Revised

Supplementary Information for

Polygonal Gold Nanoplates in a Polymer Matrix

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Synthesis and film fabrication

Different weights (3.6 mg, 7.2 mg, 14.4 mg, 21.6 mg, 32.4 mg) of hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4$) dissolved in 0.5 ml water was mixed with a solution of 90 mg of polyvinyl alcohol, PVA (Aldrich, average molecular weight = 13 - 23 kDa, % hydrolysis = 86) in 0.3 ml water to prepare the five different compositions which will be designated using the Au/PVA weight ratios, 0.02, 0.04, 0.08, 0.12, 0.18 respectively. The solution mixture was diluted by adding 0.3 ml more of water and stirred for 10 min at room temperature (27 - 30^{o}C). MilliQ purified water was used in all operations.

Glass/quartz plates were cleaned by sonication with isopropyl alcohol, methanol and finally acetone for 10 min each. A few drops of a solution of polystyrene, PS (average molecular weight = 280 kDa) in toluene (1 g in 8 ml) was spin coated on the glass substrate using a standard Photoresist Spinner at 1,000 RPM for 10 sec and dried in a hot air oven at 75 - 80^{o}C for 10 - 15 min. The $HAuCl_4$ - PVA solution was spin coated on top of the polystyrene coating at 6,000 RPM for 10 sec. Alternately, $HAuCl_4$- PVA was spin coated directly on quartz substrates without a polystyrene coating.

The film coated plates were placed in a closed stainless steel chamber and heated in a standard oil bath for different times ranging from 5 - 60 min and at temperatures ranging from 100 - 170^{o}C. A few different heating rates were also explored.

Thickness of the films were measured using an Ambios Technology XP-1 profilometer.

Electronic absorption studies

Electronic spectra of the Au-PVA films coated on quartz substrates were recorded on a Shimadzu Model UV-3101 UV-Vis Spectrometer.

FT-IR studies of free-standing films of PS, PVA/PS, $HAuCl_4$-PVA/PS and Au-PVA/PS

FT-IR spectra were recorded on a Jasco5300 FTIR spectrometer. The samples were free-standing films and the spectra were recorded in transmission mode, from 4000 – 600 cm^{-1}. All films were prepared by spin-coating : speed = 1 RPM, time = 10 sec. PS was coated as 2 layers, and PVA as 3 as well as 5 layers. The Au/PVA ratios of 0.18 and 0.36 were studied. The general characteristics were found to be reproducible in the various spectra which differ in the number of layers and gold content. The spectra shown on the following page correspond to the cases having 5-layer PVA and Au/PVA = 0.36. The heating experiments were done at 100^oC for 60 min; a free-standing film was cut into two portions and one was subjected to heating while the other one was retained at room temperature.

The spectra for PS, PVA/PS (before and after heating) and $HAuCl_4$-PVA/PS (before and after heating, the latter corresponding to Au-PVA/PS), are provided on the following page. Significant changes, if any, are observed only in the region 4000 – 1000 cm^{-1}; hence only this part is shown. The relevant peaks are marked in the spectra. It is significant to note that the spectrum of PVA/PS is unchanged on heating; this indicates that the broad peak at 3347 cm^{-1} is primarily due to the alcohol groups and not water. The peak intensity variations in $HAuCl_4$-PVA/PS are explained in the main text. A semi-quantitative assessment of the peak intensities was carried out by measuring the peak height from a baseline drawn connecting the beginning and end of each peak. The intensity is estimated by normalizing with respect to the intensity of the C=C stretch vibration from the aromatic ring of PS which remains unaffected by the heating and chemical reactions in the film. The relevant values of C=O peak intensities are provided in the table below.

Sample film	**Intensity of C=O normalized w.r.t. that of C=C**
PVA/PS (before heating)	0.38
PVA/PS (after heating)	0.38
$HAuCl_4$-PVA/PS (before heating)	0.27
$HAuCl_4$-PVA/PS (after heating) ie. Au-PVA/PS	0.51

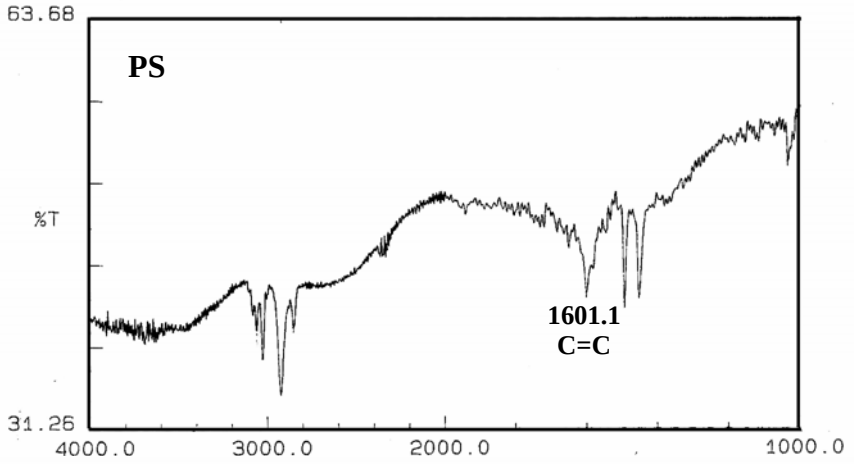
As explained in the main text, we infer that the following steps occur during the process of formation of the Au nanoparticles :

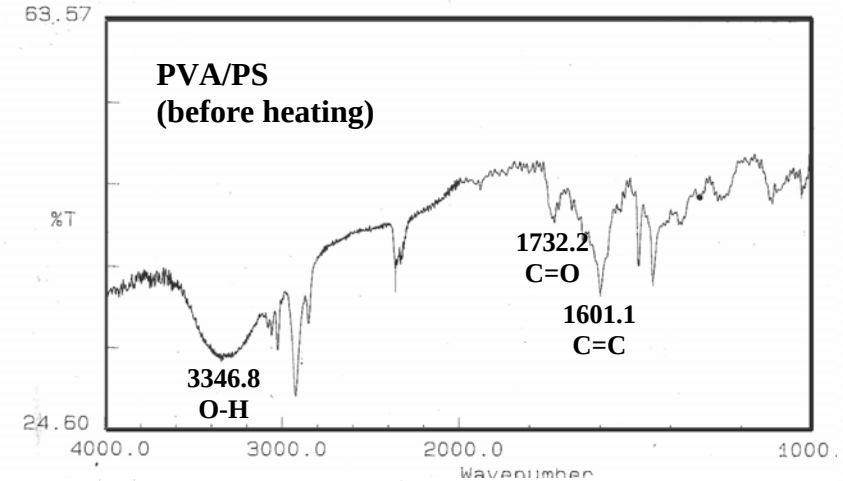
(i) When $HAuCl_4$ is added to PVA, the acid protons coordinate to the carbonyl groups of the remnant acetyl groups of PVA (note that the PVA used is only 86% hydrolyzed).

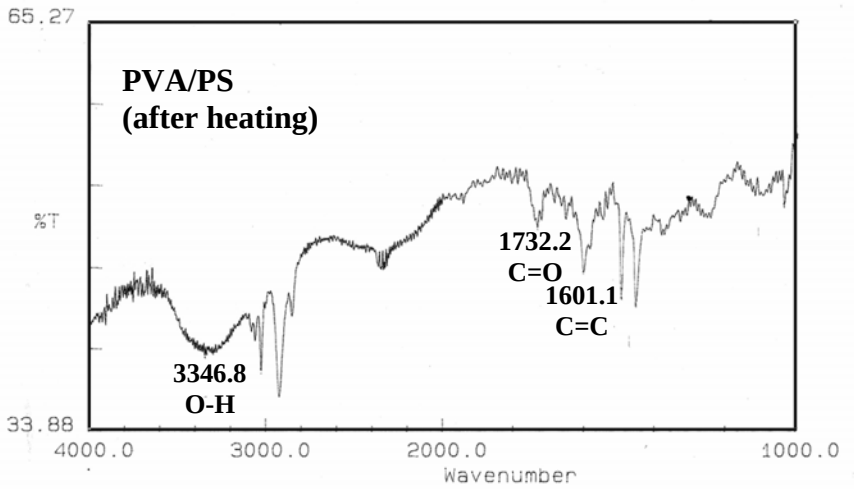
(ii) On heating, the alcohol groups of PVA reduce the $AuCl_4^-$ ion to Au; HCl is the byproduct.

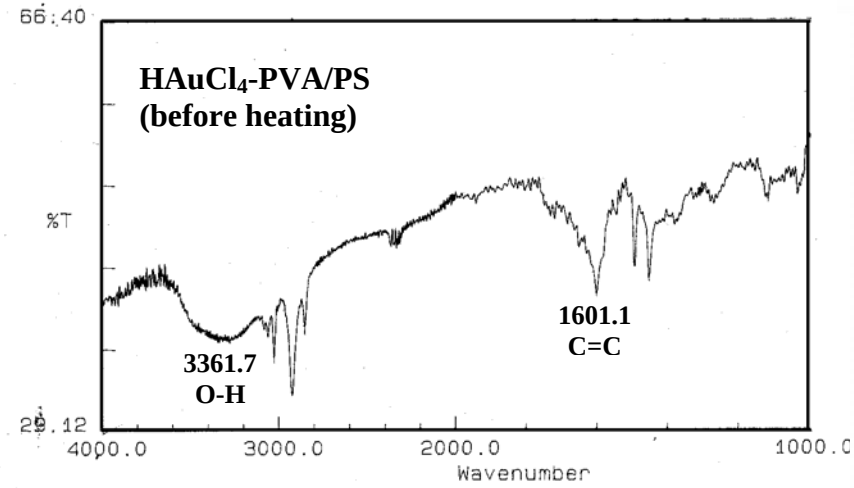
(iii) The keto groups formed from the oxidation of the alcohol as well as the original carbonyl groups on PVA are coordinated by protons from the by-product HCl.

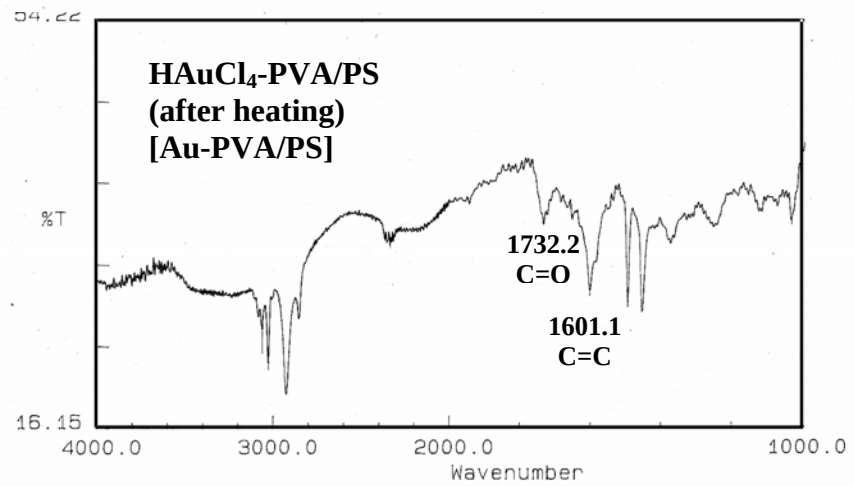
FT-IR spectra



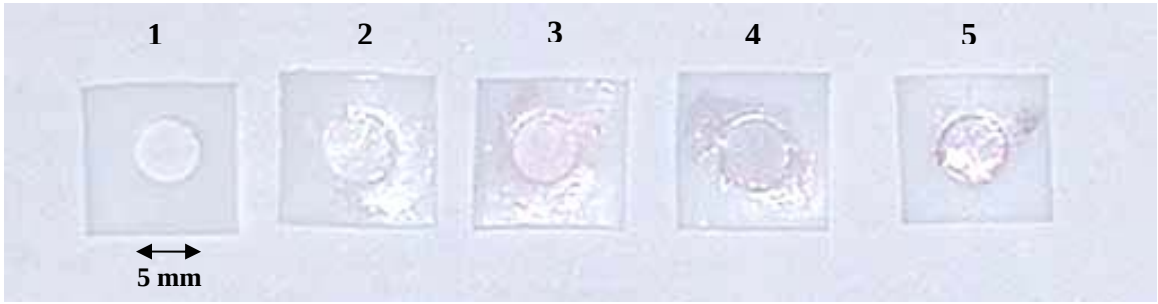








Photograph of the free-standing films of Au-PVA films placed on a teflon sheet with a hole



1 ⟶ Empty hole
2 ⟶ Au/PVA = 0.04, Thermal treatment : 130^{o}C, 5 min
3 ⟶ Au/PVA = 0.08, Thermal treatment : 130^{o}C, 30 min
4 ⟶ Au/PVA = 0.04, Thermal treatment : 100^{o}C, 60 min
5 ⟶ Au/PVA = 0.04, Thermal treatment : 100^{o}C, 60 min

Table 1. Different fabrication conditions and the shape / morphology of resulting Au nanoplates / nanoparticles

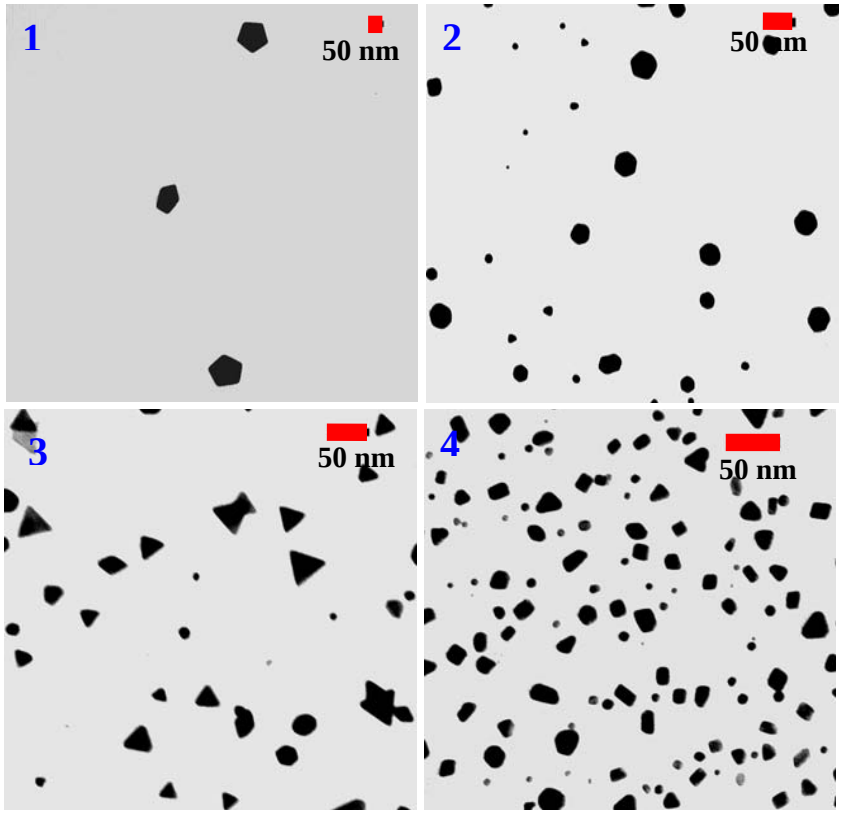
Weight of $HAuCl_4$ (mg)	Weight of PVA (mg)	Volume of solution (ml)	Au / PVA weight ratio	Temperature (^oC) / Time (min)	Shape / morphology (those given in Fig. 1 of main text are shown in bold)	TEM image number (see pages 5 - 8)
3.6	90	1.1	0.02:1	100 / 2*	Rings	5
				170 / 5	Regular pentagons	6
7.2	90	1.1	0.04:1	100 / 2*	Irregular truncated pentagons	7
				100 / 60	Twinned structures with stress patterns	14, 15
				130 / 60	Triangles with stress patterns	16
				170 / 5	**Regular pentagons**	1
14.4	90	1.1	0.08:1	100 / 2*	Irregular pentagons, hexagons	8, 9
				130 / 30	**Regular hexagons**	2
				130 / 60	Hexagons to circular with stress patterns	17
21.6	90	1.1	0.12:1	100 / 30*	Long needles	11, 12
				100 / 60	**Regular triangles**	3
				130 / 60	Triangles, pentagons	10
32.4	90	1.1	0.18:1	100 / 60	**Squares, rectangles**	4
				130 / 60	Mixed polygons	13

*The films were heated from room temperature (27 - 30^{o}C) to the designated temperature over ~3 h and held at that temperature for the time specified. In other cases, the samples were placed in the chamber heated to the designated temperature and then held at that temperature for the time specified.

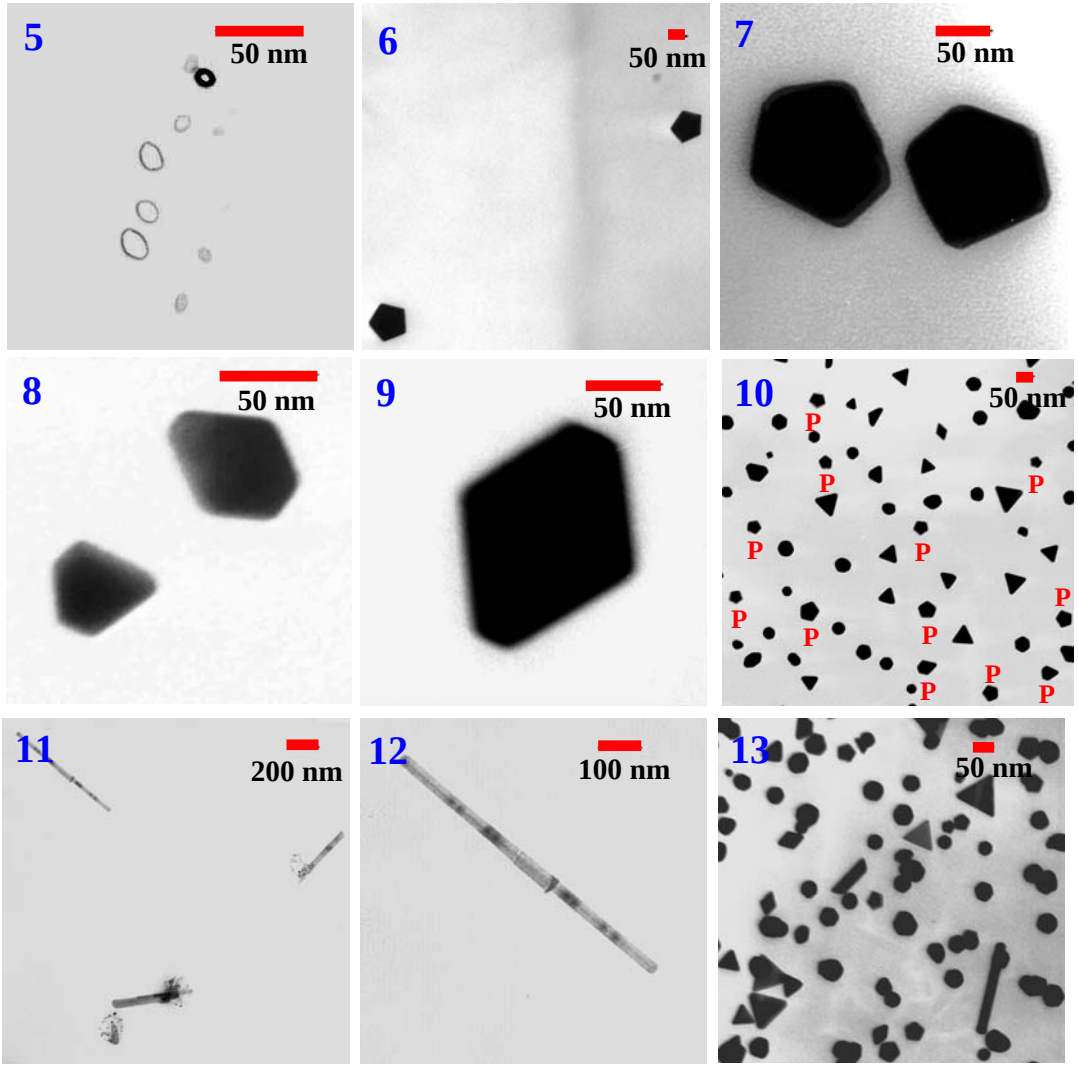
Transmission electron microscopy and selected area electron diffraction

Glass substrate with the Au-PVA/PS coating was immersed in toluene in a petri dish. The PS layer dissolved in toluene and the Au-PVA films floated to the surface in about 5 min. The film was collected directly on 100 mesh copper grid. The samples were examined in a JEOL 100CX TEM at an accelerating voltage of 100 kV using a 20 μm aperture. Electron diffraction data was collected from the particles at 100 kV accelerating voltage at a camera length of 46 or 76 cm. The patterns were photographed using beam stoppers for 4 sec. A collection of TEM images and ED patterns follow.

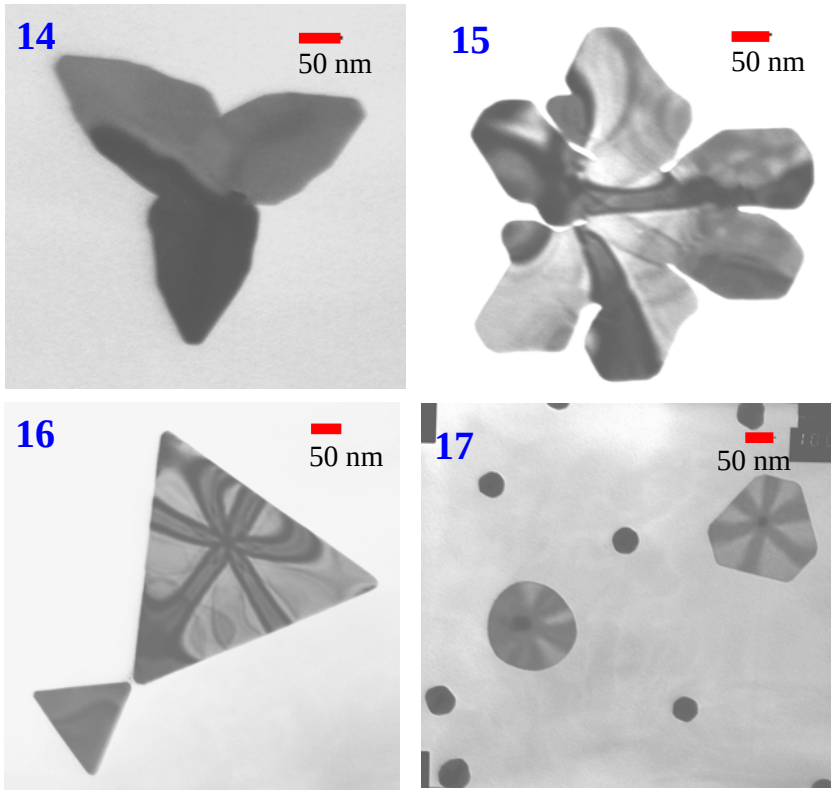
TEM images of regular polygonal nanoplates shown in Fig. 1 of main text (the fabrication conditions corresponding to each image is given in the Table 1)



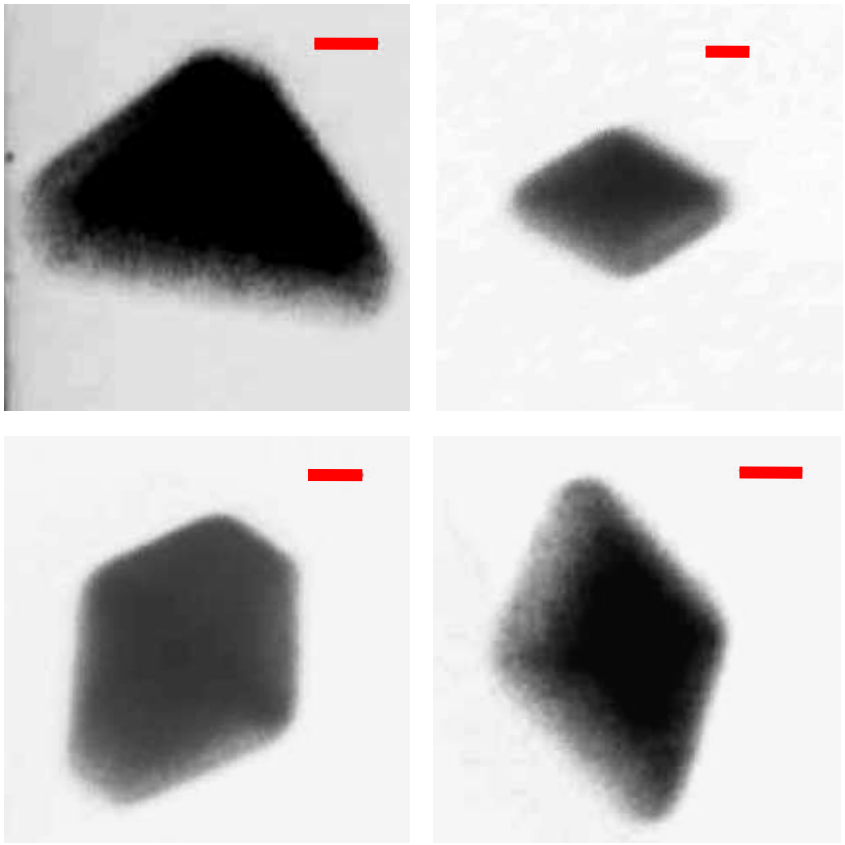
TEM images of a range of other shapes (the fabrication conditions corresponding to each image is given in the Table 1)



TEM images of nanoplates with stress patterns (the fabrication conditions corresponding to each image is given in Table 1)



TEM images of single gold polygons which reveal the plate thickness (scale bar corresponds to 10 nm)



Electron diffraction patterns (the specific nanoplate on which the ED is recorded is shown in the inset); indexing of the diffraction spots is shown on one of the patterns.