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Electronic Supplementary Information

Influence of stabilisers on the catalytic activity of supported Au colloidal nanoparticles for the liquid phase oxidation of glucose to glucaric acid: Understanding the catalyst performance from NMR relaxation and computational studies

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Characterisation of Catalysts

UV-visible spectra of the Au colloidal solutions were recorded on an Agilent Cary 3500 UV-Vis Spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'PertPRO X-ray diffractometer. A Cu radiation source (λ= 1.54 Å) was utilized, and diffraction patterns were recorded between 10–80° 2θ with 0.08° step size and acquisition time of 1300 s per step.

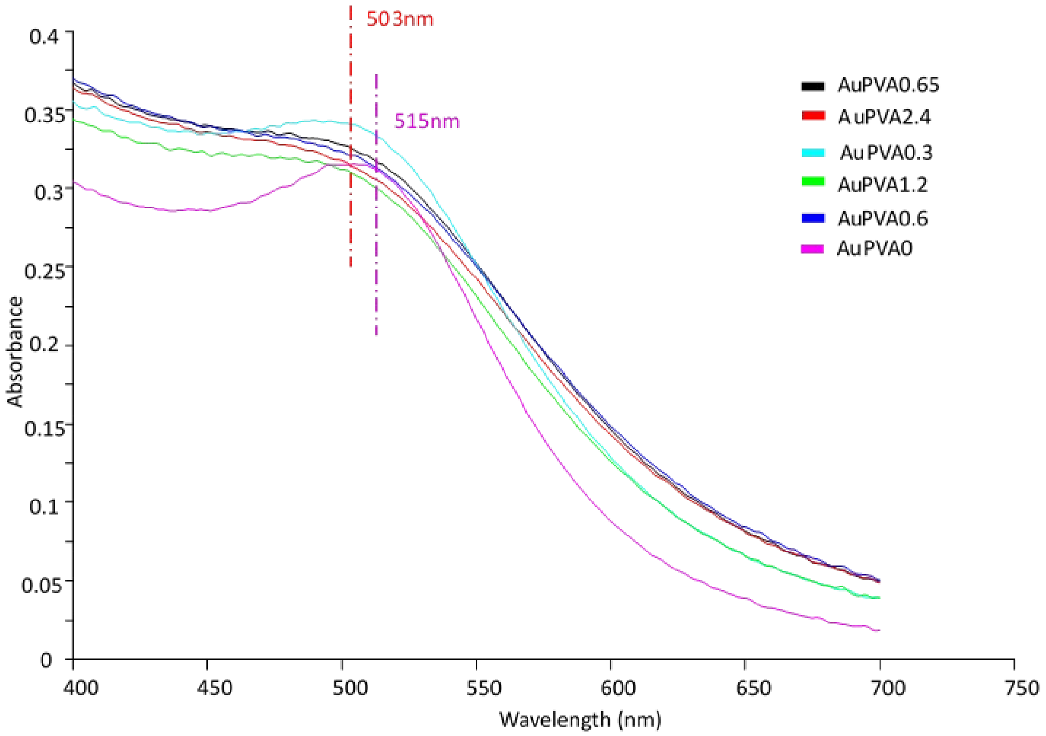


Figure S1. UV-Vis spectra of Au colloidal solutions with different PVA:Au weight ratio.

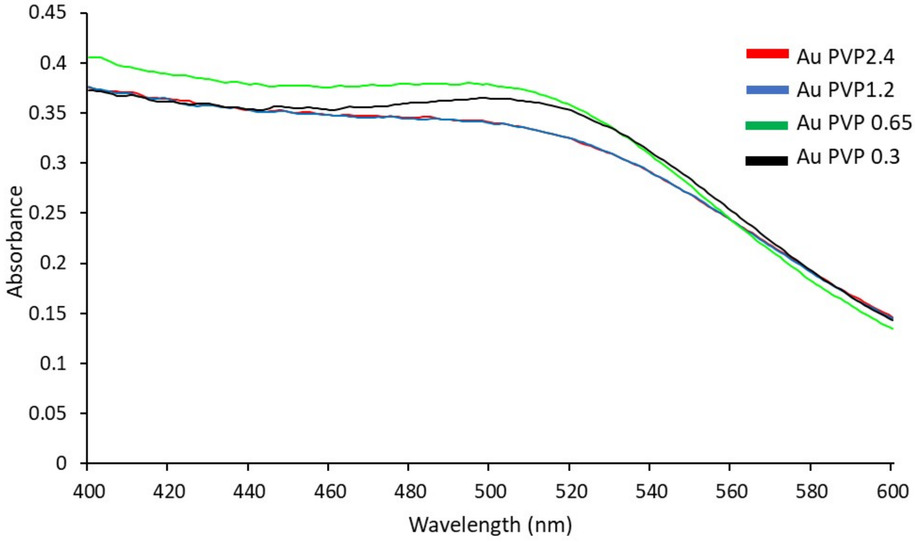


Figure S2. UV-Vis spectra for Au/AC PVP series after 25min from the addition of $NaBH_4$.

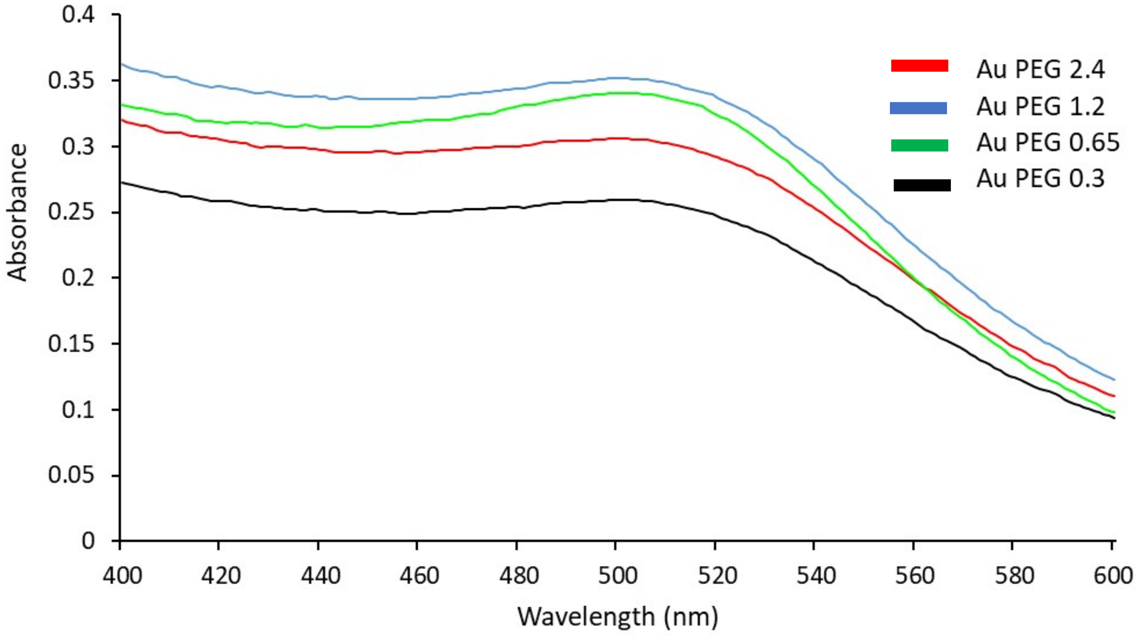


Figure S3. UV-Vis spectra for Au/AC PEG series after 25min from the $NaBH_4$ addition.

The comparison of the different UV-Vis spectra recorded (Figure S1) shows that with increasing the amount of PVA from a polymer:Au weight ratio of 0 to 2.4, the plasmonic peak became flattered and shifted to a lower wavelength. In particular, AuPVA0 shows the plasmonic peak at 515 nm and

AuPVA2.4 at 503 nm. These results indicate that a higher amount of PVA facilitates the formation of smaller Au colloidal nanoparticles. In the case of the Au colloidal nanoparticles synthesised by PVP (Figure S2) and PEG (Figure S3) the colloidal Au nanoparticles show a surface plasmon resonance peak around 500 nm and, therefore, an indication of the formation of small nanoparticles. In Table S1 it is reported the λ_{max} values. For both series, small differences are evident. The Au nanoparticles stabilised by PVP show a surface plasmon resonance which varies from 498 nm to 500 nm. The increase of PEG amount causes a slight decrease in the λ_{max} from 503 nm to 501 nm.

Table S1. SPR peak values from UV-vis spectra for Au-PVP and Au-PEG series after 25 minutes from the addition of $NaBH_4$.

PVP:Au weight ratio	**λ_{max} at 25 minutes (nm)**	**PEG:Au weight ratio**	**λ_{max} at 25 minutes (nm)**
0.3:1	498	0.3:1	503
0.65:1	500	0.65:1	503
1.2:1	497	1.2:1	502
2.4:1	497	2.4:1	501

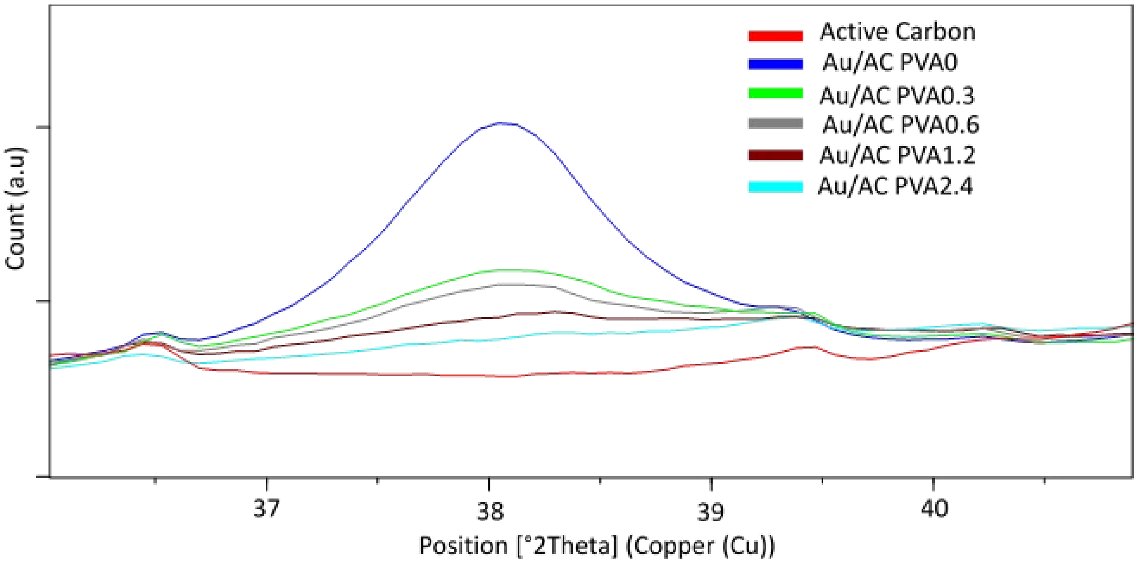


Figure S4. XRD patterns of activated carbon and Au/AC samples with different PVA:Au weight ratio.

Table S2. Mean crystallite size for Au/AC using PVA with different PVA:Au weight ratio.

Catalyst	Mean crystallite size (nm) by XRD	Mean particle size (nm) by TEM± Standard Deviation
Au/AC PVA0.3	6.4	7.9 ± 6.3
Au/AC PVA0.3	3.6	4.3 ± 3.6
Au/AC PVA0.6	3.1	2.7± 1.6
Au/AC PVA1.2	2.6	2.6± 2.1
Au/AC PVA2.4	2.2	2.4± 1.2

Table S3. Mean crystallite size for Au/AC using PVP with different PVP:Au weight ratio.

Catalyst	Mean crystallite size (nm) by XRD	Mean particle size (nm) by TEM± Standard Deviation
Au/AC PVP0.3	6.7	5.5±3.6
Au/AC PVP0.65	6.4	5.6±3.9
Au/AC PVP 1.2	8.2	7.4±4.7
Au/AC PVP2.4	8.1	8.4±4.9

X ray diffraction (XRD) is one of the techniques used and allows us to estimate the Au crystallite size presented in the described samples. Each crystal plane gives a diffraction peak in a specific position and the main ones for gold nanoparticles are:

- Au (111): ~38° 2θ
- Au (200): ~44° 2θ
- Au (220): ~64° 2θ
- Au (311): ~77° 2θ

Usually, for Au nanoparticles, the most intense peak is the one related at the (111) plane. For this reason and because of the low metal loading used (1% wt), the method used is focused in the region nearby 38° 2θ; XRD patterns as a function of the PVA amount are shown in Figure S4 as a representative example.

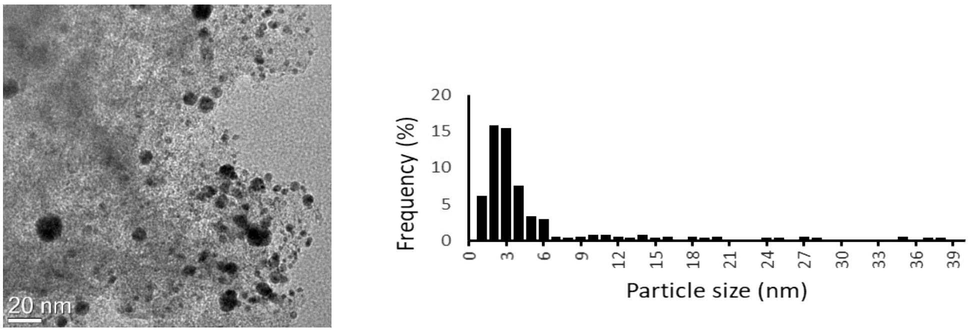
The diffraction peak present in the XRD pattern at 38.2° 2θ corresponds to the highest signal of gold, which is the plane Au (111). It was reported also the diffractogram of the activated carbon, to prove that there is no diffraction peak overlapping given by the support used. XRD pattern clearly showed a broadening of the diffraction peak of Au as PVA concentration increased. This was ascribed to the decrease of the dimension of the crystal size and with the Scherrer equation, it is possible to calculate the mean crystallite size of Au. Indeed, this formula correlates the diameter with the broadening at half the maximum intensity and the results are reported in Table S2. However, as the crystallite size of Au is lower than 5 nm, the precision and accuracy of this method are lower, therefore we focused on the trend of crystallite size to compare the results presented.

Comparison of the data using XRD and TEM analysis, showed that the dimensions obtained with the TEM are in good agreement with the one calculated with the XRD analysis, confirmed the method validity and the Scherrer equation applicability (Table S2). The analysis confirms the trend already observed by XRD analysis: the stabilising agent facilitates the formation of small Au nanoparticles, avoiding the agglomeration and the aggregation during the preparation method; the higher is the amount of PVA, the smaller is the mean particle size of the Au nanoparticles. From TEM analysis it was observed the formation of larger Au nanoparticles for the sample without stabilising agent and areas where agglomeration of Au nanoparticles was occured.

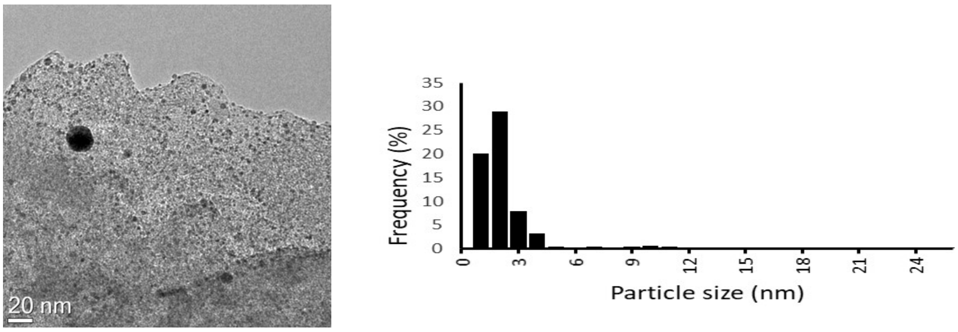
In Tables S2 and S3 are reported the values of the mean crystallite size obtained by XRD analysis with the different stabilizing agents as a function of stabilizer amount used during the synthesis and comparison with TEM analysis. For the Au/AC PVP series, a weight ratio of Au to the chosen stabiliser of 0.3 and 0.65 does not affect the crystallite size for Au/AC (6.7 nm for Au/AC PVP0.3 and 6.4 nm for Au/AC PVP0.65). It appears similar to the value obtained without a stabiliser agent (Au/AC PVA0 6.4nm). Moreover, the increase of PVP does not reduce the crystallite size, which reaches the value of 8.1 nm for Au/AC PVP2.4.

In the case of the PEG a different trend was observed. The increase of PEG from the ratio 0.3 to 0.65 leads to a decrease of Au crystallite size from 10.2 nm to 6.4 nm, then remains stable doubling the PEG amount. Finally, the maximum amount of PEG leads to the formation of large Au nanoparticles with a value of 8.1 nm. As has already been seen in the case of PVA, increasing the amount of PVA, the nanoparticles are better stabilised and lead to the formation of spherical Au nanoparticles. In the case of PVP instead is required in small quantities to form the smallest Au nanoparticles due to the fact that higher amounts can lead to the formation of Au NPs with a higher dimension. In the case of PEG, PEG can acts as a good stabiliser only at an intermediated Au to PEG weight ratio.

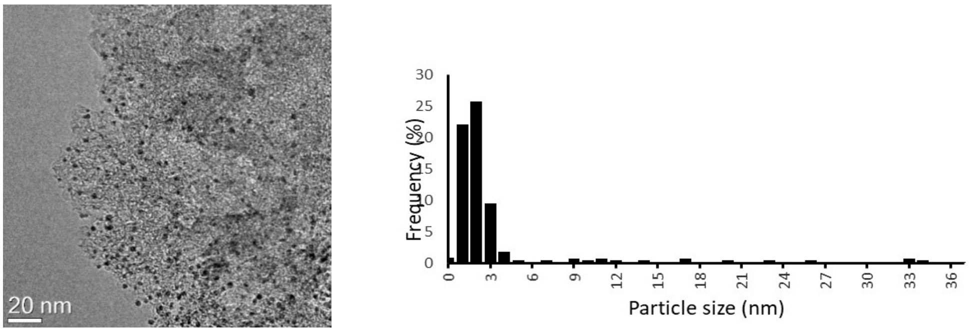
- **Au/AC (PVA/Au = 0.3)**



- **Au/AC (PVA/Au = 0.6)**



- **Au/AC (PVA/Au = 1.2)**



- **Au/AC (PVA/Au = 2.4)**

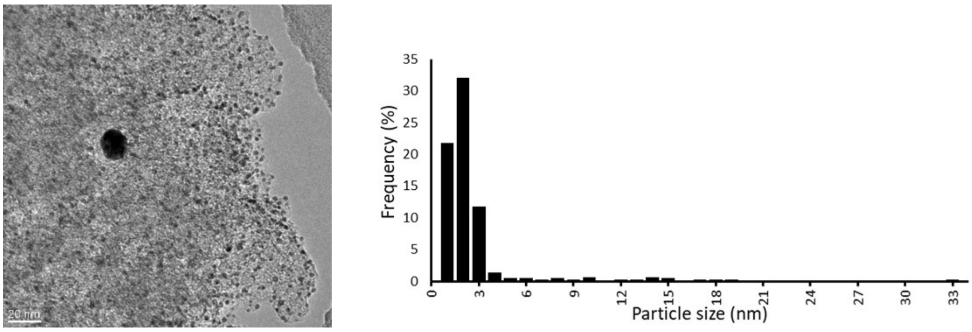
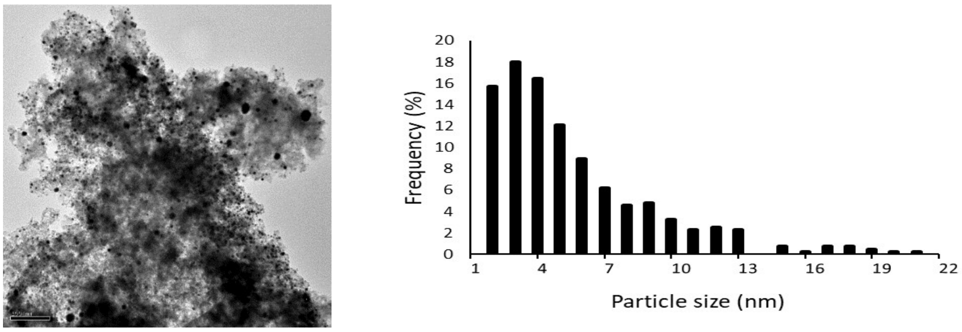
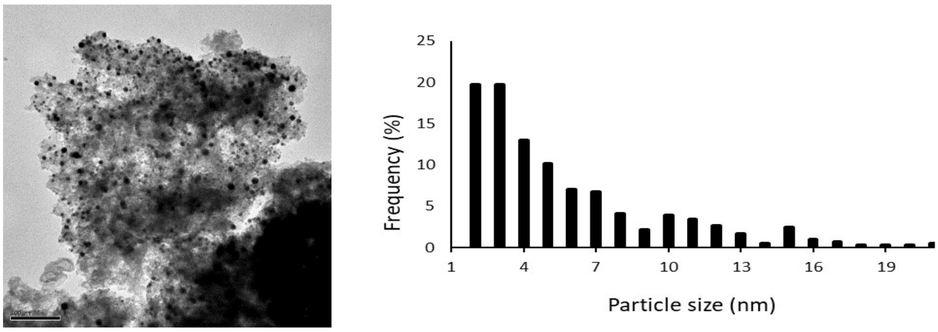


Fig. S5 TEM images and particle size distributions of Au/AC synthesised using PVA with different PVA:Au weight ratio.

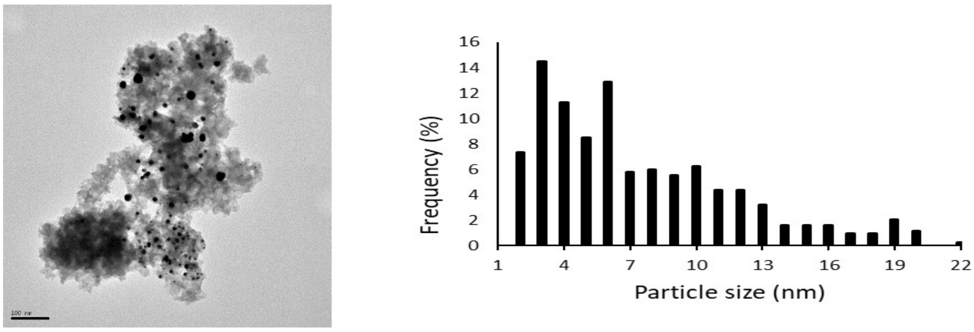
- **Au/AC (PVP/Au = 0.3)**



- **Au/AC (PVP/Au = 0.65)**



- **Au/AC (PVP/Au = 1.2)**



- **Au/AC (PVP/Au = 2.4)**

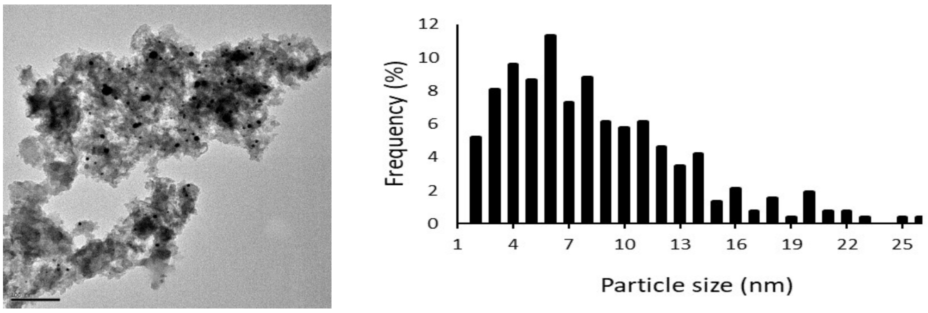
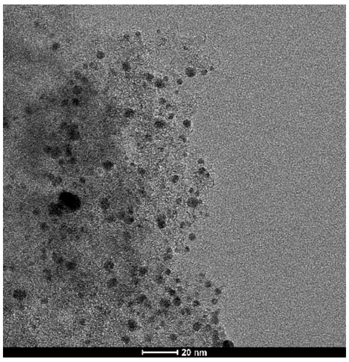
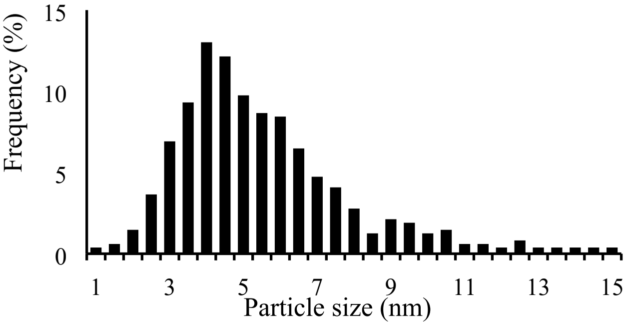


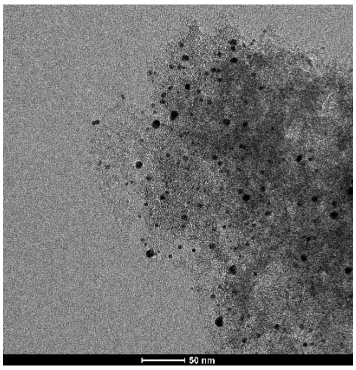
Fig. S6 TEM images and particle size distributions of Au/AC synthesised using PVP with different PVA:Au weight ratio.

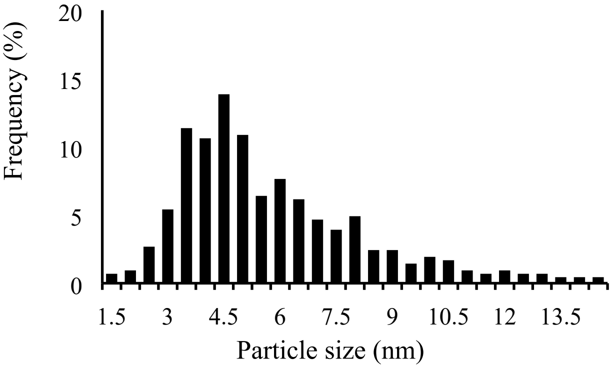
- **Au/AC (PEG/Au = 0.3)**



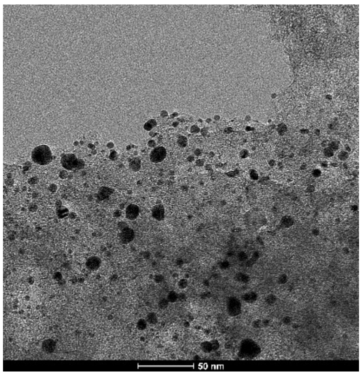


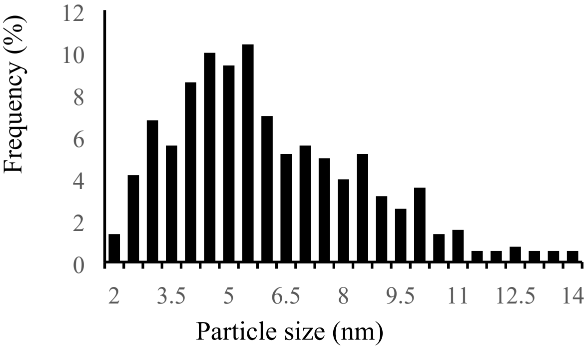
- **Au/AC (PEG/Au = 0.6)**





- **Au/AC (PEG/Au = 1.2)**





- **Au/AC (PEG/Au = 2.4)**

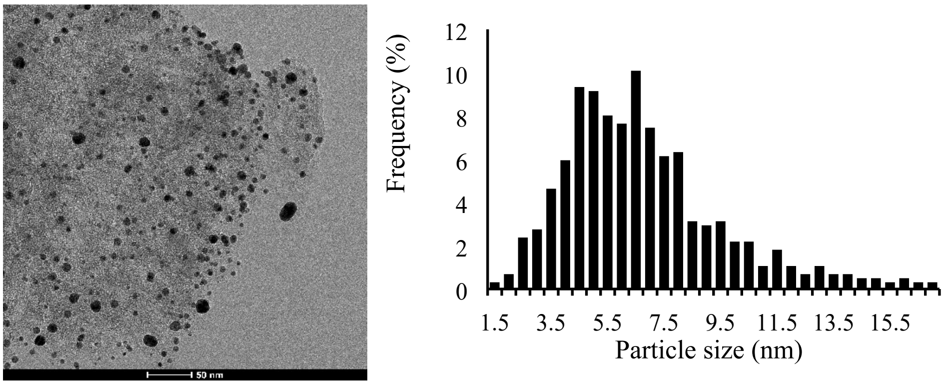


Fig. S7 TEM images and particle size distributions of Au/AC synthesised using PEG with different PEG:Au weight ratio.

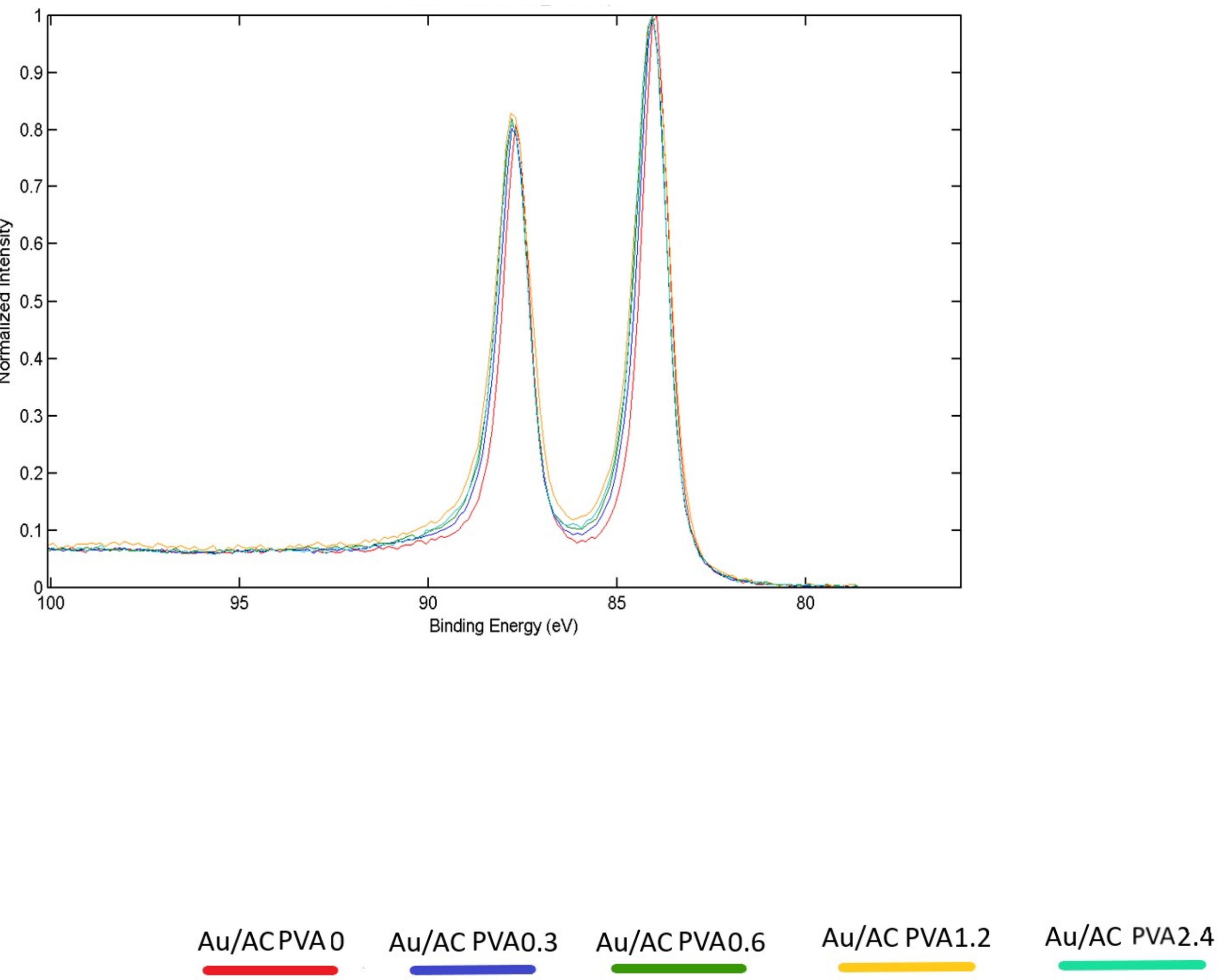


Fig. S8 XPS spectra for Au/AC using PVA with different PVA:Au weight ratio. (label "Au/AC PVA06" is the catalyst with PVA/Au=0.65 weight ratio).

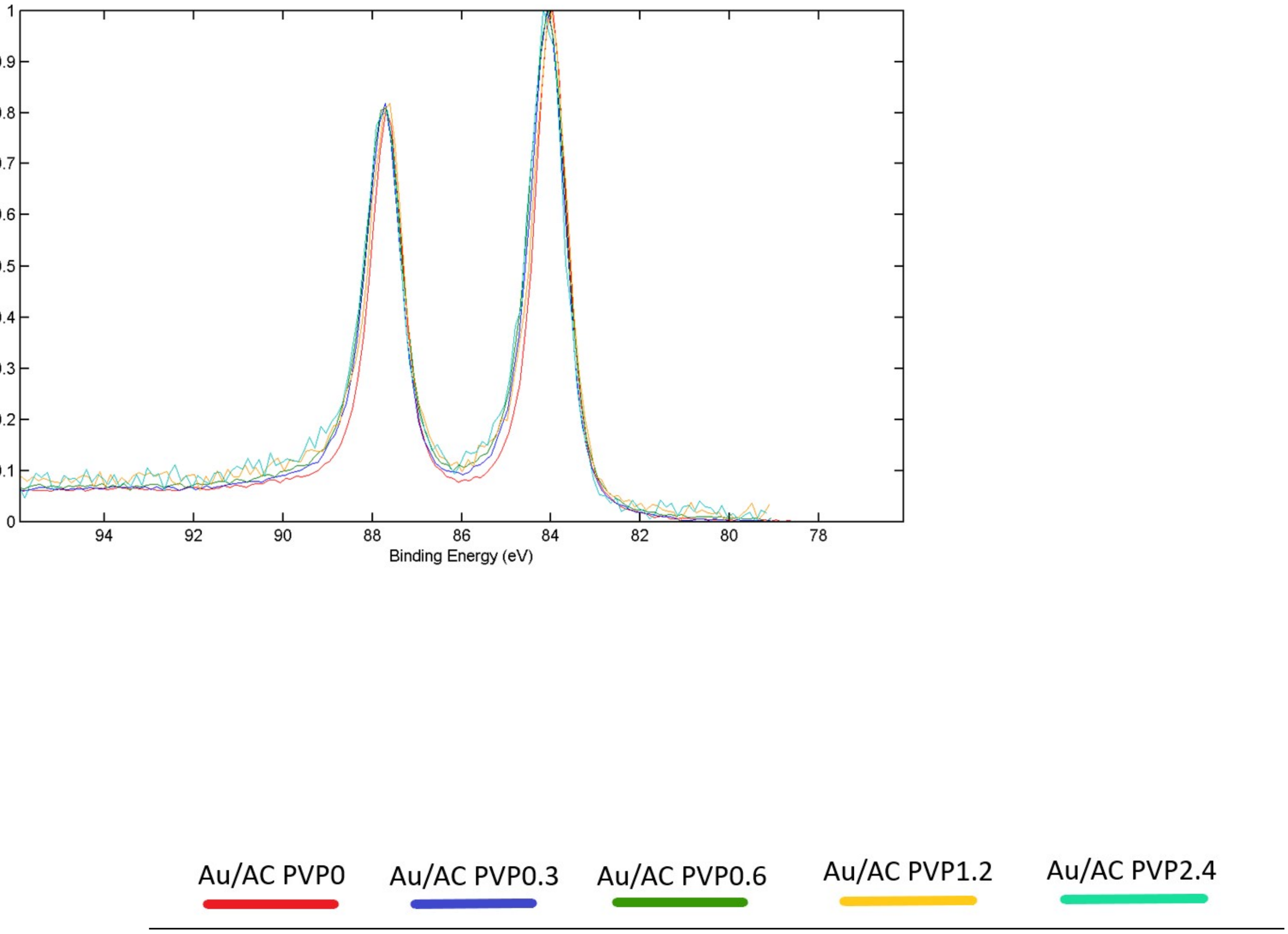


Fig. S9 XPS spectra for Au/AC using PVP with different PVP:Au weight ratio (label “Au/AC PVP06” is the catalyst with PVP/Au=0.65 weight ratio).

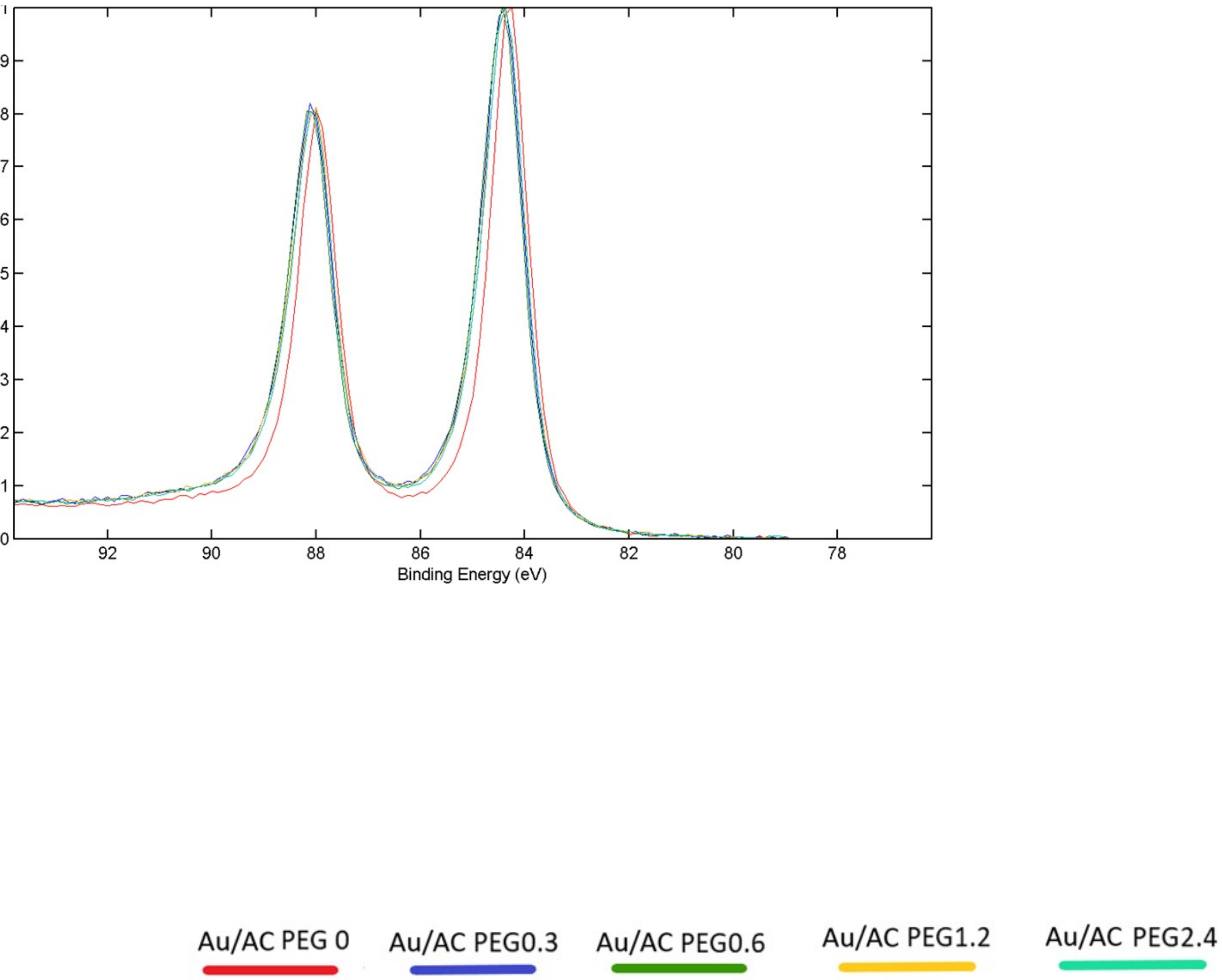


Fig. S10 XPS spectra for Au/AC using PEG with different PEG:Au weight ratio (label “Au/AC PVP06” is the catalyst with PEG/Au=0.65 weight ratio).

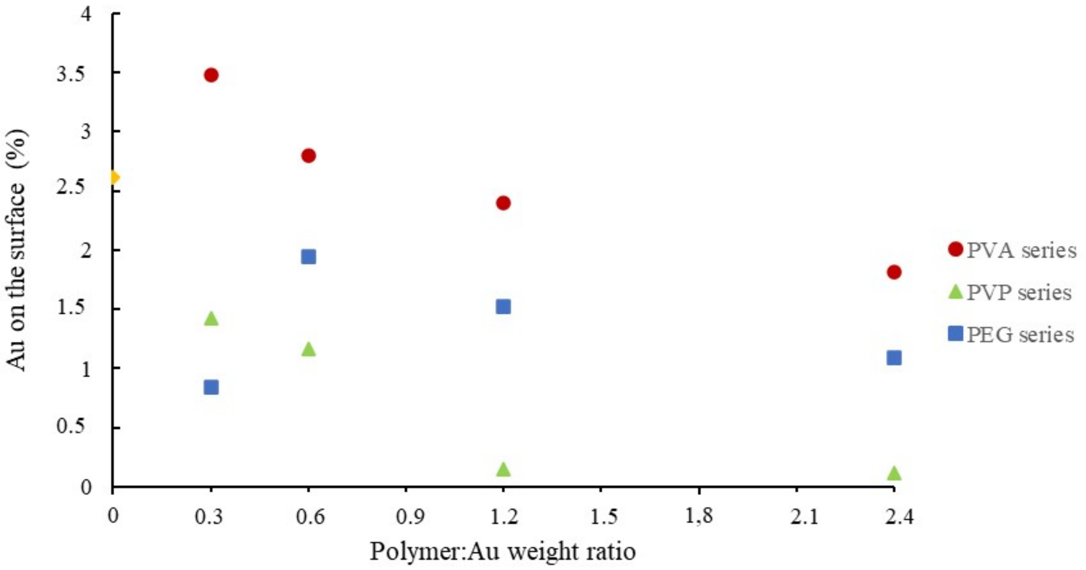


Fig. S11 Correlation between the polymer:Au weight ratio and atomic percentage of Au on the surface for PVA series, PVP series and PEG series. With yellow colour is the sample without the presence of polymer.

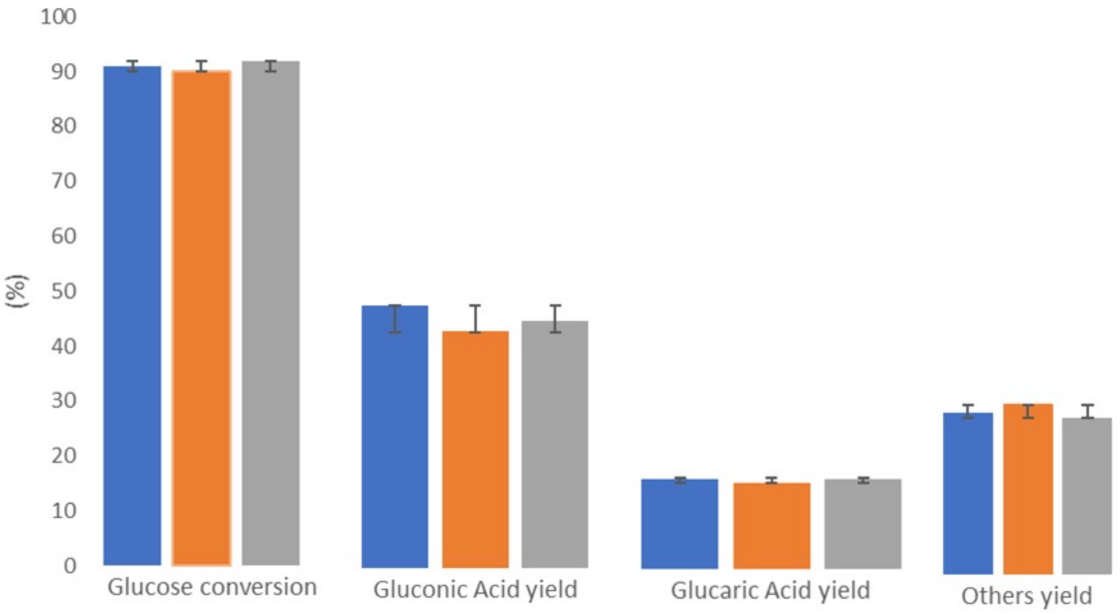


Fig. S12 Reproducibility tests of GLU conversion and formation of GO, GA and other byproducts using Au/AC_PVA_065. Reaction conditions: 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

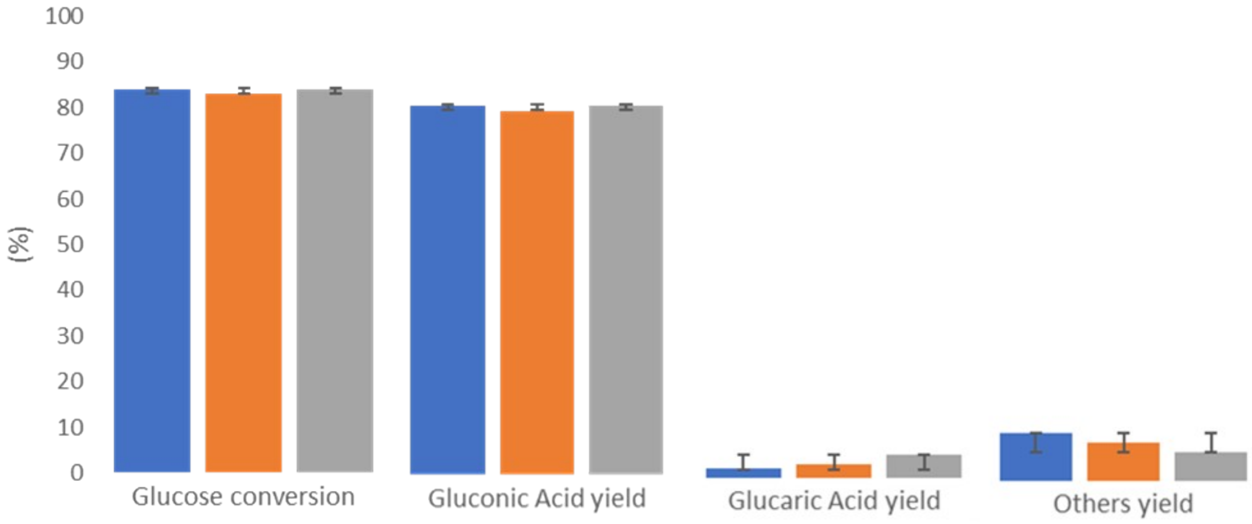


Fig. S13 Reproducibility tests of GLU conversion and formation of GO, GA and other byproducts using Au/AC_PVP_1.2. Reaction conditions: 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

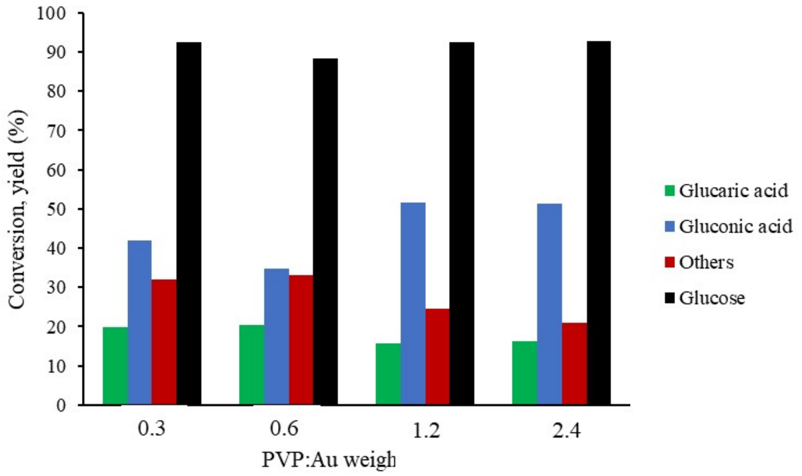


Fig. S14 Catalytic screening of catalysts Au/AC PVP series. Reaction conditions: 60 min, 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

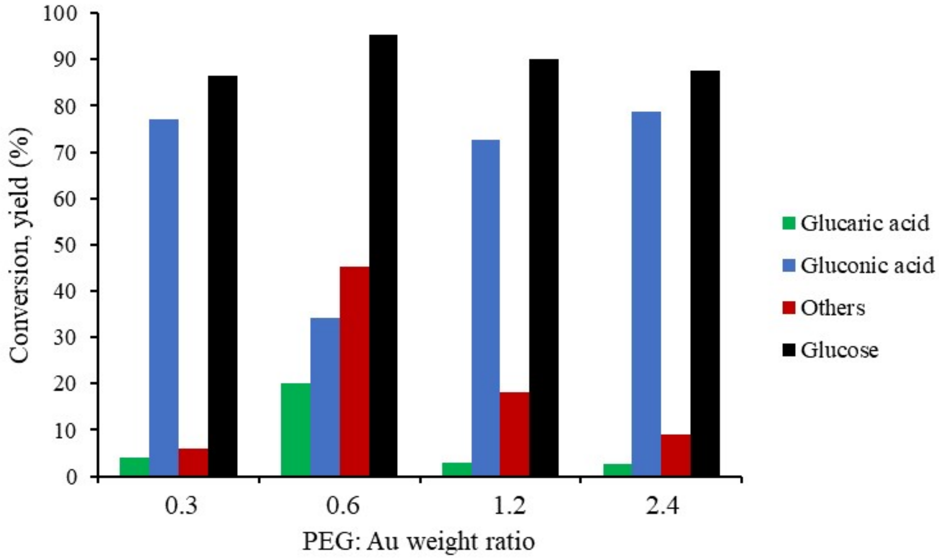


Fig. S15 Catalytic screening of catalysts Au/AC PEG series. Reaction conditions: 60 min, 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

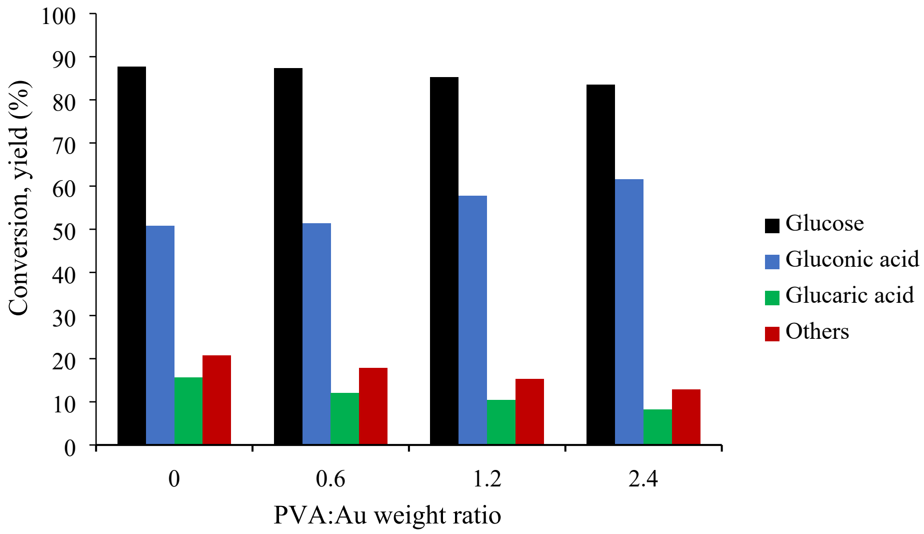


Fig. S16 Catalytic screening of catalysts Au/AC PVA series. Reaction conditions: 15 min, 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

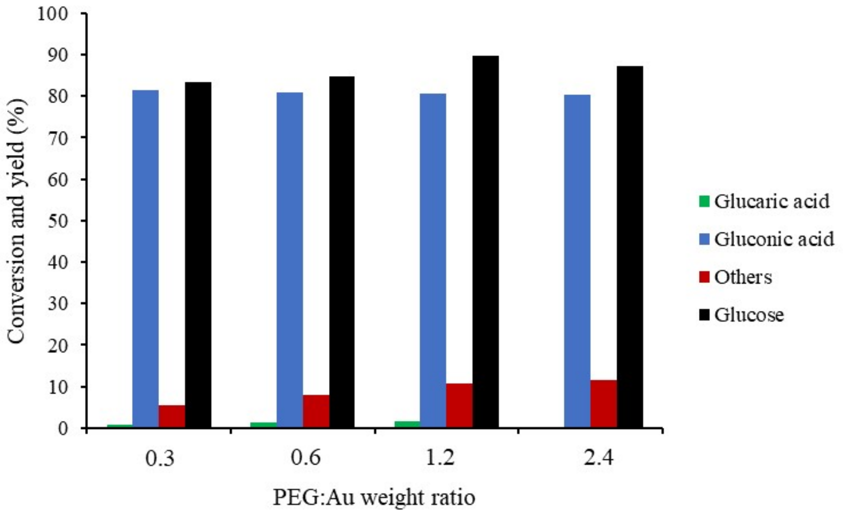


Fig. S17 Catalytic screening of catalysts Au/AC PEG series. Reaction conditions: 15 min, 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

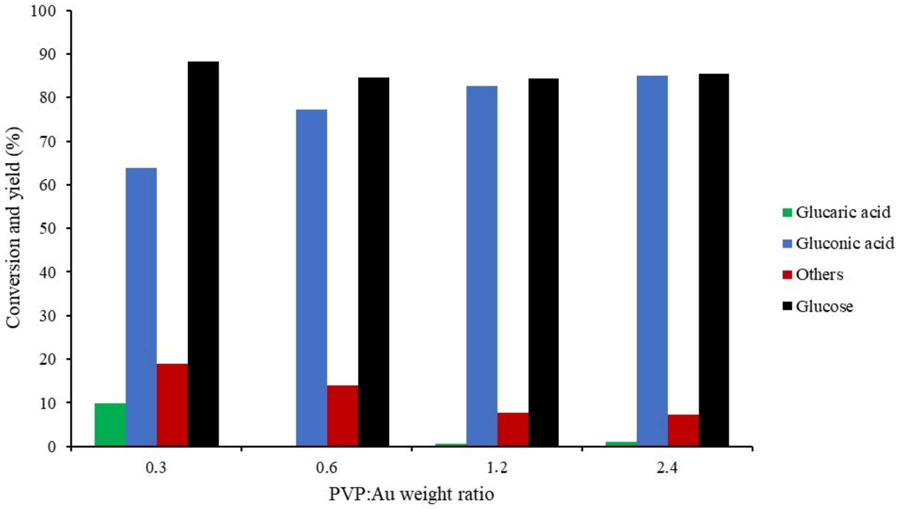


Fig. S18 Catalytic screening of catalysts Au/AC PVP series. Reaction conditions: 15 min, 60 °C, 1000 rpm, 10 bar O_2, Glu:Au:NaOH molar ratio of 1000:1:3000.

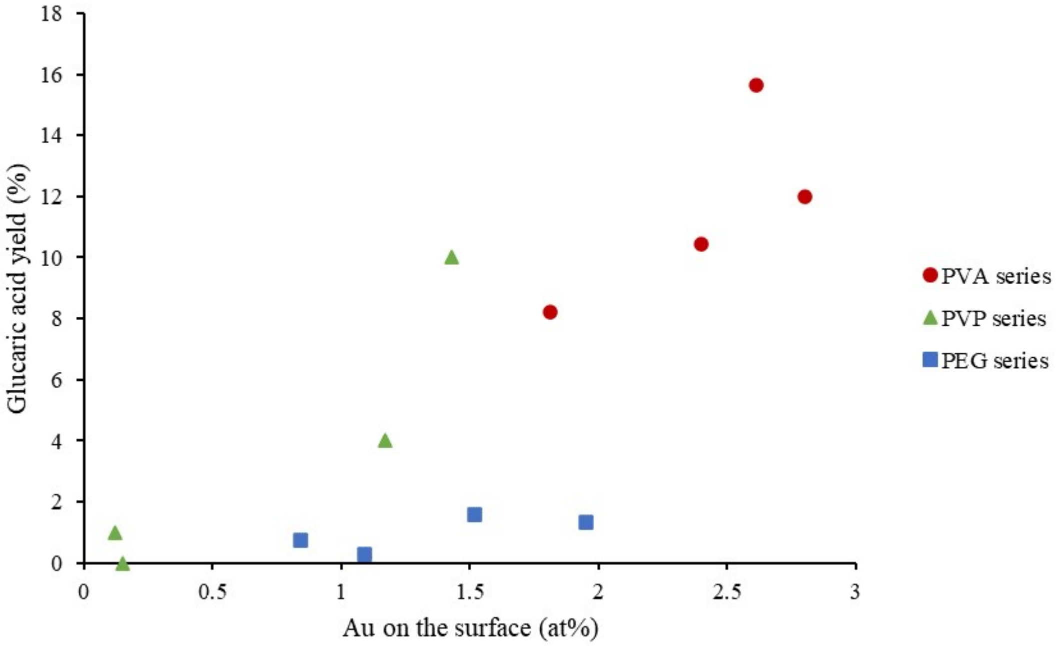


Fig. S19 Correlation between the glucaric acid GA yield and atomic percentage of Au on the surface for PVA series, PVP series and PEG series at reaction time of 15 min.

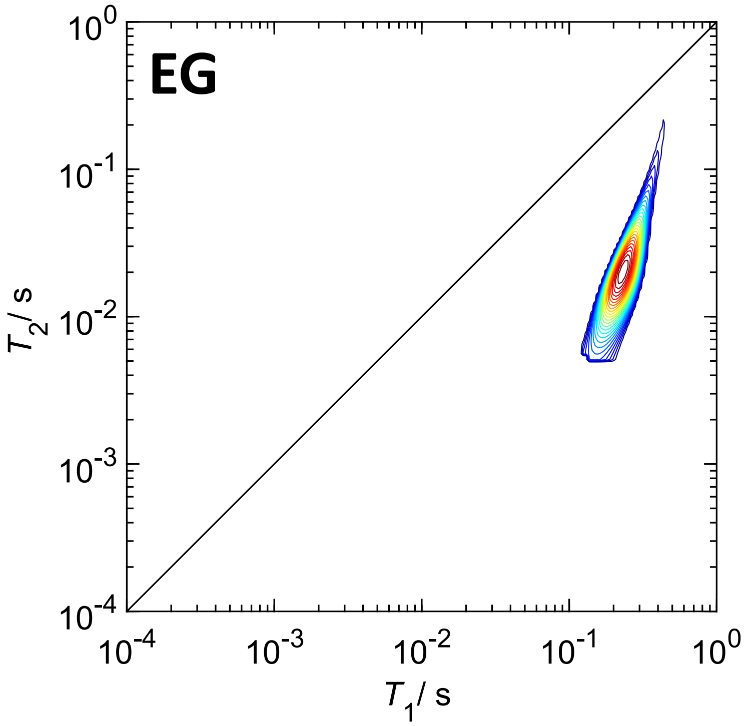


Fig. S20 2D T1-T2 correlation map for ethylene glycol imbibed within the pores of the fresh Au/AC catalyst.

Table S5 NMR relaxation times obtained using the soaking protocol starting with aqueous glucaric acid solution (0.6 M)

Soaking protocol	T_1 (ms)	T_2 (ms)	T_1/T_2 (-)
GA	79 ± 2	6 ± 1	11.3 ± 0.5
GA Dry	12 ± 1	1 ± 1	12.0 ± 0.5
GA EG	244 ± 9	29 ± 1	8.4 ± 0.3
EG Only	233 ± 7	20 ± 1	12.6 ± 0.5

Table S6 NMR relaxation times obtained using the soaking protocol starting with aqueous GO solution (0.6 M)

Soaking protocol	T_1 (ms)	T_2 (ms)	T_1/T_2 (-)
GO	79 ± 2	7 ± 1	11.3 ± 0.5
GO Dry	13 ± 1	2 ± 1	6.5 ± 0.3
GO EG	180 ± 5	23 ± 1	7.8 ± 0.3
EG Only	233 ± 9	20 ± 1	12.6 ± 0.5

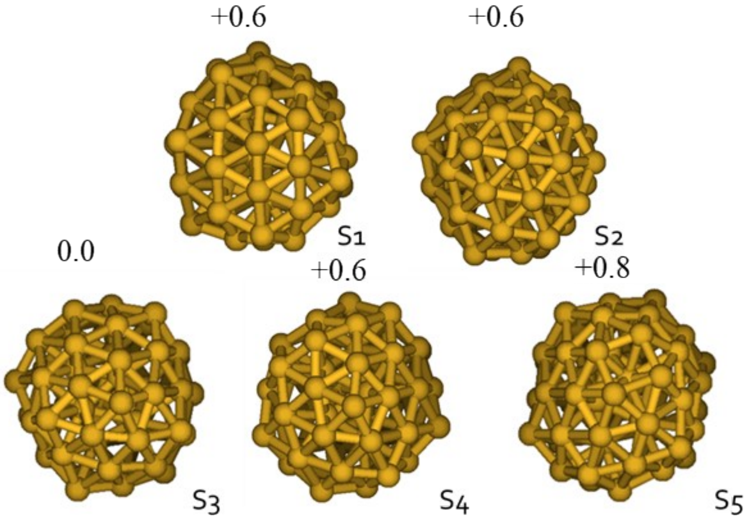


Fig. S21 The five distorted Au_{55} structures (called Sn, where n=1,2,..,5). ΔE in kcal/mol are reported.

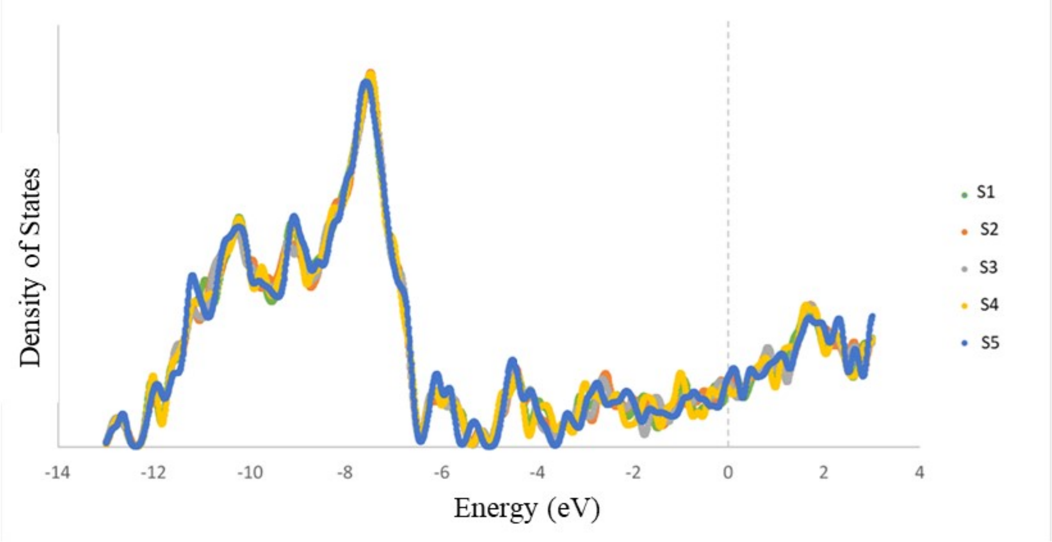


Fig. S22 Overlapped Density of States of the five distorted Au_{55} structures.