Supporting Information

High Aspect Ratio Rhodium Nanostructures for Tunable Electrocatalytic Performance

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SI-I: Transmission Electron Microscopy (TEM) of Single Nanoneedle and Nanorod:

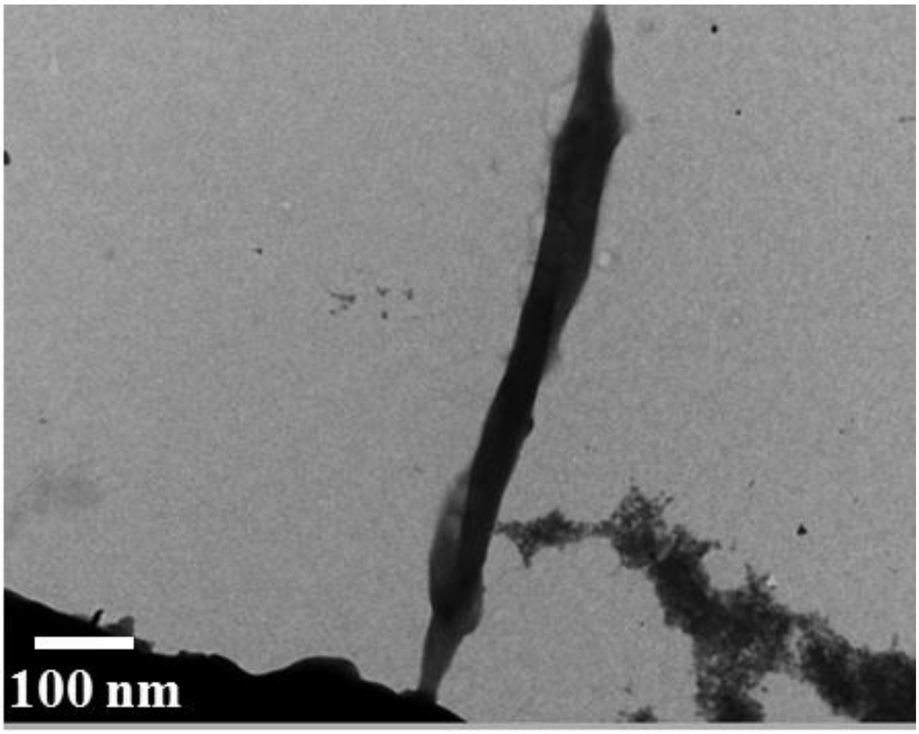

Fig. S1 TEM image of single nanoneedle (Rh-TDA) having the length of ~1 µm and thickness of ~100 nm.

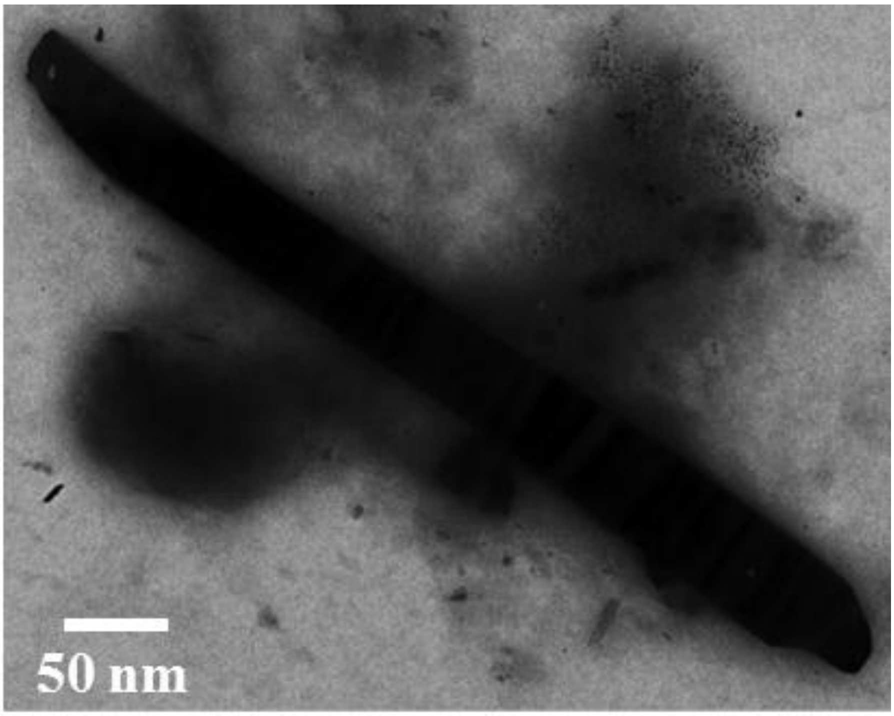

Fig. S2 TEM image of single nanorod (Rh-HTA) having the length of ~1 µm and thickness of ~60 nm.

SI-II: Furrier Transform Infra Red Spectroscopy:

Figure S3, shows a comparison of the FTIR spectra AA before and after capping with Rh. Interestingly, a comparison of these spectra reveals the disappearance of four bands in the range of 3300-3600 cm^{-1} for the nanoparticle (Rh-AA) which corresponds to the symmetric -O-H stretching of AA skeleton. The capping molecules are linked through the -O-H groups to the Rh nanoparticles. More importantly, the appearance of additional strong bands in the range of 500 cm^{-1} in case of Rh-AA is attributed to the presence of Rh-O bond. The rest of the peaks remain common in both the cases corresponding to the capping molecular skeleton. Further, the functional involvement of the passivated TDA molecules on these nanoneedles (Rh-TDA) can be obtained from the FTIR analysis, as shown in Figure S4, where the C-H stretching region (2800- 3000 cm^{-1}) is particularly informative about the orientation of methylene chains and Rh-TDA nanoneedles. In addition, Figure S4 reveals that the capping agent is intact except for the disappearance of a peak due to –N-H stretching at 3320 cm^{-1} after anchoring to Rh surface. The appearance of an additional strong band at 812 cm^{-1} is attributed to the presence of Rh-N bond. A few sharp bands near 1030 and 1358 cm^{-1}, which are absent in the spectra of TDA, could be ascribed to the coordinated N species. In addition, a broad band at 2320 cm^{-1} suggests the presence of N as a charged amine species ($-NH^+$), indicating the involvement of electrostatic interactions, especially with the nanoparticle surface. Further, the functional involvement of the passivated HTA molecules on these nanoneedles (Rh-HTA) can be obtained from the FTIR analysis, as shown in Figure

S5, where the C-H stretching region (2800- 3000 cm^{-1}) is particularly informative about the orientation of methylene chains and Rh-HTA nanoneedles.

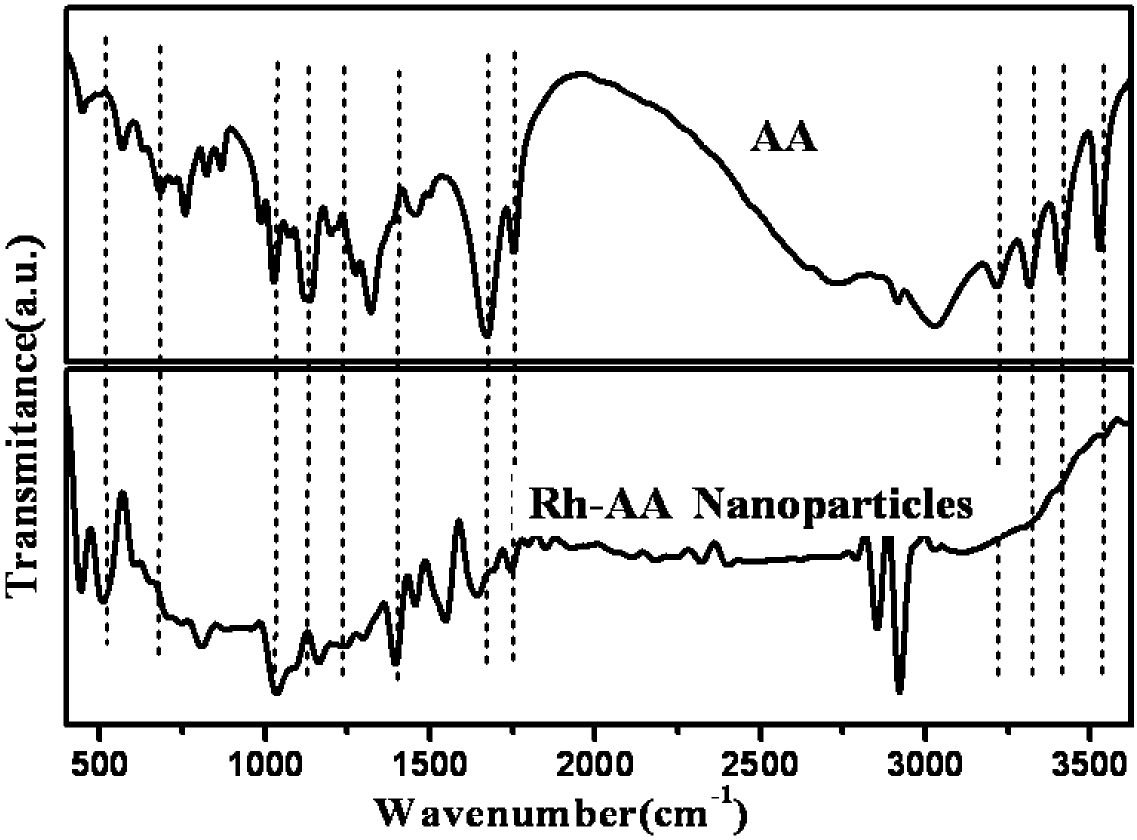

Figure S3: Superimposed FTIR spectra of AA molecules and Rh-AA nanoparticles performed in KBr matrix indicating strong peaks at 500 cm^{-1} corresponding to Rh-O linkage of Rh-AA.

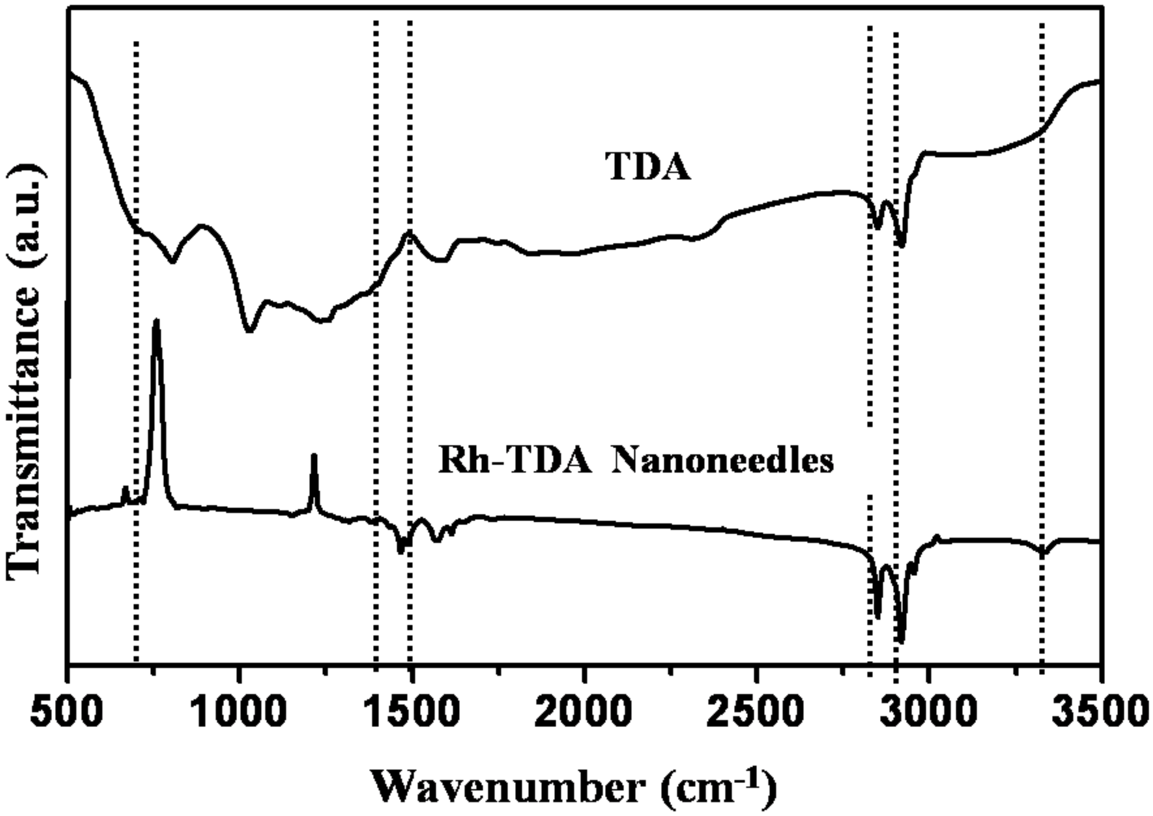

Figure S4: Superimposed FTIR spectra of TDA molecules and Rh-TDA nanoneedles performed in KBr matrix indicating strong peaks at 500 cm^{-1} corresponding to Rh-N linkage of Rh-TDA.

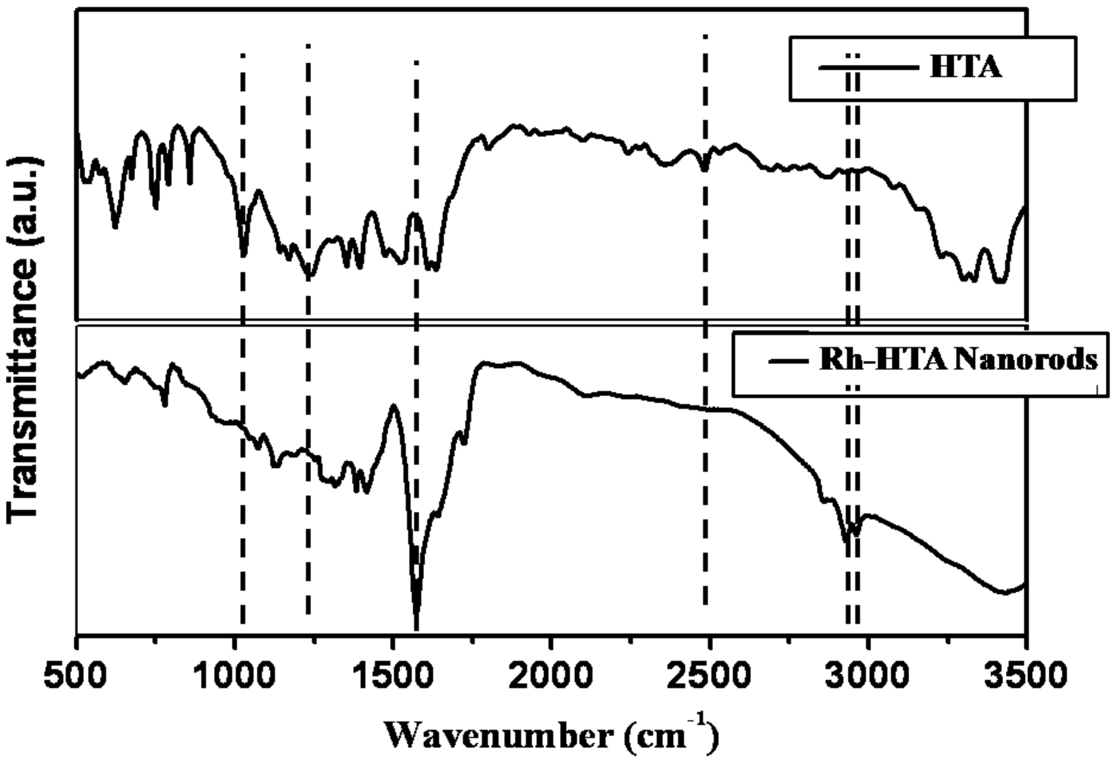

Figure S5: Superimposed FTIR spectra of HTA molecules and Rh-HTA nanorod bundles performed in KBr matrix indicating strong peaks at 600 cm^{-1} corresponding to Rh-N linkage of Rh-HTA.

References:

1. T. Shido, T. Okazaki and M. Ichikawa, *Cat. Lett*. **1993**, *20*, 37-42.
2. S. Pinchas and I. Laulicht, *Infrared Spectra of Labeled Compounds*, Academic Press: London, **1971**; Chapter 9. *NIST Vibrational Spectroscopy Database* via. Internet: http://srdata.nist.gov/vb .
3. V. M. Frolov, L. P. Shuikina, K. K. Turisbekova, and G. N. Bondarenko *Catal. (Eng. Trans.)* **1994**, *35*, 800-805.

SI-III: Scanning Electron Spectroscopy (SEM) after electrochemical studies:

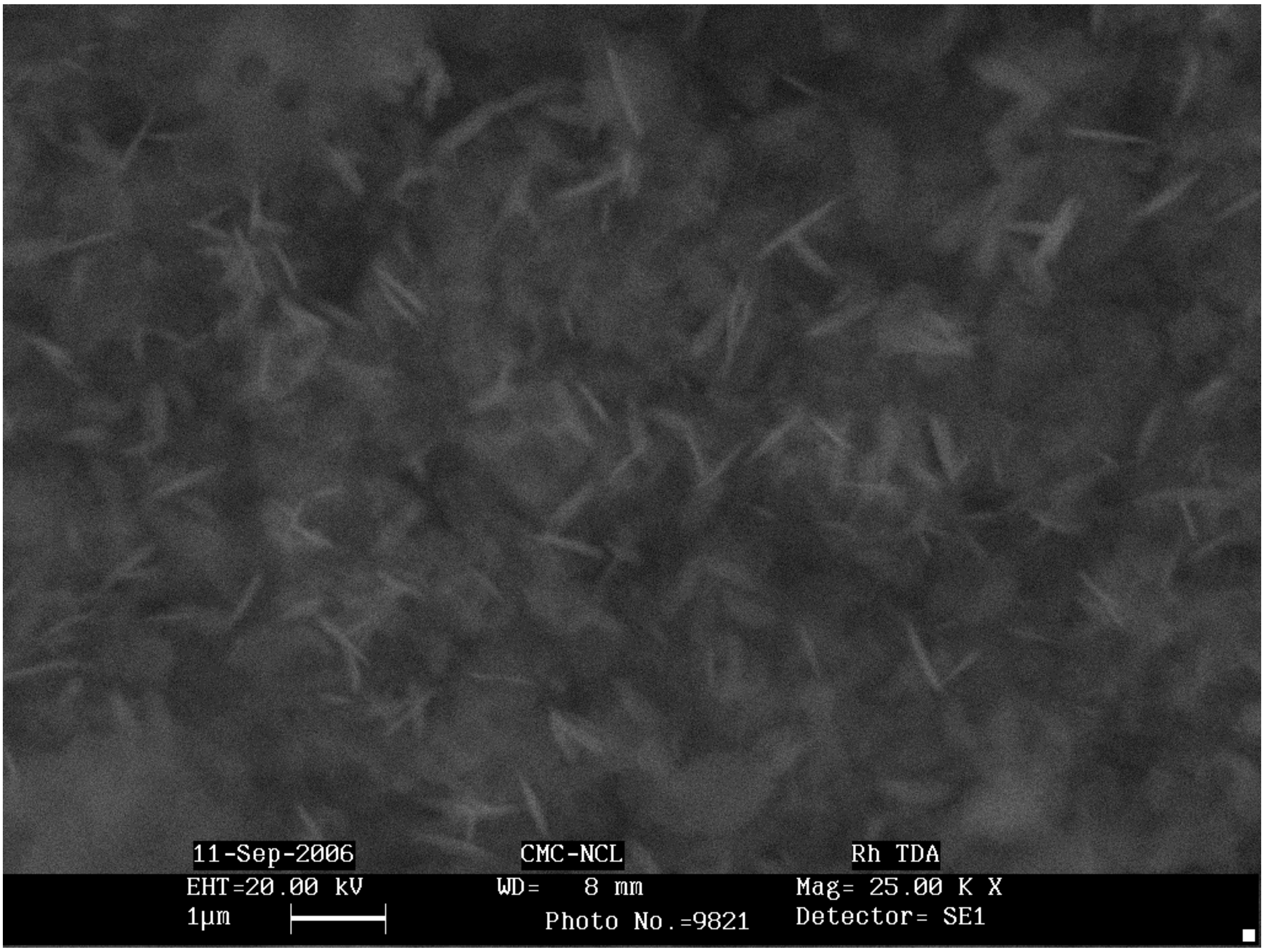

Figure S6: Scanning Electron microscopic image of nanoneedles (Rh- TDA) after electrocatalytic studies towards formic acid oxidation.

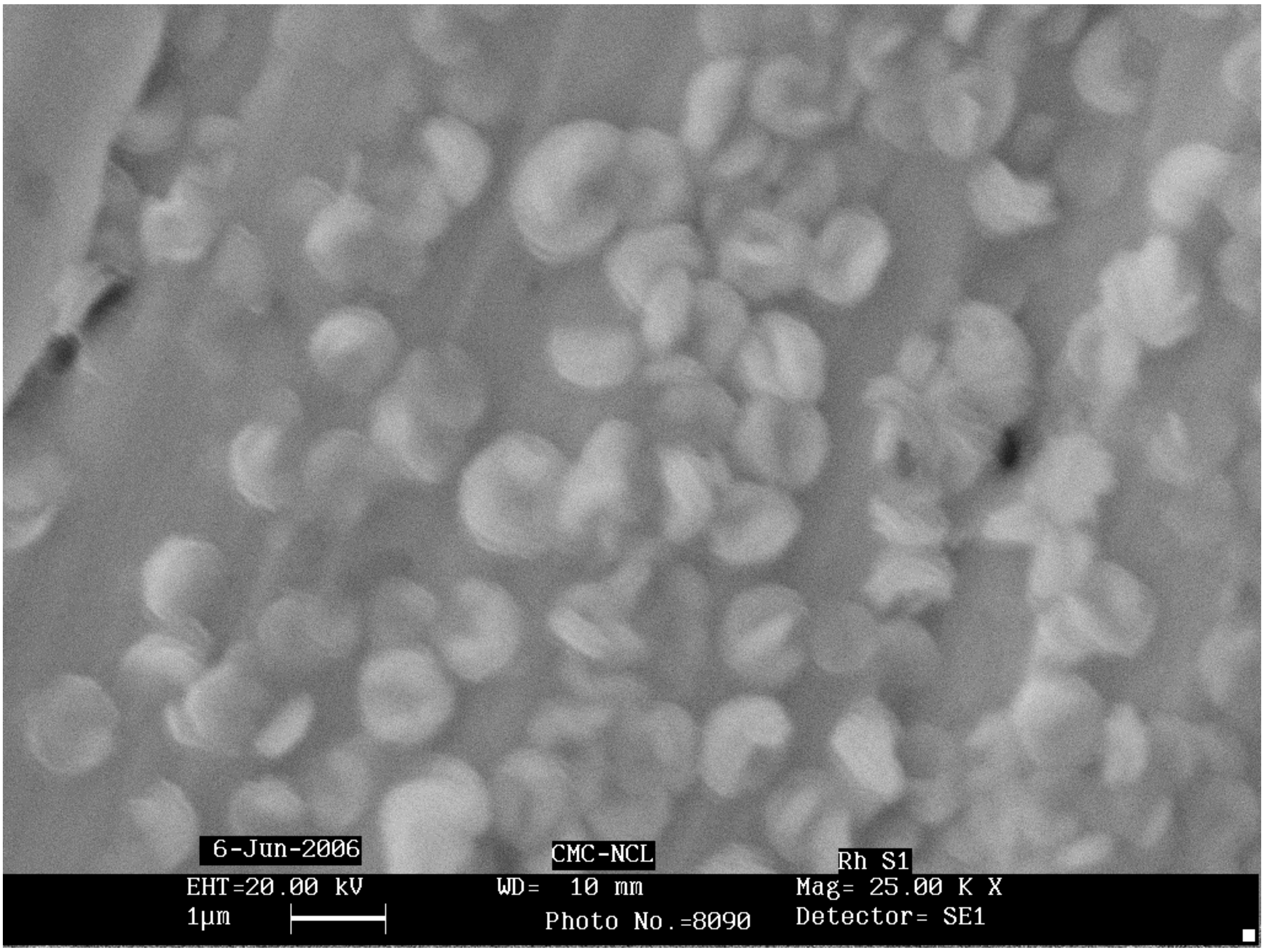

Figure S7: Scanning electron microscopic image of nanorod (Rh- HTA) bundles after electrocatalytic studies towards formic acid oxidation.