Electronic Supplementary Information

Experimental Section

Materials

Hybrid MgAl-AlP phases with an AlP/LDH ratio Q = 1, 2, 3 were prepared by the coprecipitation method. A mixed aqueous solution of $MgCl_2$ and $AlCl_3$, with Mg^{2+}/Al^{3+} molar ratio of 2 and a total concentration of metallic cations of 0.02 M, was introduced with a constant flow into a reactor containing a 1mg/ml AlP solution at 0°C. The pH was maintained constant at a value of 9.8 during all the coprecipitation by the simultaneous addition of a 0.04 M NaOH solution. The suspension was aged at 4°C under stirring and N_2 atmosphere for 24 h. The final product was centrifuged and washed several times with decarbonated water, and finally dried in air at room temperature (dried samples) or kept in suspension in water (fresh samples) (0.6 mg/ml). UV-Vis spectra at 280 nm of supernatant solutions showed that all the enzyme amount was immobilized within the inorganic host material. The samples were ever stored at -20°C.

p-Phenylene phosphate sodium salt, named HQDP, was prepared by adapting the protocols of Silverberg *et al.*[1] and Ameduri *et al*[2]. Hydroquinone (**1**) (0.02 mol, 2.2 g) was dissolved into 125 ml anhydrous acetonitrile and cooled down to -10°C. CCl_4 (10 eq) was added to the stirred solution. N,N diisopropylethylamine (4.2 eq) followed by N,N-dimethylaminopyridine (0.2 eq) were added. One minute later, a slow dropwise addition of diethylphosphite (2.9 eq) was begun and the temperature was kept constant at -10°C. The mixture was let to react for two hours at -10°C. 80 ml of 0.5 M aqueous KH_2PO_4 was added and the mixture was allowed to warm to room temperature. The mixture was extracted three times with ethyl acetate. The organic phase was washed successively with water and saturated NaCl aqueous solution. The tetraethyl phenylendiphosphate (**2**) was purified by chromatography. The yield was 76 %. Monomer **2** was dealkylated using silylating reagents[2]. 222 mg ($0.58\ 10^{-3}$ mol) of monomer **2** was solubilized in 7 ml of dichloromethane. 20 eq (1.5 ml) of $BrSiMe_3$ was added dropwise. The reaction mixture was stirred at room temperature for 16 h. 2 ml H_2O was added. The mixture was extracted with CH_2Cl_2/H_2O. HDQP 4H (**3**), a white powder, was obtained after evaporation of the solvent in 89 % yield. The sodium salt was obtained on a cationic exchange resin (Amberlite IR-120 Na). ^1H NMR (D_2O) δ = 7.09 (s, aromatic). FTIR cm^{-1}: 1180 (P-O-C_6H_5 stretching). All other reagents are of analytical grade and used as received.

Physical characterization

Powder X-ray diffraction patterns were collected on a Siemens D501 diffractometer using CuKα radiation. Patterns were recorded over the 2-70 2θ range in steps of 0.04° with a counting time per step of 8 s. ATR-FTIR analysis was performed on a Nicolet 5700 FTIR (Thermo electron corporation) spectrometer in the range 4000 to 400 cm^{-1}. Scanning electron micrographs were recorded on Zeiss supra 55-VP microscope at an electron energy of 2 kV. TEM imaging was carried out using a JEOL 1200 microscope at 80 kV. The AFM images were recorded with a MgAl-Alp coating on a silicon wafer. The AFM equipment used was a 5500 (Pico+) Agilent Technologies. Measurements in air were carried out in contact mode. Measurements in buffer solution were carried out in intermittent contact mode (Acoustic AC mode). It is an oscillating technique controlling the amplitude during (x,y) displacement. The

same Si_3Ni_4 tip was used in both cases; it had a curvature radius of 20-30 nm and Young modulus of 0.06 N/m.

Enzyme assays

28 µg of MgAl-AlP LDH were mixed in 3 ml (0.1 M Tris-HCl buffer + 10 mM $MgCl_2$ solution, pH 8.5) at 30°C for 10 min. 30 µmole *p*-nitrophenyl phosphate (100 µL of 0.3 M) were added to the solution and the variation of the concentration of enzymatic product *p*-nitrophenol *vs* time was recorded spectrophometrically at 410 nm. The residual activities (%) of immobilized enzyme were calculated in comparison with the activity obtained for the same amount of free enzyme. Under these conditions, the specific activity of free alkaline phosphatase from porcine kidney (Aldrich) was 12 U/mg of solid.

Bioelectrode preparation

The biofilm was prepared as follows: 30 µl MgAl-AlP nanohybrid (Q = 1) suspension were spread on the surface of a polished glassy carbon electrode (5 mm) and the coating was stored at 4°C overnight. Before use, the rotating disk electrode was connected to a Tacussel EDI 101T/CTV 101T (500 rpm) and the modified electrode was incubated into 0.1 M Tris-HCl buffer (pH 8.5) + 10 mM $MgCl_2$ for at least 1 h to allow the gel swelling. Permeability and amperometric measurements were performed with a potentiostat (Autolab, PGSTAT 100, Eco-Chemie) in a conventional electrochemical cell containing a three-electrode system thermostated at 30°C. The MgAl-AlP modified electrode was the working electrode, a platinum wire the auxiliary electrode and a saturated Ag/AgCl/KCl electrode served as reference electrode. Permeability, was determined by linear sweep voltammetry at rotating disk electrode, using hydroquinone as electroactive permeant [3]. The storage stability of the biosensor in buffer solution at 4°C was tested once a week over a two month period.

1. L. J. Silverberg, J. L. Dillon and P. Vemishetti, *Tetrahedron Lett.*, 1996, **37**, 771-774.
2. R. Souzy, B. Ameduri, B. Boutevin and D. Virieux, *J. Fluorine Chem.*, 2004, **125**, 1317-1324.
3. D. Shan, S. Cosnier and C. Mousty, *Anal. Chem.*, 2003, **75**, 3872-3879.