

Gold nanoparticles grown on hydrophobic and texturally-tunable PDMS-like framework

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S1. Experimental

General. Commercially available reagents and solvents were purchased from Across and Sigma-Aldrich and used without further purification. PMSi and OMSi were prepared according to literature procedures.¹ Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum 100FT-IR spectrometer on neat samples (ATR FT-IR). ¹³C and ²⁹Si CP MAS NMR spectra were acquired on a Bruker Avance 400 WB spectrometer operating at 100 MHz and 79 MHz respectively under cross-polarization conditions. Nitrogen sorption isotherms at 77 K were obtained with a Micromeritics ASAP 2010 apparatus. Prior to measurement, the samples were degassed for 8sqh at 120 °C to remove any physisorbed species. The surface area of the samples was evaluated as $S_g = Nm A r$, where Nm are the N₂ molecules adsorbed in a statistical monolayer on a gram of sample, A is the Avogadro number and r is the molecular area of adsorbed N₂ (r commonly used being 0.162 nm²). The values are taking in the range of 0.03 < p/p₀ < 0.3. Thermogravimetric analyses (TGA) were performed on a Q500 using a heating rate of 10 °C/min from room temperature to 900 °C under air. Prior to measurement, the solid sample was heated in oven at 100°C for 2 hours. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system using CuKα radiation with a step size of 0.02° in the 2θ range from 0.45 to 87°. UV spectra were measured in the 200–800 nm range using spectralon as the reference on a Perkin-Elmer Lambda 1050 spectrometer. Scanning electronic microscopy (SEM) images were obtained using a JEOL JSM 6700F. The samples were dispersed in ethanol and placed onto a carbon coated copper microgrid and left to dry before observation. (TEM) images from a JEOL JEM 2010 at an activation voltage of 200 kV.

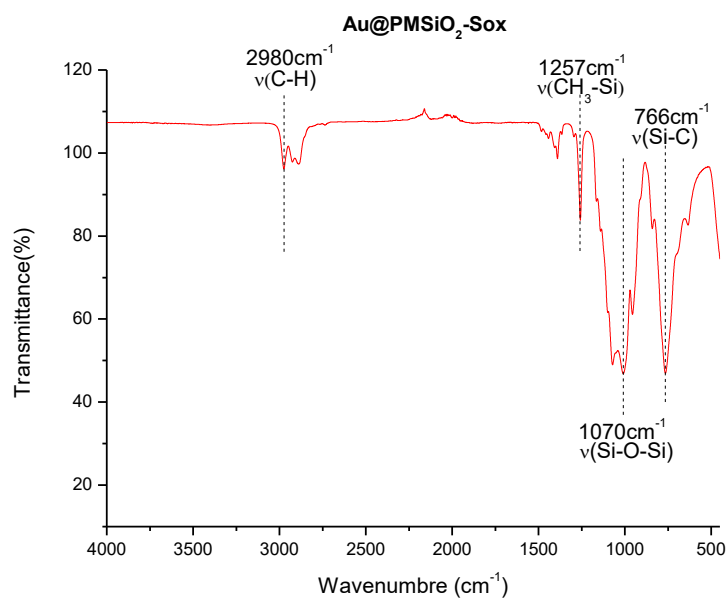
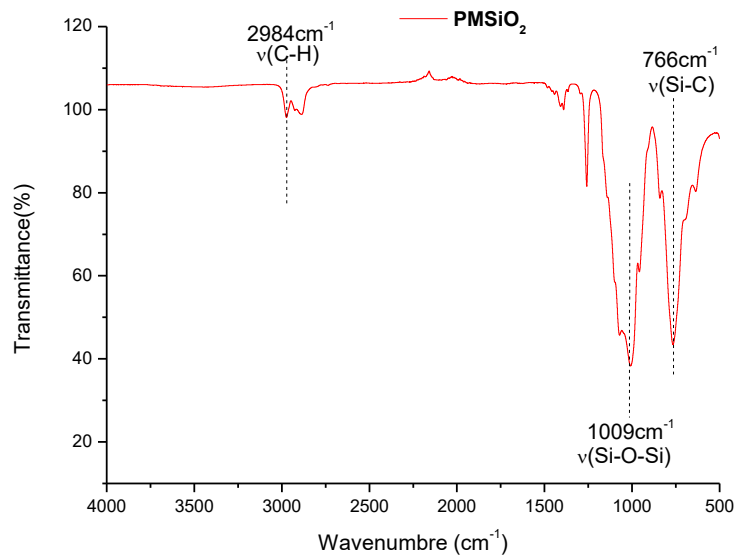
Preparation of PMSi₂-Sox and OMSi₂-Sox

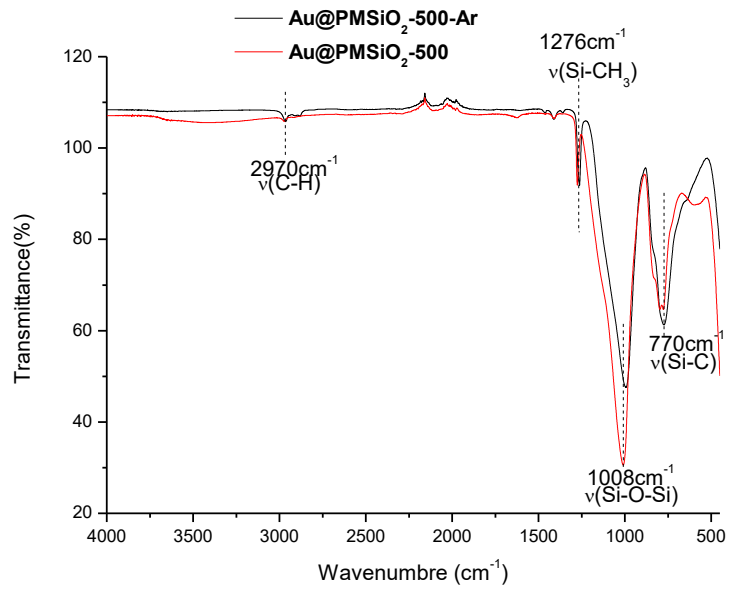
A solution of 1 g of PMSi (n = 29 repeating units) or OMSi (n = 5 repeating units) in 7.8 ml of ethanol was sonicated for 15 min. 1.47 g of CTAB is added to a water / ethanol mixture (10 ml / 7.8 ml), after 15 min with stirring, 22 ml of NH₄OH are added dropwise with stirring. This mixture was added to the first solution. The mixture is left for 24 h with stirring at room temperature, then heated at 60°C for 72 h. The solid is collected by centrifugation, washed three times with ethanol and dried overnight at 60°C. The CTAB was removed via Soxhlet extraction using refluxing EtOH/acetic acid (188 mL/12 mL) for 5 days. **PMSi₂-Sox** or **OMSi₂-Sox** were washed three times with water and dried at room temperature for 24 h and then at 80°C for an additional 24h.

Catalytic reduction of 4-NP

The catalytic activity of materials was tested with the reduction of 4-NP as a model reaction. In this typical process, 2 mg/L of the catalyst was mixed with 0.4 mL aqueous solution of 4-NP (0.2 mmol) in a glass beaker and stirred vigorously for 2 min on a magnetic stirrer. To the above mixture, 3.6 mL of freshly prepared aqueous sodium borohydride (3.6 10⁻²mmol) solution was added and stirred until the reaction mixture became colorless. The reduction process is followed by UV-visible. After fixed time intervals the solution is filtered with 0.22 μm pore size membrane filters to remove the catalyst and the concentration of 4-NP in the residual solution was determined by UV- visible spectrophotometer.

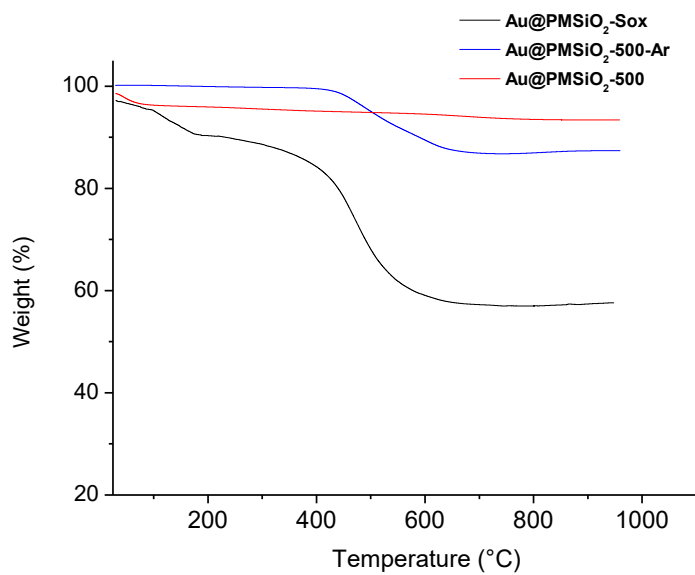
S2. Infrared spectra of PMSiO₂, Au@PMSiO₂-Sox, Au@PMSiO₂-500 and Au@PMSiO₂-500-Ar



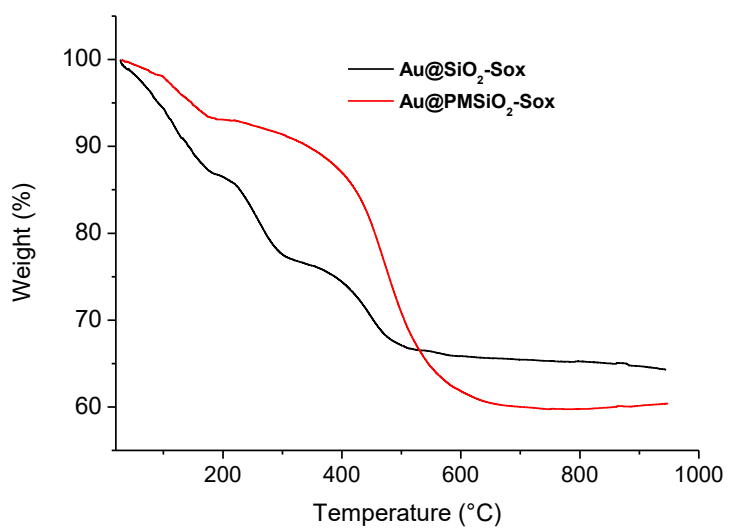


S3. TGA curves of Au@PMSiO₂-Sox, Au@PMSiO₂-500-Ar, Au@PMSiO₂-500 and Au@SiO₂-Sox

S3a. TGA curves of Au@PMSiO₂-Sox, Au@PMSiO₂-500-Ar and Au@PMSiO₂-500



S3b. TGA curves of Au@PMSiO₂-Sox and Au@SiO₂-Sox



S4. Digital photos of **Au@PMSiO₂-Sox**, **Au@PMSiO₂-500-Ar**, **Au@PMSiO₂-500**, **Au@SiO₂-500-Ar**, and **Au@SiO₂-500** dispersion in aqueous solution



Au@PMSiO₂-Sox



Au@PMSiO₂-500-Ar



Au@PMSiO₂-500



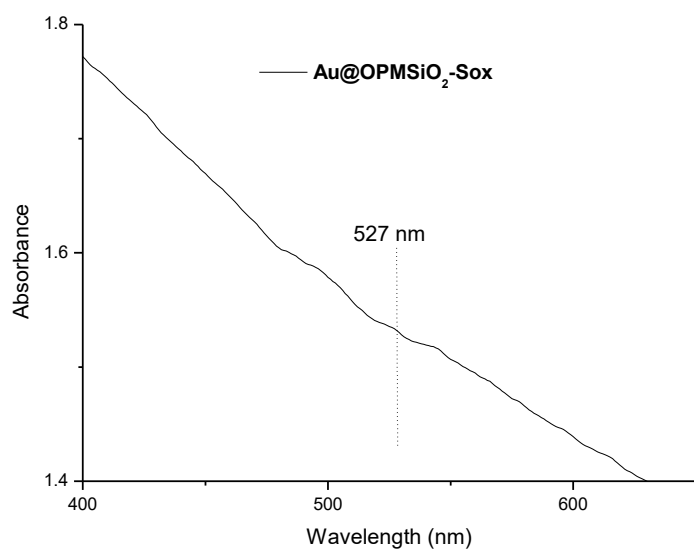
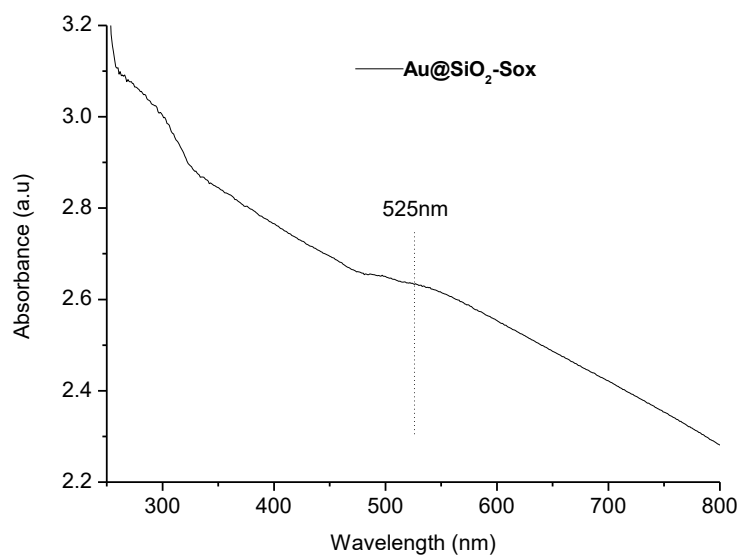
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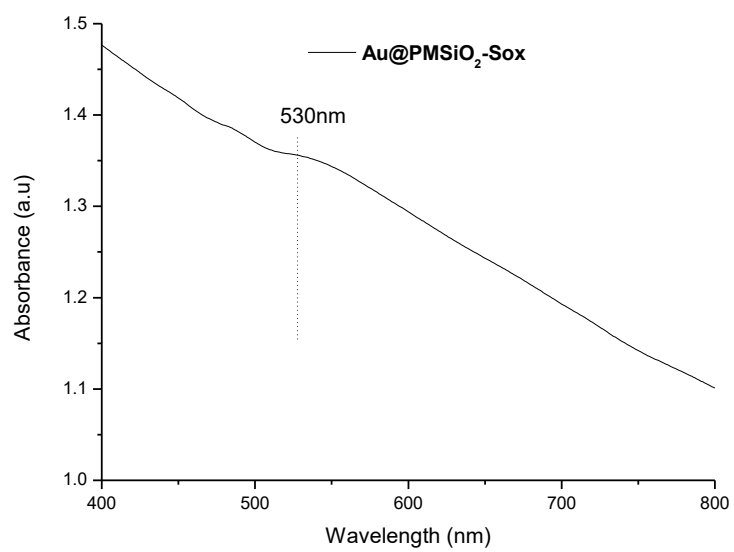


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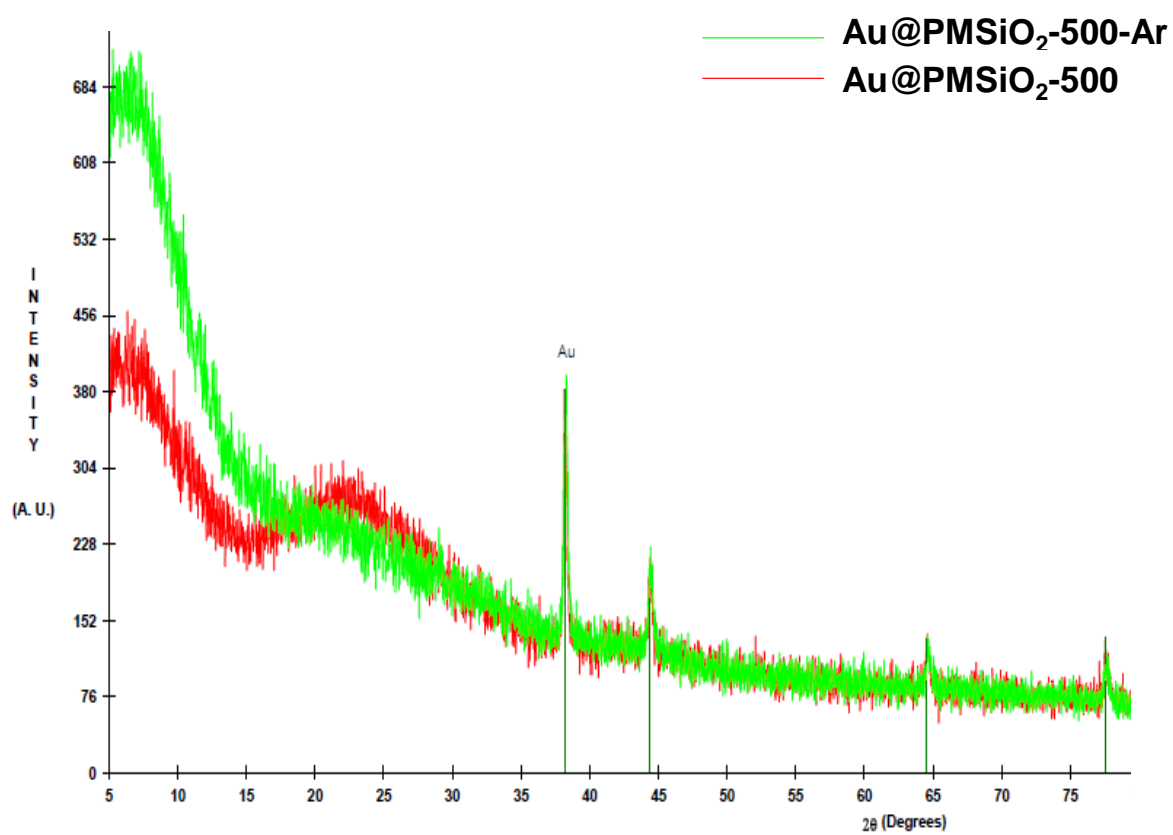
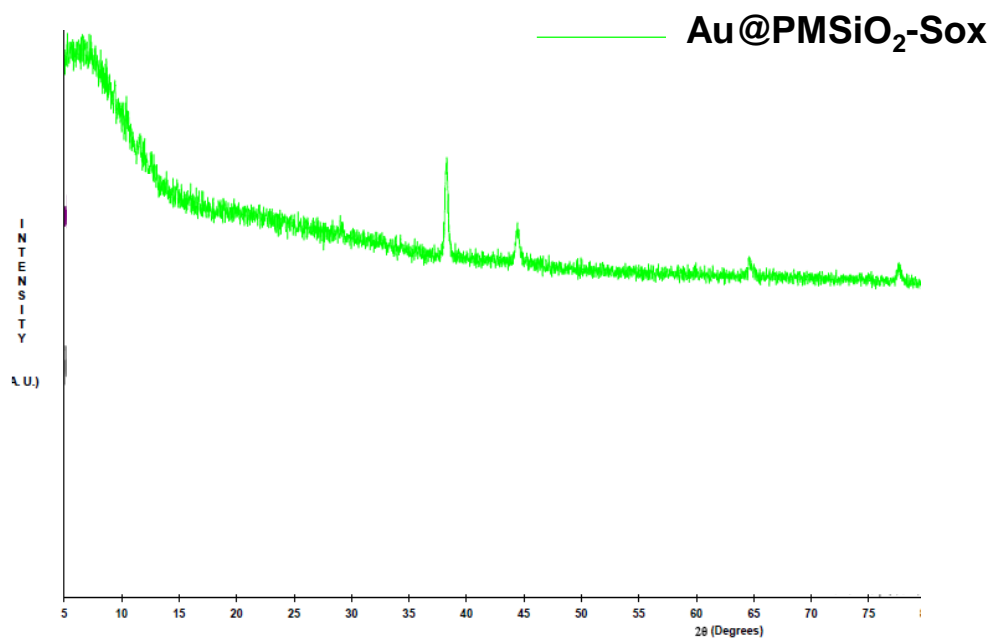
(a) **Au@PMSiO₂-500-Ar**, (b) **Au@PMSiO₂-500**, (c) **Au@SiO₂-500-Ar**, (d) **Au@SiO₂-500**

S5. UV spectra of **Au@SiO₂-Sox**, **Au@OMSiO₂-Sox** and **Au@PMSiO₂-Sox**

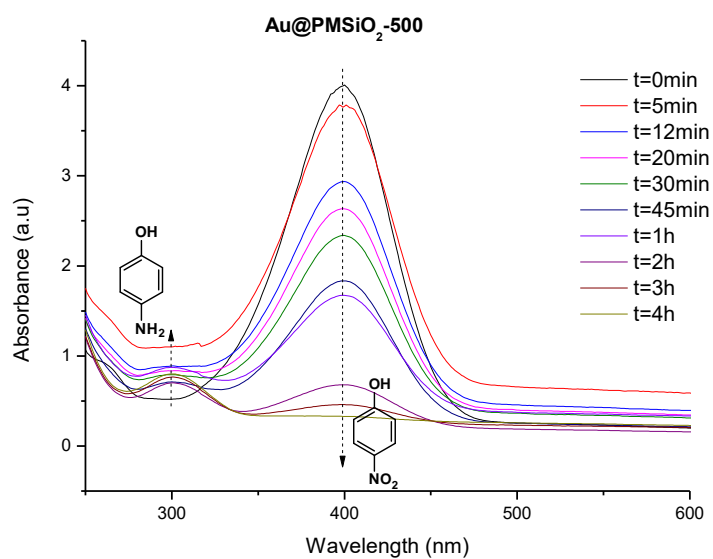
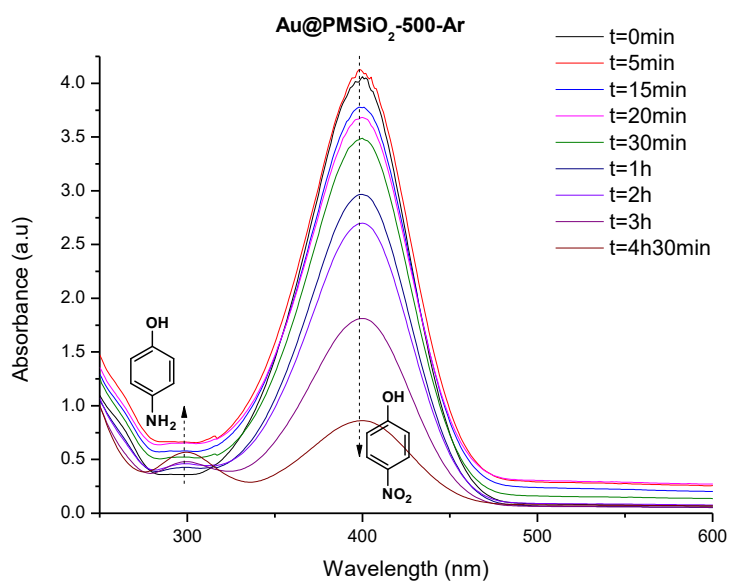
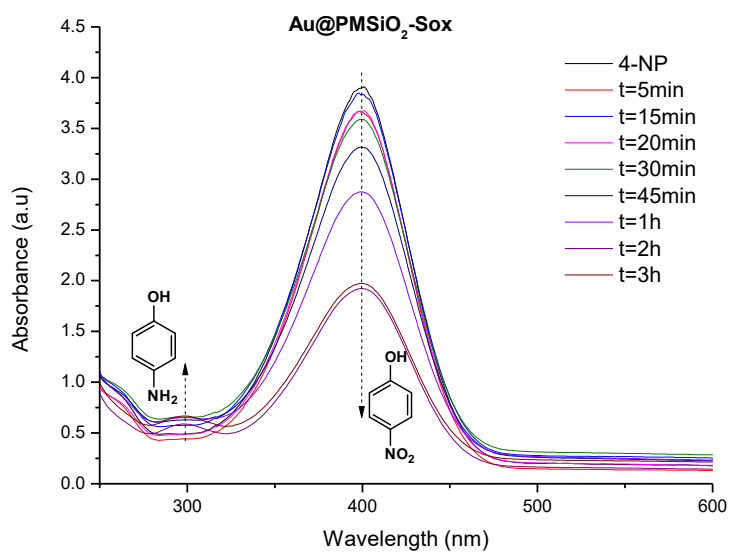




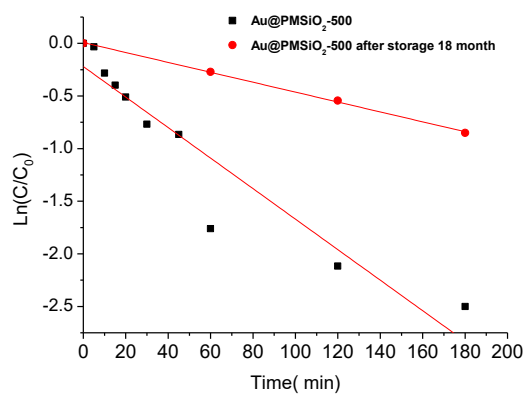
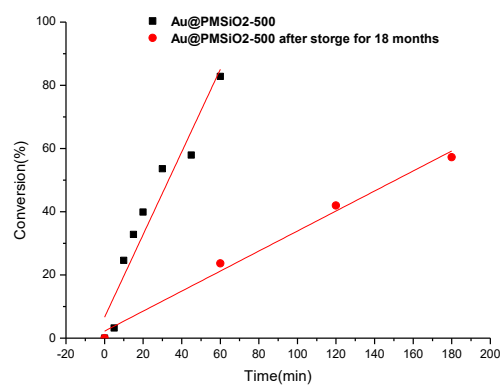
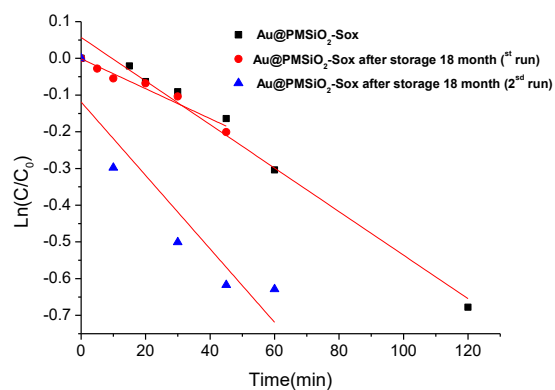
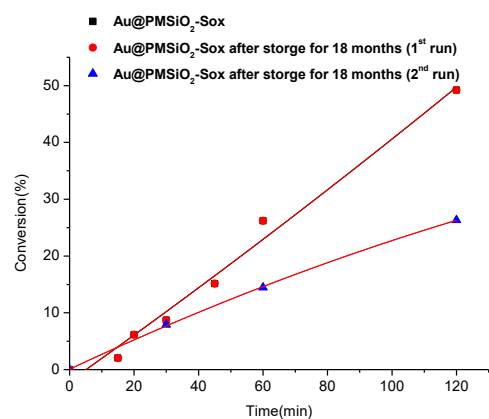
S6. XRD pattern of Au@PMSiO₂-Sox, Au@PMSiO₂-500-Ar, Au@PMSiO₂-500



S7. UV-Visible spectrum reveals the reduction of 4-nitrophenol with Au@PMSiO₂-Sox, Au@PMSiO₂-500-Ar and Au@PMSiO₂-500



S8. Recycling experiments after storage for 18 months of Au@PMSiO₂-Sox



1. A. E. Kadib, A. Finiels, N. Marcotte and D. Brunel, *Chem. Commun.*, 2013, **49**, 5168-5170.