Electronic Supplementary Material (ESI) for RSC Advances
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Supplementary Information

Electrochemical Synthesis of Flower-like Pd Nanoparticles with High Tolerance Toward Formic Acid Electrooxidation

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Pd architectures reproducibility

The reproducibility of the electrochemical syntheses of the different Pd architectures was determined using scanning electron microscopy (SEM) and cyclic voltammetry (data not shown). Three different syntheses (triplicate) were carried out with the same conditions for each electrochemical method.

In Figure S1 different SEM images are presented for the system IV: Pd with coral-reef architecture prepared by second harmonic AC voltammetry for three separate syntheses. In the micrographs the nanostructures can be observed. The architecture coral-reef is observed all cases. Also, the sizes of the coral-reef Pd architecture were kept in the same order as well as the nanostructure. This procedure was carried out for all architectures obtaining the same result in each case.

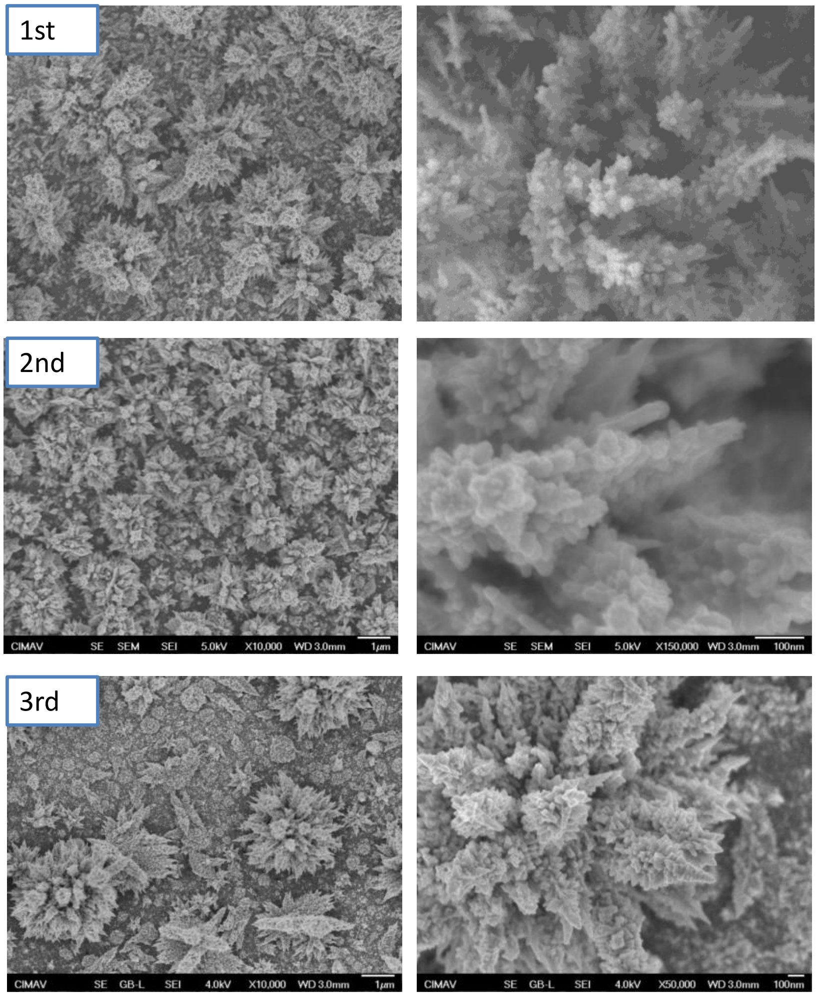

Fig. S1 SEM images of the Pd with coral-reef architecture for three different syntheses using the conditions of the system IV.

Conditions of electrochemical methods

The potential-time programs used for the fourth electrochemical methods of synthesis: cyclic voltammetry, differential pulse amperometry, square wave voltammetry and second harmonic AC voltammetry are shown in the figure S2.

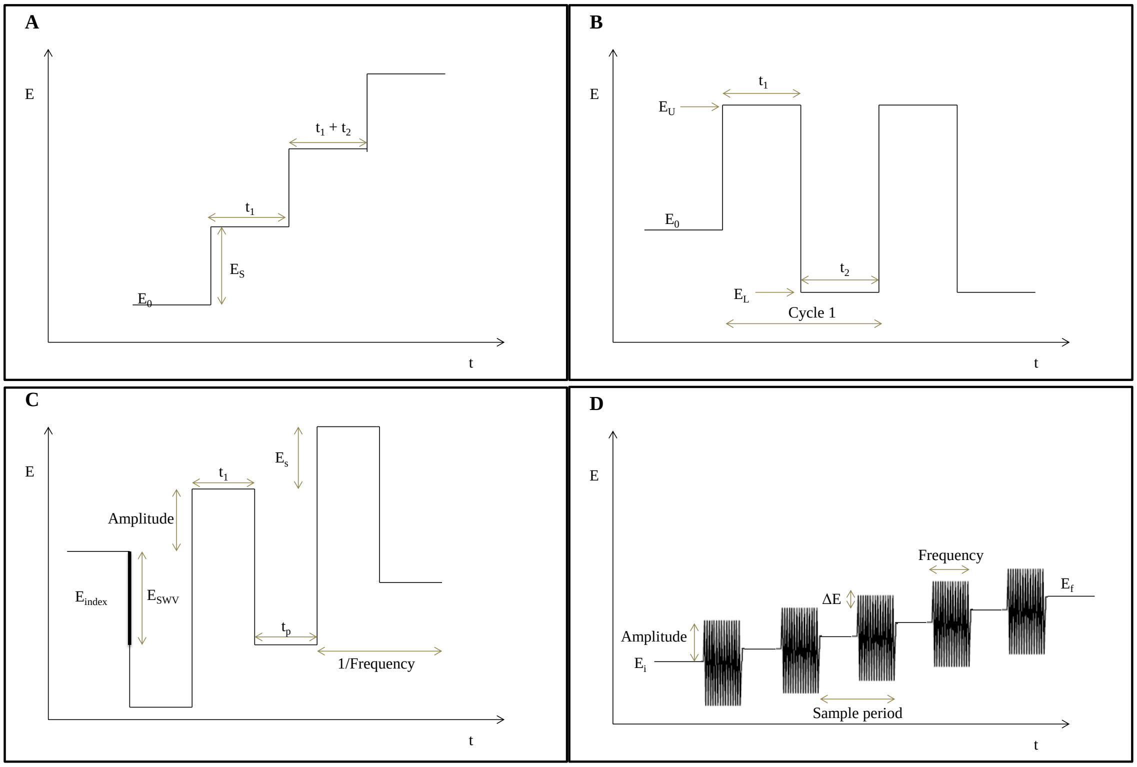

Fig. S2 Potential-time programs for the different electrochemical techniques: A) cyclic voltammetry (system I), B) differential pulse amperometry (system II), C) square wave voltammetry (system III) and D) second harmonic AC voltammetry (system IV).

In figure S2-A, the cyclic voltammetry program is presented (namely system I). E_0 is the equilibrium potential; E_S is the step potential, $t_1$and t_2 indicate the duration of the applied potentials. For the synthesis of Pd, the step potential was of 1 mV s^{-1}, the duration was determined in terms of the number of cycles and the potential range, in this case 20 cycles and a potential range between -0.35 to 1.1 V *vs.* SCE. The equilibrium potential was of 0.65 V *vs.* SCE.

In figure S2-B the potential-time program for the differential pulse amperometry (system II) is showed. E_U indicates the upper potential (0.8 V *vs.* SCE), in other words is a potential where the reduction of Pd ions cannot occur. And consequently, E_L (lower potential, 0.2 V *vs.* SCE) is a potential where the reduction of Pd ions to metallic take place; t_1 and t_2 are the duration of each potential, in this case 0.1 s each one. The duration of each applied potential results in a cycle. For the synthesis of Pd by this technique, the pulse potentials were applied for 5000 cycles.

The potential-time program for the system III (Pd synthesised by square wave voltammetry) is shown in the figure S2-C. The index potential is referred to the half of the pulse potentials $\{(E_1+E_2)/2\}$; in our case E_1 was of 0.8 and E_2 -0.2 V *vs.* SCE. t_1 and t_p are the durations of the first pulse and the consecutive pulses. In square wave voltammetry $t_1=t_p$ and for the synthesis of Pd was of 0.01 s. The step potential (E_s) was of 3 mV s^{-1}. Finally, the frequency was of 20 Hz. The experiment was repeated 50 times.

The potential-time program for the system IV (Pd synthesised by second harmonic AC voltammetry) is shown in the figure S2-D. In this program, two potentials are defined, the initial potential (E_i, 0.8 V *vs.* SCE) and the final potential (E_f, -0.2 V *vs.* SCE). The amplitude was of 1 mV rms, the frequency of 1 Hz. The duration of the sample period was determined by the frequency, the modulation time and the interval time, the modulation time was of 2 seconds, and the interval time 4 seconds.