Effect of heat treatment of TiO_2 nanotubular layer on electrocatalytic activity of Au nanoparticles/TiO_2 system in oxygen electroreduction reaction

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Oxygen reduction reaction (ORR) significantly limits widespread applications of fuel cells due to relatively slow kinetics of oxygen formation and decomposition on most electrodes [1]. Platinum and its alloys are mostly used as anode and cathode catalysts in these applications, but this metal is costly and of limited reserve. Therefore, recently extensive research efforts have been devoted to the development of non-platinum electrocatalysts. Gold in alkaline medium can display effectiveness in ORR close to that of platinum. In order to achieve a high specific surface area and particularly minimize the cost, gold is typically dispersed in the form of nanoparticles (NPs) and immobilized on solid surface [2]. However, the catalytic activity of NPs can depend strongly on the nature of the substrate.

In the present report, to study the influence of heat treatment of the substrate on electrocatalytic activity of gold NPs, electrochemically synthesized TiO_2 nanotubular layers on Ti were annealed at 350 ^oC, 450 ^oC and 550 ^oC for 3 h. Colloidal Au NPs were prepared by mixing $HAuCl_4$, sodium citrate and sodium boronhydride solutions. Aqueous colloidal suspension of Au NPs was coated onto the TiO_2 surface and then dried at room temperature. After Au loading, the samples were briefly post-heated at 200 ^oC to eliminate water and to assure more intimate contact between the NPs and TiO_2 surface. The electrocatalytic activity of the Au/TiO_2 electrodes in ORR was then examined by cyclic voltammetry (CV) using an Autolab potentiostat in 0.1 M KOH solution saturated with O_2.

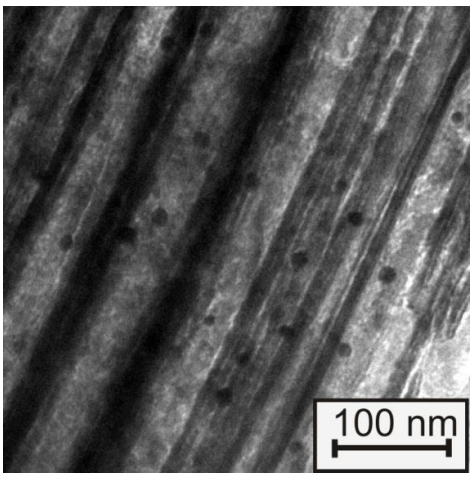

Fig 1. TEM image of Au nanoparticles within TiO_2 nanotubes

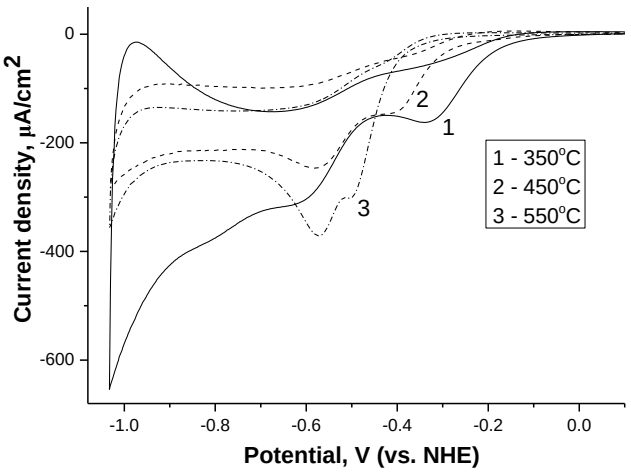

Fig 2. CV curves of ORR in 0.1 M KOH solution on nanotubular TiO_2 layers heated at different temperatures and then loaded with Au nanoparticles

Fig. 1 shows TEM image of the Au-loaded TiO_2 nanotubular layer, the average size of Au NPs is 7−10 nm. CV curves for TiO_2 samples without Au NPs have one wave of ORR at potentials more negative than -0.5 V (Fig. 2). For Au/TiO_2electrodes an additional wave corresponding to O_2 electroreduction on the Au surface appears at less negative potentials. This wave is shifted to the negative direction with increasing the temperature of TiO_2 substrate annealing. This substrate-dependent influence on the Au-catalized ORR can be rationalized if we take into account the variation of semiconductor properties of TiO_2 as a result of its annealing.

References

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2. J. M. Macak, F. Schmidt-Stein, P. Schmuki. *Electrochem. Commun*. (2007) 9: 1787.