Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supporting material

The electrochemical synthesis of Pt particles on ZrO_2-ERGO modified electrodes with high electrocatalytic performance for methanol oxidation

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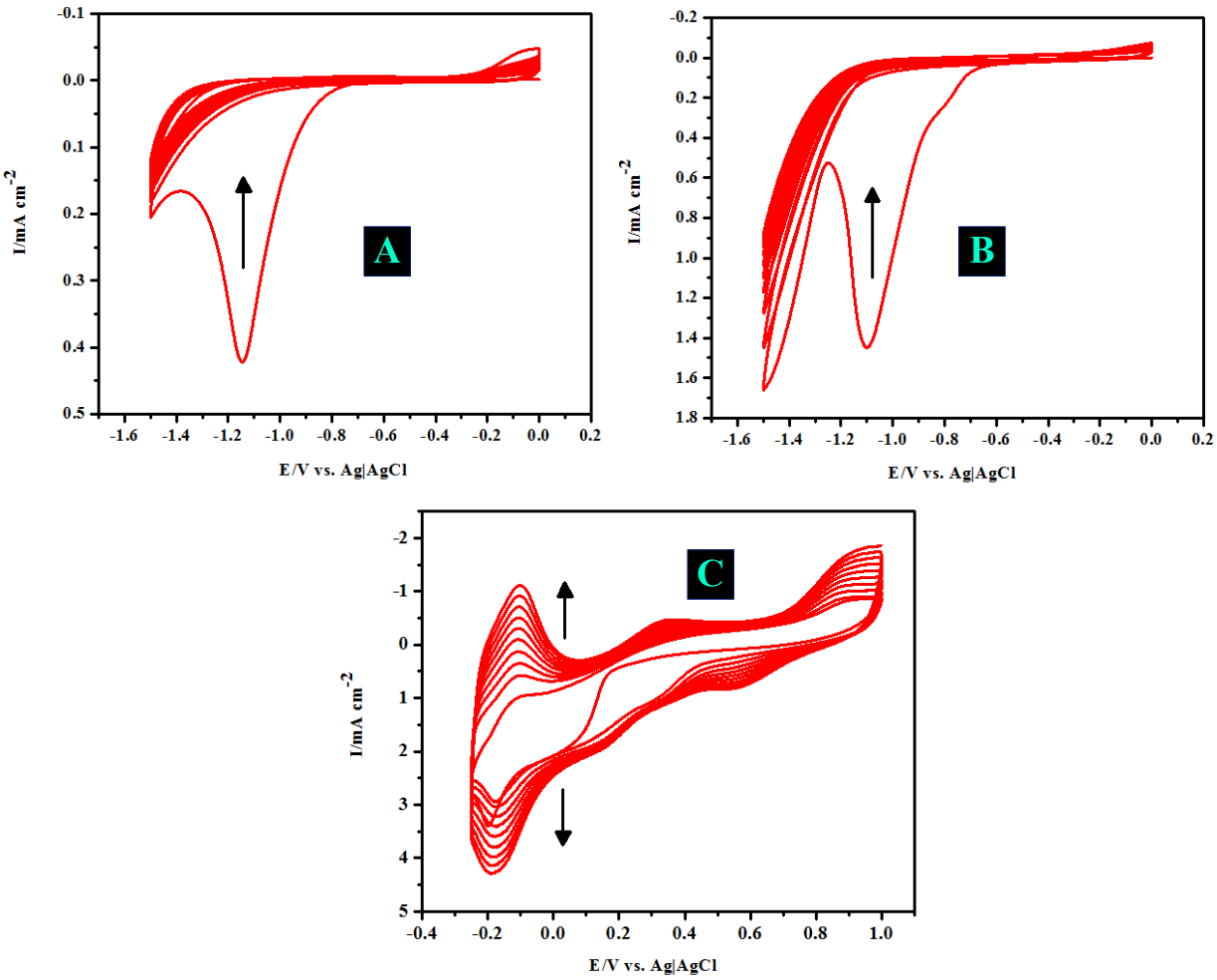

Fig. S1. (A) 30 consecutive cyclic voltammograms recorded for a GO modified GCE in N_2 saturated 0.05 M PBS (pH 5.0) at a scan rate of 50 mV s^{-1}. (B) 10 consecutive cyclic voltammograms recorded for a GO-modified GCE in 5.0 mM $ZrOCl_2$ containing N_2 saturated 0.05 M PBS (pH 5) at a scan rate of 20 mV s^{-1}. (C) Repeated cyclic voltammograms for a nano Pt film electrodeposited on ZrO_2-ERGO/GCE from 0.5 M H_2SO_4 containing 1 mM of K_2PtCl_6 and a potential scan rate between -0.25 to 1.0 V for 10 cycles (Scan rate of 0.05 V s^{-1}).

Electrochemical deposition of Pt nano particles on ERGO-ZrO_2 film

Electrochemical reduction of pristine GO was obtained for the GO modified GCE placed in an electrochemical cell containing 0.05 M PBS (pH 5) at 50 mV s^{-1} for successive cyclic voltammograms, as shown in Fig S1A. A large cathodic peak appeared at around -1.0 V, corresponding to the reduction of abundant oxygen functionalities (carboxyl, hydroxyl and epoxy) residing on the edge and basal plane of the GO. There was a drastic reduction in the magnitude of the current in subsequent cycles with the peak disappearing after 15 cycles, showing the completion of reduction. The simultaneous electrochemical reduction of GO and electro deposition of ZrO_2 was obtained by placing the GO modified GCE in another electrochemical cell containing 5.0 mM $ZrOCl_2$ and 0.05 PBS (pH 5) at 20 mV s^{-1} (see Fig S1B). In the first cycle, a large cathodic peak appeared at -1.0 V corresponding to the reduction of oxygen functionalities, as in the case for pristine GO. After 15 cycles the cathodic peak disappeared suggesting that the electrochemical reduction of GO to ERGO had reached its maximum. In the course of the electrochemical experiments, a new cathodic peak appeared at -0.75 V in the first cycle, which could be associated with the formation of ZrO_2. The obtained electrode, denoted as ZrO_2-ERGO/GCE was then transferred into another electrochemical cell containing 0.5 M H_2SO_4 + 1 mM of K_2PtCl_6 (Fig S1C). Pt nanoparticles were deposited by cyclicvoltammetry in the potential range between -0.25 and 1.0 V at 10 mV s^{-1}. It can be observed that the two peaks associated with the reduction of Pt particles in the hydrogen adsorption-desorption process, which takes place in the range of -0.2 V. The gradual increase in the current magnitude with subsequent cycles suggests the successful formation of Pt nanoparticles on the ZrO_2-ERGO/GCE electrode surface. [3]The same preparation procedure was followed for all modified electrodes. The electrochemical behavior after the deposition of Pt

particles on various modified electrodes (such as ZrO_2, ERGO surface) was also investigated. The Pt loadings clearly show that the ERGO/Pt modified electrode can be used to improve the methanol oxidation performance, with better performance being achieved with a Pt loading of 106 μg. An If/Ib value of 101 was achieved with the ZrO_2/Pt electrode (See Fig 3A) with a Pt loading of 90 (μg). To achieve a better methanol oxidation performance for Pt/ZrO_2-ERGO electrode, a Pt loading of 176 (μg) s needed, which is much higher than in the case described above. In other words, a significant increase in the Pt loading is needed. The larger surface area of the ERGO/ZrO_2 electrode allows a significant increase in the Pt loading needed to achieve good methanol oxidation performance. However, the Pt/ZrO_2-ERGO has better methanol oxidation than Pt/C with the same Pt loading.

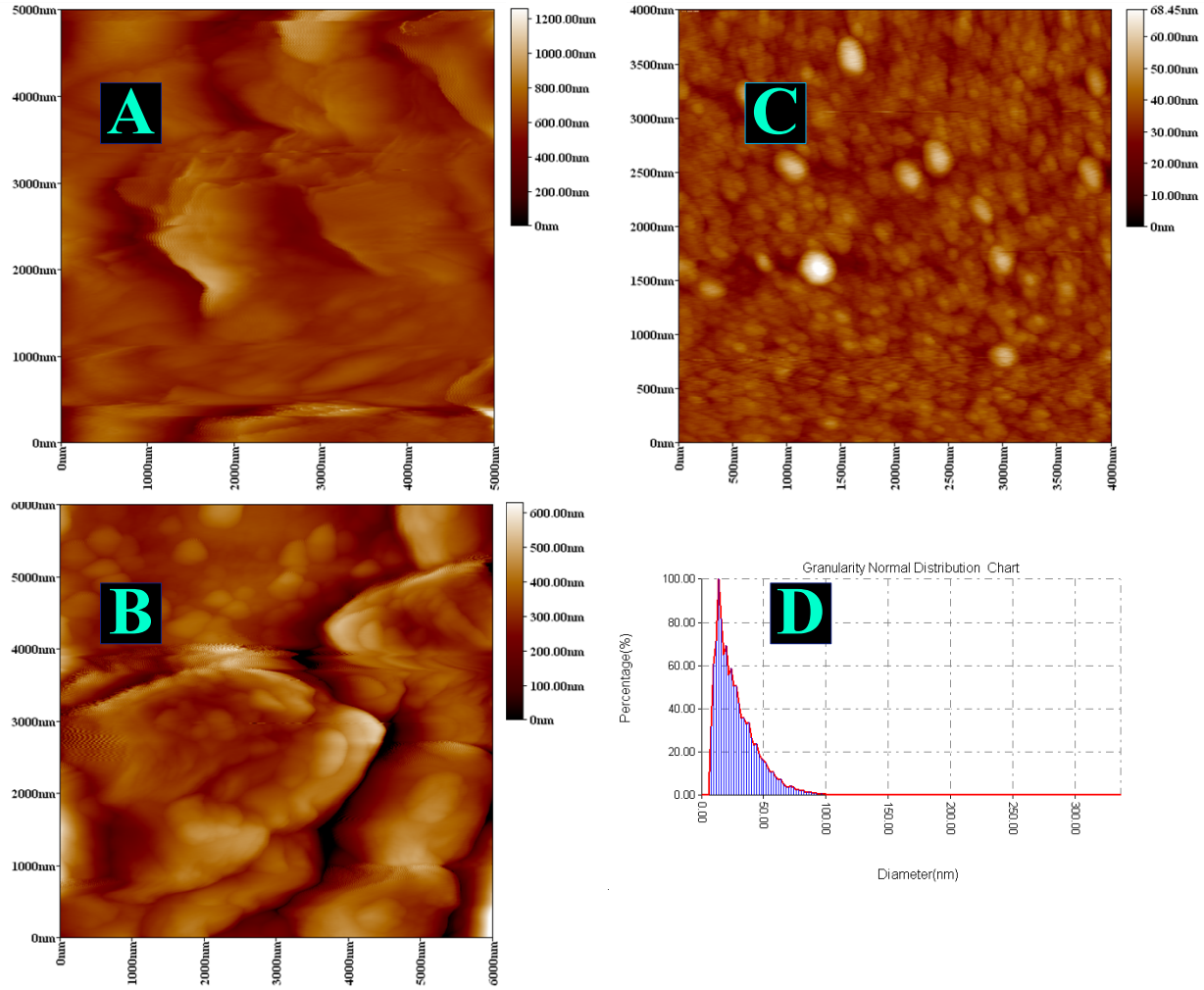

Fig. S2 AFM images of the (A) ERGO/ITO, (B) ZrO_2-ERGO /ITO, (C) ZrO_2-ERGO /ITO and granularity normal distribution chart for the Pt nano particles deposited on the ZrO_2-ERGO sample.

AFM analysis of the Pt/ZrO_2-ERGO composites

Fig. S2 shows AFM images of ERGO, ZrO_2-ERGO and Pt nanoparticles deposited on the ZrO_2-ERGO sample. From this image we can find that there are ERGO sheets with some overlapping regions near the edges, which can be more clearly seen in the higher resolution image (Fig. S2A). Fig S2B shows the increased overlapping of the ERGO sheets and folding at the edges. The sheets are uniformly distributed and have some wrinkles. The wrinkles are observed on the surface of single as well as overlapped ZrO_2-ERGO sheets. The layered

structure with its wrinkles and folds can be clearly seen in the AFM images (Fig. S2B) as indicated by arrows. These show the characteristic features of single-layer ERGO sheets decorated with ZrO_2 nanoparticles. The enlarged AFM image (Fig. S2C) shows Pt nanoparticles decorating the ZrO_2-ERGO sheet to a thickness of less than 15 nm. The size distribution of Pt nanoparticles is presented in the granularity normal distribution chart (Fig. S2D). The average diameter is 20 nm. It is obvious that such a narrow distribution of Pt nanoparticles is associated with the most efficient Pt/ZrO_2-ERGO electro catalysts. On the other hand, the ZrO_2-ERGO is uniformly covered with Pt nanoparticles with an average size of 20nm. The average sizes of the particles of all the resultant Pt/ZrO_2-ERGO electro catalysts as calculated from the XRD data are consistent with the AFM micrograph results. As can be seen from the XRD observations (Fig. 2C), small Pt nanoparticles with a well-defined size distribution were deposited on the ZrO_2-ERGO by electrochemical deposition.

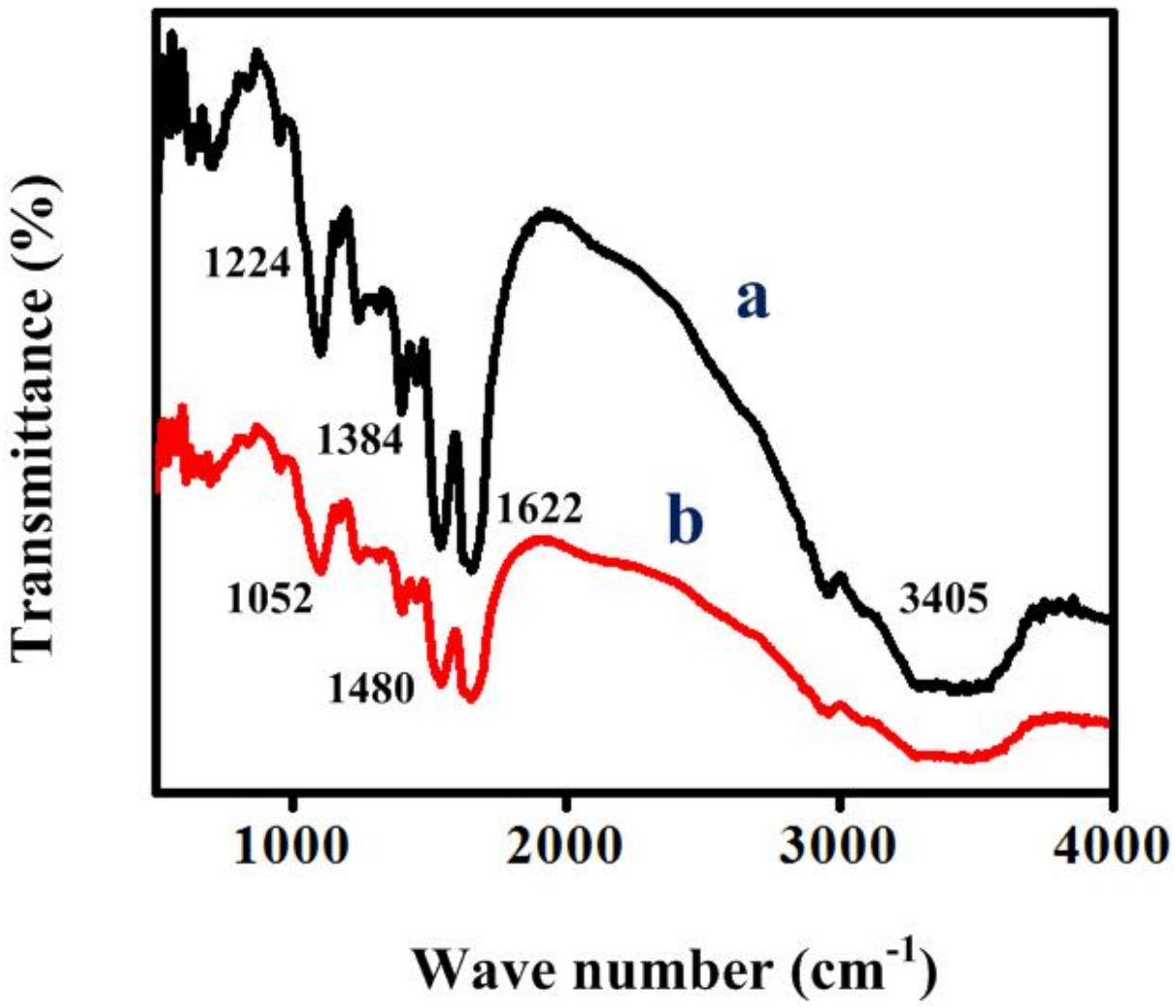

Fig. S3 FTIR spectra of the (a) ERGO and (b) ZrO_2-ERGO composite.

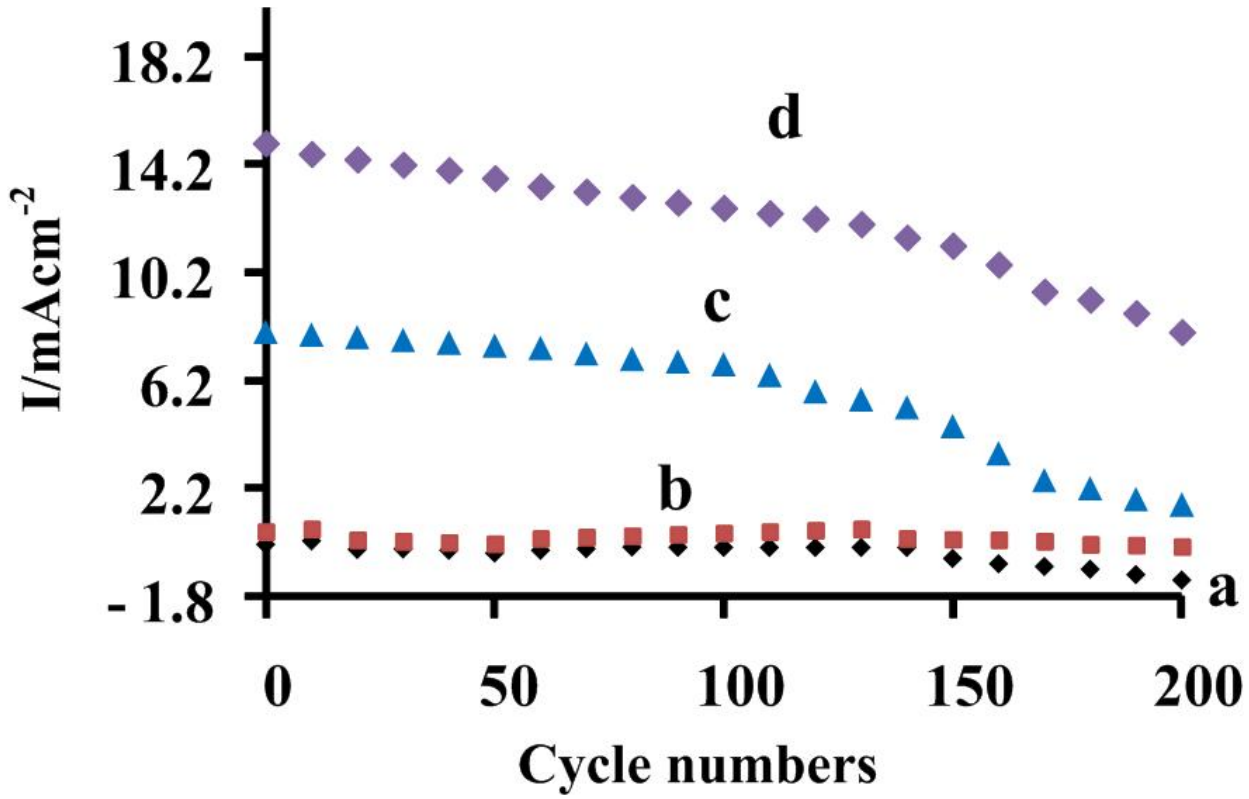

Fig. S4. Long-term cycle stabilities of the (a) Pt/C (b) Pt/ZrO_2 (c) Pt/ERGO and (d) Pt/ZrO_2-ERGO/GCE electrodes in the mix solution of 1M $HClO_4$ + 1M CH_3OH aqueous solutions at a scan rate of 50 mV s^{-1}.

References

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