nanomaterials

MDPI

Supplementary Materials

Effect of Polyvinyl Alcohol Ligands on Supported Gold Nano-Catalysts: Morphological and Kinetics Studies

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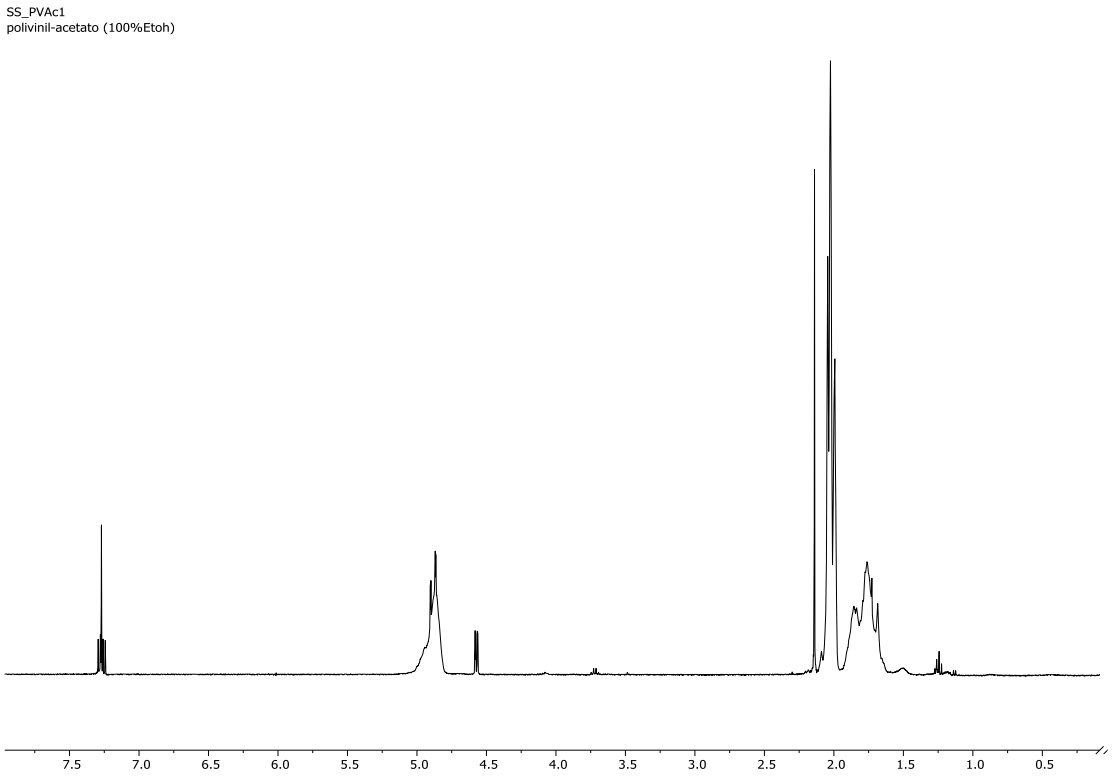
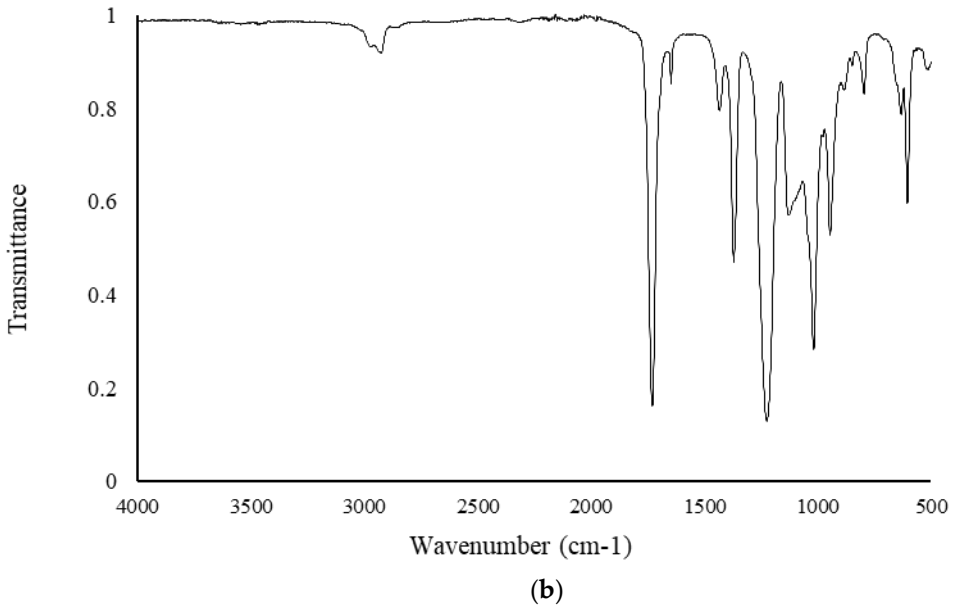
-Poly vinyl alcohol synthesis and characterization

To characterize polymer synthesized by radical polymerization of vinyl acetate NMR as well as FT-IR spectra were recorded and reported in **Figure S1**. By ^{1}H-NMR spectrum, reference peak of the CH_3 derived from acetate group was observed at 2 ppm. The other aliphatic hydrogen signals were observed at 1.75 ppm and 4.9 ppm. **Figure S1b** shows FT-IR spectra of PVAc where typical reference bands at 1729 and 1300–1000 cm^{-1} related to the stretching vibrations of C=O and C–O group are present.



(**a**)



(**b**)

Figure S1. (**a**) ^{1}H-NMR (Proton nuclear magnetic resonance) in $CDCl_3$ and (**b**) FT-IR (Furier Transform Infra-Red Spectroscopy) spectra of poly-vinyl acetate (PVAc).

Table 1. GPC (Gel Permeation Chromatography) data.

	$\overline{M_n}$	$\overline{M_w}$	*Polidispersity*
PVAc1	23,300	44,700	1.9
PVAc2	32,800	60,500	1.8
PVAc3	92,300	221,500	2.4
PVAc4	161,500	616,400	3.8

Poly-vinyl alcohol synthesized by direct saponification process was characterized by means of NMR and FT-IR spectroscopies. By ^{1}H-NMR spectrum reported in **Figure S2.** it is possibile to confirm the presence of full-hydrolyzed PVA due to the absence of CH_3 peak at 2 ppm.

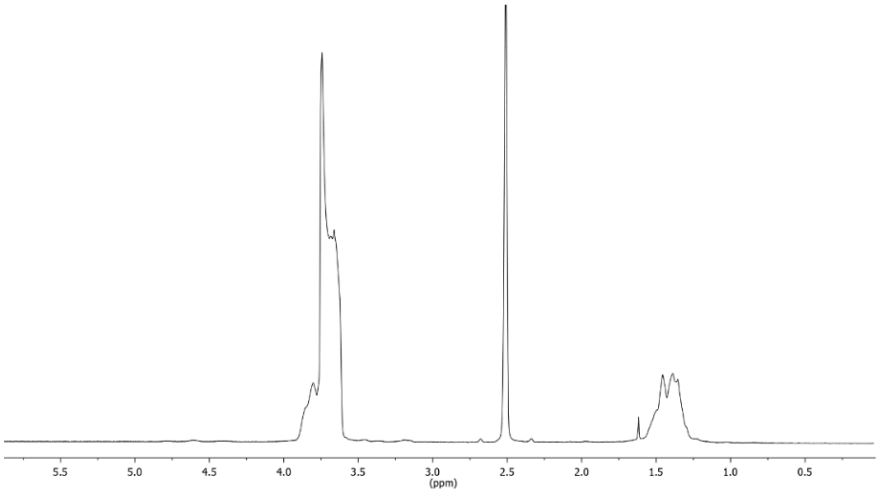


Figure S2. ^{1}H-NMR spectrum in d_6-DMSO-D_2O of full hydrolyzed poly-vinyl alcohol.

By using a reference peak, the intensity of C=O stretching band at 1729 cm^{-1}, the hydrolysis degree in PVA partially hydrolyzed was evaluated. **Figure S3** showed the FT-IR spectra of the synthesized polymers.

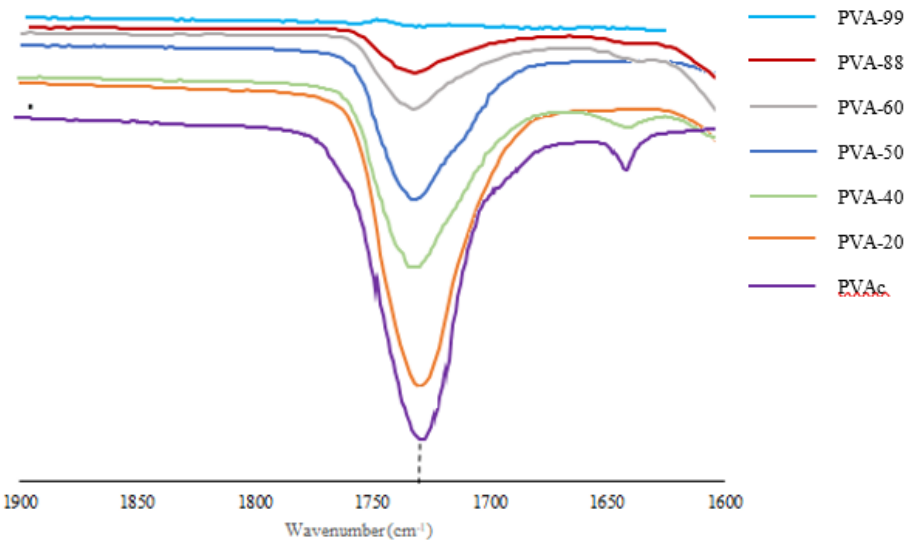


Figure S3. FT-IR spectra of poly-vinyl alcohol partially hydrolysed: focus on the C=O stretching at 1729 cm^{-1}.

-Nanoparticles characterization: effect of molecular weight

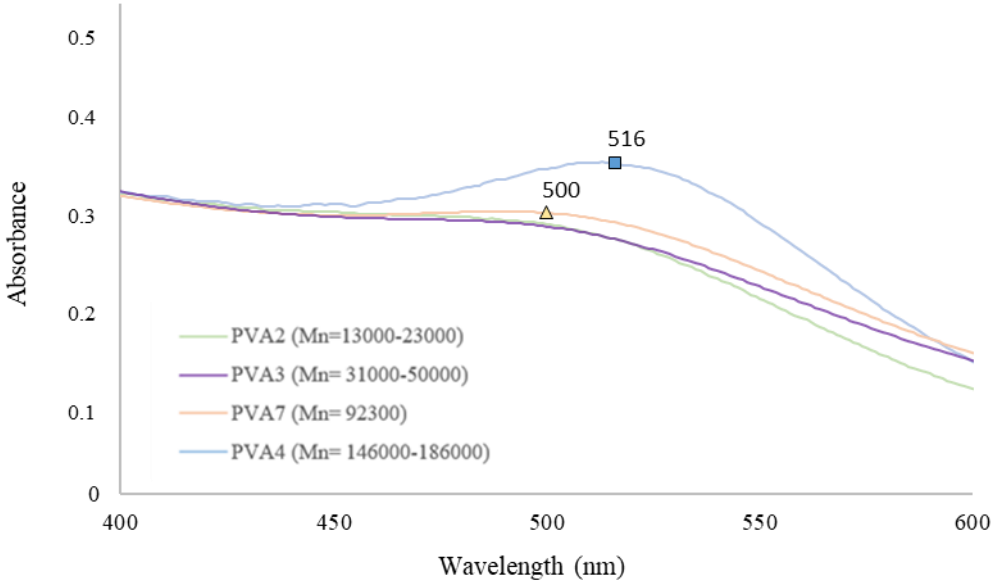


Figure S4. UV-visibile spectra and positions of the surface plasmon resonance peak of the Au colloidal nanoparticles obtained by PVA as a function of molecular weight.

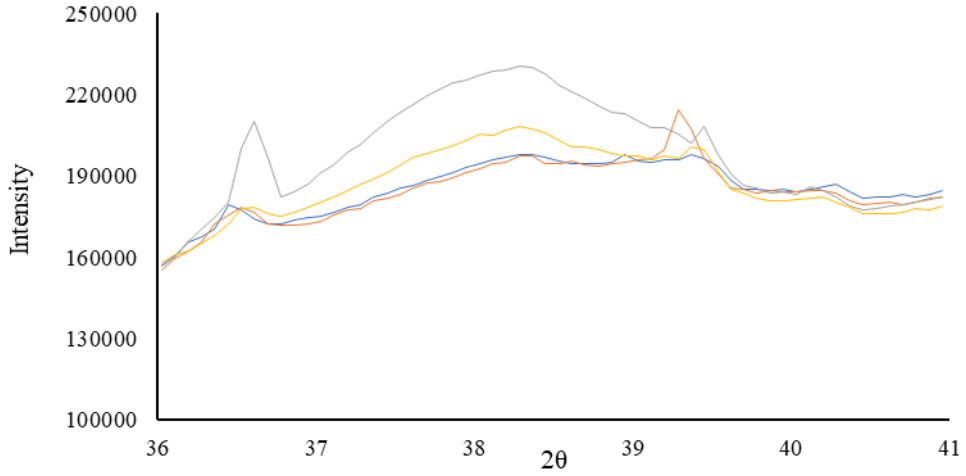


Figure S5. XRD patterns of the Au supported colloidal nanoparticles obteined by PVA as a function of molecular weight.

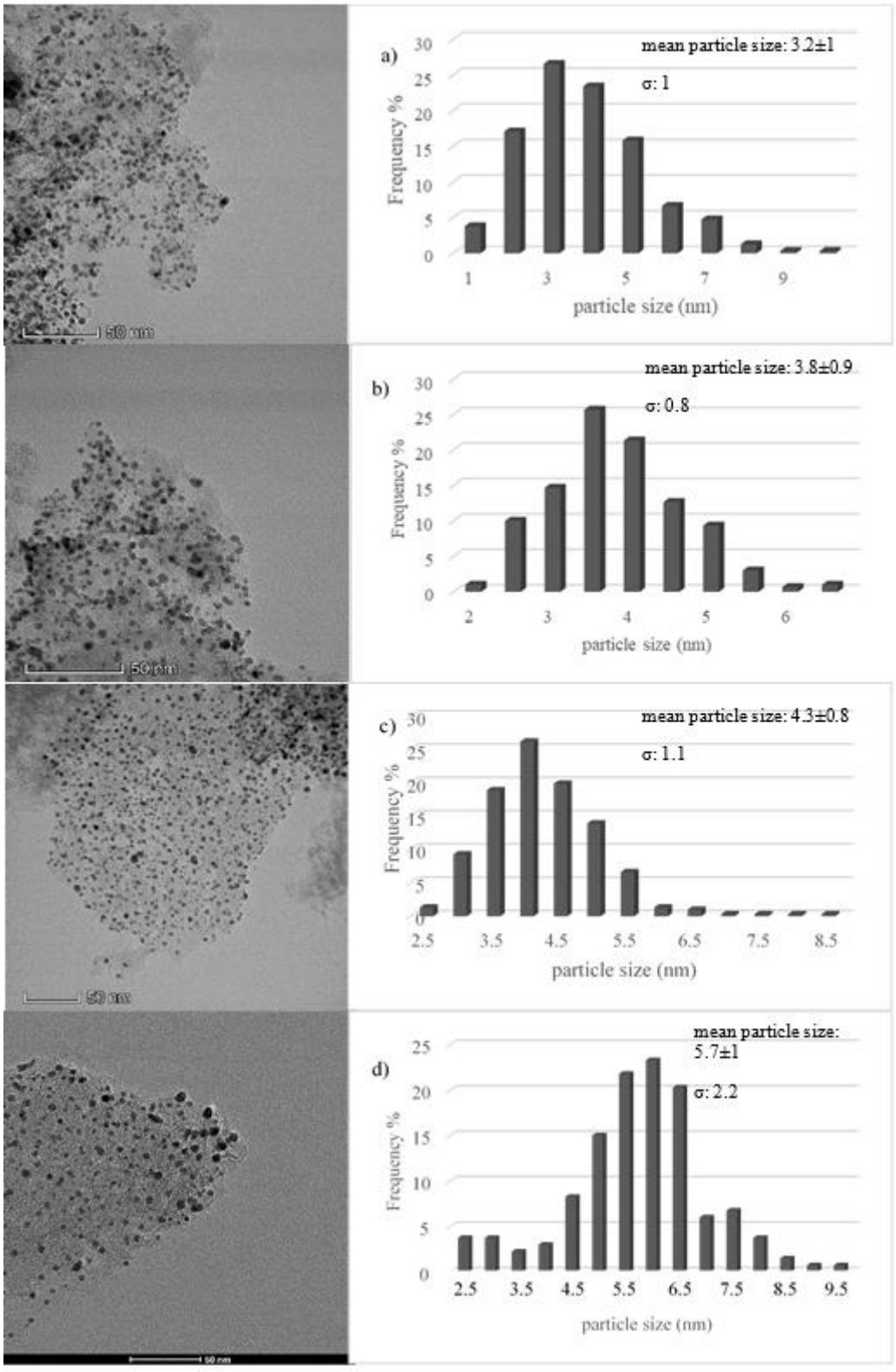


Figure S6. TEM images and particle size distributions of Au/AC synthesized using different molecular weights: (**a**) M_n= 13,000–23,000; (**b**) M_n= 31,000–50,000; (**c**) M_n= 92,300 and (**d**) M_n= 146,000–186,000.

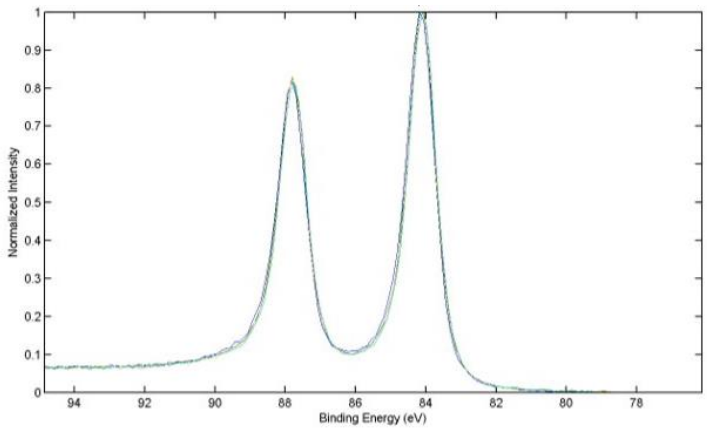


Figure S7. XPS spectra for 1% wt Au/AC synthesized using PVA-99 with different molecular weights.

-Nanoparticles characterization: effect of hydrolysis degree

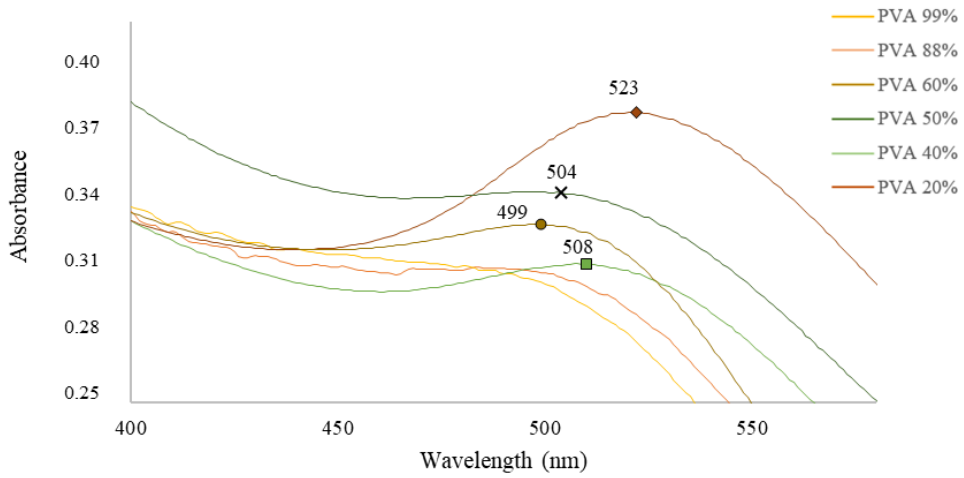


Figure S8. UV-visibile spectra relative to gold nanoparticles obtained by PVA (Mn:23,300) with different hydrolysis degree: focus on surface plasmon resonance peak.

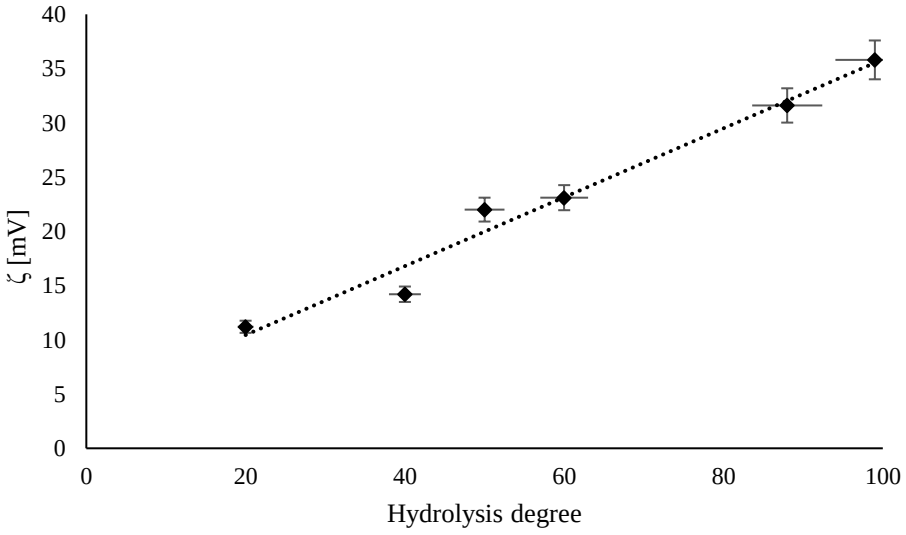


Figure S9. Zeta potential (ζ) of gold nanoparticles versus poly-vinyl alcohol hydrolysis degree (Mn:23,300).

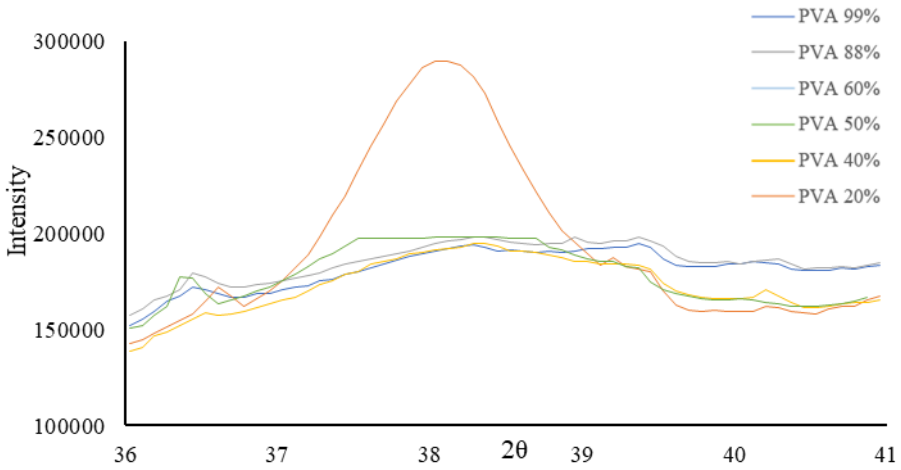
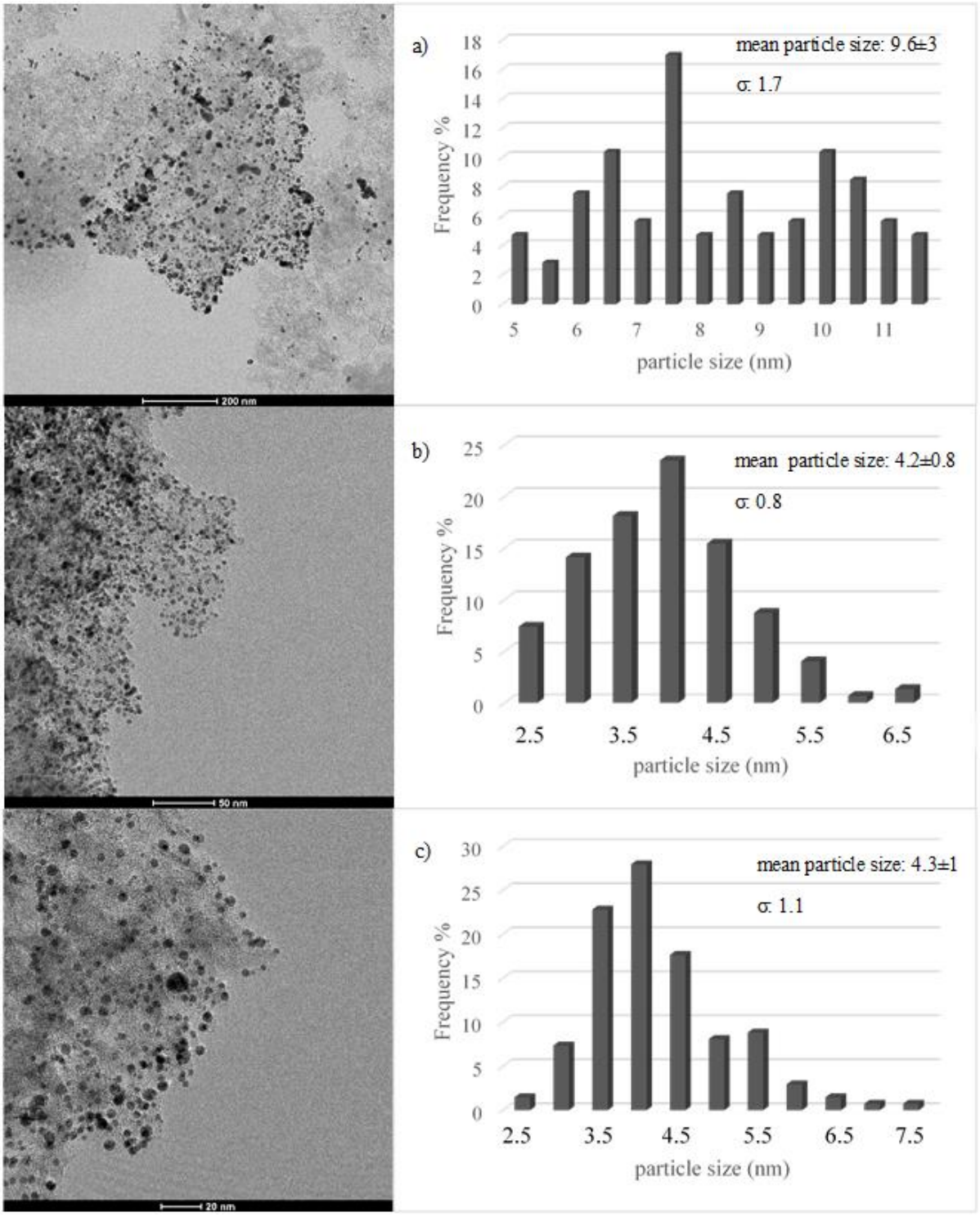


Figure S10. XRD patterns of the Au supported nanoparticles obtained by PVA (Mn:23,300) as a fucntion of the hydrolysis degree.


200 nm
a)
mean particle size: 9.6±3
σ: 1.7
Frequency %
particle size (nm)
50 nm
b)
mean particle size: 4.2±0.8
σ: 0.8
Frequency %
particle size (nm)
20 nm
c)
mean particle size: 4.3±1
σ: 1.1
Frequency %
particle size (nm)

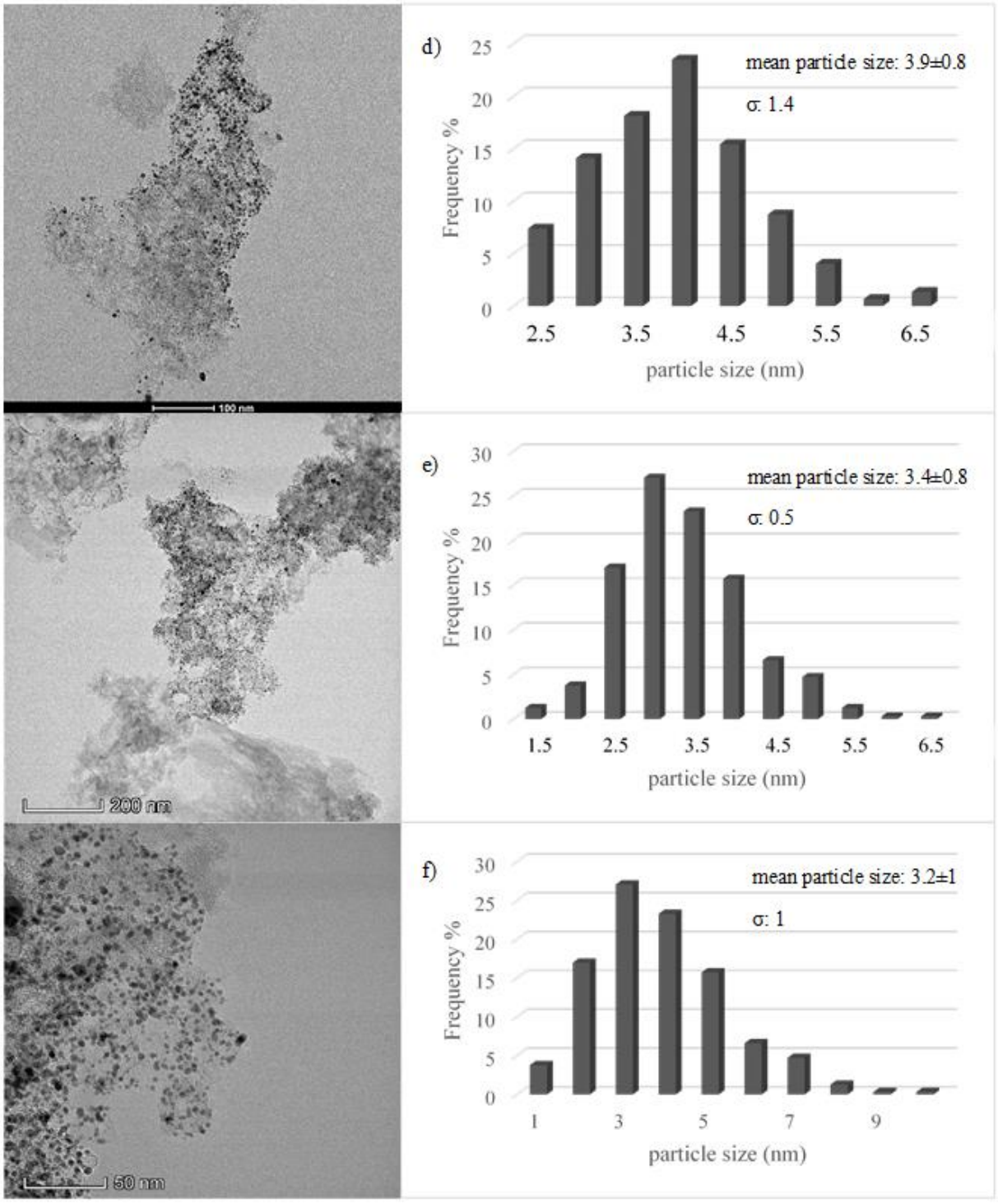


Figure S11. TEM images and particle size distributions of Au/AC synthesized using different hydrolysis degree: (**a**) 20%; (**b**) 40%; (**c**) 50%; (**d**) 60%; (**e**) 88% and (**f**) 99%.

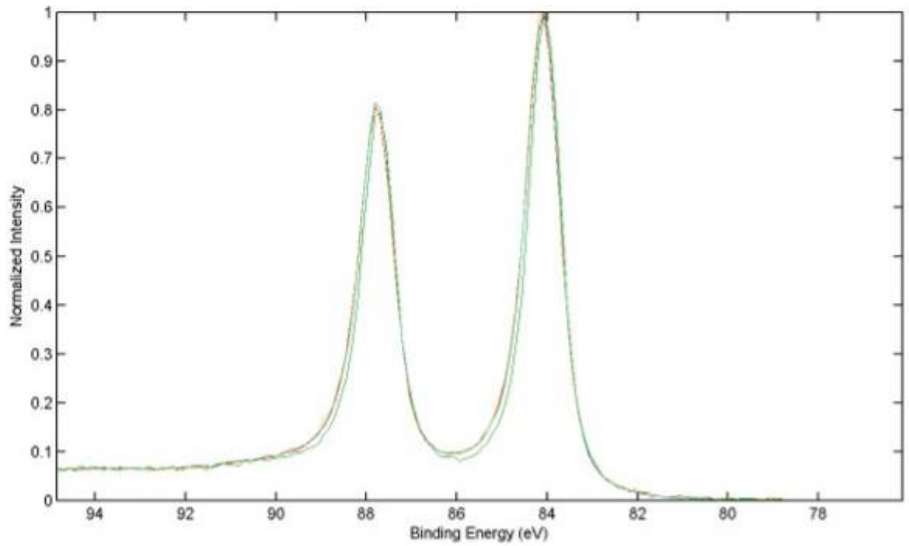


Figure S12. XPS spectra for 1% wt Au/AC synthesized using PVA (Mn:23,300) with different hydrolysis degree.

-Effect of molecular weight

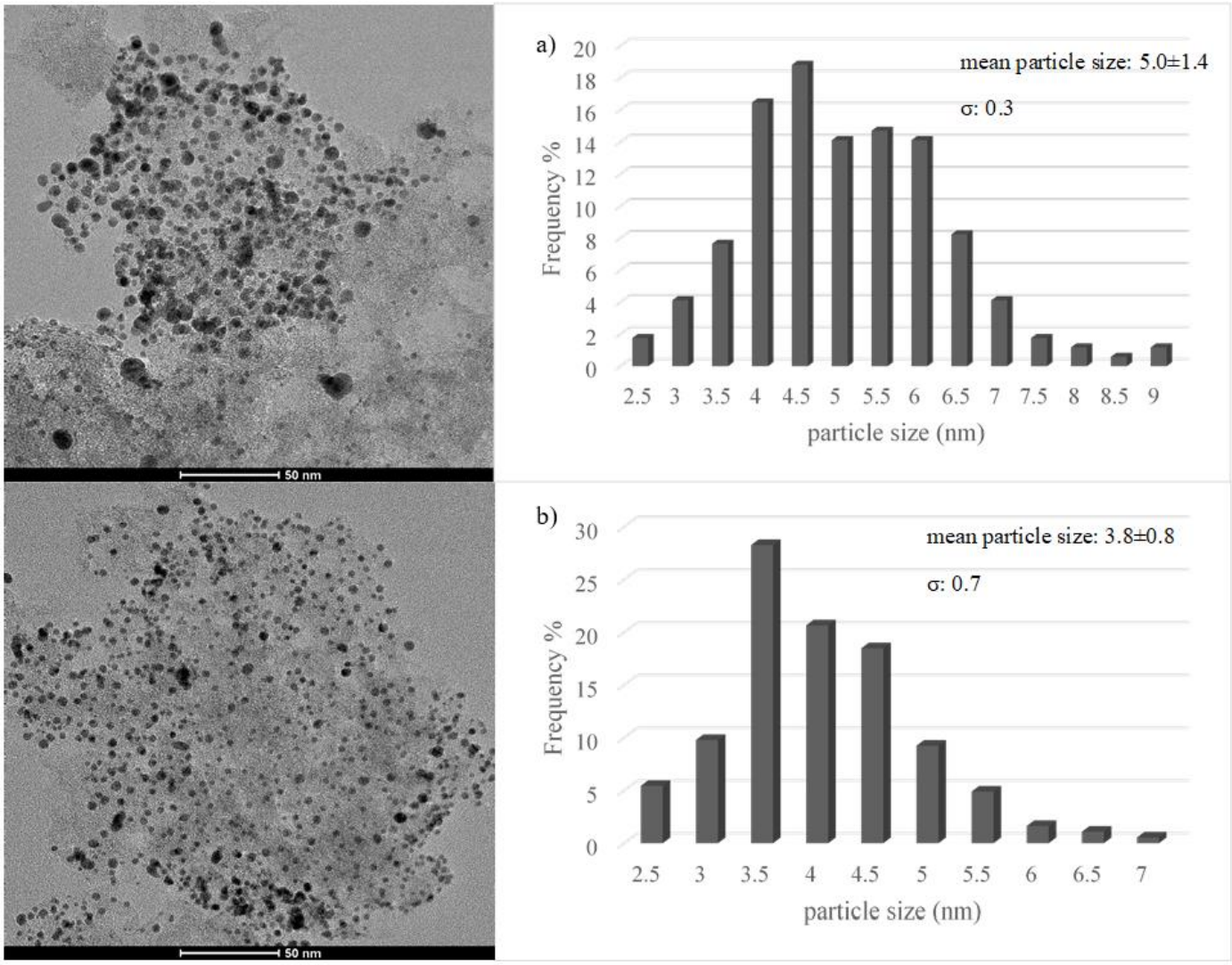


Figure 13. TEM images and particle size distributions of Au/AC synthesized using PVA2 (Mn=13,000–23,000) with different Au:PVA weight ratio: (**a**) ratio 1:0.15(Au:PVA); (**b**) ratio 1:0.33(Au:PVA).

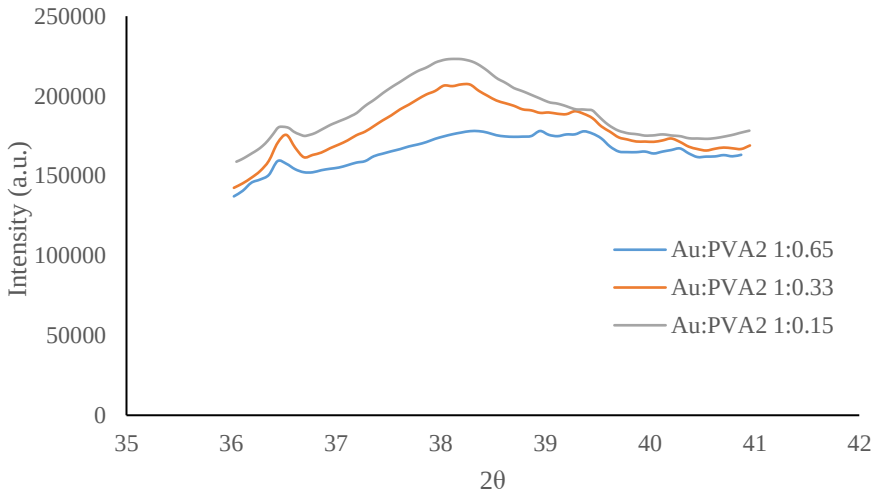


Figure S14. XRD patterns of the Au supported nanoparticles obtained by PVA2 (Mn:13,000–23,000) with different Au:PVA weight ratio.

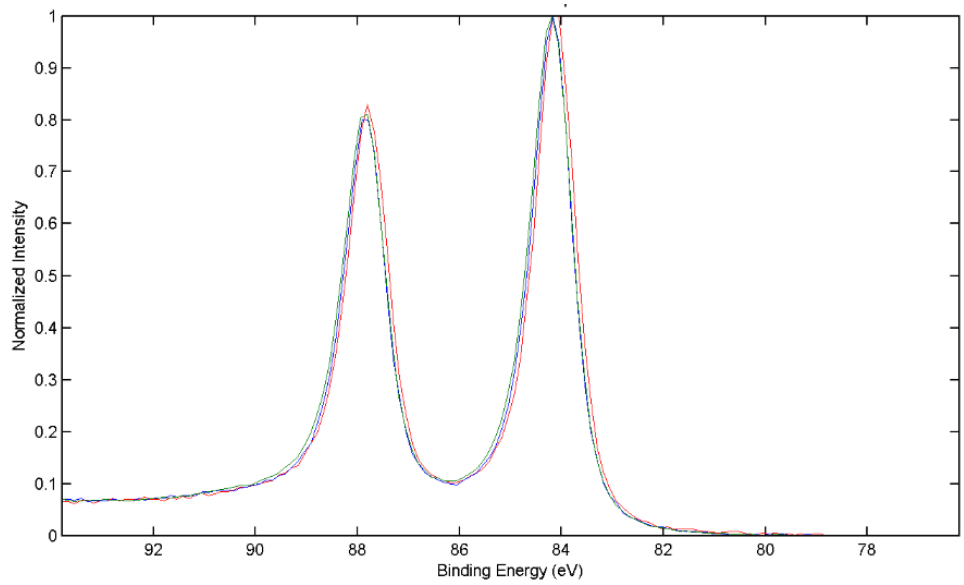


Figure S15. XPS spectra for 1% wt Au/AC synthesized using PVA2 (13,000–23,000) with different Au:PVA weight ratio.

-Effect of hydrolysis degree

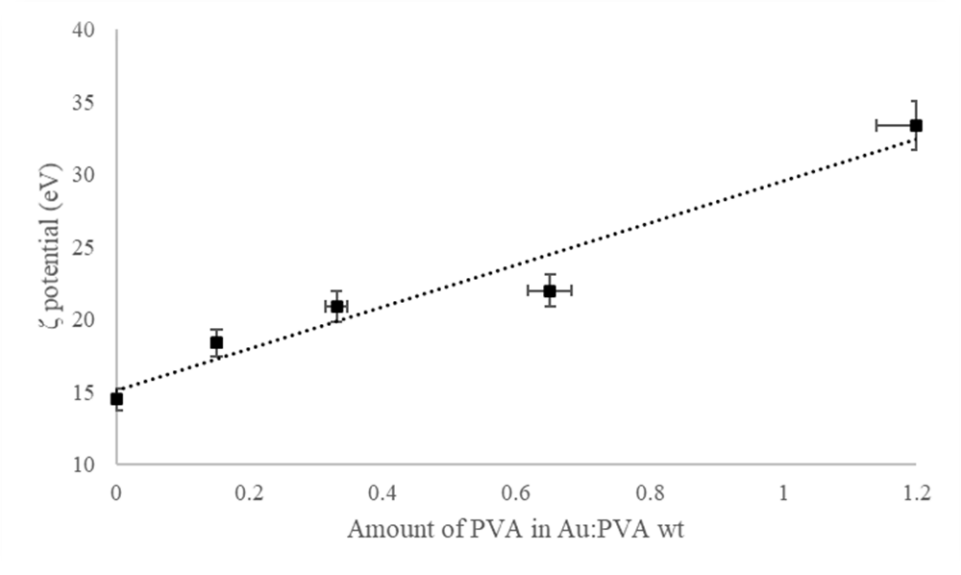
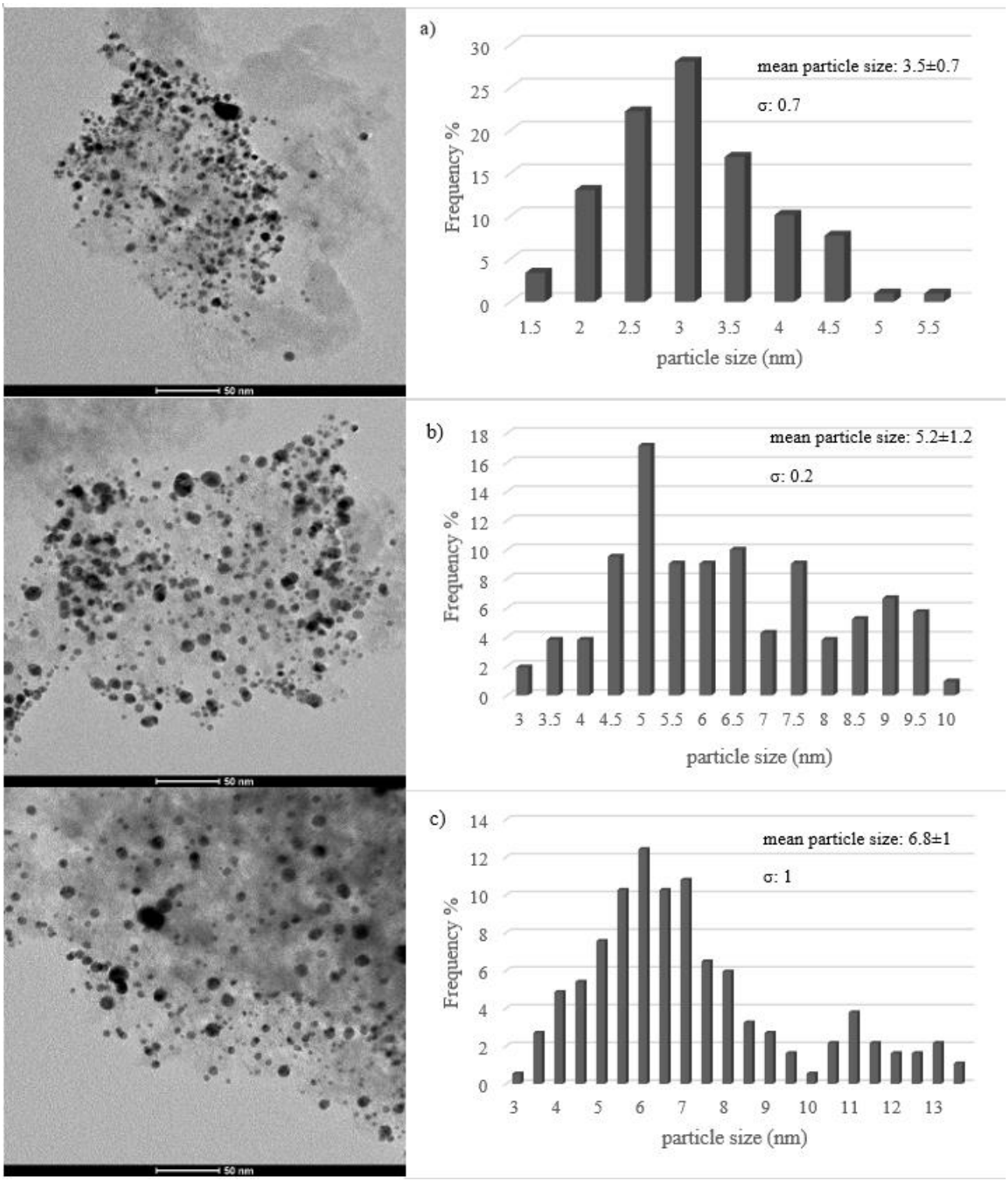


Figure S16. Zeta potential (ζ) of gold nanoparticles versus amount of PVA-60 (Mn:23,300) in Au:PVA weight ratio.


a)
mean particle size: 3.5±0.7
σ: 0.7
Frequency %
particle size (nm)
b)
mean particle size: 5.2±1.2
σ: 0.2
Frequency %
particle size (nm)
c)
mean particle size: 6.8±1
σ: 1
Frequency %
particle size (nm)

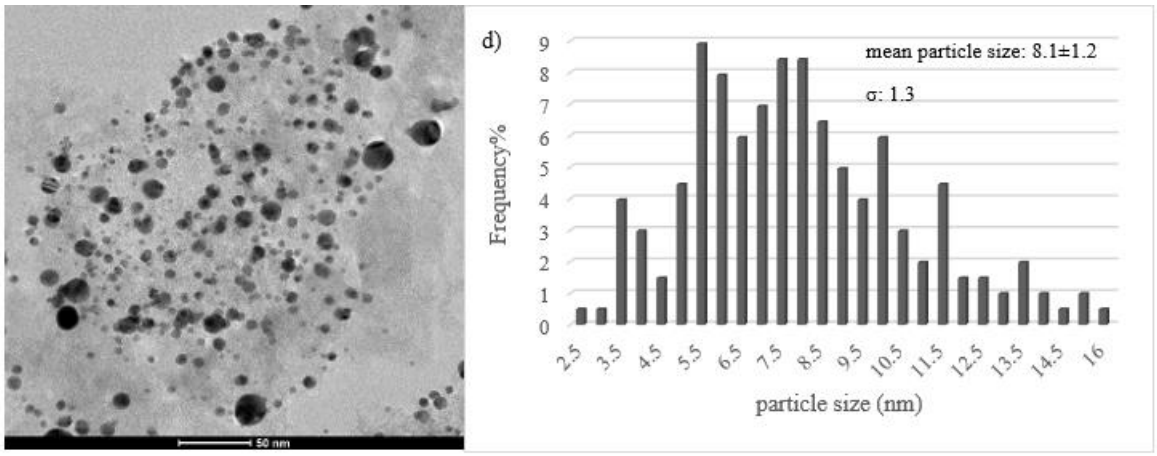


Figure S17. TEM images and particle size distributions of Au/AC synthesized using PVA-60 (Mn = 23,300) with different Au:PVA weight ratio: (**a**) ratio 1:1.2(Au:PVA); (**b**) ratio 1:0.33(Au:PVA); (**c**) 1:0.15 (Au:PVA); (**d**) 1:0 (Au:PVA).

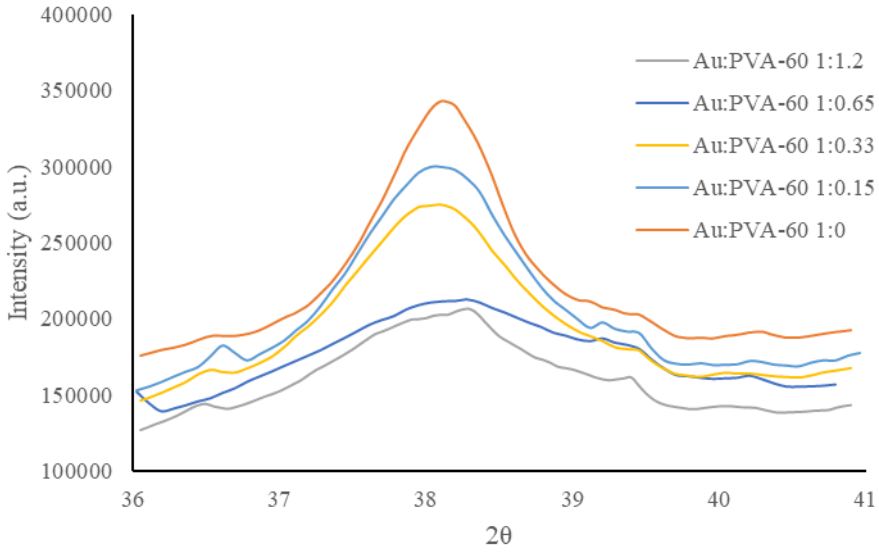


Figure S18. XRD patterns of the Au supported nanoparticles obtained by PVA-60 (Mn:23,300) with different Au:PVA weight ratio.

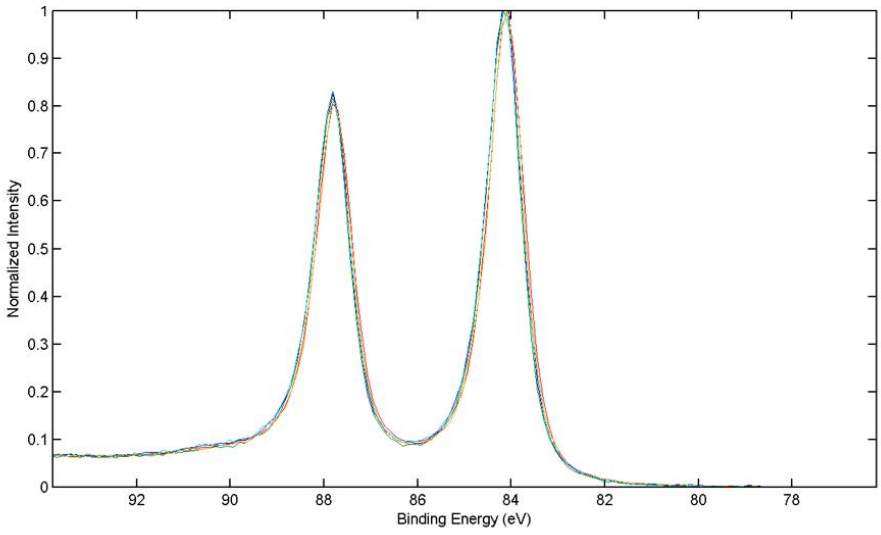


Figure S19. XPS spectra for 1% wt Au/AC synthesized using PVA-60 (23,000) with different Au:PVA weight ratio.

-Reusability test

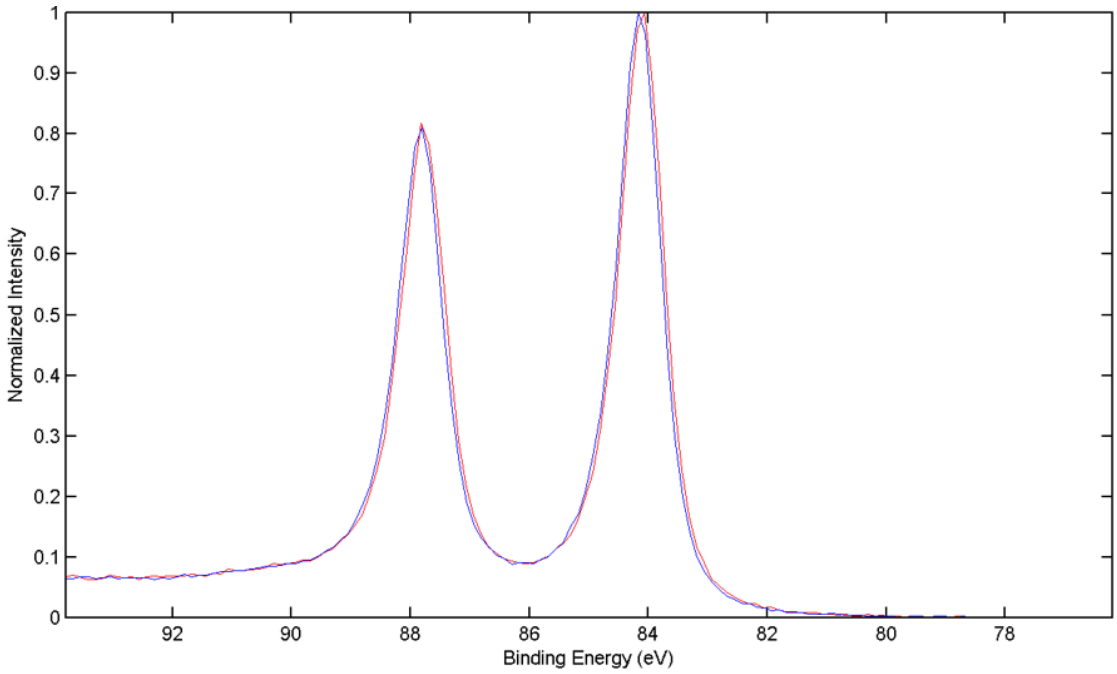


Figure S20. XPS spectra for 1% wt Au/AC synthesized using PVA-60 (23,000) with Au:PVA of 1:0.33: comparison beetween fresh and used catalyst.

Table S2. XPS data for 1% wt Au/AC synthesized using PVA-60 (Mn = 23,300) with Au:PVA of 1:0.33: comparison beetween fresh and used catalyst.

	Au:PVA (w/w)	*BE Au 4f$_{7/2}$ (eV)*	*Au on Surface (% atomic)*	*C on Surface (% atomic)*	*Surface atomic ratio Au/C*
PVA-60 fresh	1:0.33	84.1	1.38	93.2	0.02
PVA-60 used	1.0.33	84.1	1.87	92.9	0.02

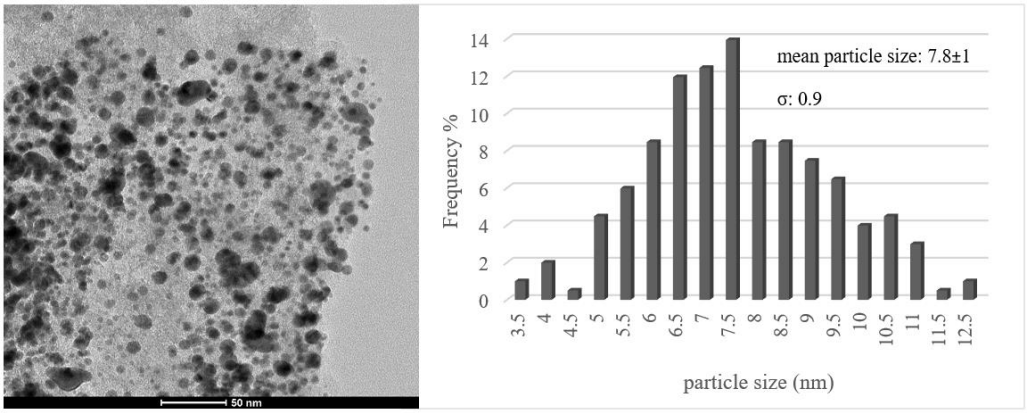


Figure S21. TEM images and particle size distributions of Au/AC used catalyst synthesized with PVA-60 (Mn = 23,300) Au:PVA of 1:0.33.