Experimental conditions  Monodisperse PS beads with an average diameter of 450 nm (± 10 nm) were purchased from Aldrich. The polystyrene colloidal crystals were obtained by self-assembly using gravitational sedimentation. A polished Pt plate (1x1 cm) was placed into a vessel and an aqueous suspension of PS beads (0.5 weight%) was added. Then, the solution was let to evaporate at room temperature until crystal growth was achieved. The well ordered colloidal crystal obtained was further used as template. An electrochemical cell (20 ml) with a three-electrode system was used, including a SCE reference electrode, a platinum basket as counter electrode and the Pt plate coated with the PS colloidal crystal as working electrode. Firstly, the PS sphere modified Pt electrode was carefully immersed into a solution of 0.03 M metal salts (2Ni(NO$_3$)$_2$, Al(NO$_3$)$_3$) and 0.3 KNO$_3$ for 30 min to permit to the solution to infiltrate the template. Secondly, the electrosynthesis of NiAl-NO$_3$ films were carried by applying a constant potential of -0.9 V. Different deposition times were tested (30, 60, 120 and 200 s) and 60 s appeared as an optimal deposition time for the template LDH electrosynthesized. After template LDH electrosynthesis, the working Pt electrodes were quickly removed from the solution, deeply rinsed with deionised water and let to dry at room temperature. To remove the PS template and access to macroporous LDH structure, the Pt electrodes were further soaked twice with toluene for 12 h each.

For comparison, a untemplated NiAl film was prepared under the same conditions. A bare Pt electrode was immersed into a solution of 0.03 M metal salts (2Ni(NO$_3$)$_2$, Al(NO$_3$)$_3$) and 0.3 KNO$_3$ and a constant potential of -0.9 V was applied for 60 s to electrosynthesize NiAl-NO$_3$ film. Then, the working Pt electrode was quickly removed from the solution, deeply rinsed with deionised water and let to dry at room temperature. Glucose oxidase (GOx) (EC 1.1.3.4 from Aspergillus niger, 180 U mg$^{-1}$ solid) was purchased from Sigma-Aldrich. Immobilization of GOx on both LDH films was performed by adsorption. 200 µl of an aqueous solution of GOx (1 mg/ml) was spread on the LDH modified Pt electrode surfaces and dried in a fridge overnight. Before use, bielectrodes were exposed 15 min to saturated glutaraldehyde vapor (25 %) to cross-link the adsorbed biomolecules. Next they were soaked in PBS (pH 7) for 15 min under stirring to rehydrate the biofilm and remove glutaraldehyde traces.
**Apparatus** Cyclic voltammetry and chronoamperometry experiments were carried out with a potentiostat Autolab PGSTAT 100. Powder X-ray diffraction patterns were recorded on a Panalytical X’pert pro diffractometer in $\theta$/$\theta$ geometry equipped with a real-time multistrip X’celerator detector using CuK$_\alpha_{1/2}$ radiation. Diffractograms were on powder removed from the electrodes surface by scratching recorded and deposited on a Si support in the range of 2-70° 2θ (continuous mode, step 0.013°). The ordered macroporous electrodes were characterized using a Zeiss supra 55-VP Field-emission scanning electron microscope working at an electron energy of 3 kV. The film thicknesses were measured with an Alpha-step IQ surface profiler (KLA Tencor) and the AFM images recorded using a scanning Probe Microscope Vista 100, Burleigh instrument.
Electronic supplementary figures:

Figure ESI 1 FESEM and AFM images of the starting PS sphere (Ø 450 nm) colloidal crystal obtained by evaporation method on Pt plate.

Figure ESI 2 FESEM images of the Pt modified electrodes with the 3D-OME NiAl films obtained after applying a constant potential of -0.9 V for 30 s (left) and 120 s (right).
**Figure ESI 3** FESEM image of untemplated electrosynthesised NiAl film (-0.9 V for 60 s)

**Figure ESI 4** FESEM micrograph of 3D-OME NiAl- obtained after applying a constant potential of -0.9 V for 60 s showing in detail the wall surface.