

# Highly Active TiO<sub>2</sub> Photocatalysts for Hydrogen Production through a Combination of Commercial TiO<sub>2</sub> Material Selection and Platinum Co-Catalyst Deposition Using a Colloidal Approach with Green Reductants

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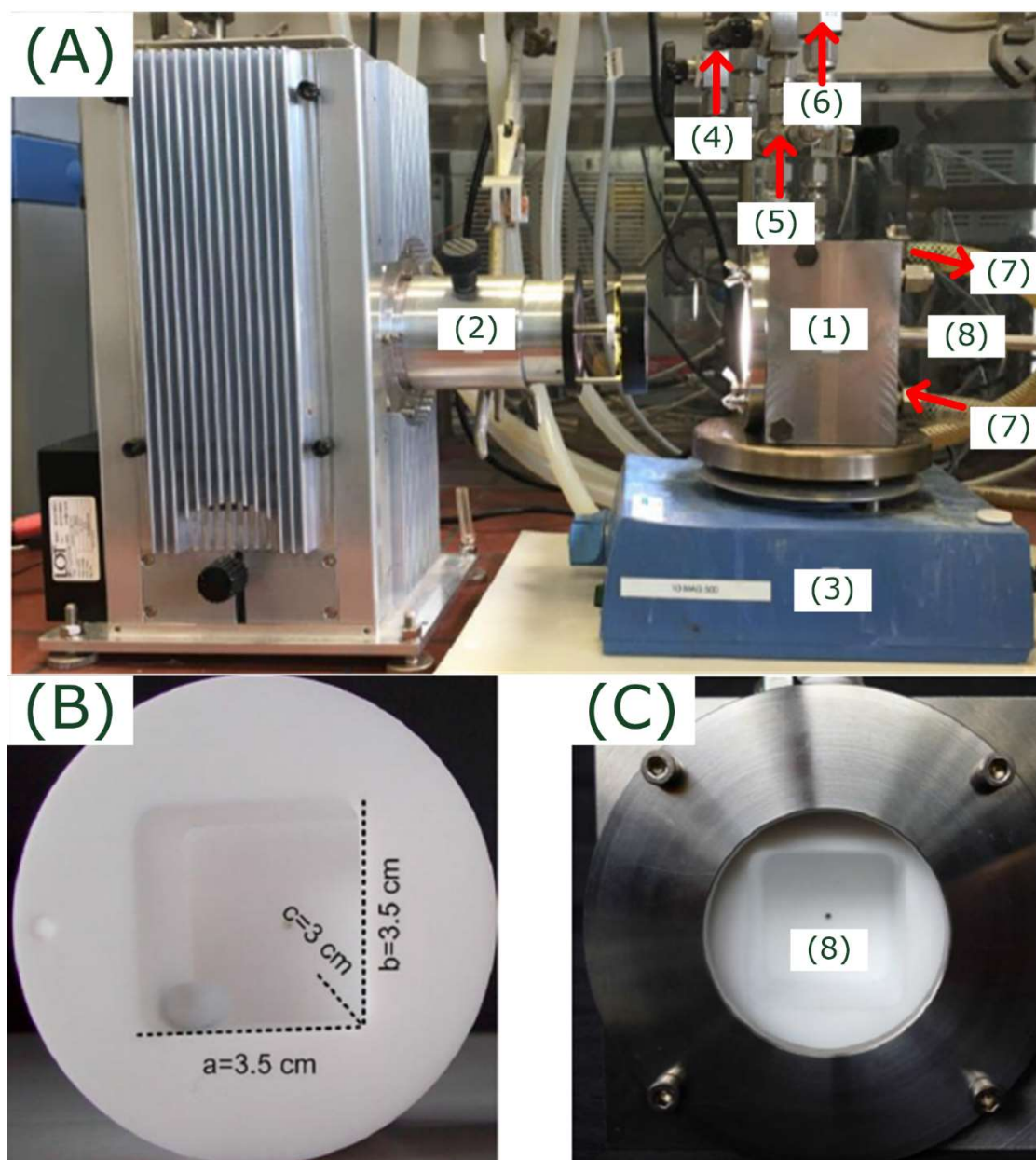
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## 1. Photocatalytic Experiments – Setups



**Figure S1.** Setup for the screening of TiO<sub>2</sub> photocatalysts (1: photoreactor, 2: stirrer, 3: 300 W Xe lamp (no filter), and 4: thermostat).

Further investigations were done in a photoreactor with defined geometry with a 300 W Xe lamp (full spectrum) via side irradiation.



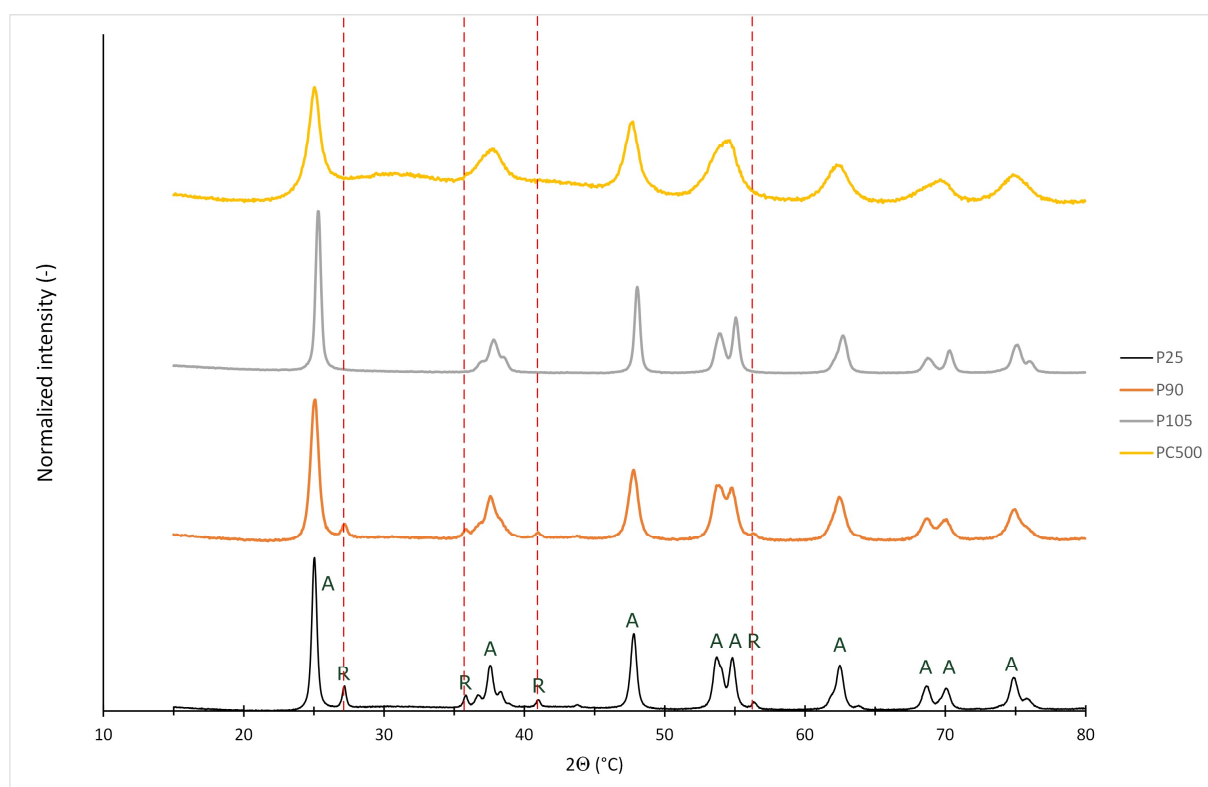
**Figure S2.** Setup for defined photocatalytic experiments (A) with used Teflon inlet (B) and photoreactor front view (C) (1: photoreactor with quartz glass window, 2: 300 W Xe lamp with filter holder, 3: stirrer, 4: pressure indicator, 5: pressure sensor, 6: gas sampling valve, 7: thermostat, and 8: temperature sensor).

In both cases, after irradiation, a gas sample was collected and analyzed by gas chromatography to obtain the gas phase composition.

## 2. Characterization of Photocatalysts

### 2.1 XRD

Commercial TiO<sub>2</sub> photocatalysts were characterized by XRD to verify the different compositions of anatase and rutile phases. XRD patterns of Pt@PC500 were measured, but no change was observed. Peaks for Pt were not obtained due to the small size of the nanoparticles and low loading of TiO<sub>2</sub> with Pt. Further characterizations (e.g., BET) are in the main text.



**Figure S3.** XRD pattern of investigated commercial TiO<sub>2</sub> photocatalysts (A: anatase phase, R: rutile phase).

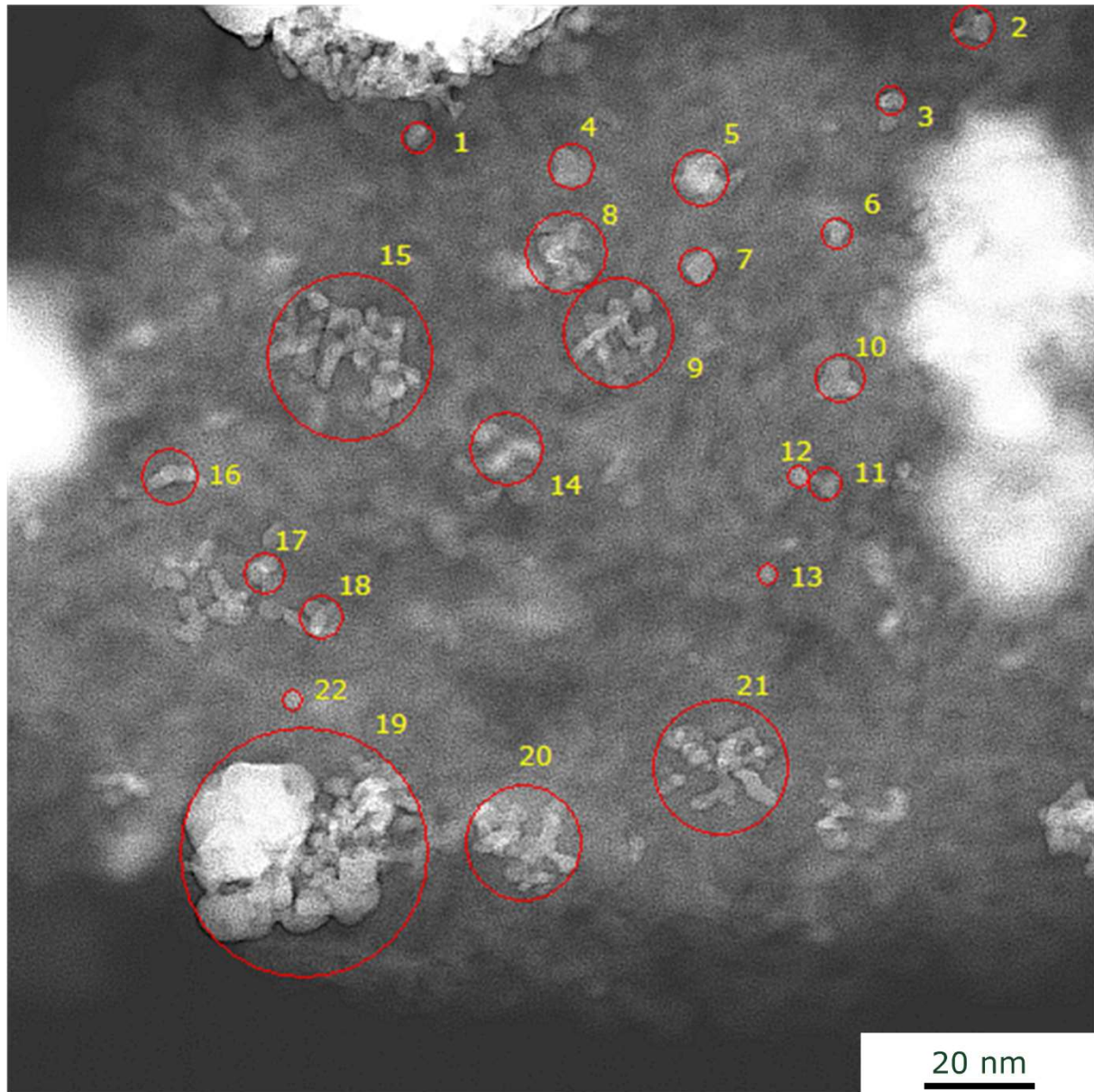
### 2.2 Particle Size and Distribution

From the prepared Pt@TiO<sub>2</sub> photocatalysts, STEM HAADF images were recorded and evaluated using Gatan digital micrograph to obtain the mean particle size and the particle size distribution. Counted particles and/or agglomerates are marked with red circles. The data were evaluated using equations 1-3, with N being the number of particles and  $x_i$  the size of the selected particle. To obtain a better contrast between the Pt particles and the porous TiO<sub>2</sub> photocatalyst, the “sharpen” function of the software was applied to the images.

Mean value  $\bar{x} = \frac{\sum x_i}{N}$  (1)

Error of mean value  $\Delta\bar{x} = \frac{s}{\sqrt{N}}$  (2)

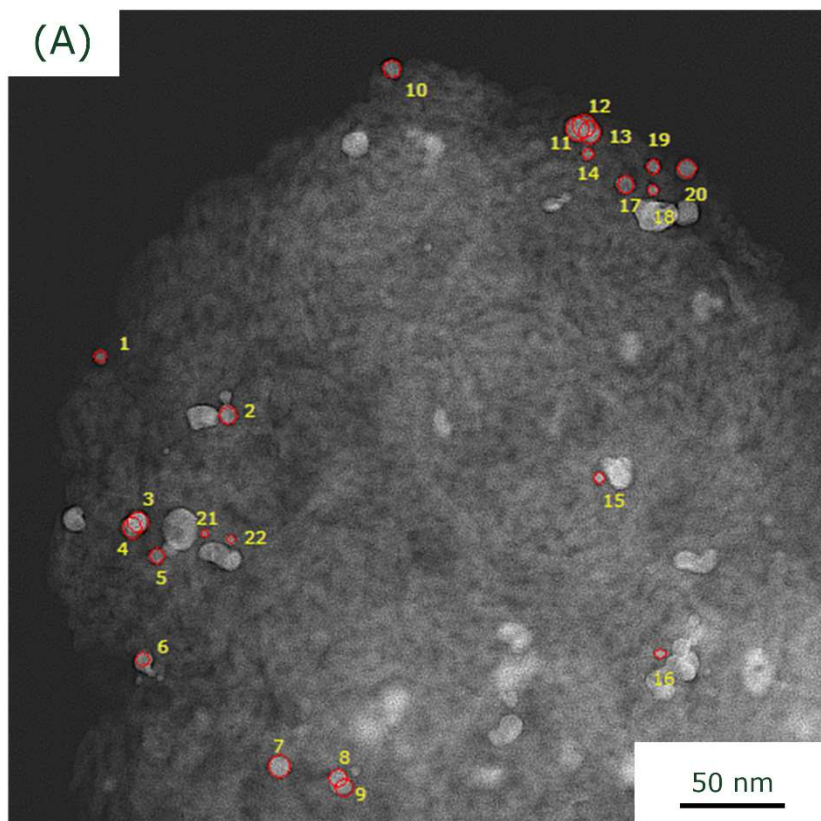
Standard deviation  $s = \sqrt{\frac{(\bar{x} - x_i)^2}{N - 1}}$  (3)



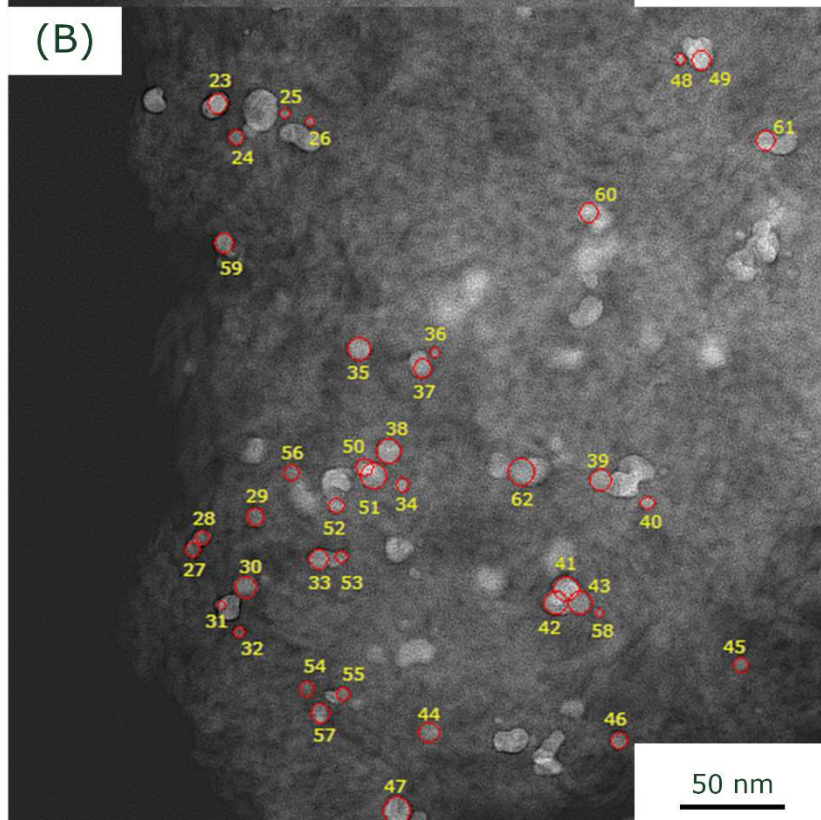
**Figure S4.** STEM HAADF image of Pt@PC500 that was prepared by simple photoreduction. It was not possible to get a mean particle size and distribution because of strong PtNP agglomeration.

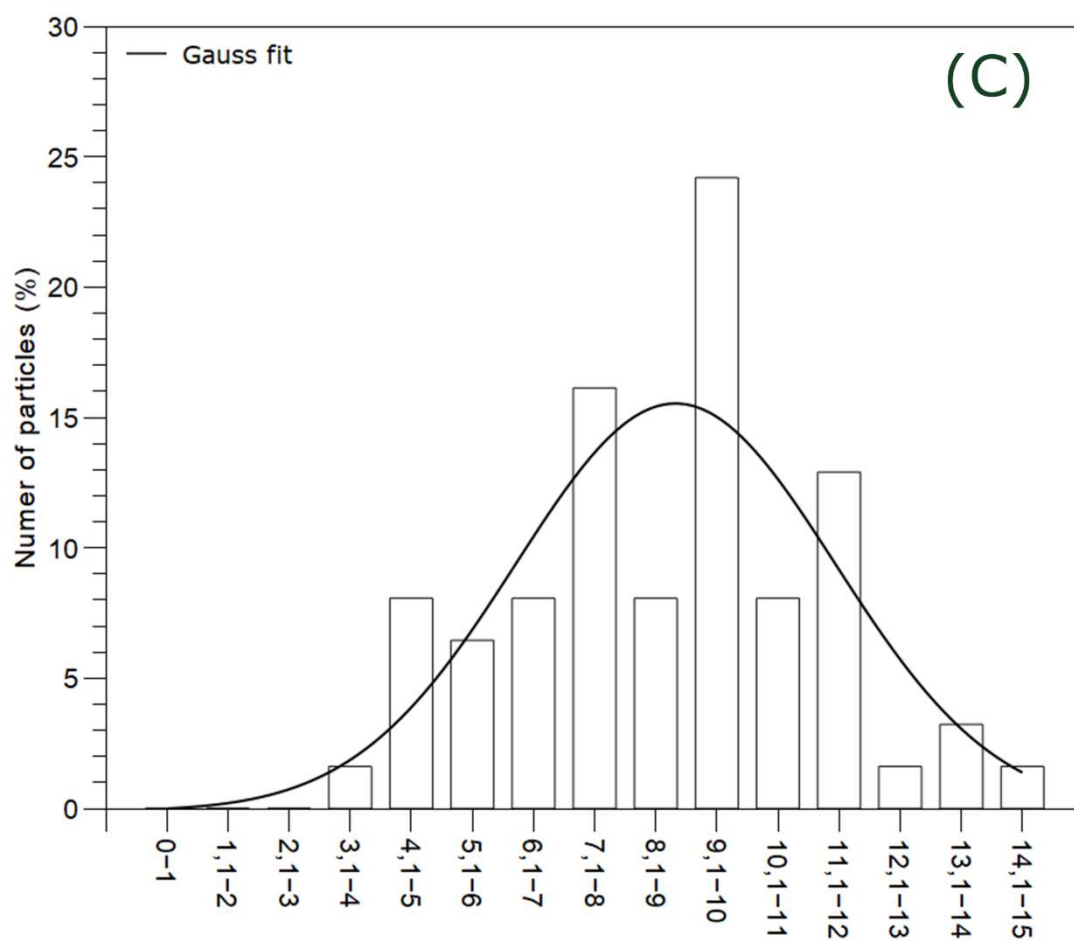


(A)



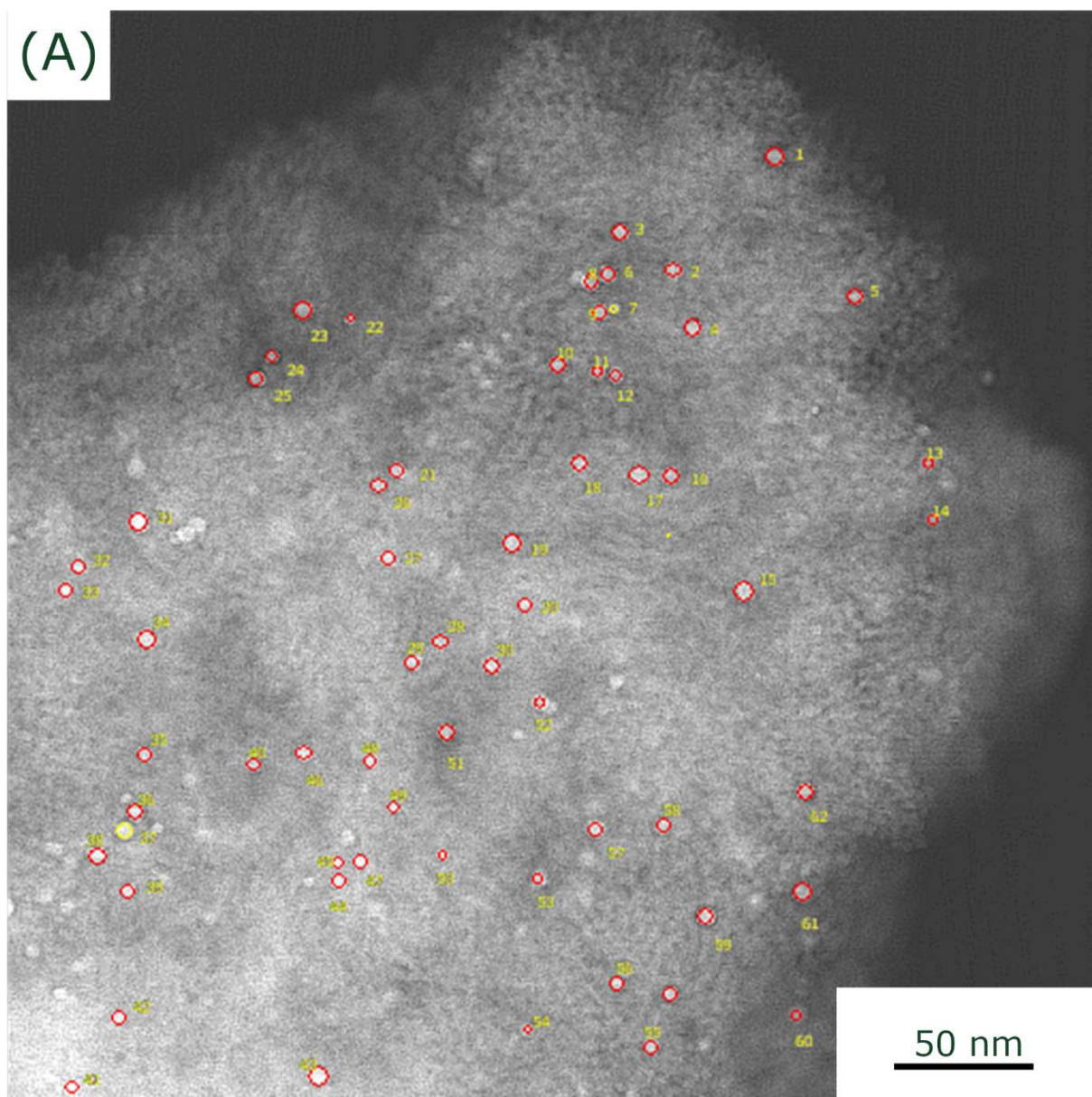
(B)

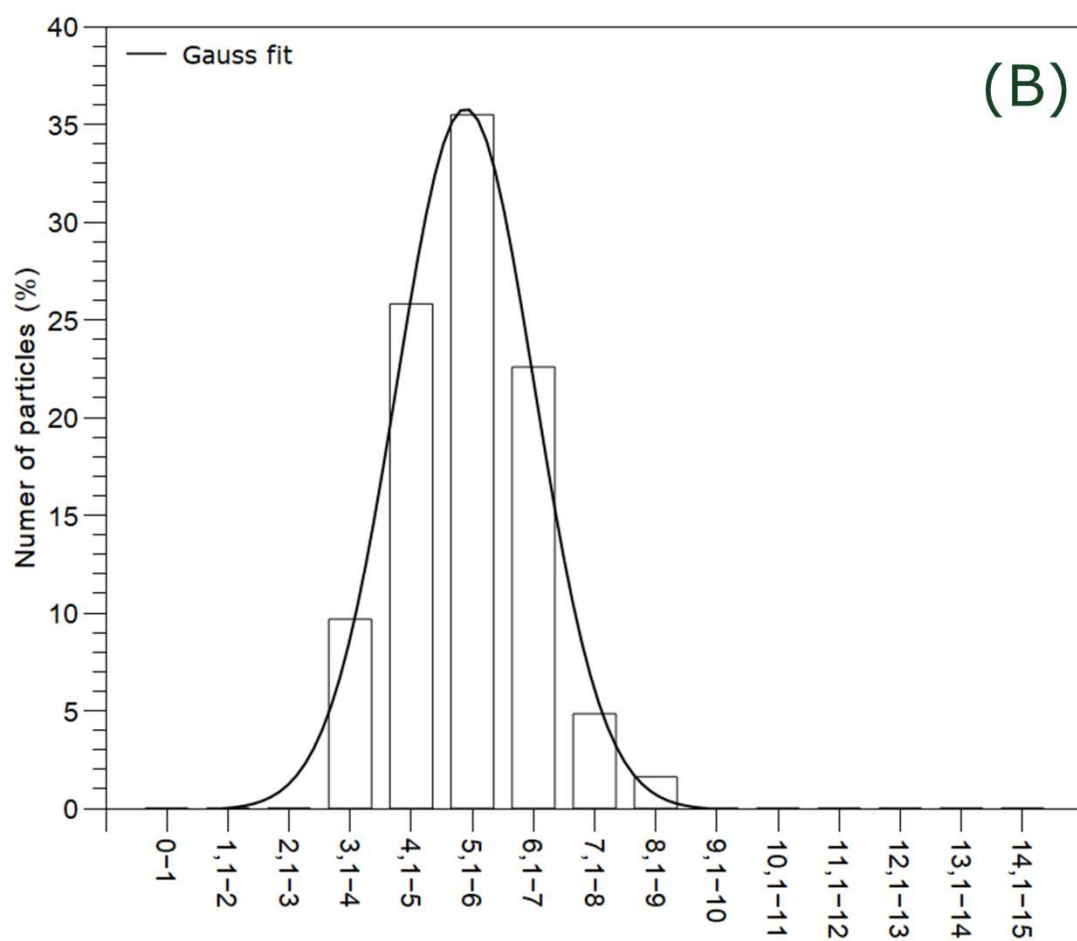




**Figure S5.** STEM HAADF images (A, B) and particle size distribution (C) of Pt@PC500 prepared by the colloidal method with ascorbic acid as the reducing agent

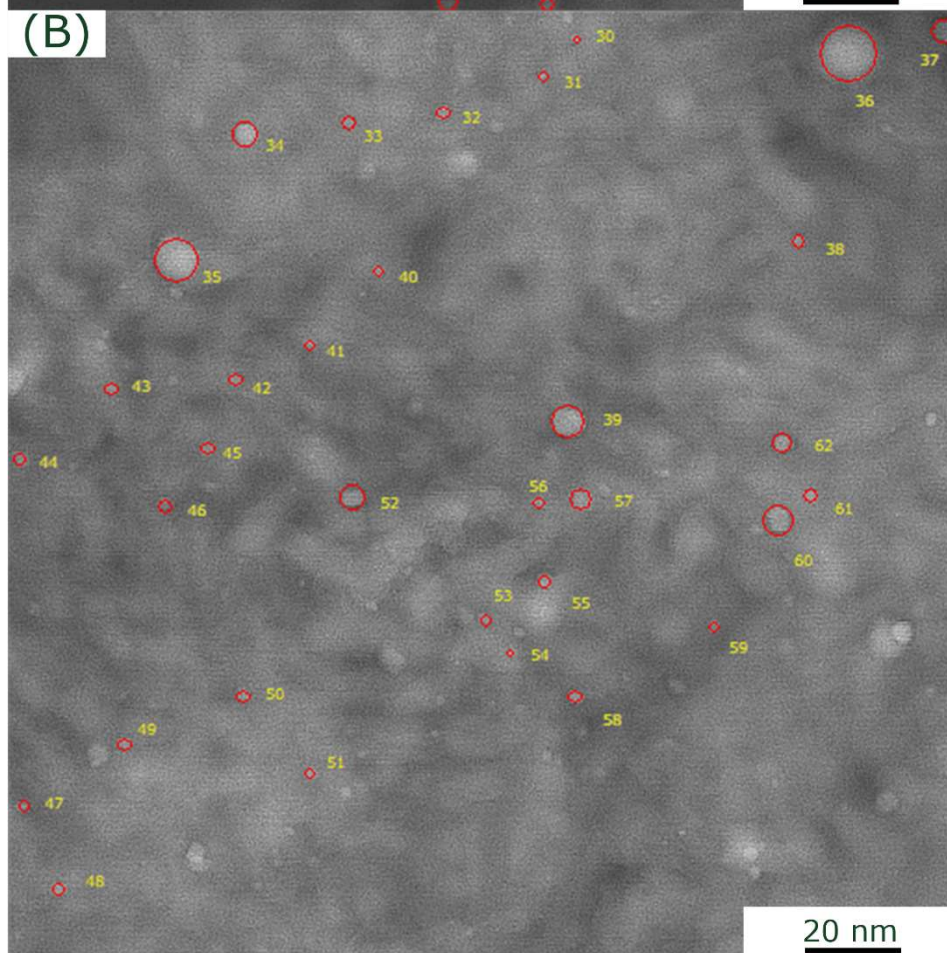
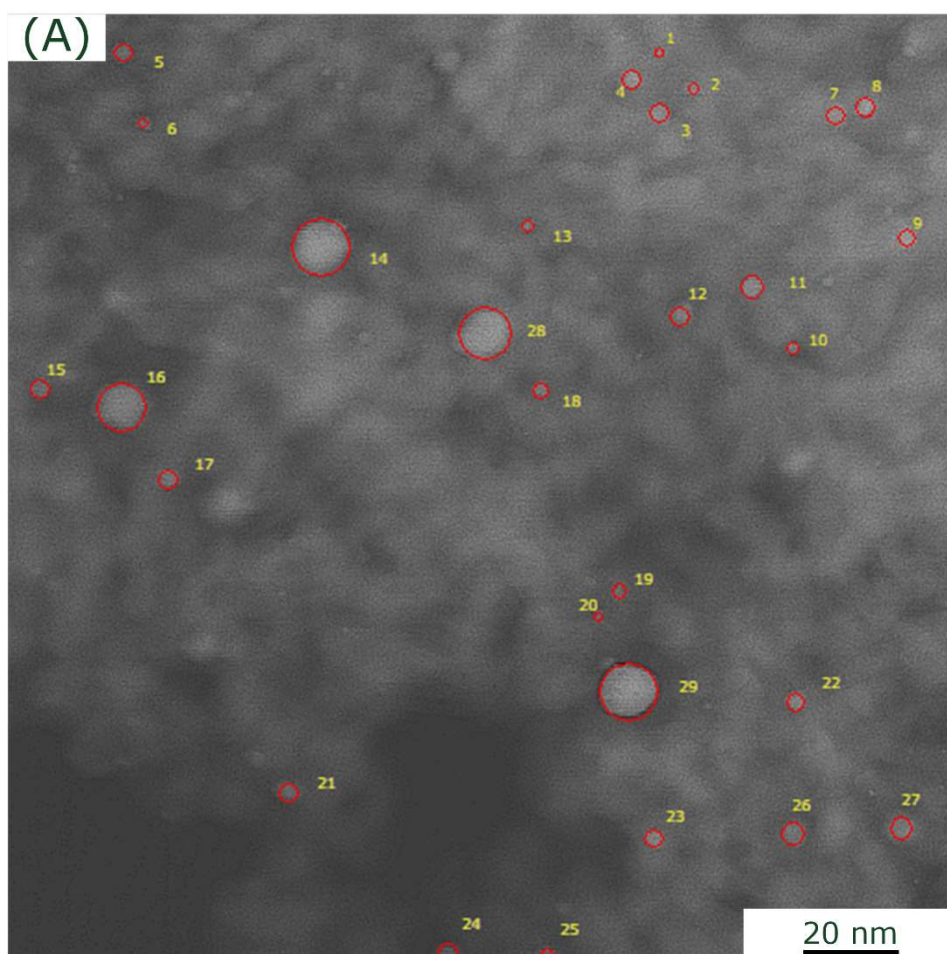
(A)

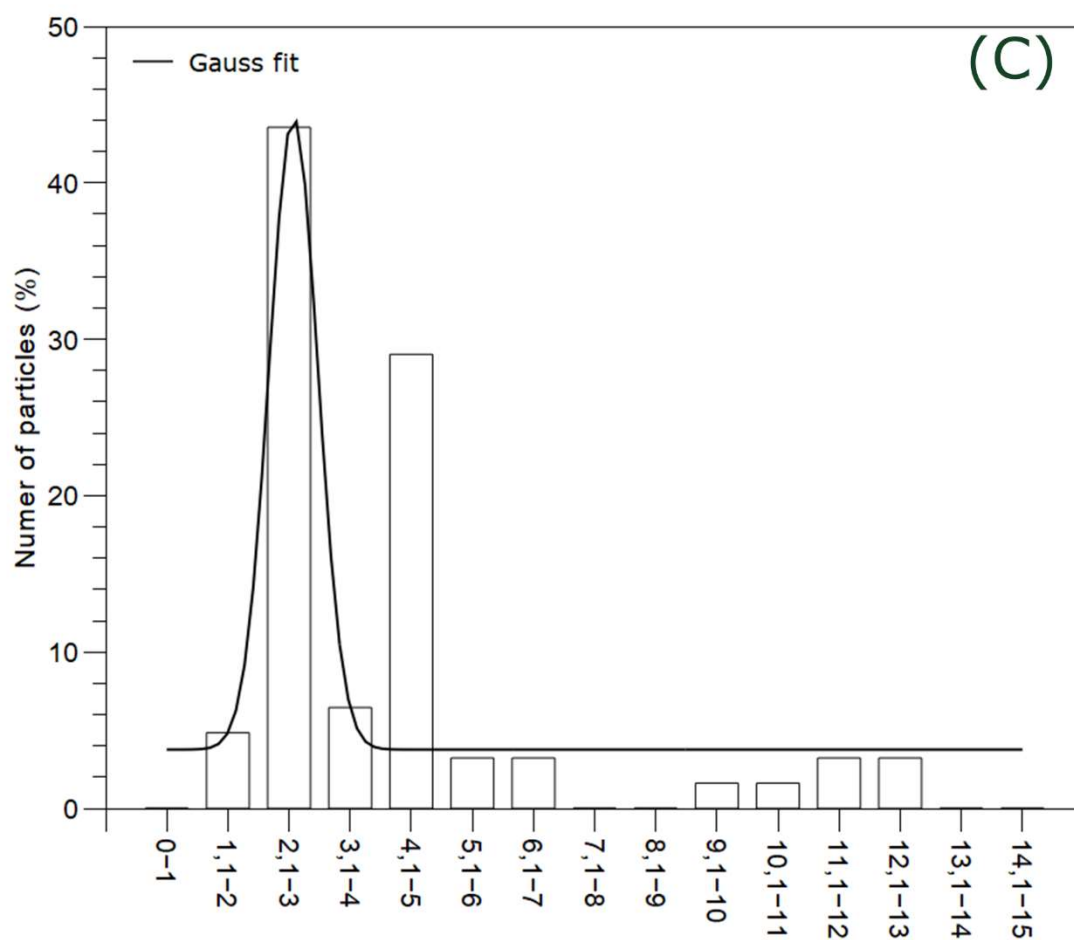




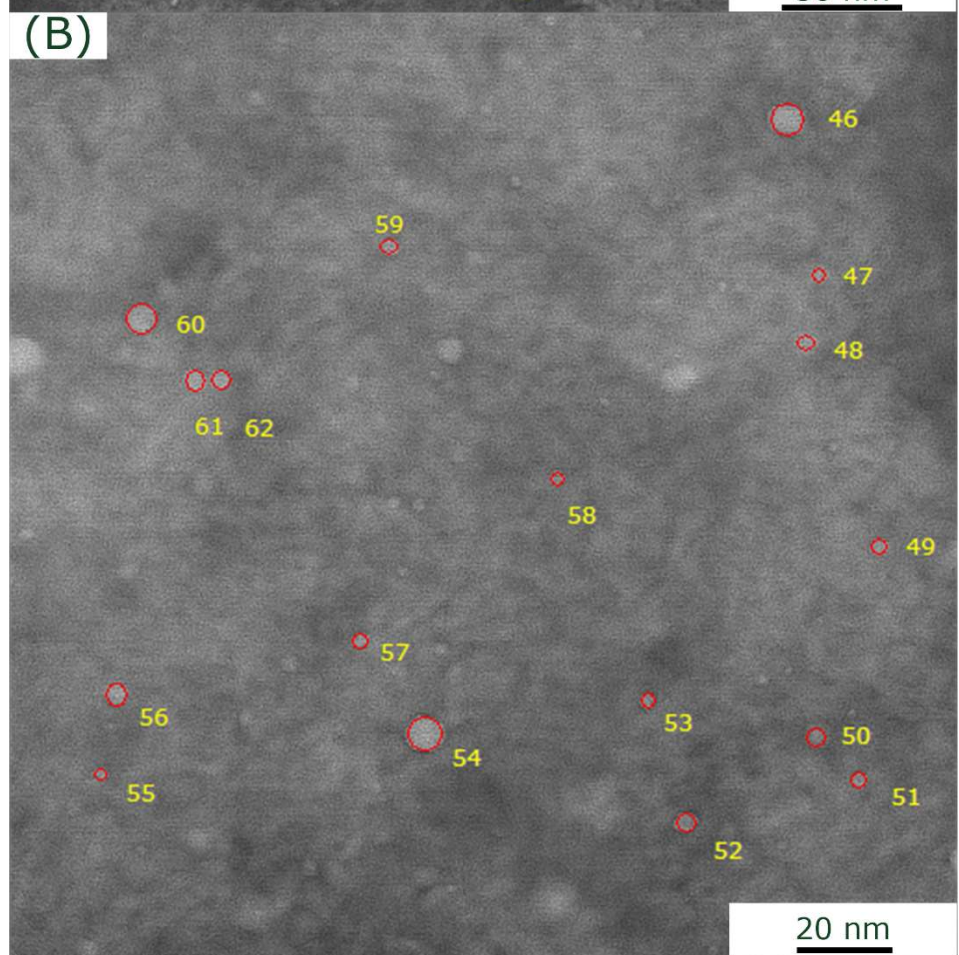
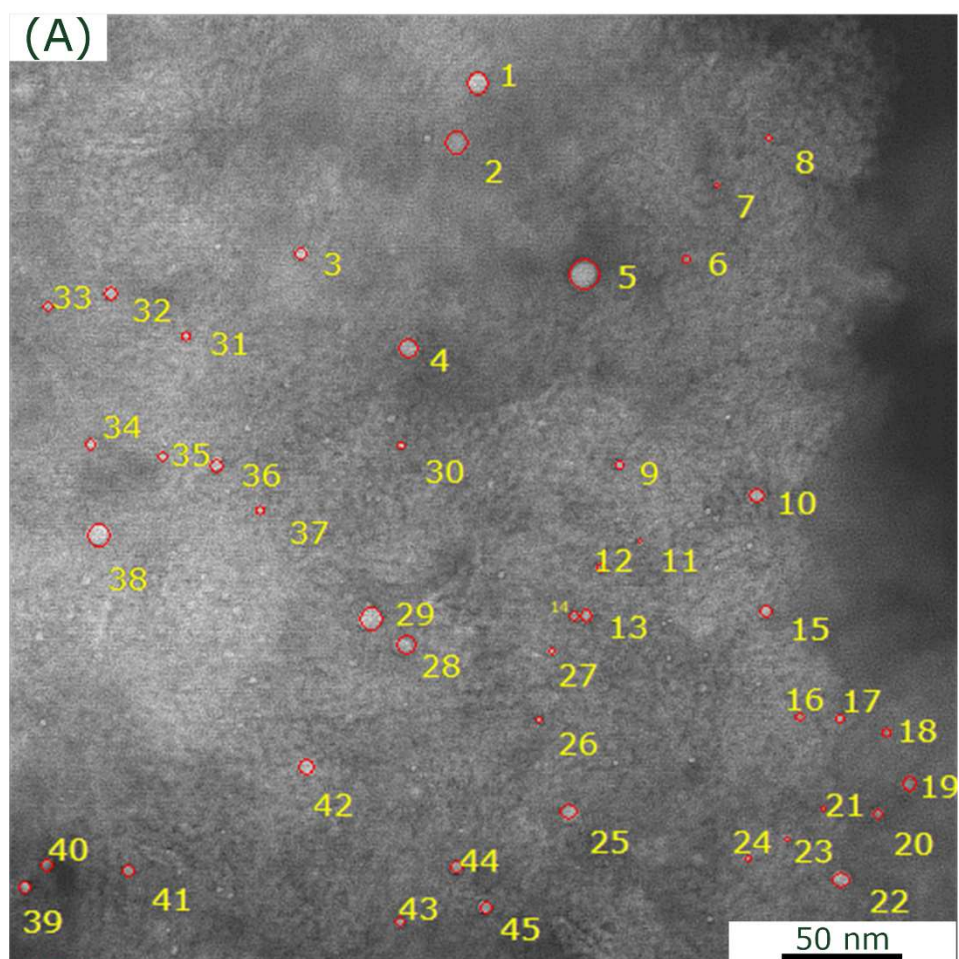
**Figure S6.** STEM HAADF image (A) and particle size distribution (B) of Pt@PC500 prepared by the colloidal method with clove as the reducing agent

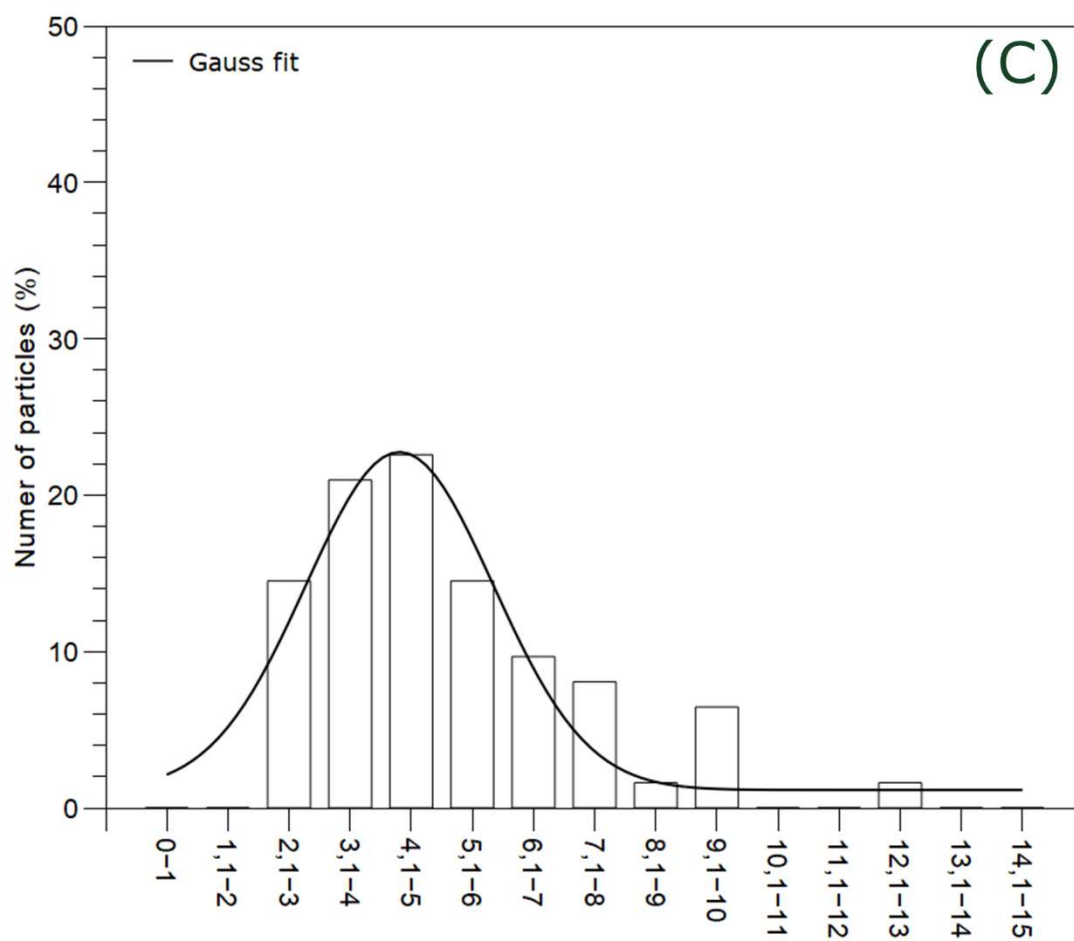






**Figure S7.** STEM HAADF images (A, B) and particle size distribution (C) of Pt@PC500 prepared by the colloidal method with grape seed as the reducing agent.



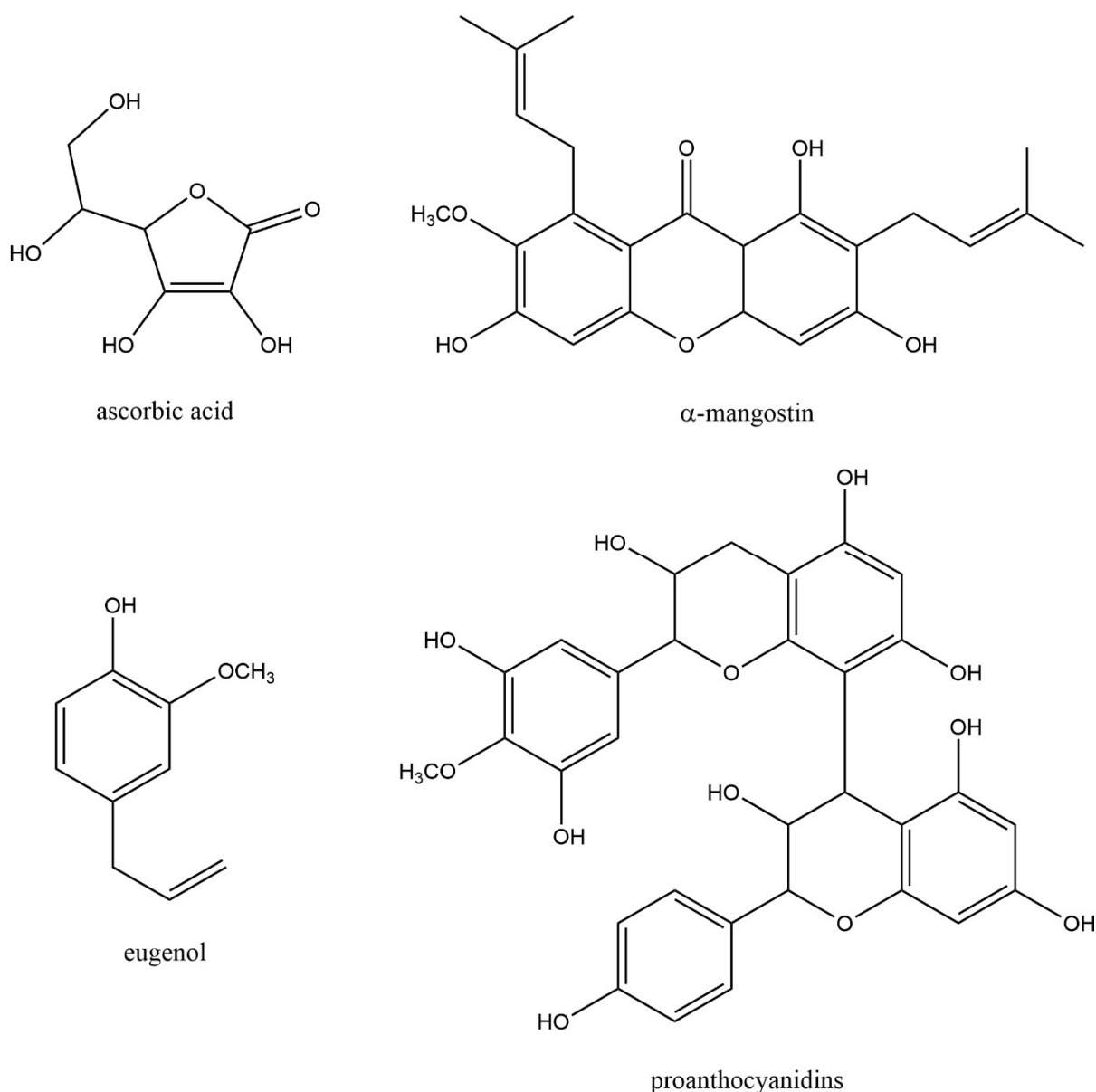


**Figure S8.** STEM HAADF images (A, B) and particle size distribution (C) of Pt@PC500 prepared by the colloidal method with mangosteen seed as the reducing agent.



### 3. Reducing Agents

Different reducing agents were used in the colloidal deposition method to prepare Pt@PC500. Except for ascorbic acid, all reducing agents (clove, grape seed, and mangosteen) are mixtures of different molecules. The main active compounds are shown below.



**Figure S9.** Chemical structures of active compounds in used reducing agents.