ION-INDUCED QUANTIZED CHARGING OF
IMMOLIZED HYDROPHILIC GOLD
CLUSTERS

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INTRODUCTION

Metallic nanoclusters have potential for nanometer-scale
electronics, sensors, and electro-optics applications.
When they are very small, the clusters exhibit a strong
electrical non-linearity via the Coulomb blockade
mechanism and this physics is strongly sensitive to local
changes associated with electrical gating, or with
adsorption of a chemical species of interest.
In this study we describe the self-assembly of water-
soluble gold nanoclusters (2 nm diameter) coated with a
tri(ethylene oxide) shell. AuEO3 [1] onto a gold electrode
modified with a mixed monolayer of alkane thiol/dithiol.
The interaction of this system with the hydrophobic
anion, PF6-, is explored by CV and ACV, performed in
aqueous supporting electrolyte. Gold nanoclusters that
are soluble in water may readily be functionalized with
bio-molecules, and the resulting bio-nanoconjugates can
be used as sensor elements.
Chen and Pei [2] investigated the ion-induced
rectification of the quantized capacitance charging of
alkanethiol protected nanoclusters adsorbed onto the
surface of bare Au electrodes. The new type of gold
clusters and the novel architecture described in this paper
allow for faster electron transfer in aqueous media than
for the previously reported system.

EXPERIMENTAL

Working electrodes were gold disks (0.04 cm²) or coiled
gold wires (0.5 cm²). Mixed monolayers were obtained
with 1-octane thiol (OT, 99%) and 1,9-nonane dithiol
(NDT, 98%), self-assembled on the clean gold surface
from 10:1 mol/mol solution in ethanol (total thiol
concentration: 2.2 mM), for 16 h at room temperature
(RT). Gold clusters AuEO3 were prepared according to
previously reported methods [1] and were attached to
modified Au electrodes, from aqueous solution (12 h at
RT).
Three-electrode mode electrochemical measurements
were performed with a chemically modified Au working
electrode, a Pt counter, and Ag/AgCl, 3 M KCl reference,
Ag(RE). Supporting electrolyte was 0.1 M NH4 PF6 in
denatured water, buffered to pH 7 with 0.01 M phosphates.
Cyclic voltammetry (CV) was recorded from 0.30 to 0.50
V vs. Ag(RE), at 0.100 V s⁻¹. AC voltammograms
(ACVs) were acquired in the stepped mode, with 10 mV
rms amplitude. Data points were recorded every 10 mV
at fixed frequency values (1-10000 Hz). CV and ACV
were performed with a Model 660a Electrochemical
Workstation (CH Instruments, Austin, TX) equipped with
a Faraday cage.

RESULTS

Fig. 1 displays the schematic of the self-assembled
system. AuEO3 gold clusters are anchored to a mixed
OT-NDT monolayer via the free thiol group of NDT, by
an exchange reaction.
The ACV in Fig. 2 shows small peaks related to the
presence of the hydrophobic PF6-anion in the supporting
electrolyte. No such peaks have been observed in media
based exclusively on phosphates.
The rate constant of the electron transfer between
the clusters and the electrode surface was derived from ACV
scans taken at different fixed frequencies by plotting the
Io/Ia against frequency (where Io is the peak current and Ia
is the background current), according to Wooster and
Creager [3].

Due to the hydrophilic coating of the electron transfer
in the system is approximately 4 times faster than that
reported for the alkanethiol-coated clusters [2].
A possible explanation of the enhanced charge transfer
rate may reside in the partitioning of PF6 ions between
the hydrophilic coating layer of the Au clusters and the
bulk phase (i.e., aqueous supporting electrolyte).

Fig. 1: Schematic of the Au clusters with hydrophilic
coating tethered to a SAM-coated gold electrode

Fig. 2: ACV recorded with the system in Fig.1 (200 Hz)

REFERENCES

1. E. E. Foos, A. W. Snow, M. E. Twigg and M. G.