



**Experiment title:** Spatial and electronic structure of Au-nanoclusters in calibrated cucurbit[n]uril cavities

**Experiment number:**  
CH-4182

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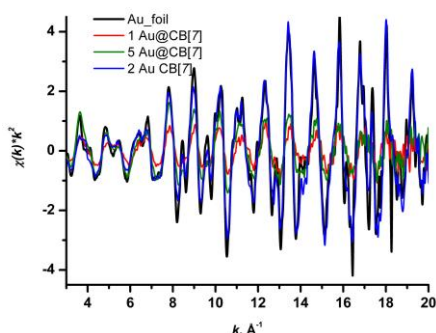
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## Report

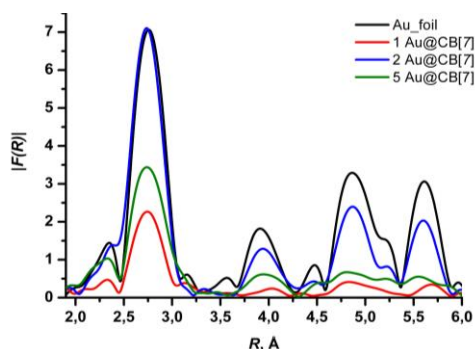
The physical and chemical properties of nanoparticles are known to be significantly different from the properties of the corresponding bulk materials. In particular, Au nanoparticles of less than 5 nm in size supported onto various metal oxides including alumina exhibit the extraordinary high catalytic activity in some reactions (low-temperature CO oxidation, alkene epoxidation and etc.) [1-3]. This effect may be attributed to the difference in the spatial and electronic structures of “infinite” bulk materials and nanoparticles.

Capsules of cucurbit[n]uril (organic molecules  $C_{6n}H_{6n}N_{4n}O_{2n}$  (CB[n]),  $n = 5 - 10$ ) are the most suitable “hosts” for “calibrating” by size and shape gold nanoparticles  $\leq 1$  nm (“guests”). In our studies gold nanoparticles were encapsulated into CB[6,7] by using liquid-phase process.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy in high-energy-resolution fluorescence detection (HERFD) mode are the powerful tools allowing to determine local atomic and electronic parameters of nanosized systems and were used to characterize the spatial and electronic structure of monodisperse metallic “guests” in cucurbit[6,7]uril cavities.



**Fig.1** Experimental  $k^2\chi(k)$   $Au_{L_{III}}$  EXAFS spectra ( $k^2$ -weighted) of the 1, 2, 5 samples and Au foil measured at 12 K.

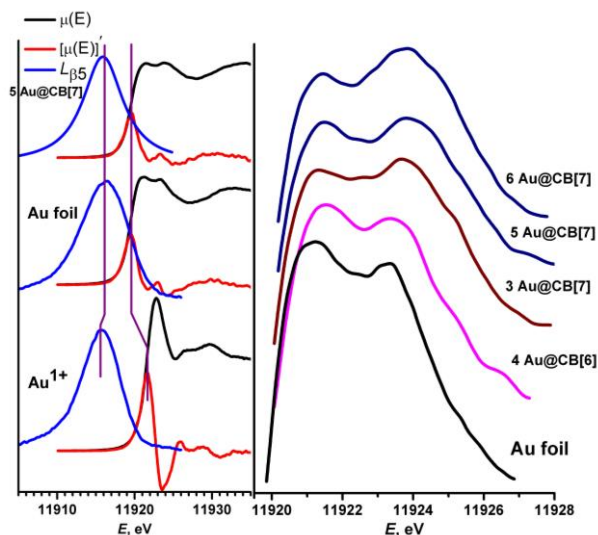


**Fig.2** Fourier transform magnitude  $|F(R)|$  of  $k^2\chi(k)$   $Au_{L_{III}}$  EXAFS spectra of the 1, 2, 5 samples and Au foil measured at 12 K.

Sample		$N_1$	$N_2$	$R_1, \text{Å}$	$R_2, \text{Å}$	$\sigma^2$
1	CB[7]	12 (15%)	6.1 (85%)	2.87	2.84	0.0073
2	CB[7]	11.9 (>90%)		2.87		0.0045
3	CB[7]	12 (65%)	5.7 (35%)	2.87	2.84	0.0078
4	CB[6]	12 (89%)	5.1 (11%)	2.87	2.84	0.0080
5	CB[7]	12 (55%)	8.7 (45%)	2.87	2.85	0.0086
6	CB[7]	12 (70%)	7.8 (30%)	2.87	2.85	0.0090
Au foil		12		2.87		0.0030

Table 1.  $Au_{L_{III}}$   $k^2\chi(k)$  EXAFS data fit parameters for the samples 1 - 6 and Au foil (bi-dispersive molel).

Coordination numbers and interatomic distances:  $N_1, R_1$  – for large particles and Au foil;  $N_2, R_2$  – for small clusters in cavities.  $\sigma^2$ -the Debye-Waller factor.



**Fig.3** On the left: spectra for gold in the oxidation state  $I+$  ( $Au^{1+}$ ), for Au foil and for a sample 5 containing gold nanoparticles in cavities of Au@CB [7]. AuL<sub>III</sub> HERFD spectra - black curves; first derivatives (AuL<sub>III</sub> HERFD)' - red; spectra of the valence band AuLβ<sub>5</sub> ( $5d - 2p$ ) - blue. On the right: top of the "white line" Au L<sub>III</sub> HERFD spectra of gold foil and inclusion compounds Au@CB[6, 7].

EXAFS, XANES and HERFD spectra of the AuL<sub>III</sub> absorption edge were measured for samples containing Au nanoparticles encapsulated in CB[6,7] (Fig.1, 2). Experimental data were processed using the programme packages: FEFF 9.0, EXCURV 98.

### Summary and conclusion

1. It has been found, that gold clusters in cavities of cucurbit[7]uril are characterized by smaller ( $0.03\text{\AA}$ ) interatomic distances and as compared to bulk gold and a considerable reduction in the first shell Au-Au coordination numbers ( $N_{\text{Au-Au}} \leq 6$ ) (Table 1) and with average size of clusters  $d \sim 0.7-1.0$  nm.
2. It has been found for all samples that Au clusters size distribution have two maximums: 1) finely divided Au within the cavities of cucurbituril molecules with narrow size distribution and 2) larger particles of gold (Table 1).
3. Fitting the EXAFS spectra measured at 12 K permits detecting large (threefold) increase of the Debye-Waller factor for the most dispersed samples Au@CB[7] in comparison with bulk metal (Table 1) and correspondingly the valuable increase in the structural disorder for the smallest Au particles in comparison with the bulk Au metal.
4. No visible differences in the the position of the AuL<sub>III</sub> absorption edge and in the charge state of Au for samples with Au@CB[6,7] and the bulk Au metal were detected. (This conclusion is illustrated in Fig.3, on the left). Revealed changes in the electron state spectra of samples with small Au clusters (see Fig.3., on the right) can be related to size effects and the appearance of a gap between the occupied and unoccupied electronic states [4]. Such changes can cause of small gold particles properties changes.

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[3] V.I. Bucktiyarov, Uspechi Chimii, (in Russian) 76(6) (2007) 596-627.

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