Continuous Flow Synthesis of Rh and RhAg Alloy Nanoparticle Catalysts Enables Scalable Production and Improved Morphological Control

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Table S1. Reaction parameters for flow reactions carried out under μwI.

Flow Mode	Flow Rate (cm^3h^{-1})			Length of Tubing (m)	Residence Time (min)
Single–phase	30			7.6	9
Single–phase	30			3.8	4.6
Single–phase	15			7.6	18
Single–phase	7.5			7.6	35
Two–phase	160 (Carrier Fluid)	64 (PVP)	16 ($RhCl_3.xH_2O$)	7.6	1
Two–phase	80 (Carrier Fluid)	32 (PVP)	8 ($RhCl_3.xH_2O$)	7.6	2
Two–phase	80 (Carrier Fluid)	32 (PVP)	8 ($RhCl_3.xH_2O$)	30.5	6
Two–phase	80 (Carrier Fluid)	32 (PVP)	8 ($RhCl_3.xH_2O$)	30.5	9
Two–phase	20 (Carrier Fluid)	8 (PVP)	2 ($RhCl_3.xH_2O$)	30.5	30

Table S2. Ratio of intensity values corresponding to 111 and 200 obtained from PXRD analyses.

Sample	I_{111}/I_{200}
Rh multipods_μwI_120°C_9 min	1.94
Rh multipods_CvH_120°C_9 min	1.48
Batch reaction_no syringe pump_Rh NPs_μwI_120°C_9 min	1.77
Rh NPs_μwI_120°C_9 min_$RhCl_3.xH_2O$ and PVP injected using syringe pump	1.76

Table S3. Statistical analysis of Rh multipods formed after different thermal treatment conditions.

Sample Identity	**Original Average Appendage Length/Diameter (nm)**		**Thermal Treatment Conditions**		**Reaction Time (min)**	**Size of Multipods (nm)**	**Size of Non-multipods (nm)**	**Size of Small Seeds (nm)**
	Multipods	Non-multipods	Mode of Heating	Reaction Temperature (°C)				
Rh multipods-μwI	6.75±1.40	3.67±0.64	μwI	150	15	6.64±1.54		
RhMP multipods-μwI			μwI	175	15	6.13±1.14		
Rh multipods-μwI			μwI	175	60	6.94±1.49		
Rh multipods-CvH	6.81±1.68	3.93±0.98	μwI	150	15	7.25±1.39	5.05±0.81	
Rh multipods-CvH			μwI	175	15	7.27±1.51	5.07±0.79	2.19±0.30
Rh multipods-CvH			CvH	175	15	6.31±1.48	4.33±0.65	
Rh multipods-CvH			CvH	175	60	6.96±1.24	4.55±0.71	

Table S3. ICP analysis of Rhodium multipods supported on amorphous silica.

Sample	Rh wt%	SSTOF (surface site^{-1} s^{-1}) Value
Rh multipods_μwI_120°C_9 min	1.362	8.5
Rh multipods_CvH_120°C_9 min	3.345	6.8

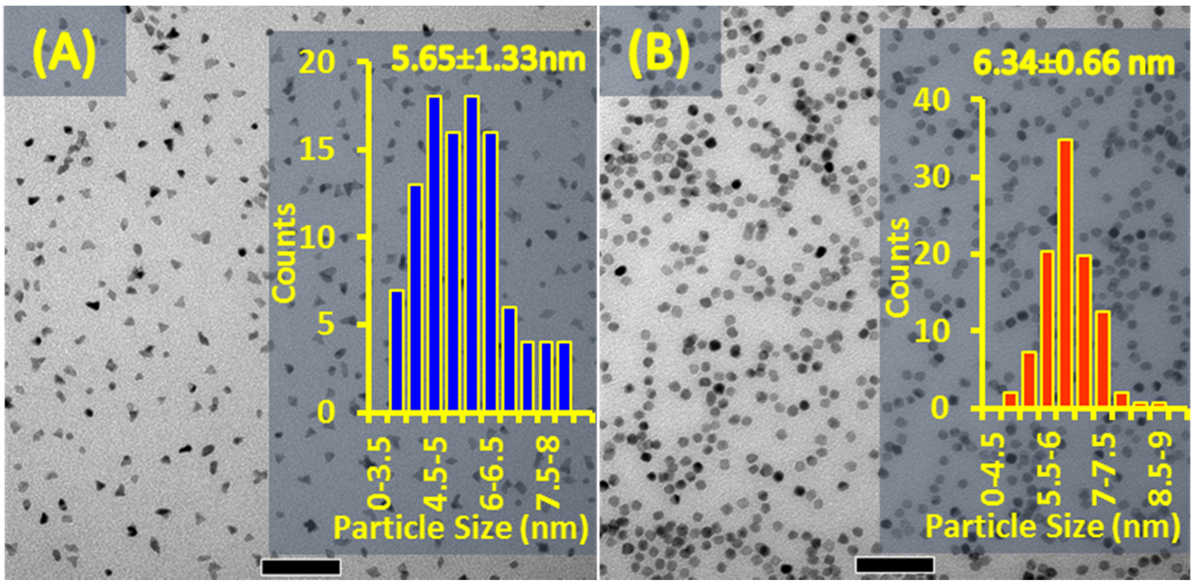

Figure S1. TEM images of Rh NPs using control reactions. **(A)** Products isolated from control batch reaction carried out under μwI at 120 °C for 9 minutes while not using a syringe pump. **(B)** Products isolated from control reaction carried out under μwI at 120 °C for 9 minutes and adding $RhCl_3.xH_2O$ and PVP dissolved in EG injected using separate syringes.

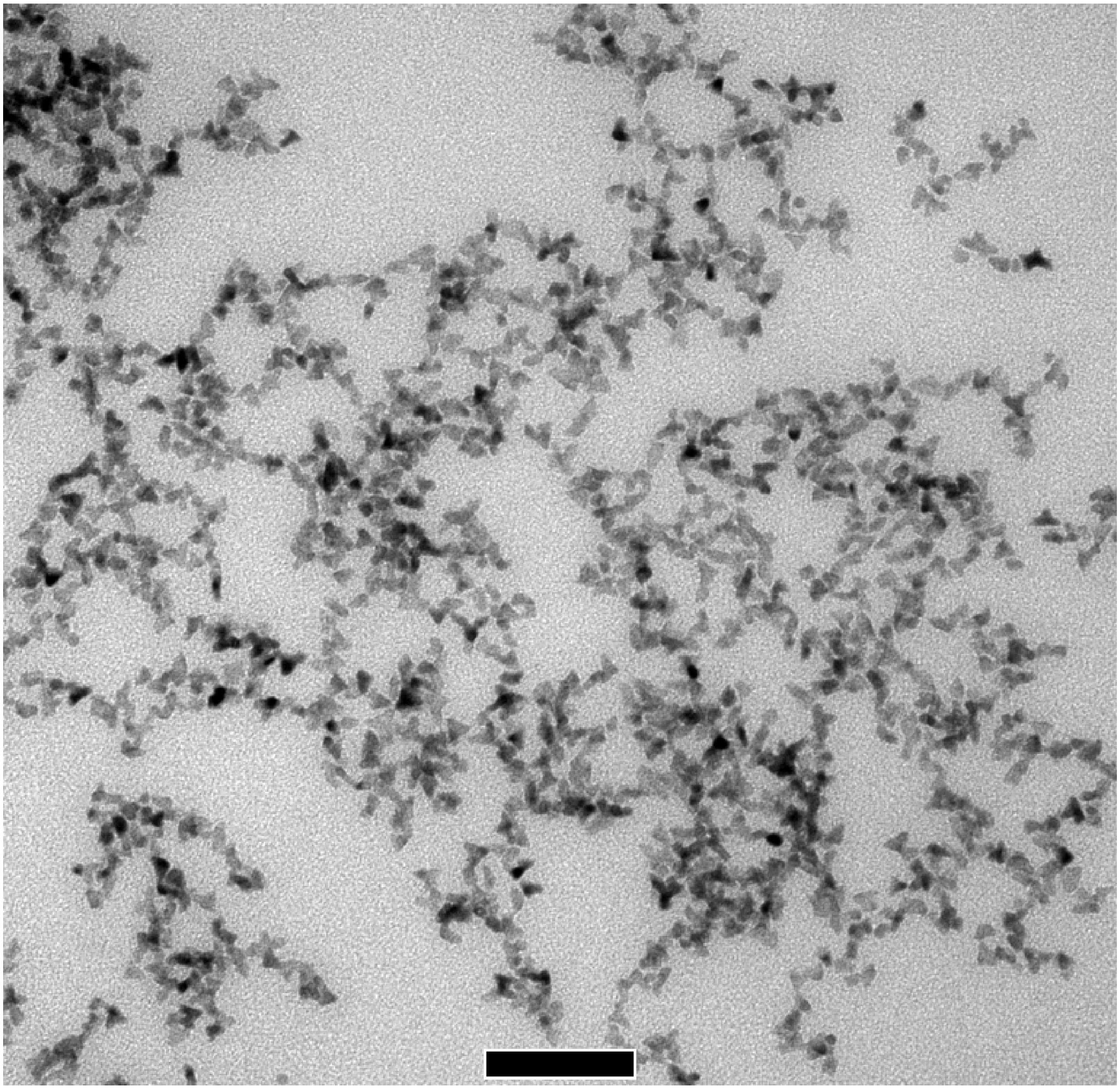

Figure S2. Microwave assisted thermal treatment at 150 °C for 15 min of Rh multipods synthesized using μwI at 120°C in EG in 9 min. Scale bar is 50 nm.

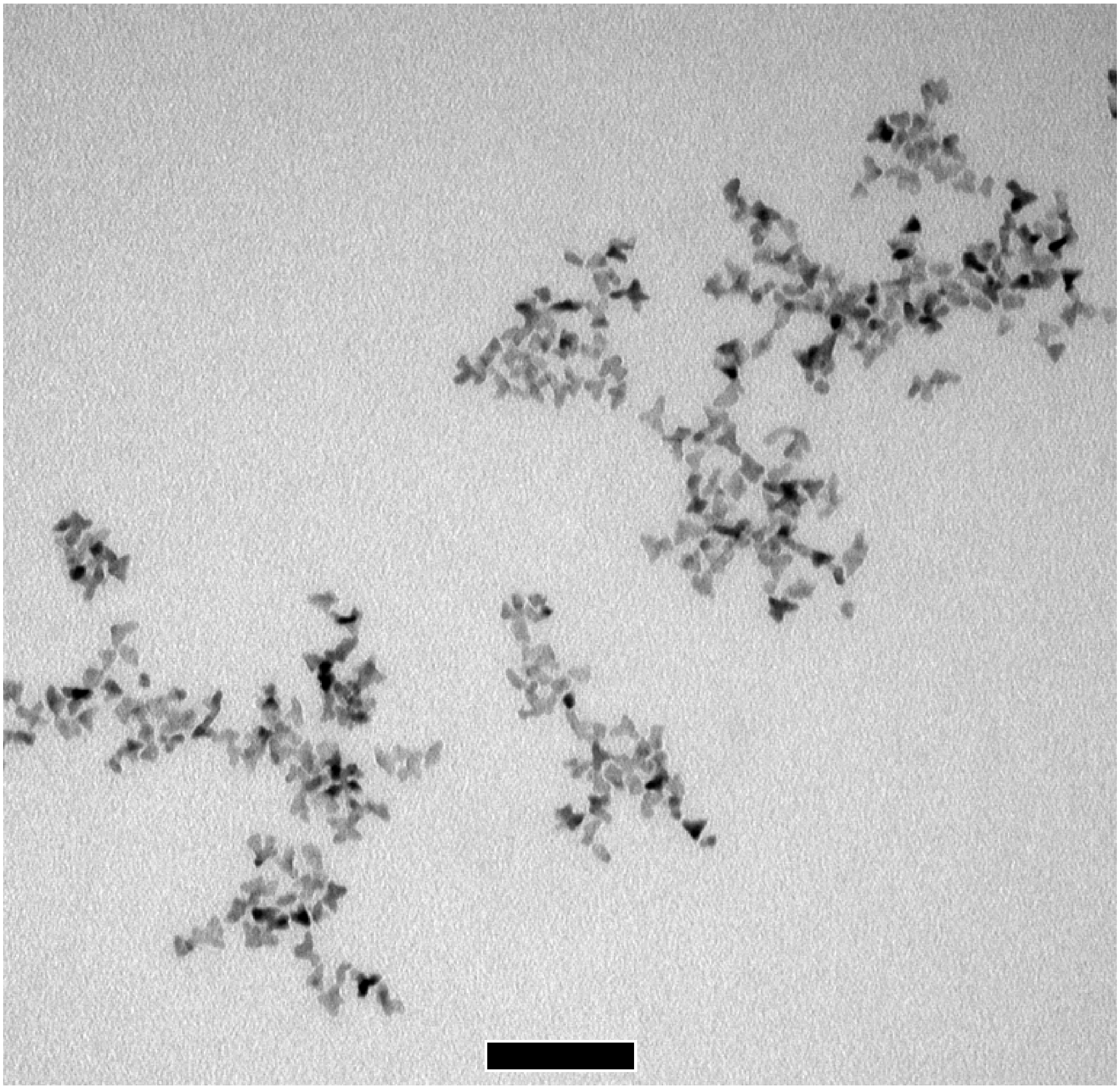

Figure S3. Microwave assisted thermal treatment at 175 °C for 15 min of Rh multipods synthesized using μwI at 120°C in EG in 9 min. Scale bar is 50 nm.

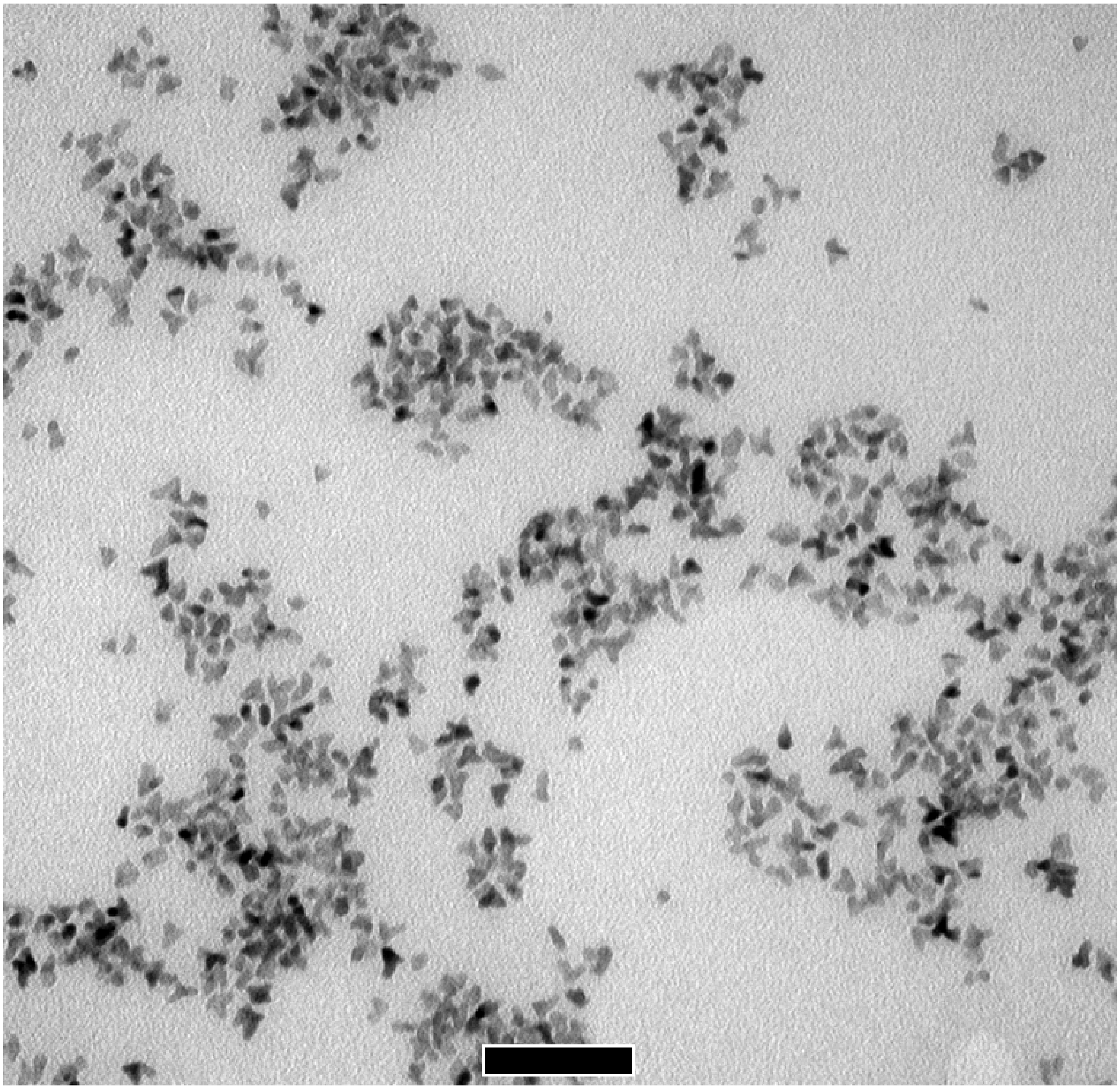

Figure S4. Microwave assisted thermal treatment at 175 °C for 60 min of Rh multipods synthesized using μwI at 120°C in EG in 9 min. Scale bar is 50 nm.

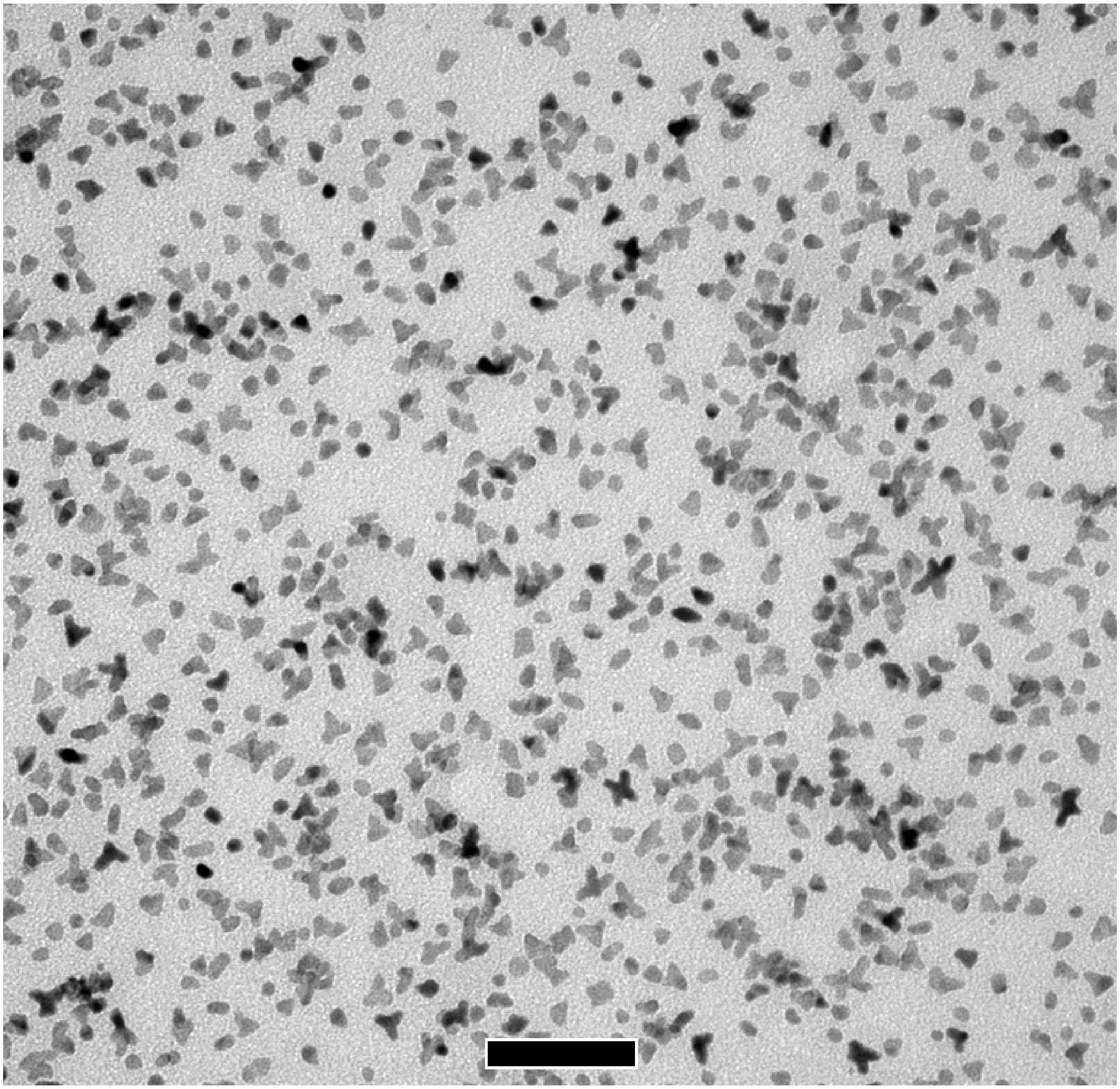

Figure S5. Oil bath assisted thermal treatment at 150 °C for 15 min of Rh multipods synthesized using CvH at 120°C in EG in 9 min. Scale bar is 50 nm.

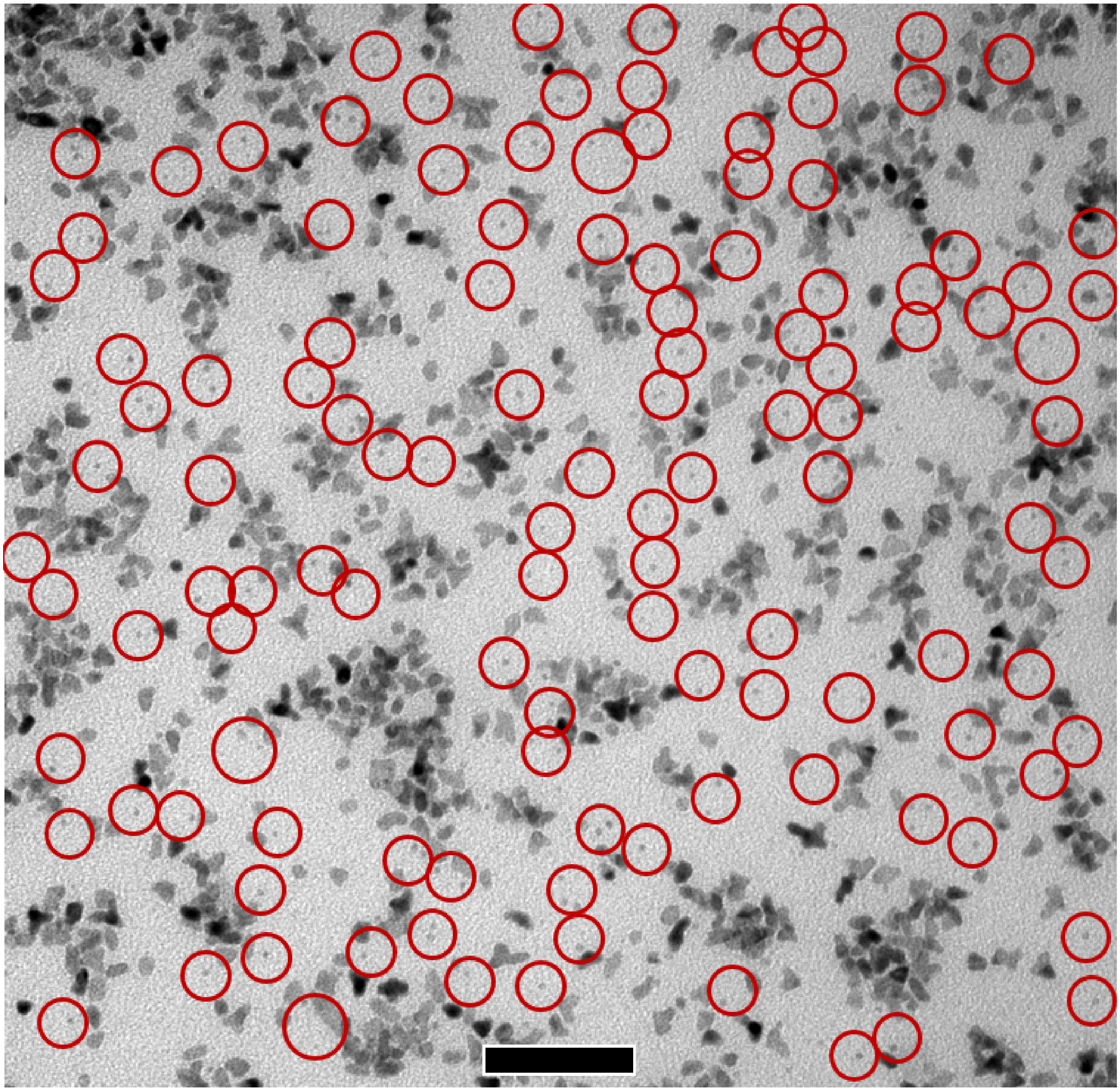

Figure S6. Microwave assisted thermal treatment at 175 °C for 15 min of Rh multipods synthesized using CvH at 120°C in EG in 9 min. Red circles indicate small Rh seeds. Scale bar is 50 nm.

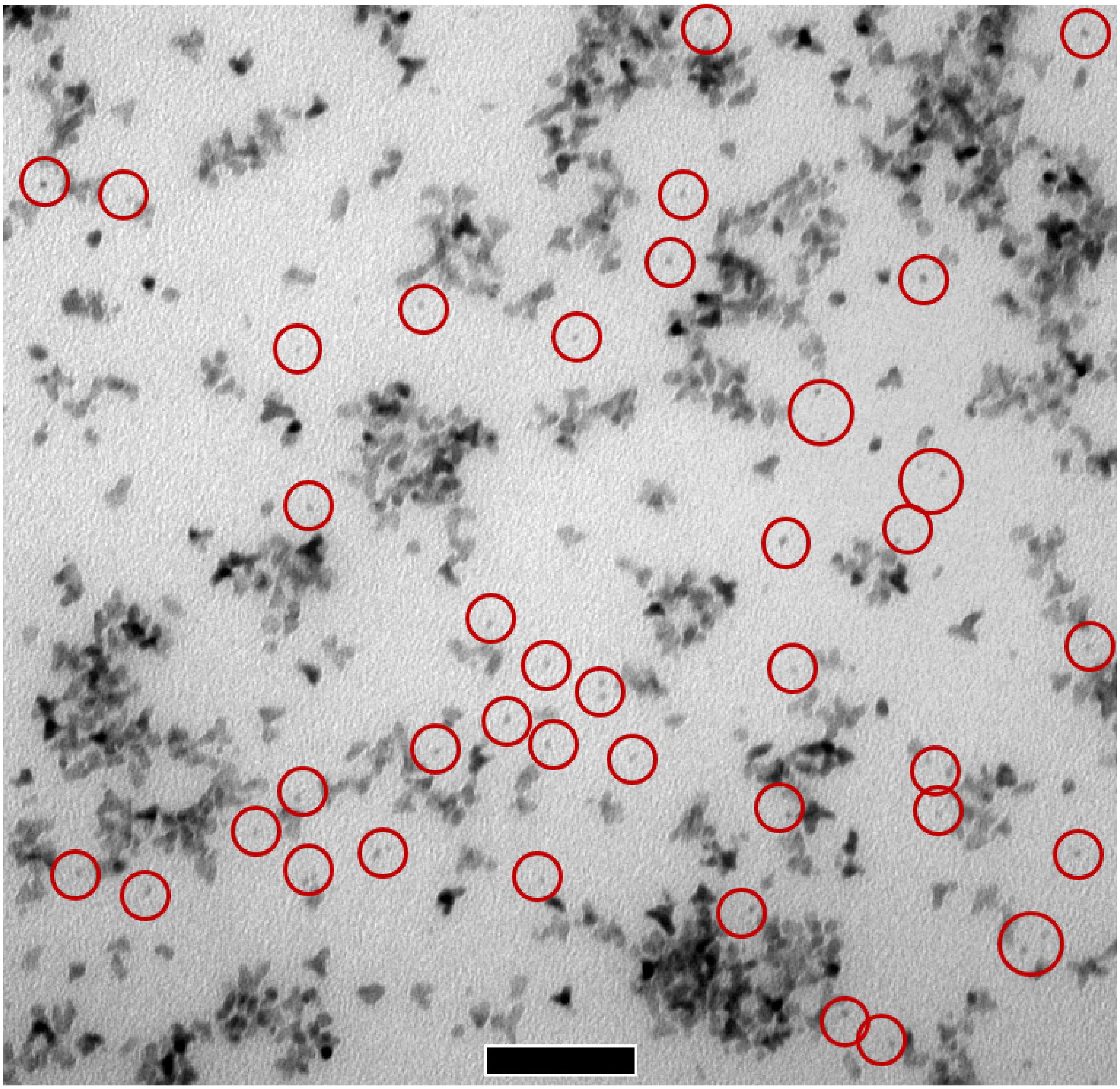

Figure S7. Oil bath assisted thermal treatment at 175 °C for 15 min of Rh multipods synthesized using CvH at 120°C in EG in 9 min. Red circles indicate small Rh seeds. Scale bar is 50 nm.

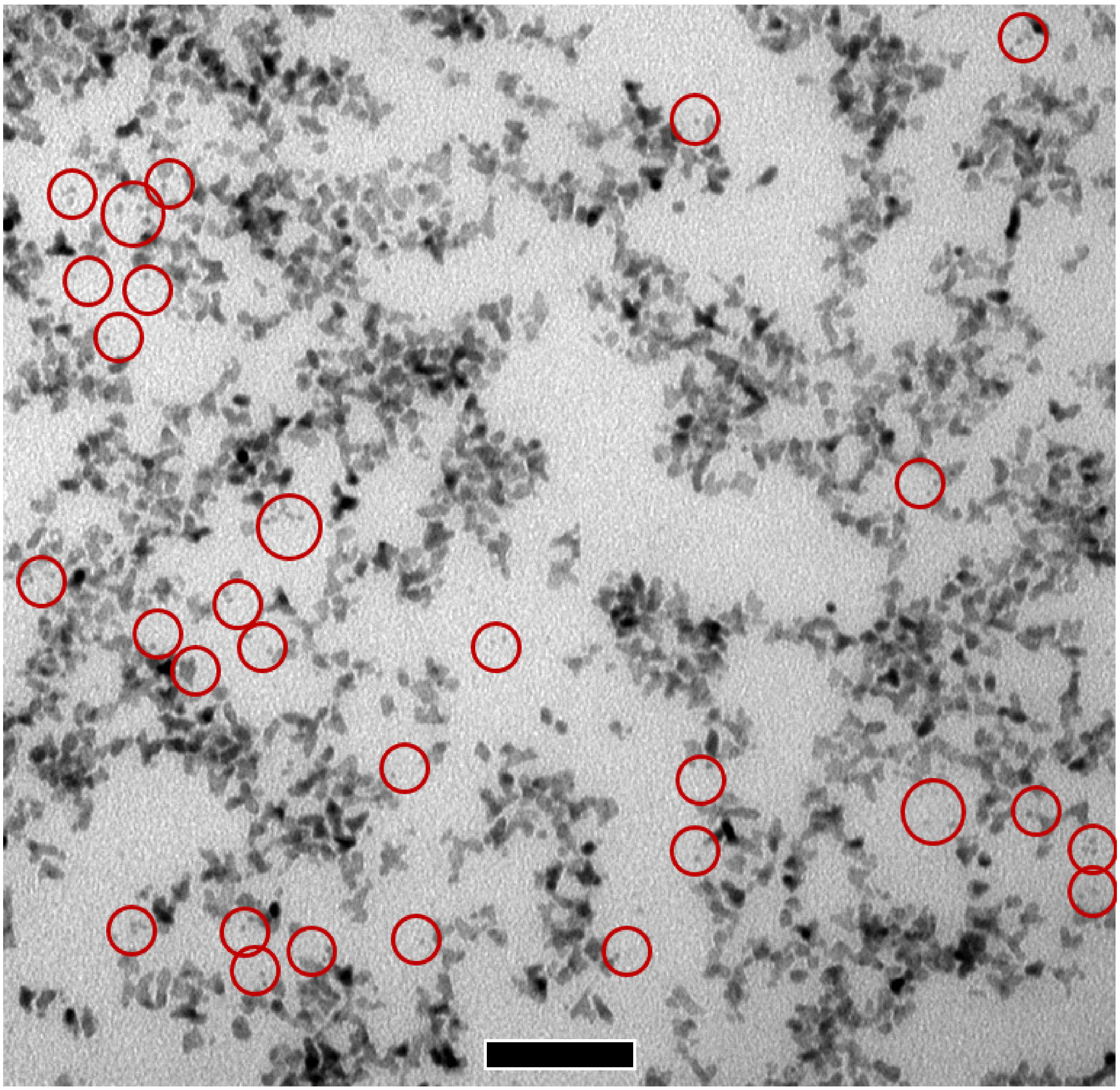

Figure S8. Oil bath assisted thermal treatment at 175 °C for 60 min of Rh multipods synthesized using CvH at 120°C in EG in 9 min. Red circles indicate small Rh seeds. Scale bar is 50 nm.

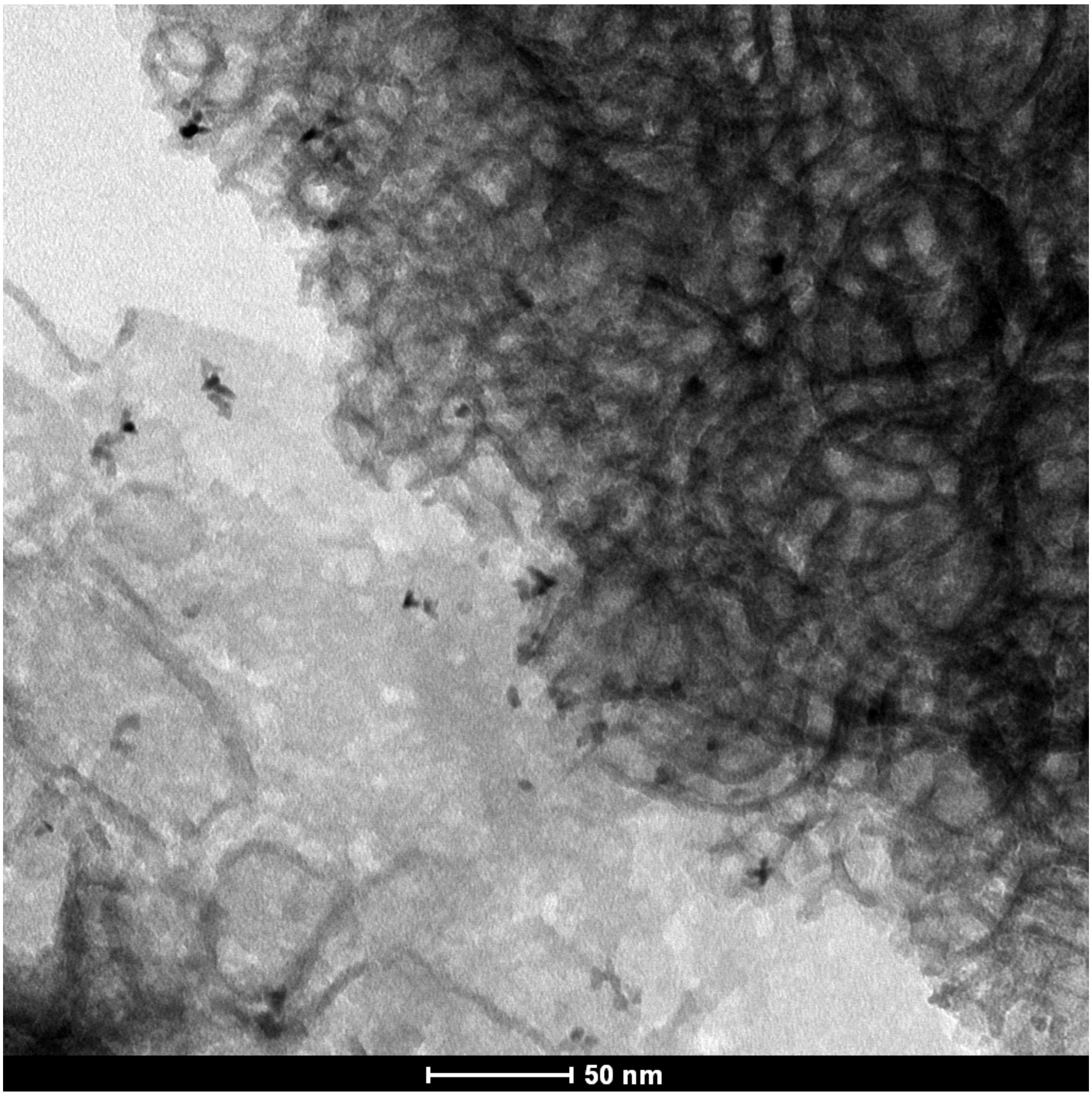

Figure S9. TEM image of Rh multipods synthesized under μwI using two phase flow reaction at 120 °C for 9 minutes after being supported on amorphous silica; scale bar is 50 nm.

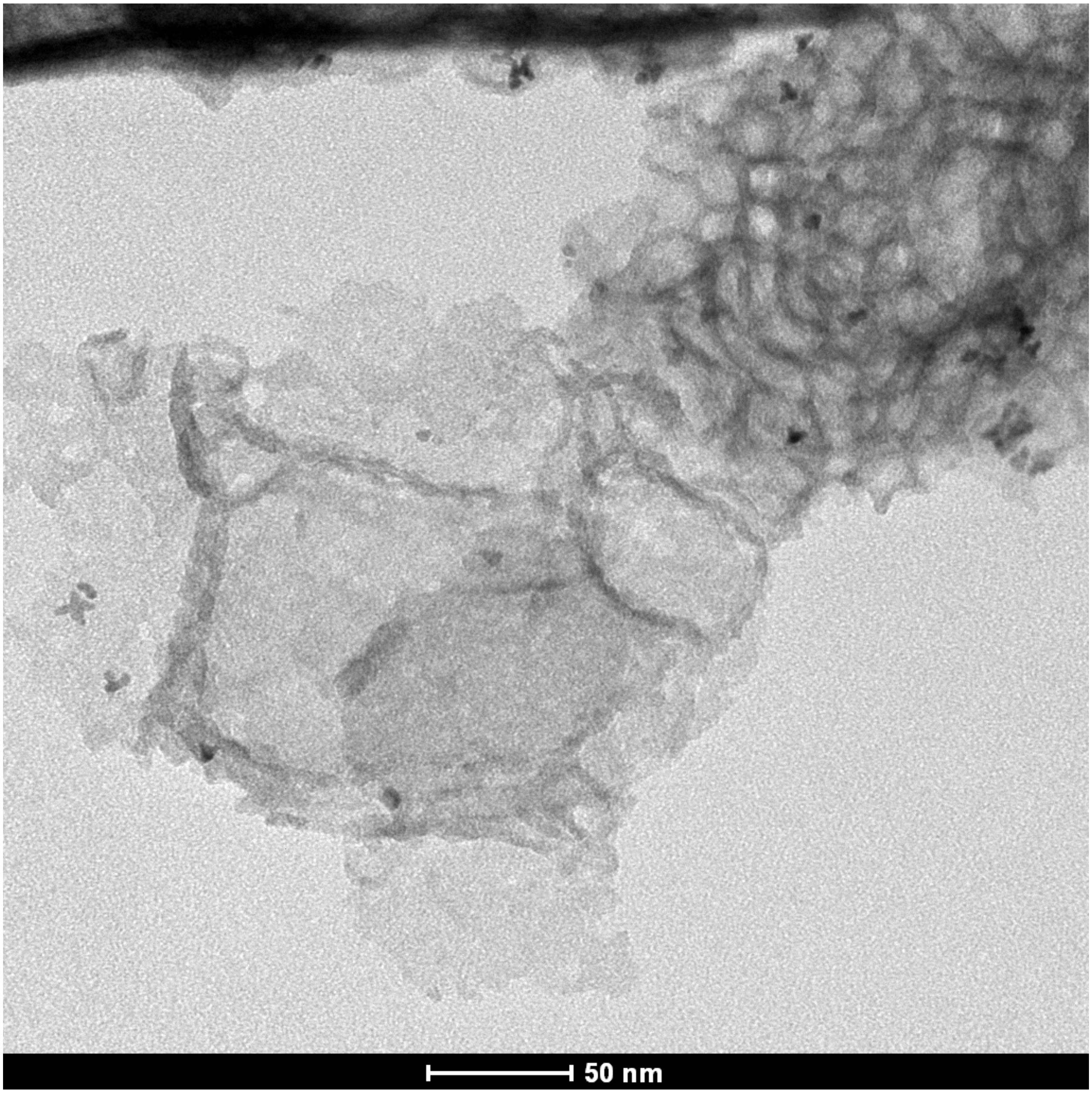

Figure S10. (A) TEM image of post-catalytic Rh multipods synthesized under μwI using two phase flow reaction at 120 °C for 9 minutes after being supported on amorphous silica; scale bar is 50 nm.

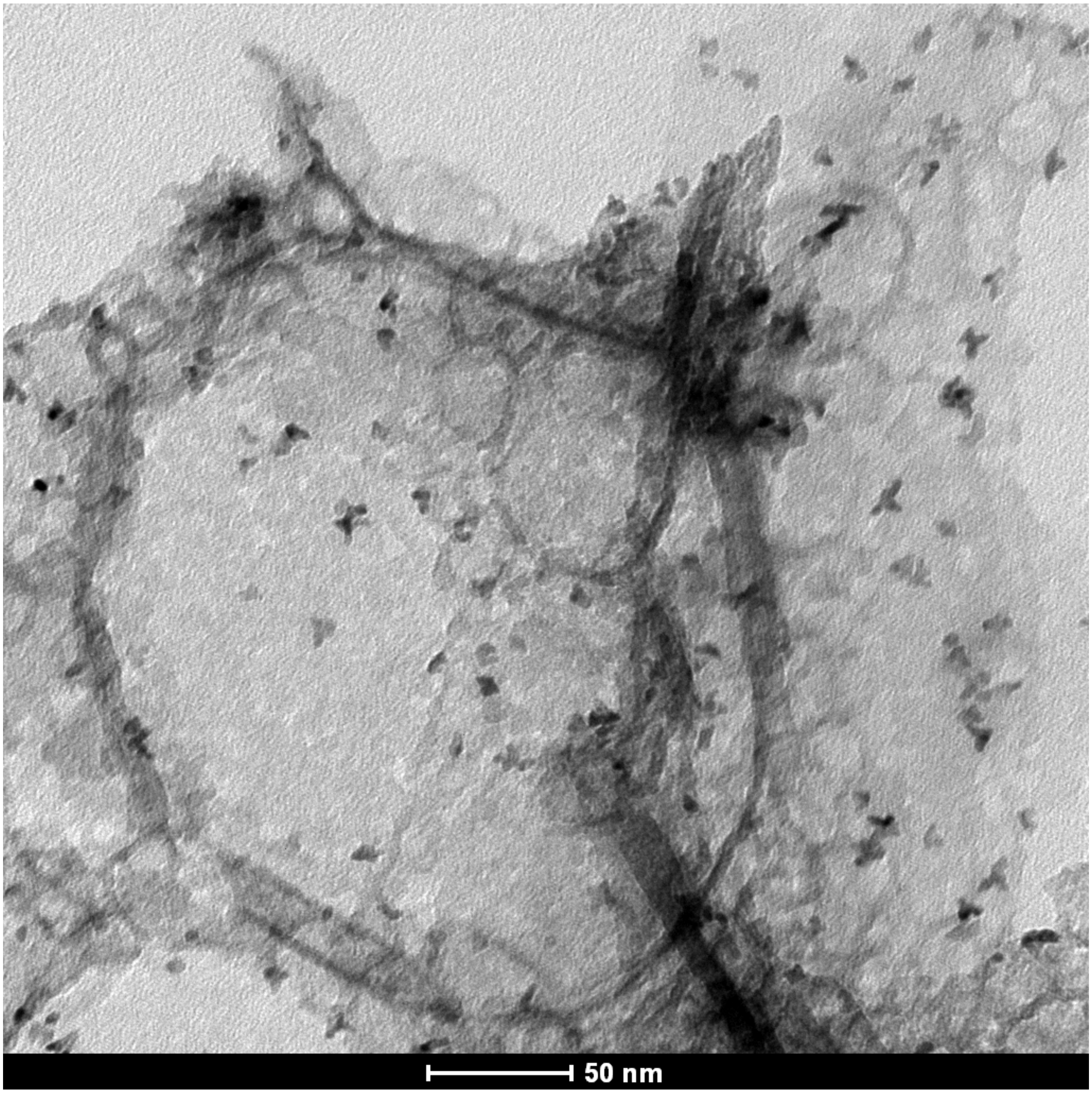

Figure S11. TEM image of Rh multipods synthesized under CvH using two phase flow reaction at 120 °C for 9 minutes after being supported on amorphous silica; scale bar is 50 nm.

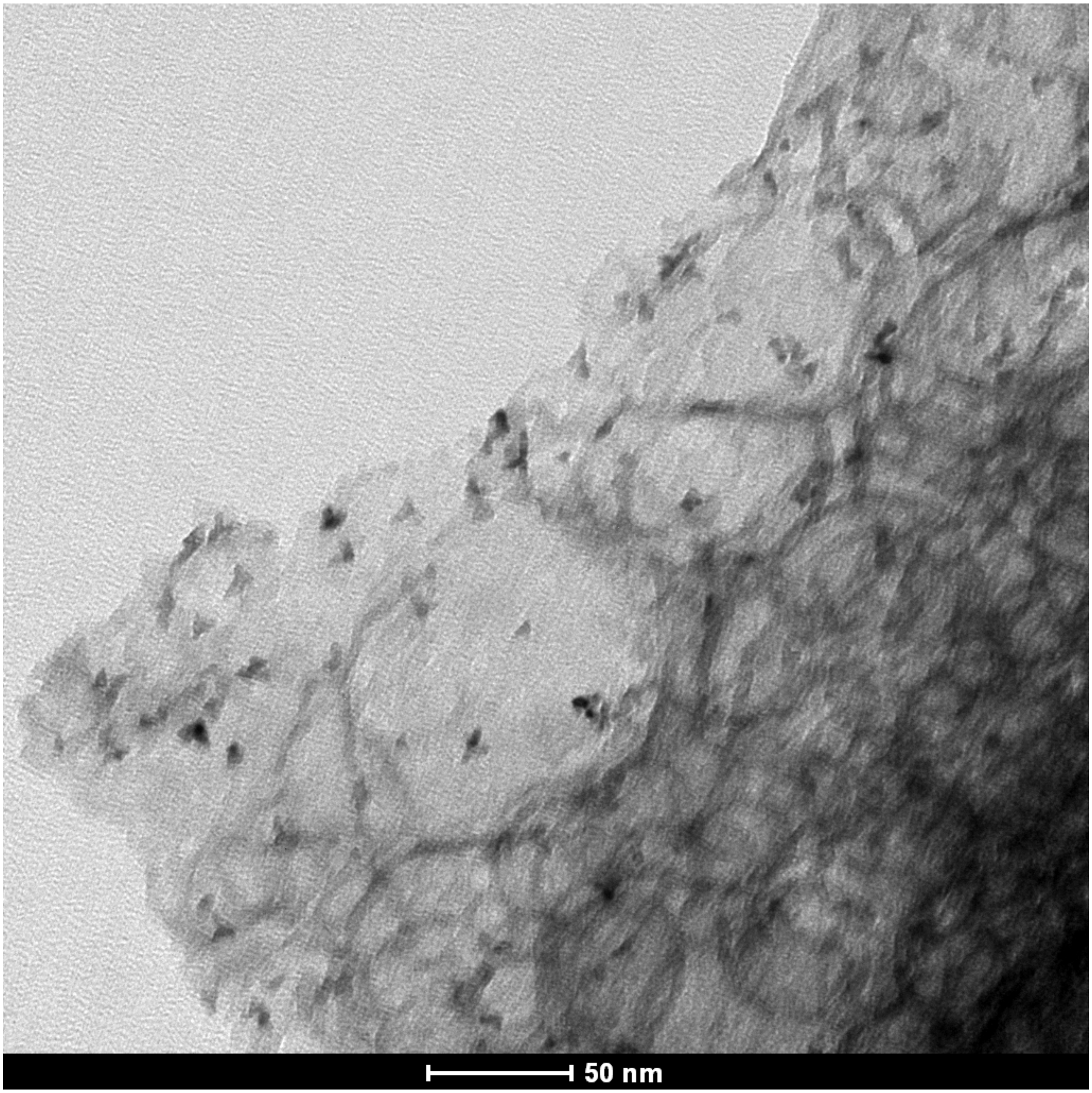

Figure S12. TEM image of post-catalytic Rh multipods synthesized under CvH using two phase flow reaction at 120 °C for 9 minutes after being supported on amorphous silica; scale bar is 50 nm.

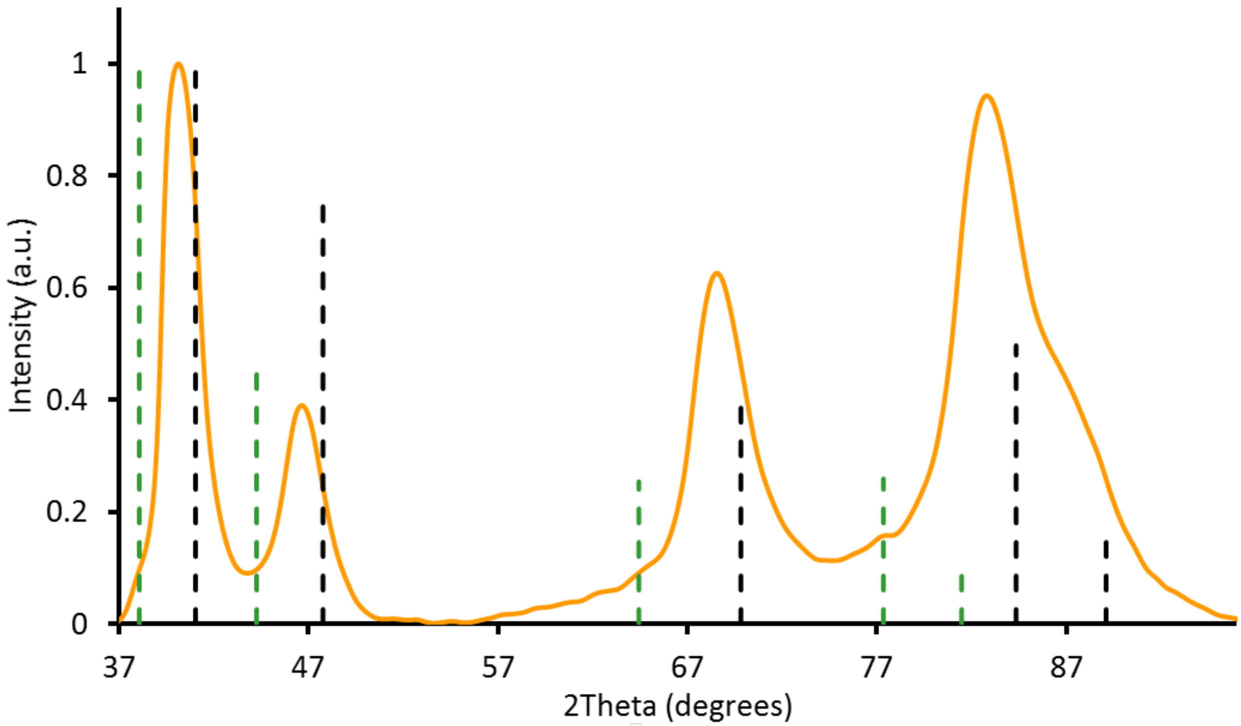

Figure S13. PXRD of $Rh_{70}Ag_{30}$ alloy NPs using two phase flow reaction.

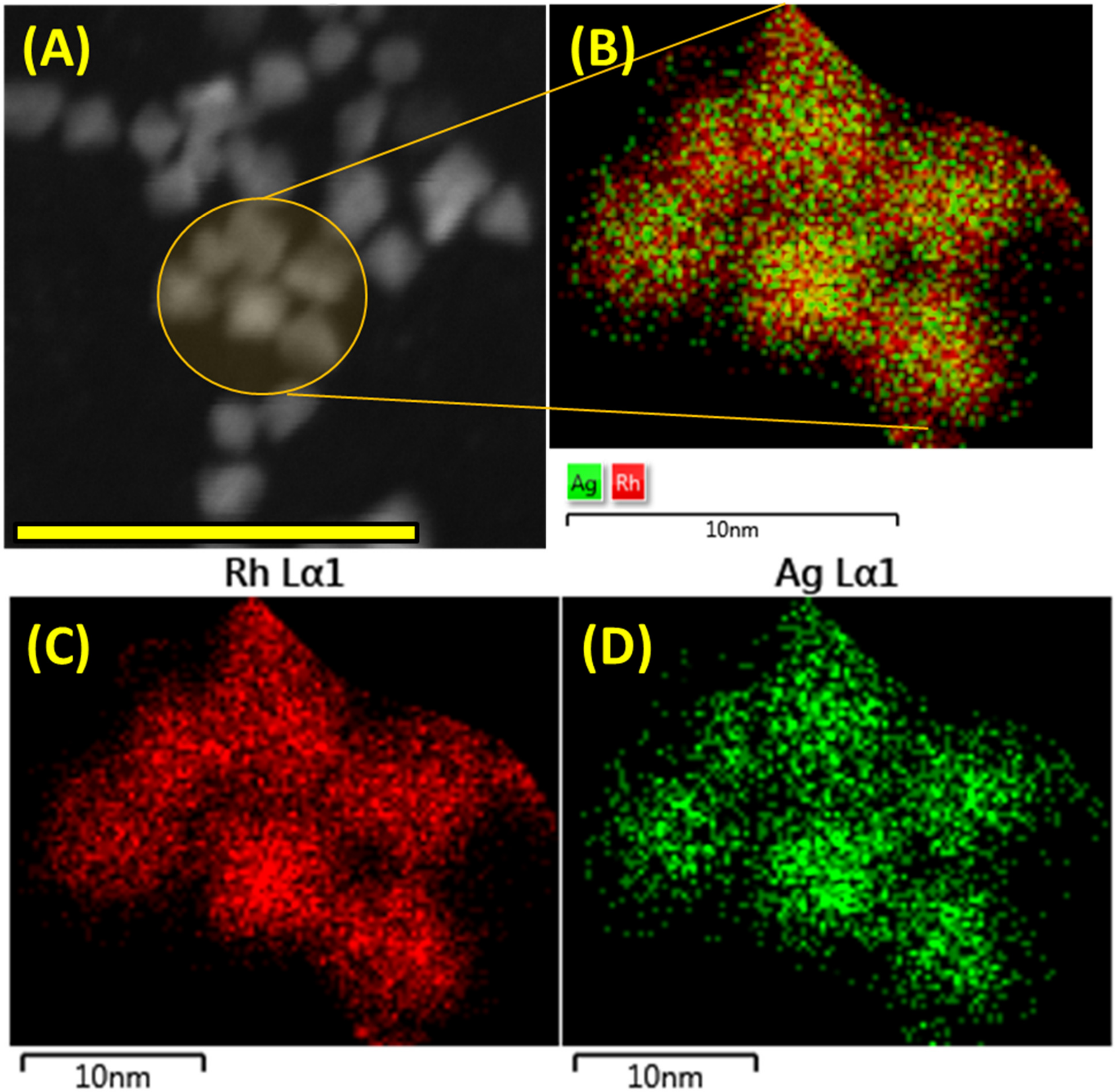

Figure S14. (**A**) HAADF-STEM images of $Rh_{70}Ag_{30}$ alloy NPs synthesized using two phase flow reaction; **(B)-(D)** show 2D EDS mapping results. Scale bar is 50 nm.

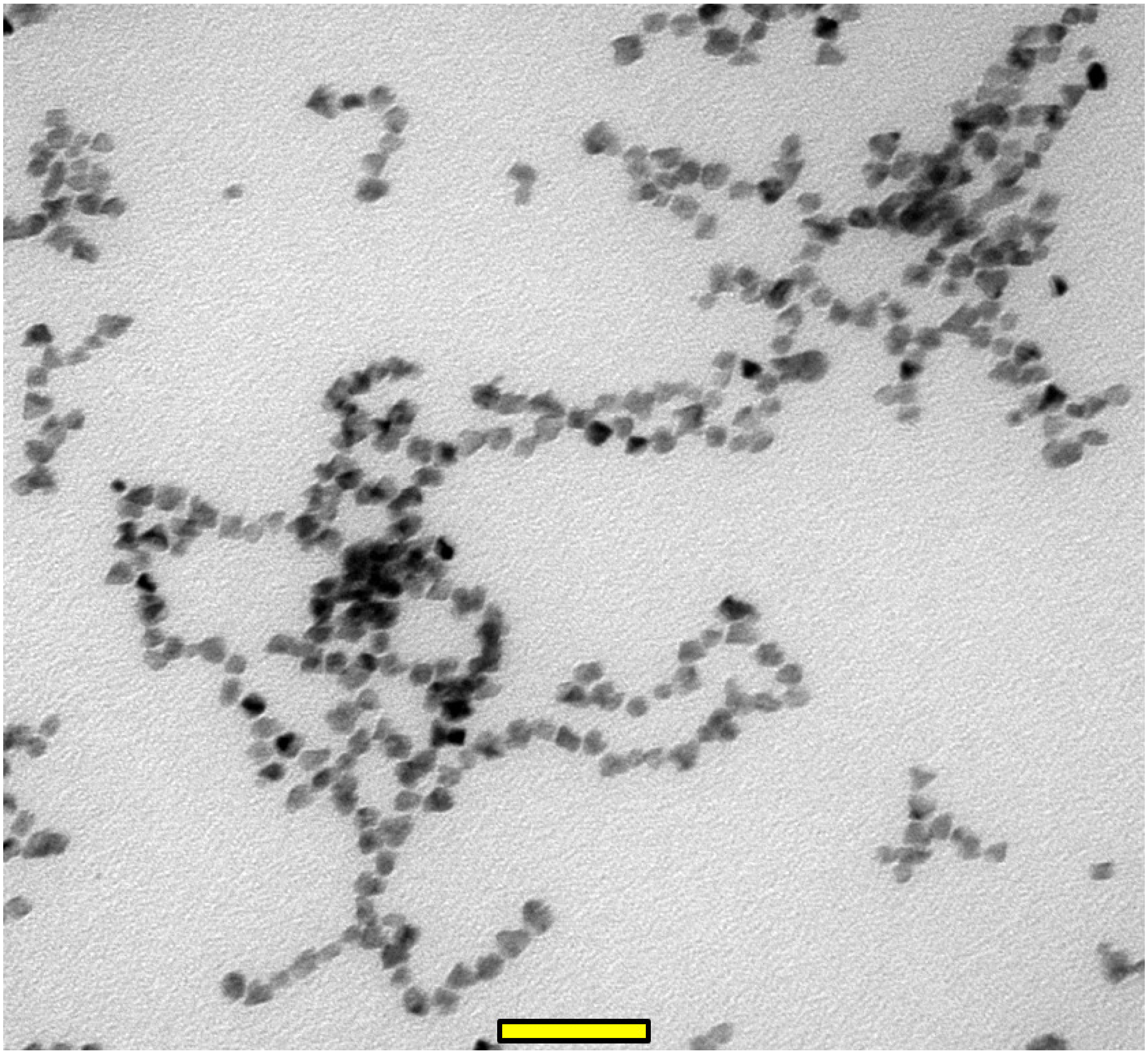

Figure S15. TEM images of $Rh_{70}Ag_{30}$ alloy NPs using two phase flow reaction; scale bar is 50 nm.

Equation S1. Activity was calculated using the following formula:

$$Activity\ (\mu mol g^{-1} s^{-1}) = \left(\frac{1}{Mass\ of\ catalyst\ used\ (g)} * \frac{C6H10\ flow\ \left(\frac{mol}{min}\right) * 10^{6}}{60\ \left(\frac{s}{min}\right)} * \frac{\left(\frac{(Area\ counts\ for\ cyclohexane)}{(MW\ of\ cyclohexane)}\right)}{\left(\frac{(Area\ counts\ for\ cyclohexane)}{(MW\ of\ cyclohexane)}\right) + \left(\frac{(Area\ counts\ for\ cyclohexene)}{(MW\ of\ cyclohexene)}\right)}\right.$$

Turnover frequency normalized for Rh loading was calculated using the formula:

$$\text{TOF}\ (\text{S}^{-1}) = \frac{Activity * 10^{-6} (mol/(\mu mol)}{\frac{(Wt\%\ of\ Rh)}{(MW\ of\ Rh)}} * \frac{1}{\left[\text{percentage of} \left(\frac{(Surface\ area)}{(Volume)}\right) for\ the\ NPs\right]}$$

Kinetic studies and determination of activation energies.

The catalytic run was started at 25 °C and temperature was changed to 30 °C after attainment of steady state conversion of cyclohexene to cyclohexane at 25 °C. Temperature was held constant at 30 °C until the steady state was achieved again. This process was repeated for temperature values of 24, 18, 12, and 6 °C respectively. The activation energy values were obtained using the slope of the best fit line by plotting Ln (activity) *vs.* $\frac{1}{T(K)}$. The activity values were averaged using at least four points corresponding to steady state of the catalysts.