The Size Effect of Nano Au Particles Electrodeposited on Poly Au Microelectrode on the Kinetics of $Co(bpy)_3^{2+/3+}$ and $MV^{1+/2+}$ Redox Reactions

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More and more experiments show that outer sphere redox reactions such as $Fe(CN)_6^{3-/4-}$, $Co(bpy)_3^{2+/3+}$, $Ru(bpy)_3^{2+/3+}$ and $MV^{+/0}$ also depend on the states of electrode surface and components of electrolytes to some extent[1]. It is worthwhile to explore the behaviors of these reactions on the electrodes with nano size particles. However there have been no relevant reports so far. In this abstract the size effect of Au nano particles electrodeposited on poly-crystal Au micro disc electrodes (denoted as AuME-nanoAu) on the kinetics of the redox-reaction of $Co(bpy)_3^{2+/3+}$ and methyl viologen (1,1'-dimethyl-4,4'-bipyridilium) $MV^{+1/2+}$ is presented.

The Au nano particles with different size were electrodeposited on poly Au microelectrode by double pulses potential step method. The morphology, distribution and sizes of particles on the electrode surface were observed by SEM (XL FEG/SFEG/Sirion) and estimated by electrochemical methods. The results of the two methods were in reasonable agreement. The redox kinetics were studied using fast cyclic voltammetry (20 - 1000 V s^{-1})

The cathodic and anodic peak separations ($\triangle \boldsymbol{E}_P$) on the CV curves of $Co(bpy)_3^{2+/3+}$ and $MV^{1+/2+}$ redox reactions were found to increase with the increase of Au particle size (Fig. 1). The apparent rate constant, $\boldsymbol{k}$ (cm s^{-1}), of $Co(bpy)_3^{2+/3+}$ and $MV^{+1/0}$ redox reactions can be calculated according the Nicholison's equation [2].

$$\psi = k\left(\frac{D_O}{D_R}\right)^{\alpha/2} / \left(\pi D_O \nu \frac{nF}{RT}\right)^{1/2} \qquad (1)$$

where ψ is a dimensionless parameter which has been obtained by numerical calculation in the literature[1]; $\boldsymbol{D}_O$, $\boldsymbol{D}_R$, □ and □ are the diffusion coefficients of the oxidized and the reduced forms, electron transfer coefficient and potential scanning rate (V s^{-1}), respectively; other symbols have their usual significance. The apparent heterogeneous electron transfer rate constants $\boldsymbol{k}$ of $Co(bpy)_3^{2+/3+}$ and $MV^{1+/2}$ redox reactions calculated from the data of fast CV was found to increase exponentially with decreasing Au particle size, as shown in Fig. 2. When the particle size is below 60 nm, the rate constant was larger than that for a smooth Au MDE. The $\boldsymbol{k}$ value for the electrode with 60 nm Au particles was close to the value for the smooth Au MDE. The $\boldsymbol{k}$ values for the electrode deposited with 5 nm Au particles for $Co(bpy)_3^{2+/3+}$ and $MV^{1+/2+}$ redox reactions were 0.37 cm s^{-1} and 0.63 cm s^{-1}, respectively. These values came out to be larger than the upper limits found in literature, i.e., 0.22 cm s^{-1} for $Co(bpy)_3^{2+/3+}$ on Pt (111) electrode in KCl containing SCN^- [2] and >0.1 cm s^{-1} for $MV^{1+/2+}$ on the GC.

However the roughness of electrode surface decreased with decrease of particle sizes (Fig. 3). After correcting for the effect of roughness factor the rate constants, $\boldsymbol{k}^0$, still increased exponentially with decrease of particle diameters, $\boldsymbol{d}$. The Similar results were obtained for the redox-reaction of $Fe(CN)_6^{3+/2+}$ on AuME-nanoAu in our early work[3]. The above described phenomenon implies that the increase of rate constant $\boldsymbol{k}$ could not be simply ascribed to the increase of electrode surface area. These findings may be in line with Haruta's opinion[5] that the surface adsorption and reactivity of Au can be tuned by down-sizing or scratching to create defective surface structures.

References

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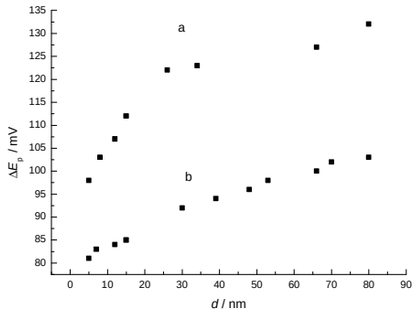

Fig. 1 Dependence of peak separations □$E_p$on particle diameters d. a, for $Co(bpy)_3^{2+/3+}$ and b, for $MV^{1+/2+}$ redox reactions.

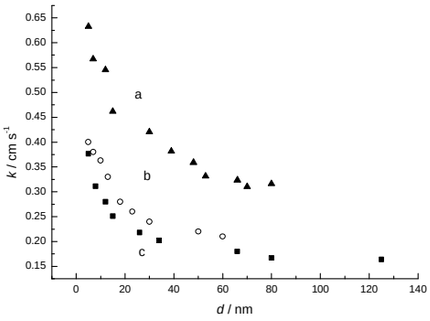

Fig. 2 Dependence of the apparent rate constant on Au nano-particle diameters d at 250mV/s. a, for $MV^{1+/2+}$redox reaction in 5mM MV^{1+} +1M KCl. b, for $Fe(CN)_6^{3-/4-}$ in 1mM $Fe(CN)_6^{3-}$+ 1M KCl.
c, $Co(bpy)_3^{2+/3+}$redox reaction in 3 mM $Co(bpy)_3(ClO_4)_3$+ 1M KCl.

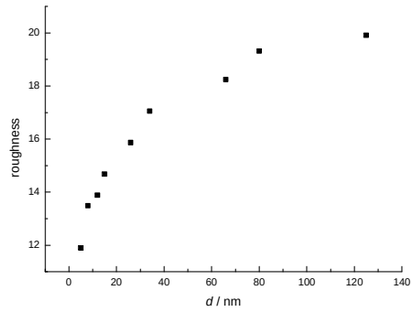

Fig. 3 Dependency of surface roughness of electrode on particle diameters *d*.