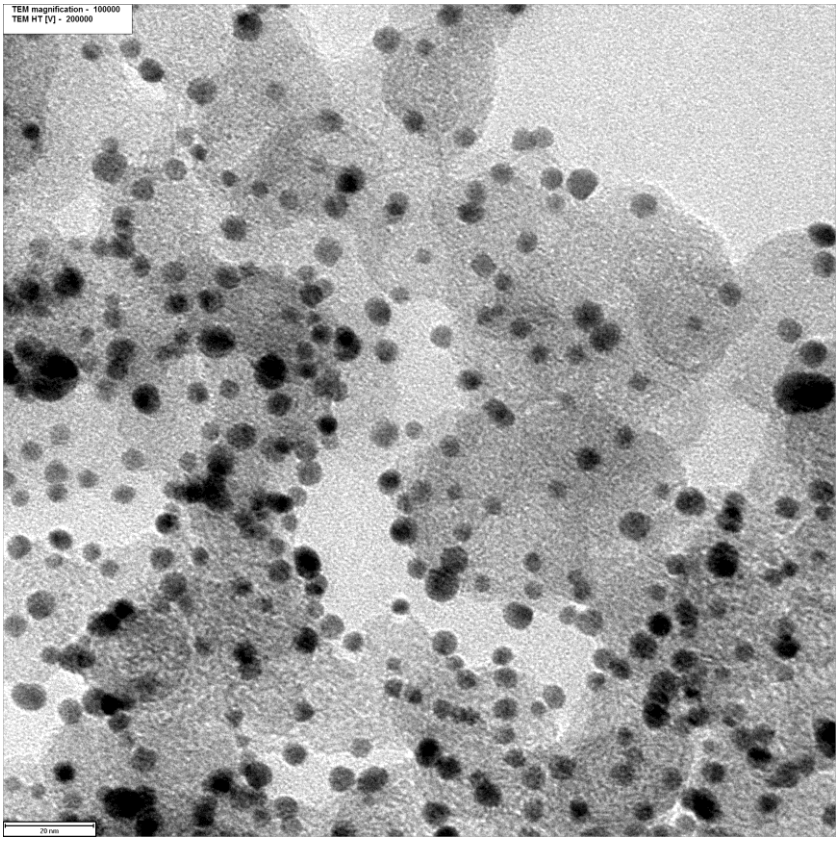
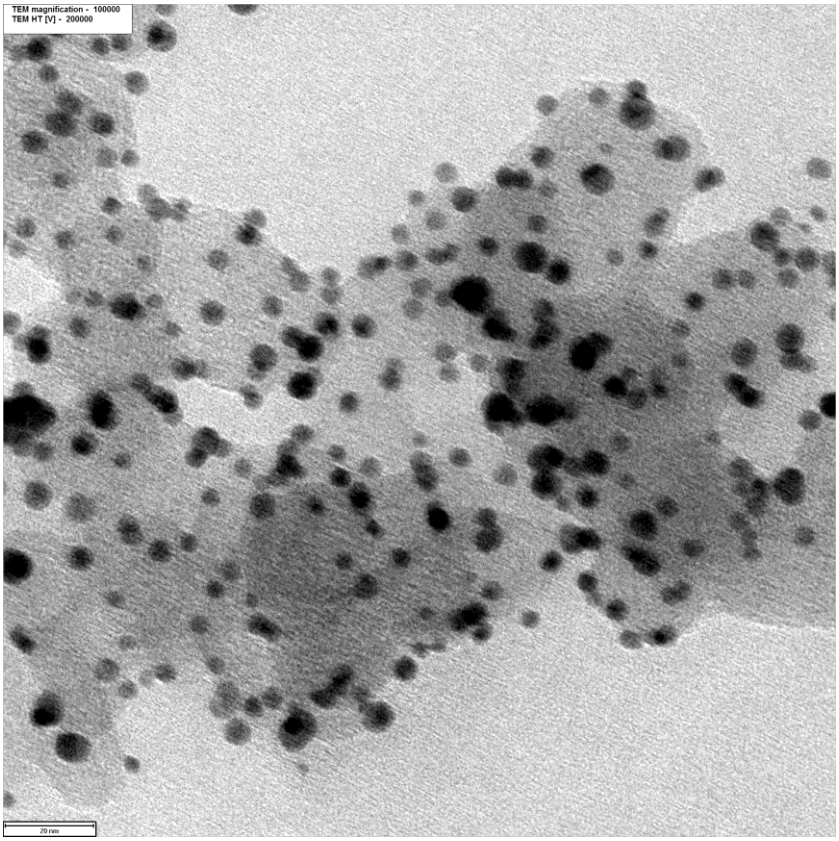


Figure A.13 TEM image at magnification of 40,000x. of 20 wt% Au on untreated carbon

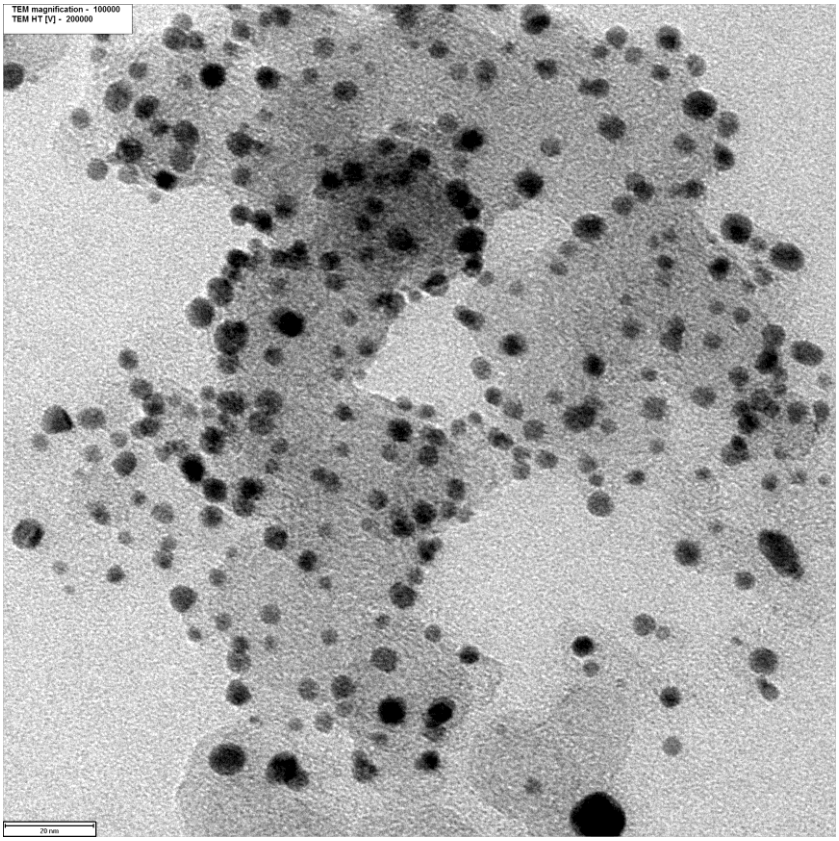


(a)

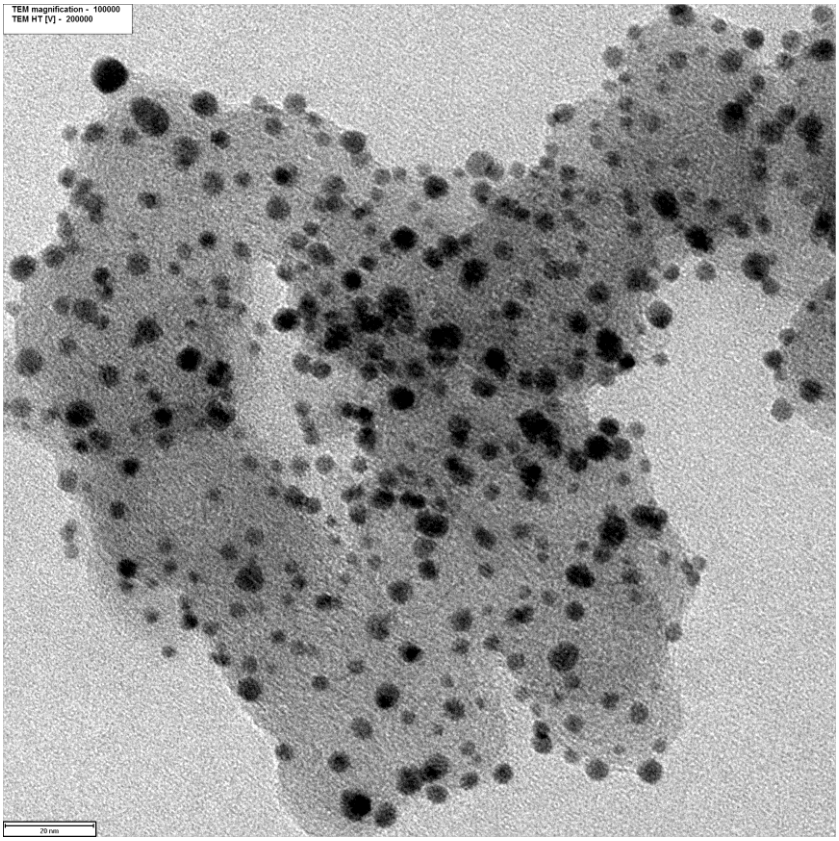


(b)

Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon

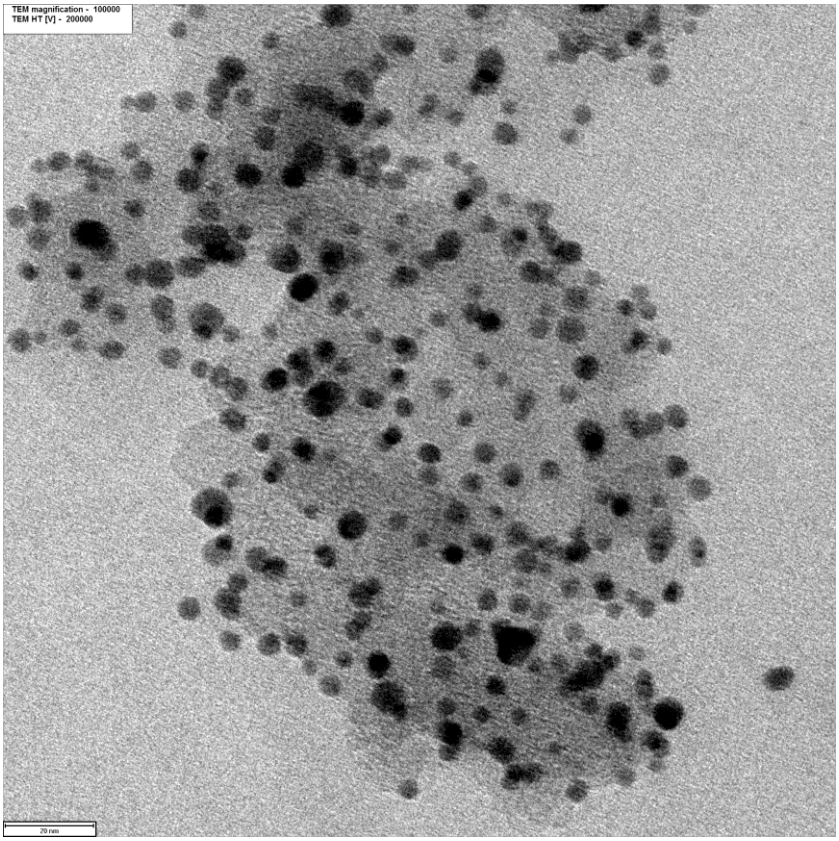


(c)



(d)

Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)



(e)

Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)

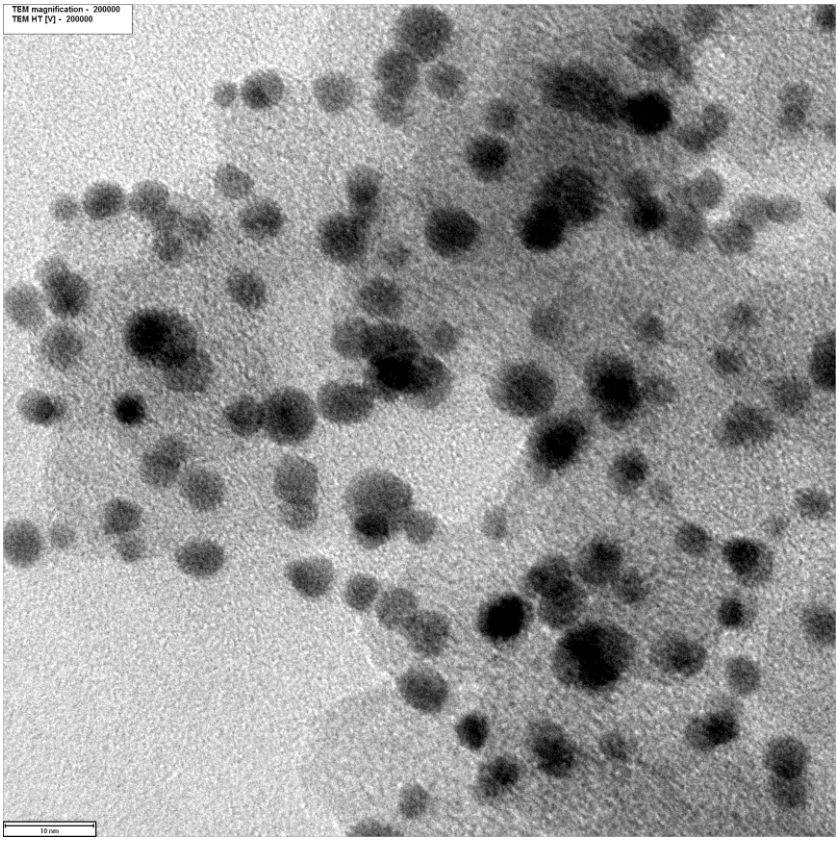


Figure A.15 TEM image at magnification of 200,000x. of 20 wt% Au on untreated carbon

2. 20% Au/ treated Carbon

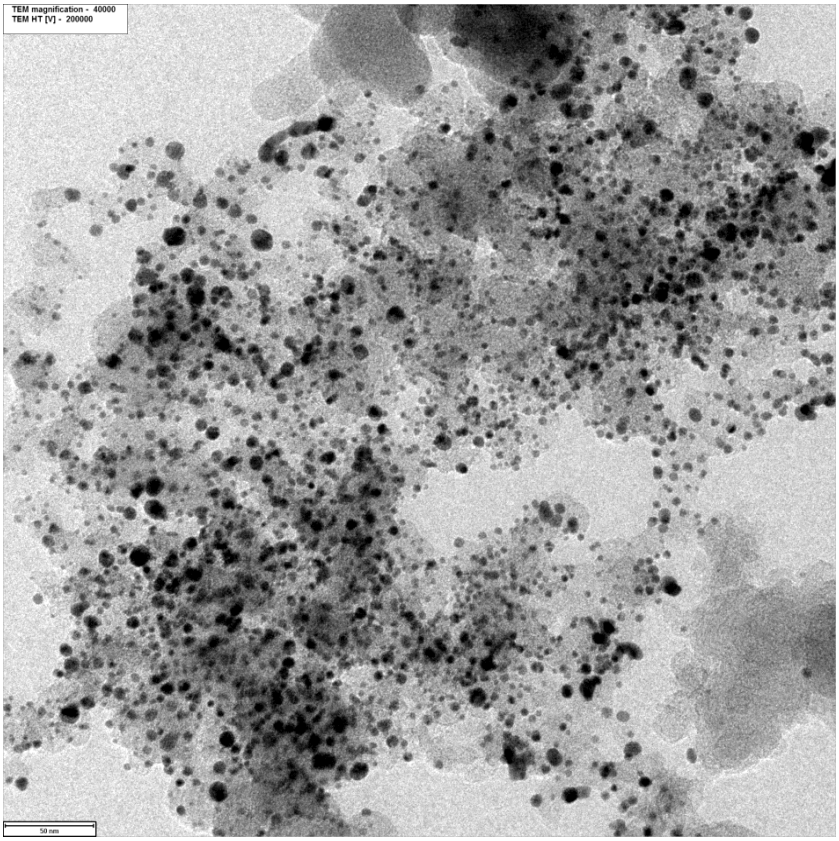
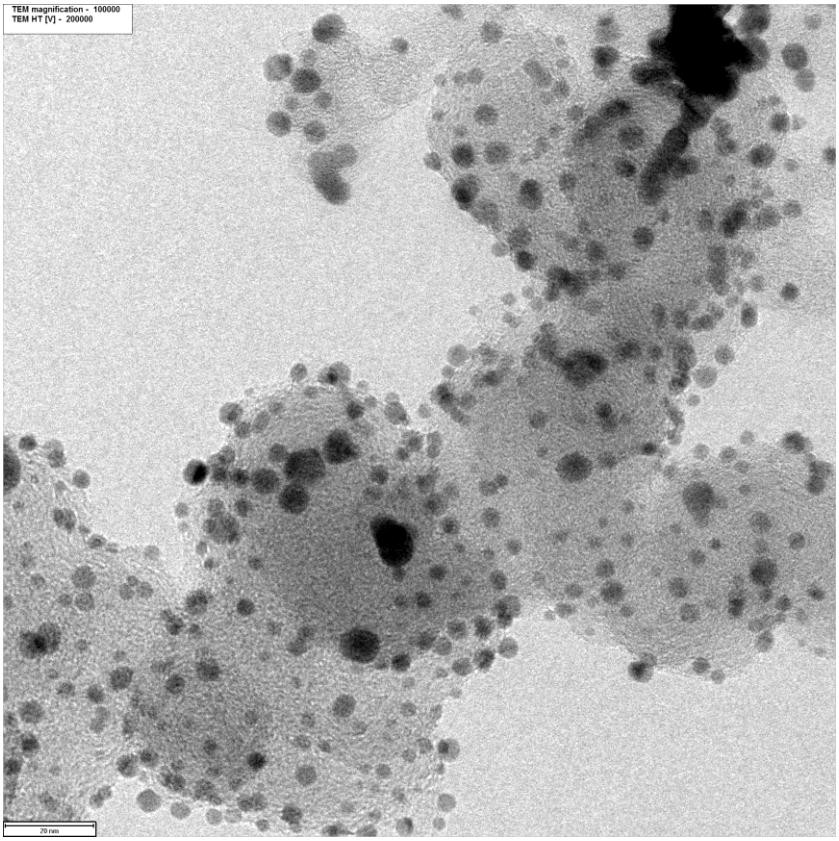
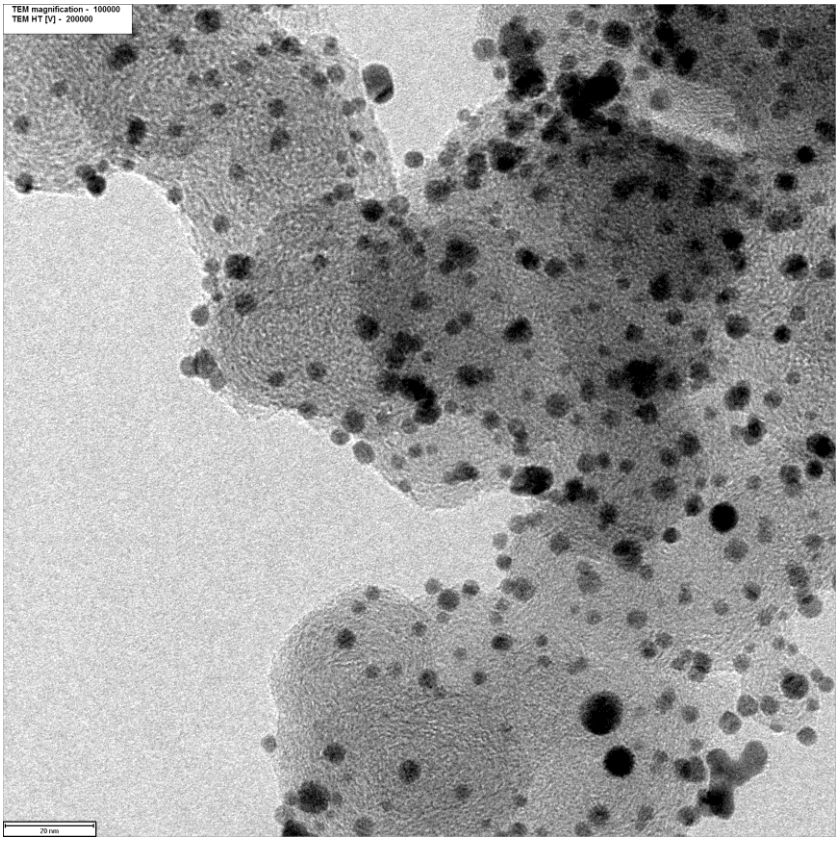


Figure A.16 TEM image at magnification of 40,000x. of 20 %wt Au on treated carbon

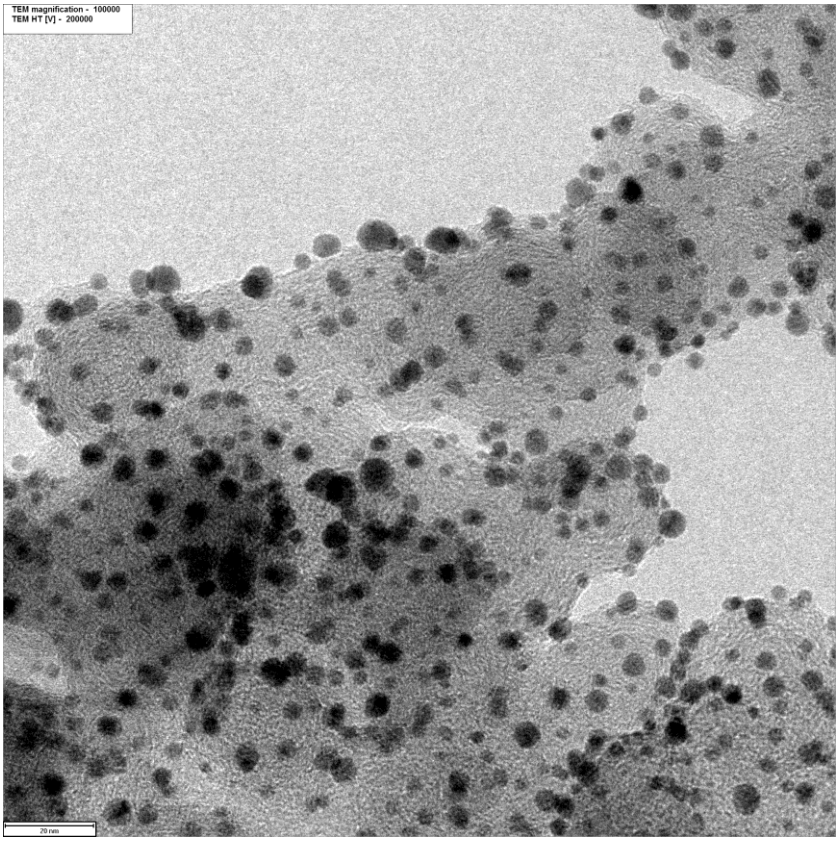


(a)

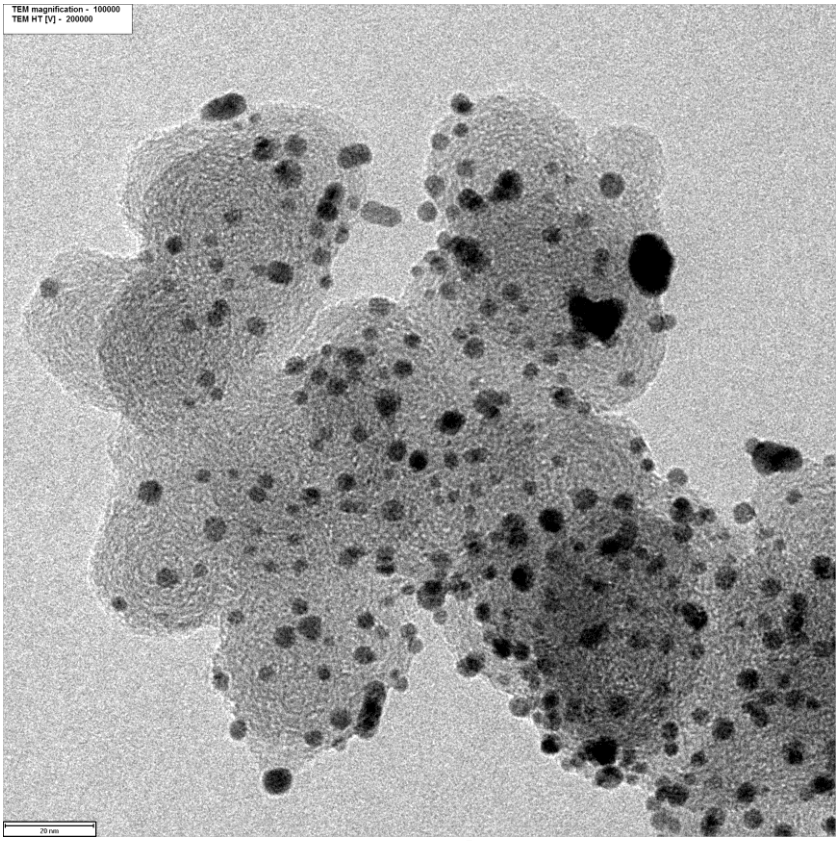


(b)

Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon

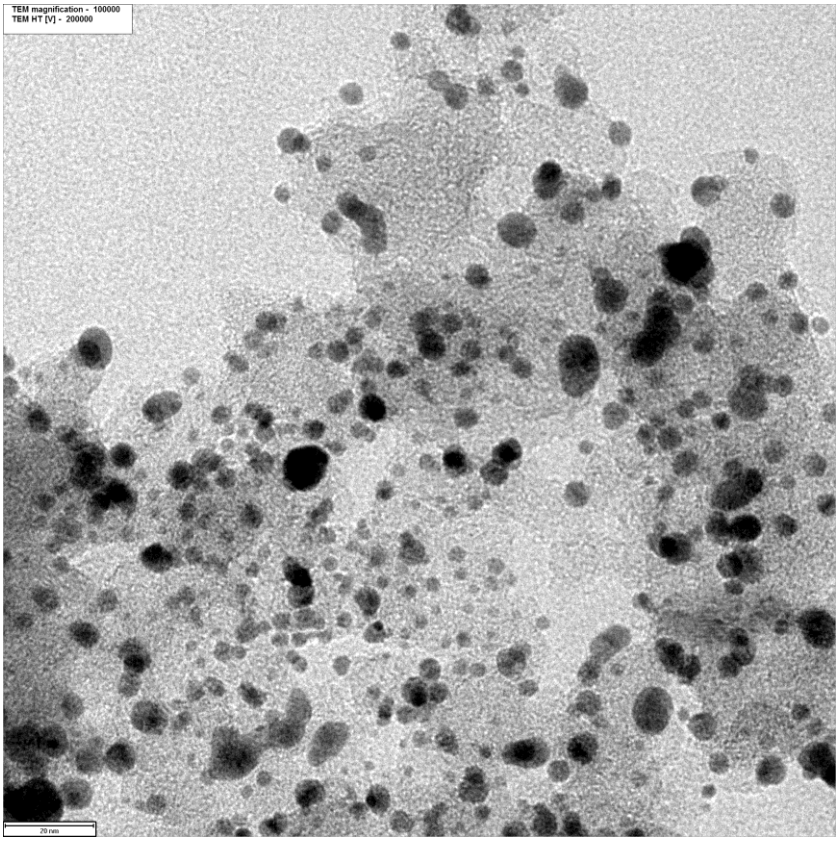


(c)



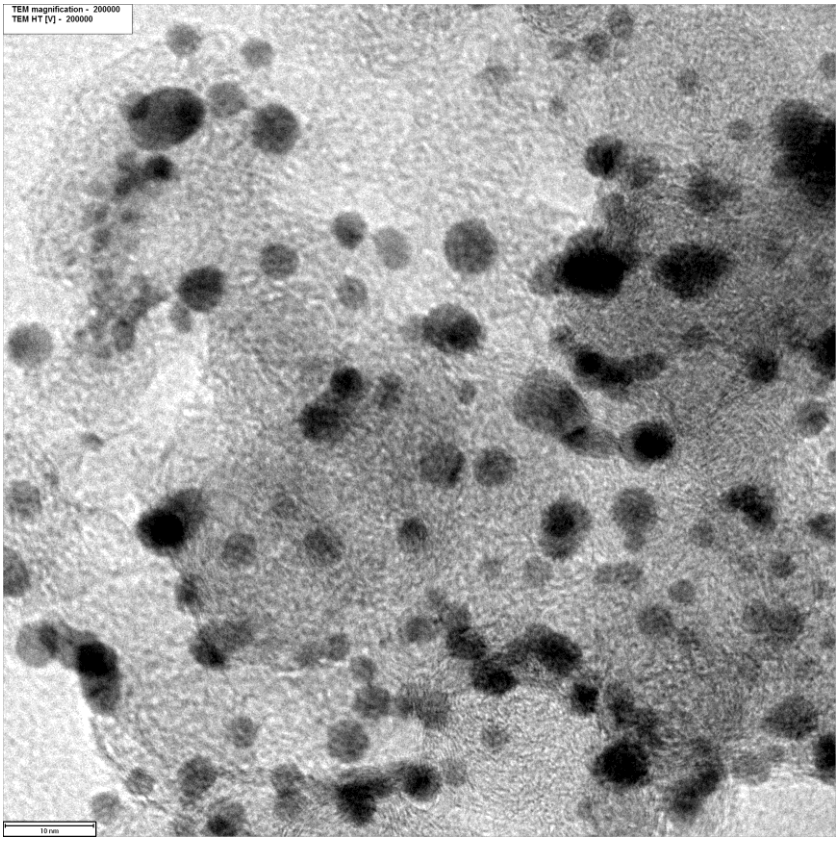
(d)

Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon (continue)

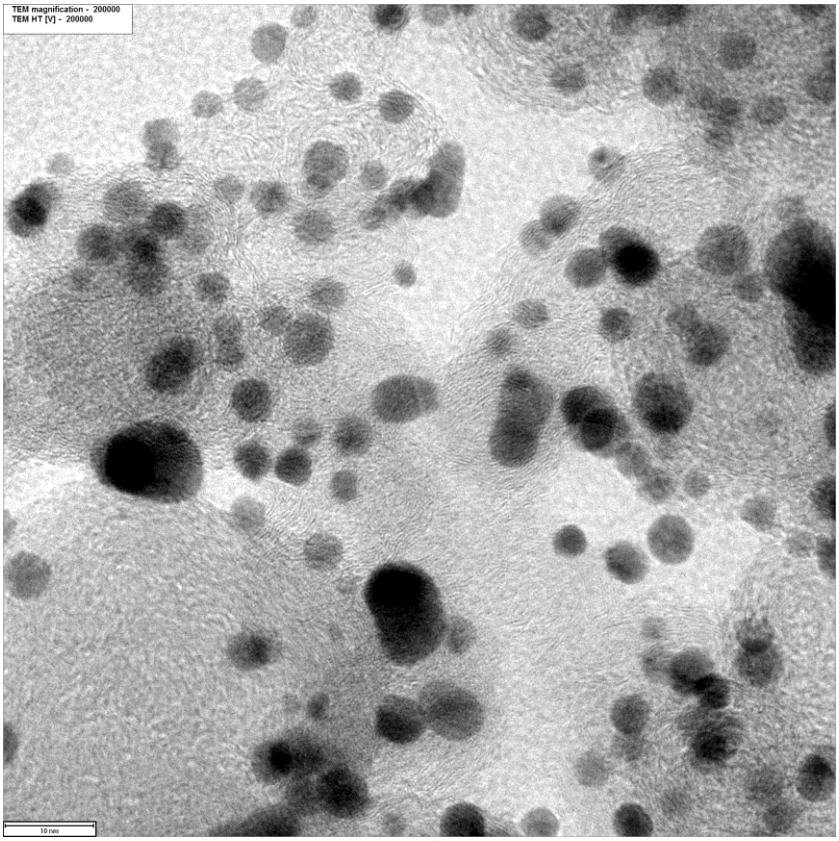


(e)

Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon (continue)



(a)



(b)

Figure A.18 (a)-(b) TEM image at magnification of 200,000x. of 20 wt% Au on treated carbon

3. 30% Au/ treated Carbon

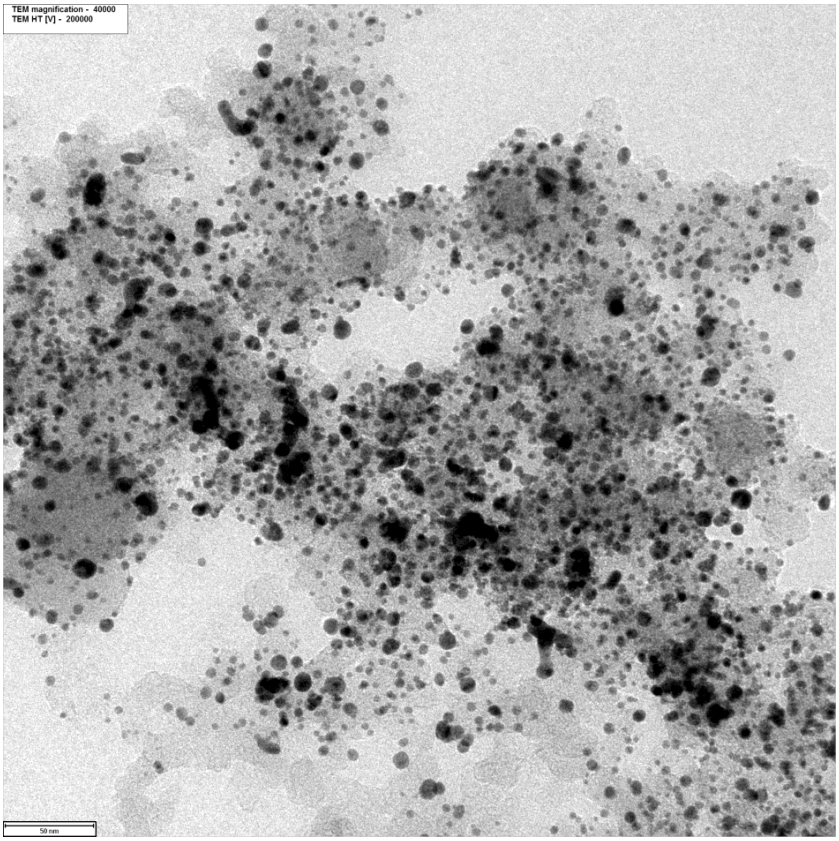
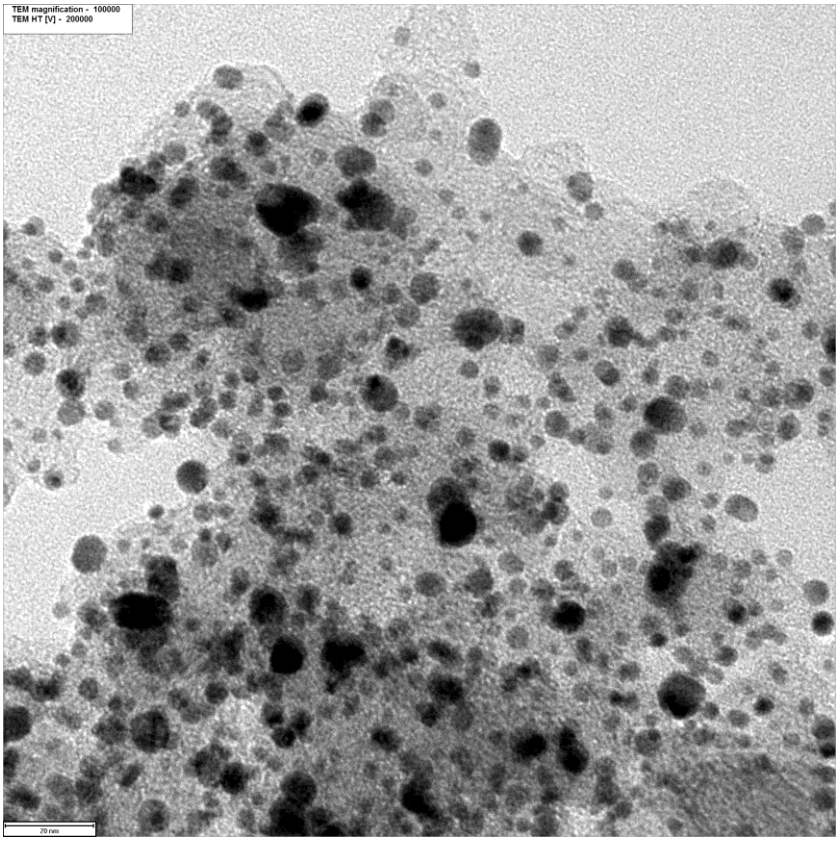
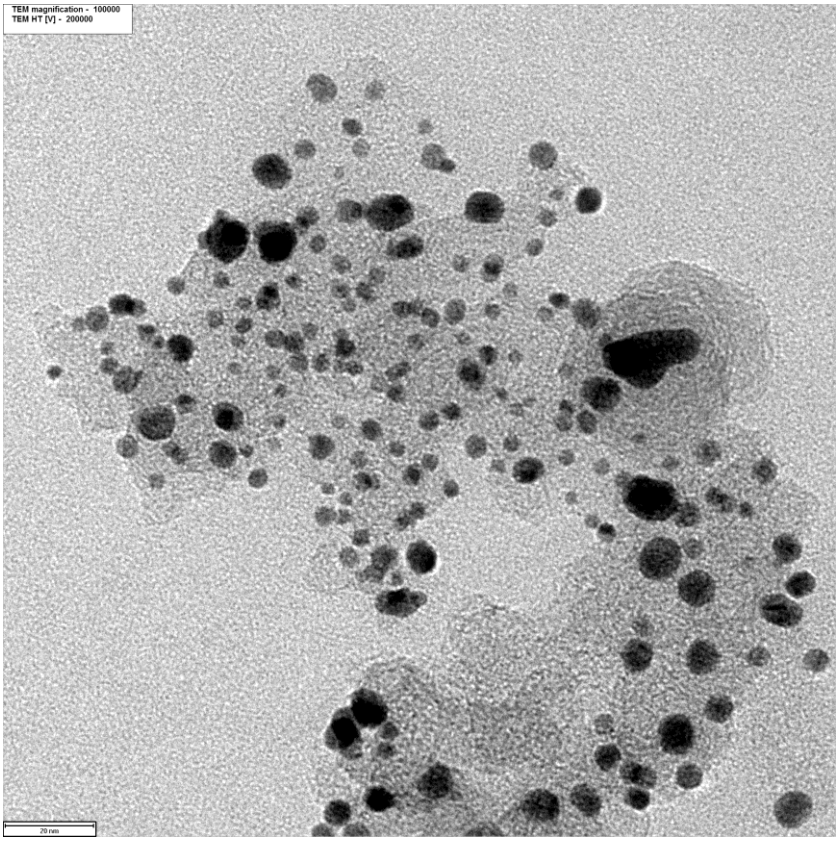


Figure A.19 TEM image at magnification of 40,000x. of 30 %wt Au on treated carbon

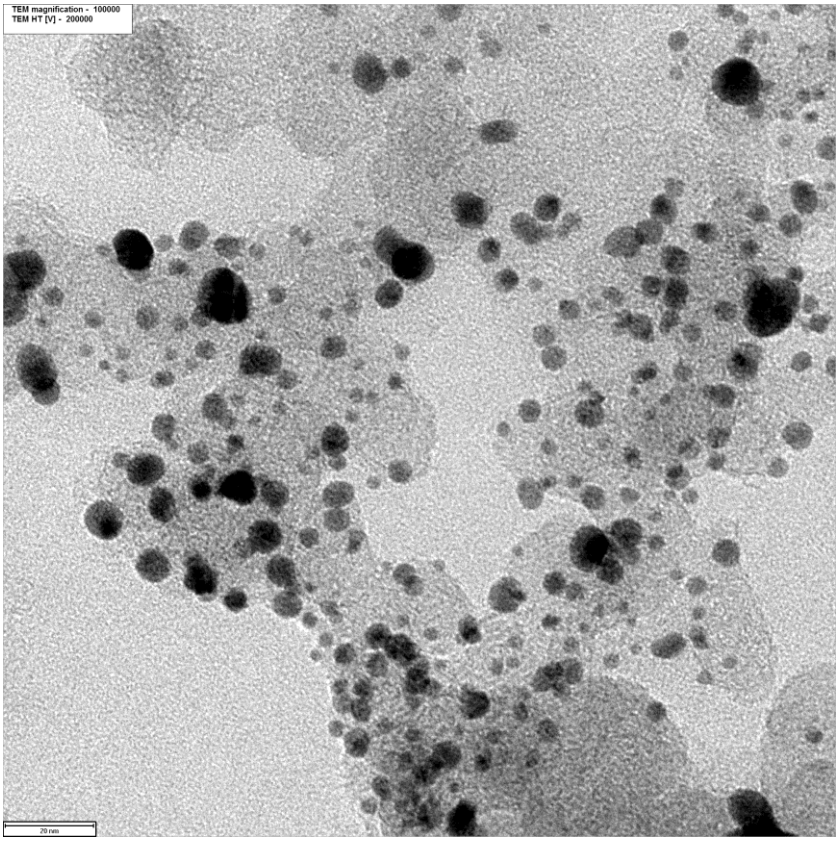


(a)

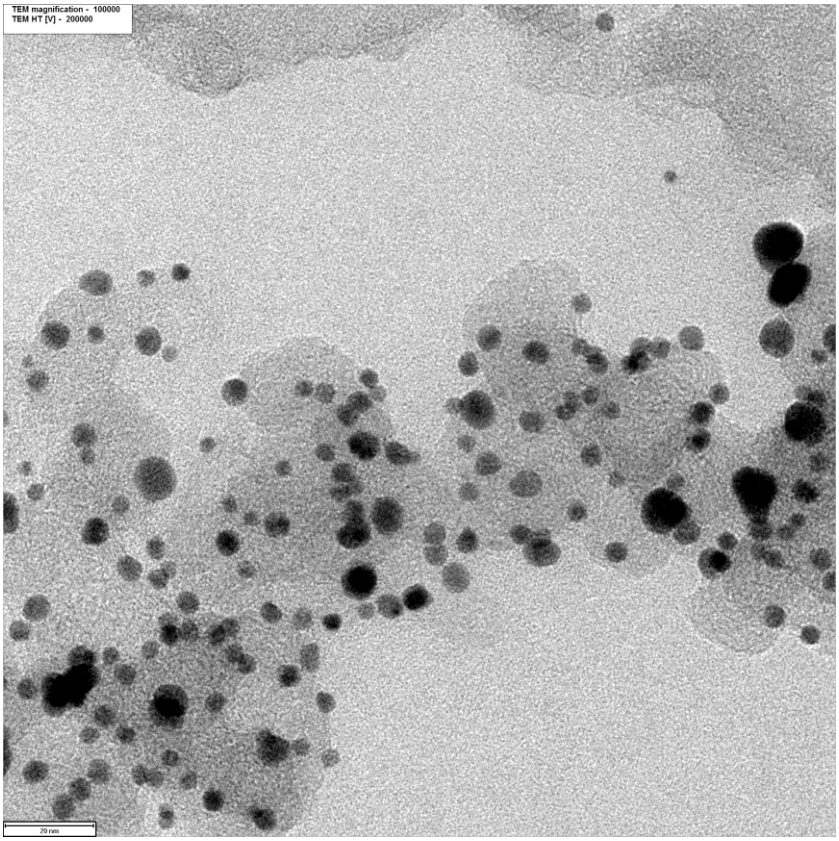


(b)

Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon

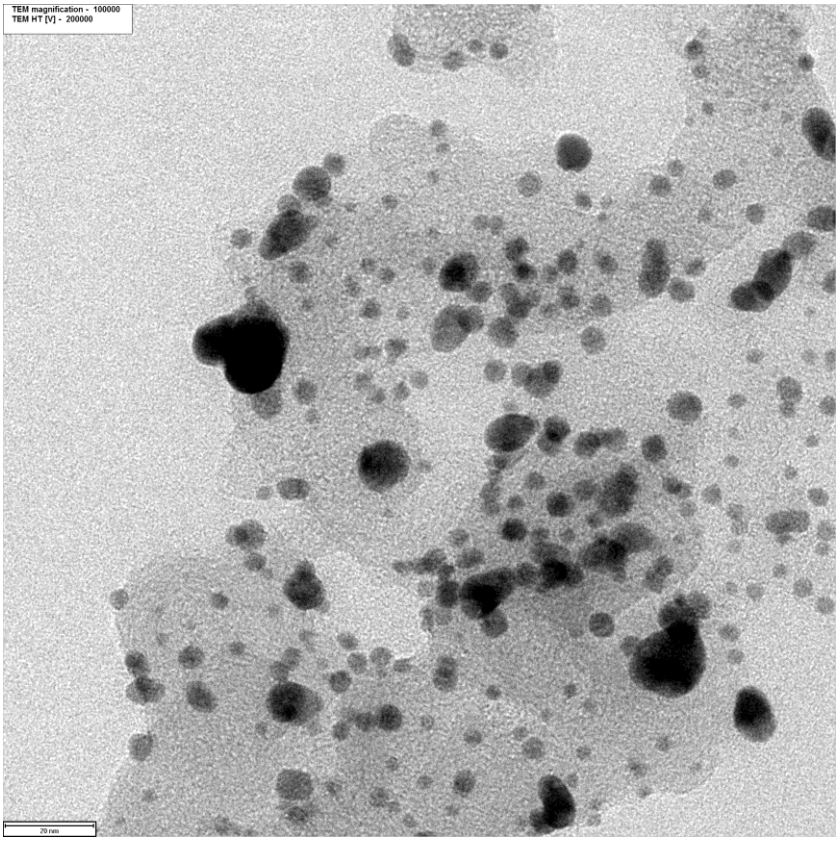


(c)



(d)

Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)



(e)

Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)

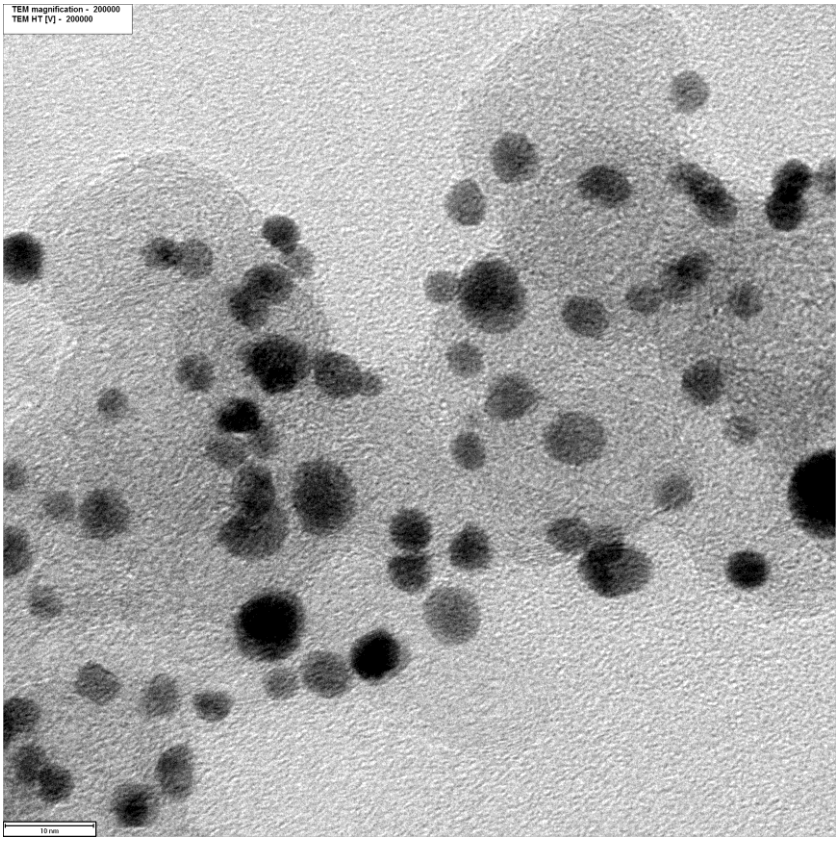


Figure A.21 TEM image at magnification of 200,000x. of 30 wt% Au on treated carbon.

4. 40% Au/ treated C

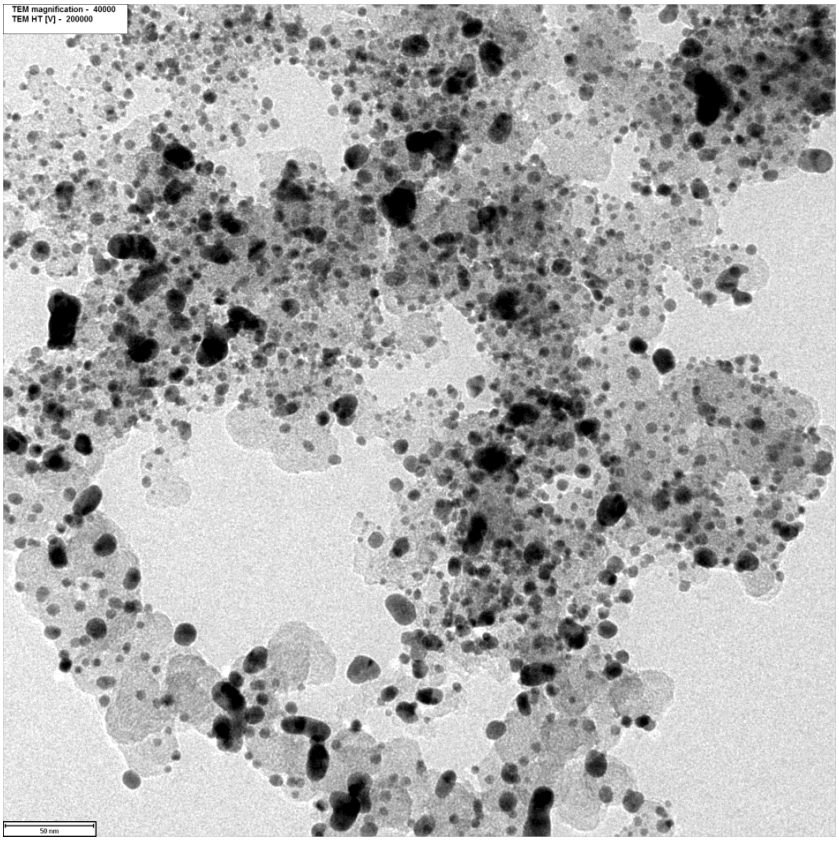
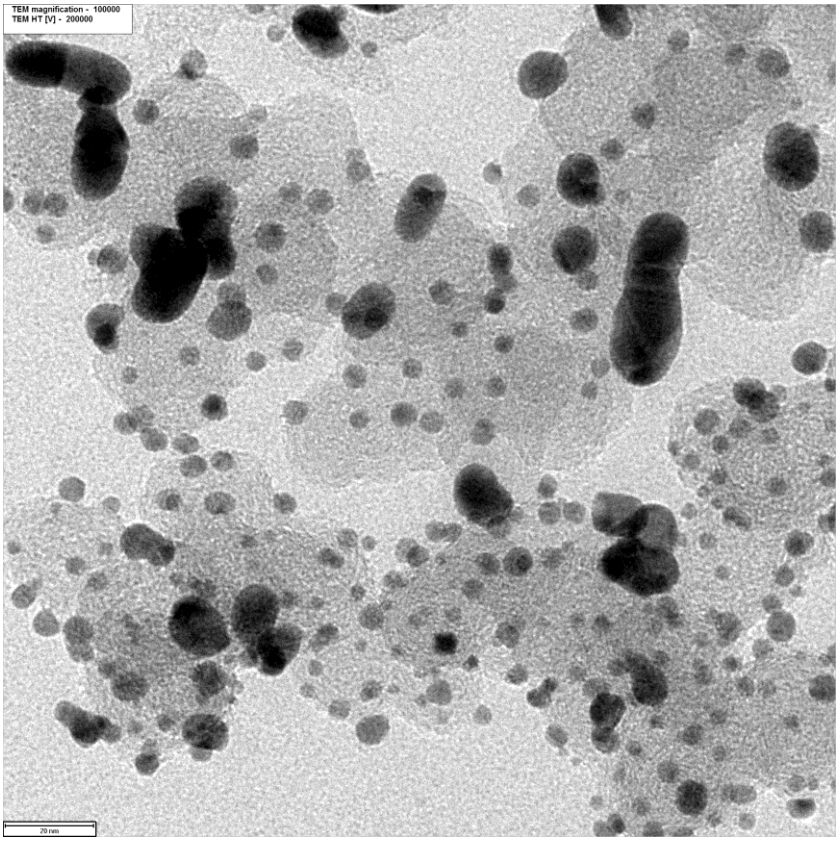
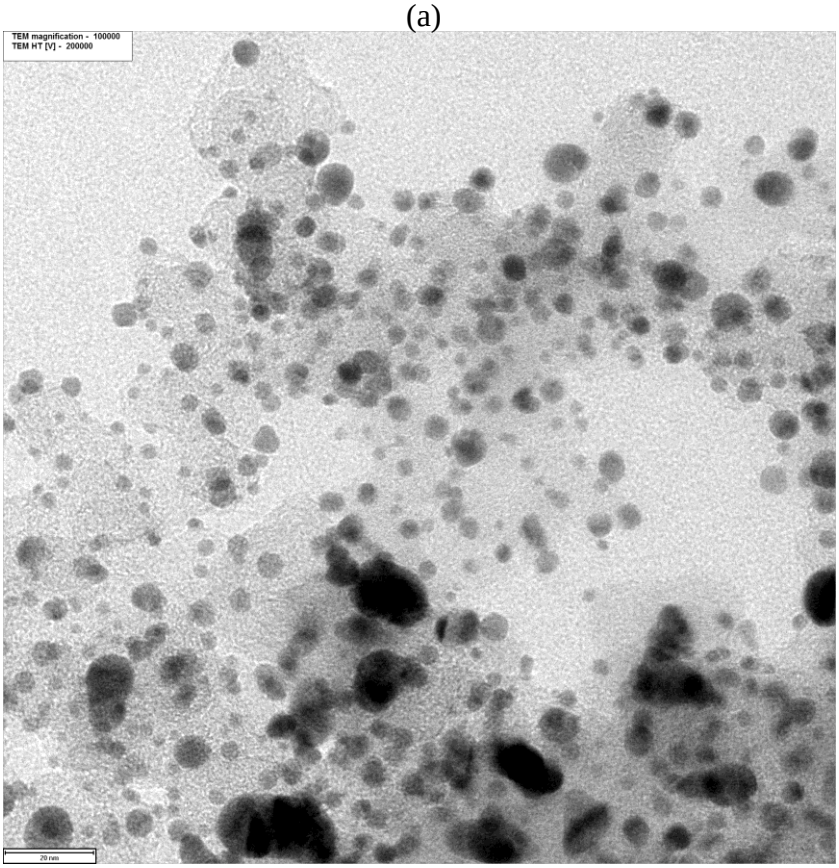


Figure A.22 TEM image at magnification of 40,000x. of 40 wt% Au on treated carbon.

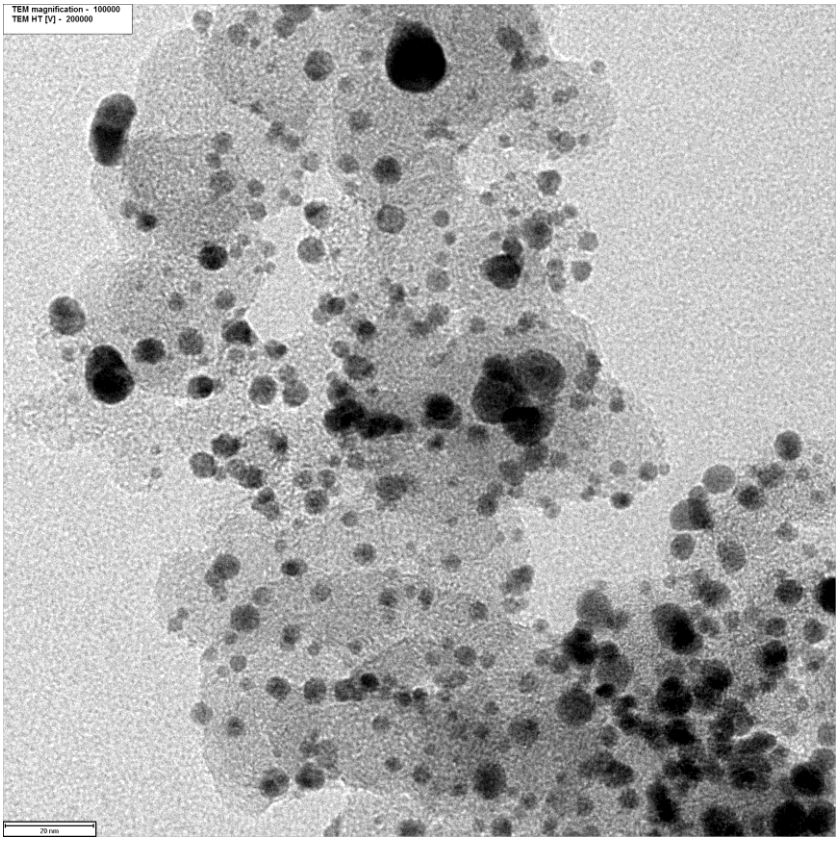


(a)

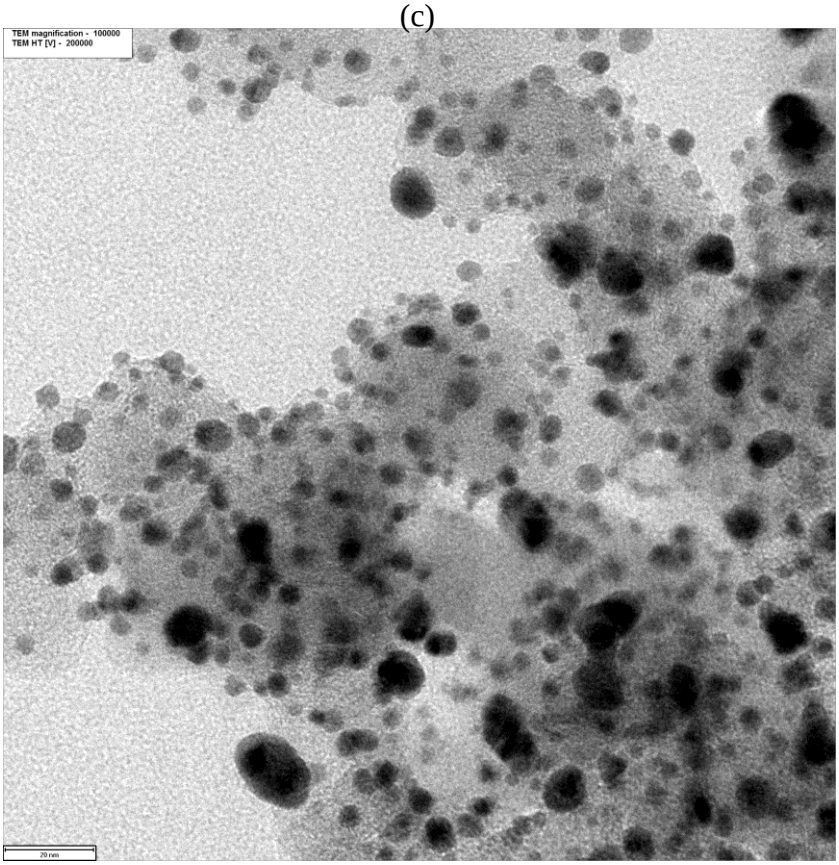


(b)

Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon

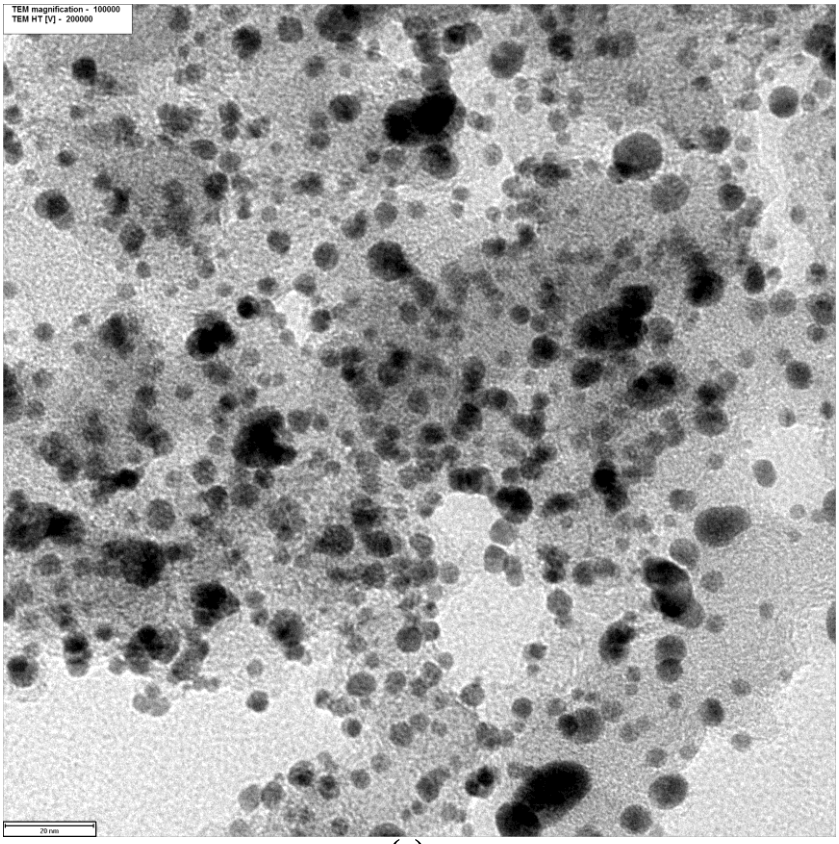


(c)

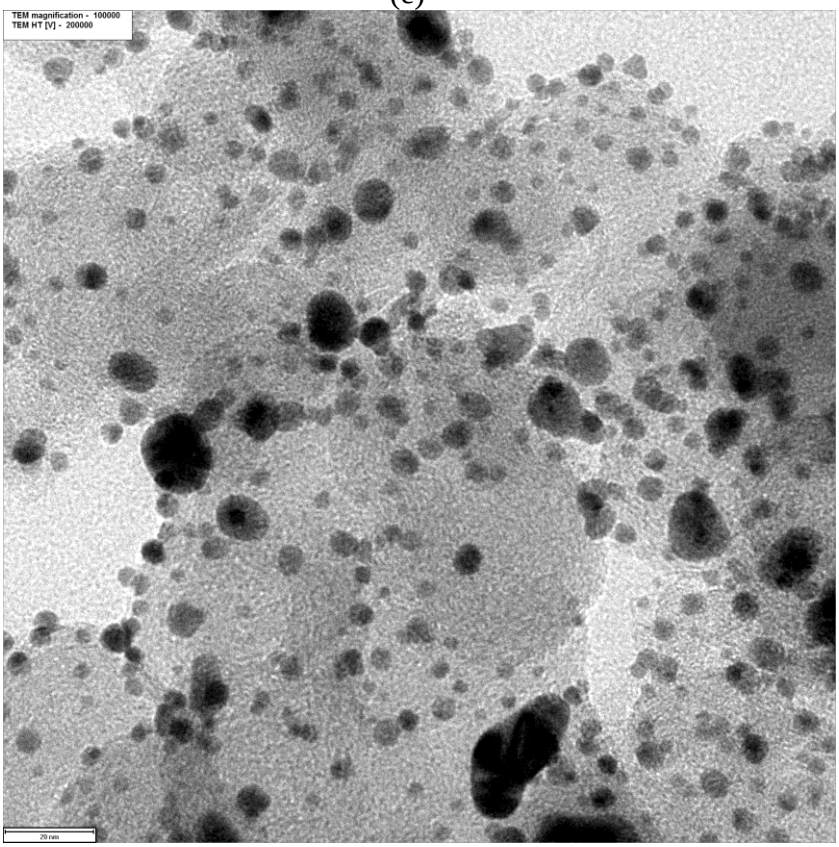


(d)

Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)

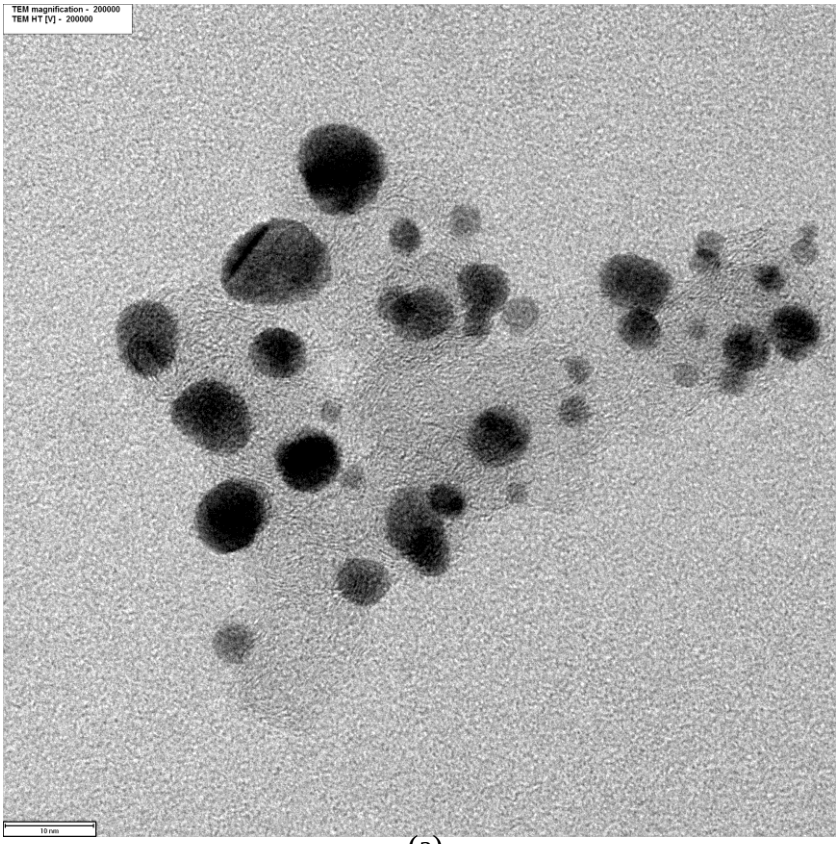


(e)

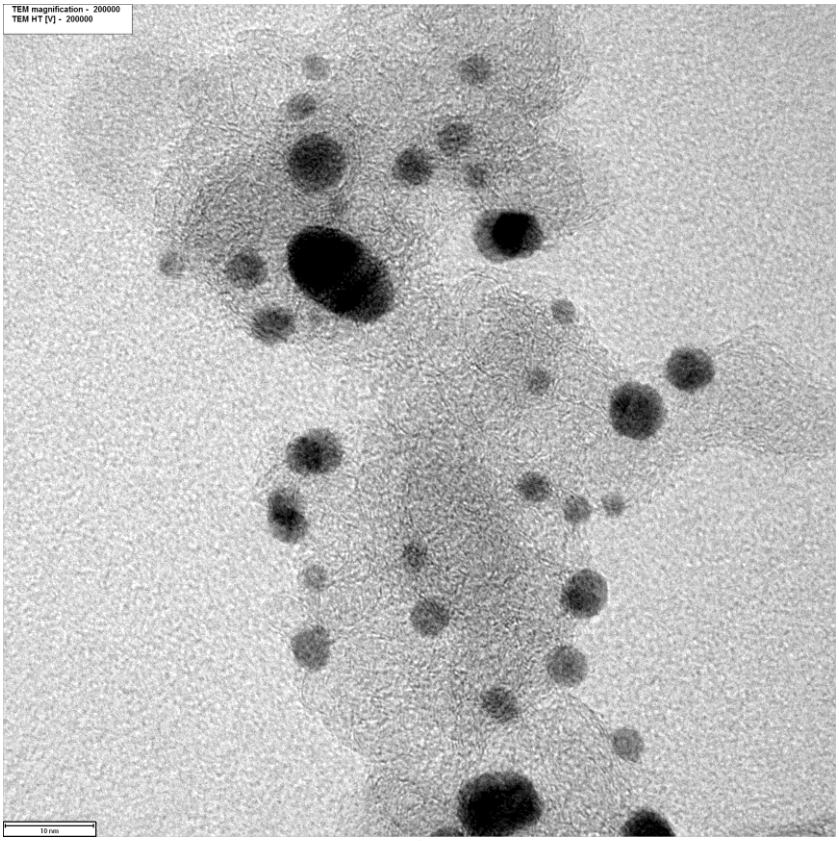


(f)

Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)



(a)



(b)

Figure A.24 (a)-(b) TEM image at magnification of 200,000x. of 40 wt% on treated carbon

A.4 Electrochemical Surface Area (ESA)

The example to determine the ESA of 20 wt% Au catalyst by PVA method;

$$\text{Reduction Peak Area} = \frac{0.0055732\ \text{C/cm}^2\ \text{(G.C)}}{0.000386\ \text{C/cm}^2\text{Au}} \begin{matrix}\longrightarrow \text{From CV result (Table A.7)} \\ \longrightarrow \text{From Literature [16]}\end{matrix}$$

$$= 14.44\ \text{cm}^2\text{Au}/\text{cm}^2\text{(G.C)}$$

Ink volume 0.2 ml contain catalyst 10 mg

Thus, Ink volume 0.0114 ml contain catalyst 0.057 mg

Since, G.C. area = 0.2827 cm^2, the amount of are catalyst on electrode per crossectional area of electrode was equal to

$$\frac{0.057\ \text{mg cat}}{0.2827\ \text{cm}^2\ \text{(G.C.)}} = 0.2016\ \text{mg cat/ cm}^2\ \text{(G.C.)}$$

There are 20 wt% of Au on catalyst, thus the amount of Au per crossectional area of electrode was

$$0.2016 \times 0.2 = 0.0403\ \text{mg Au/cm}^2\text{(G.C)}$$

Thus,

$$\text{ESA} = \frac{14.44\ \text{cm}^2\text{Au/cm}^2\text{(G.C)}}{0.0403\ \text{mgAu/cm2(G.C)}}$$

$$\text{ESA} = 358.10 \frac{\text{cm}^2\text{Au/cm}^2\text{(G.C)}}{\text{mgAu/cm}^2\text{(G.C)}}$$

Table A.8 Reduction Peak Area used to determine the ESA

Catalyst	**Reduction Peak Area (C/cm^2)**		
	(set 1)	**(set 2)**	**(set 3)**
PVA method			
20%Au/ untreated C	0.0055732	0.0058280	0.0049212
20%Au/ treated C	0.0052525	0.0056989	0.0047427
30%Au/ treated C	0.0060622	0.0058588	0.0062568
40%Au/ treated C	0.0056798	0.0046540	0.0050430
Citrate method			
20%Au/ untreated C	0.0043392	0.0048039	0.0039633
20%Au/ treated C	0.0042643	0.0049486	0.0033474
30%Au/ treated C	0.0062427	0.0066683	0.0067422
40%Au/ treated C	0.0057020	0.0053630	0.0044400