

Electronic Supplementary Information for

**A Beneficial Role of Exfoliated Layered Metal Oxide
Nanosheet in Optimizing the Electrocatalytic Activity and
Pore Structure of Pt–Reduced Graphene Oxide
Nanocomposite**

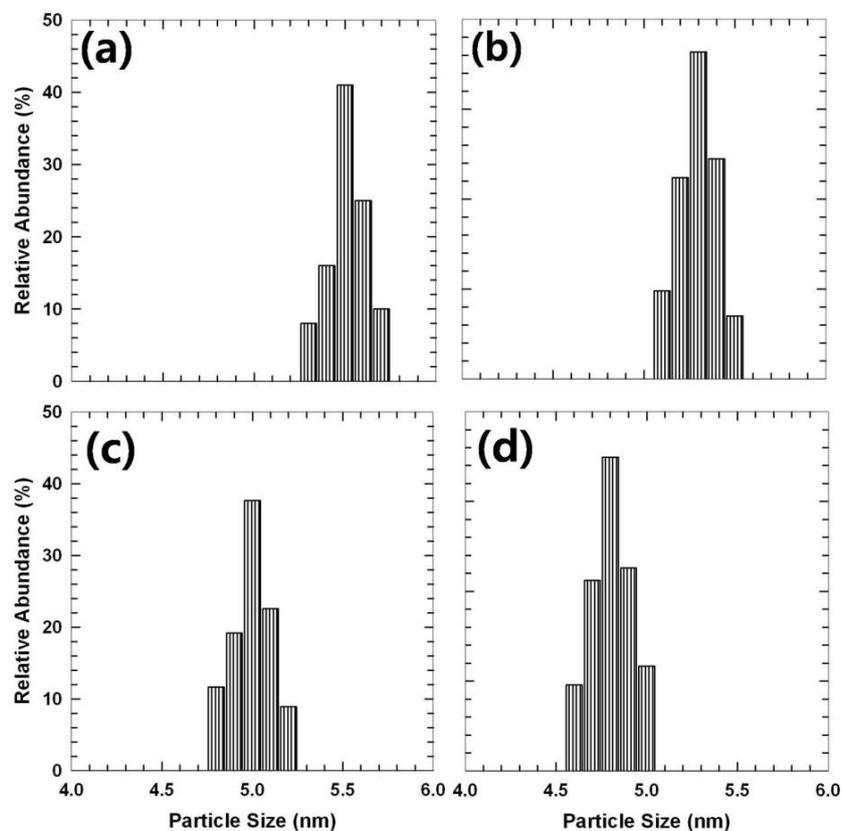
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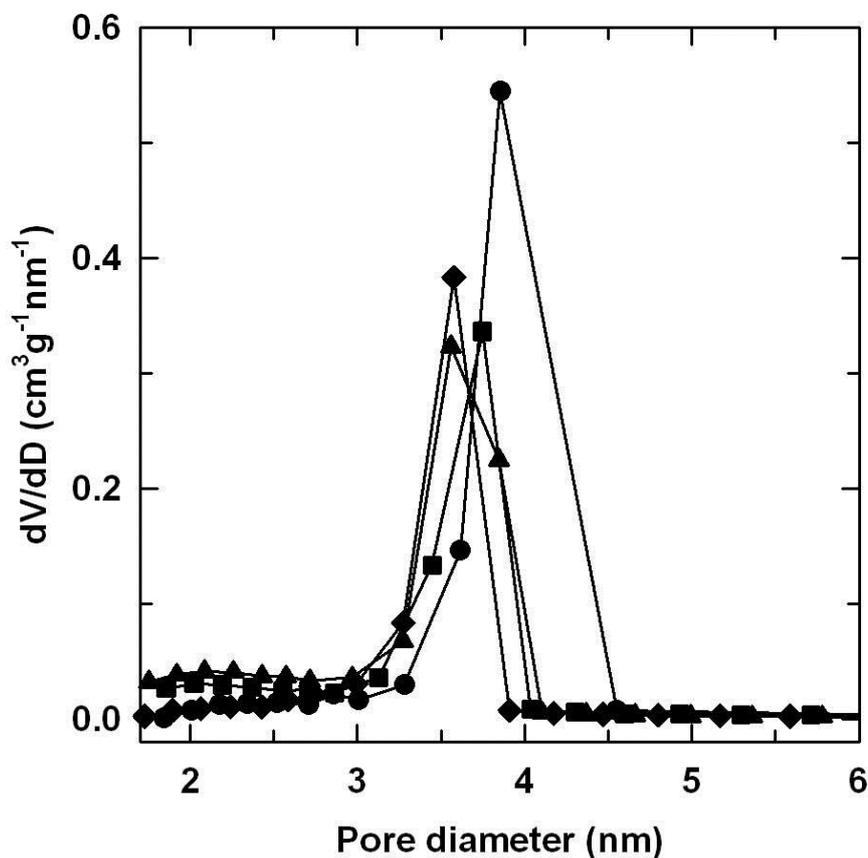
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Fig. S1. Pt particle size distribution data of the Pt–RGO–layered titanate nanocomposites of (a) PGT1, (b) PGT2, (c) PGT3, and (d) PGT4.



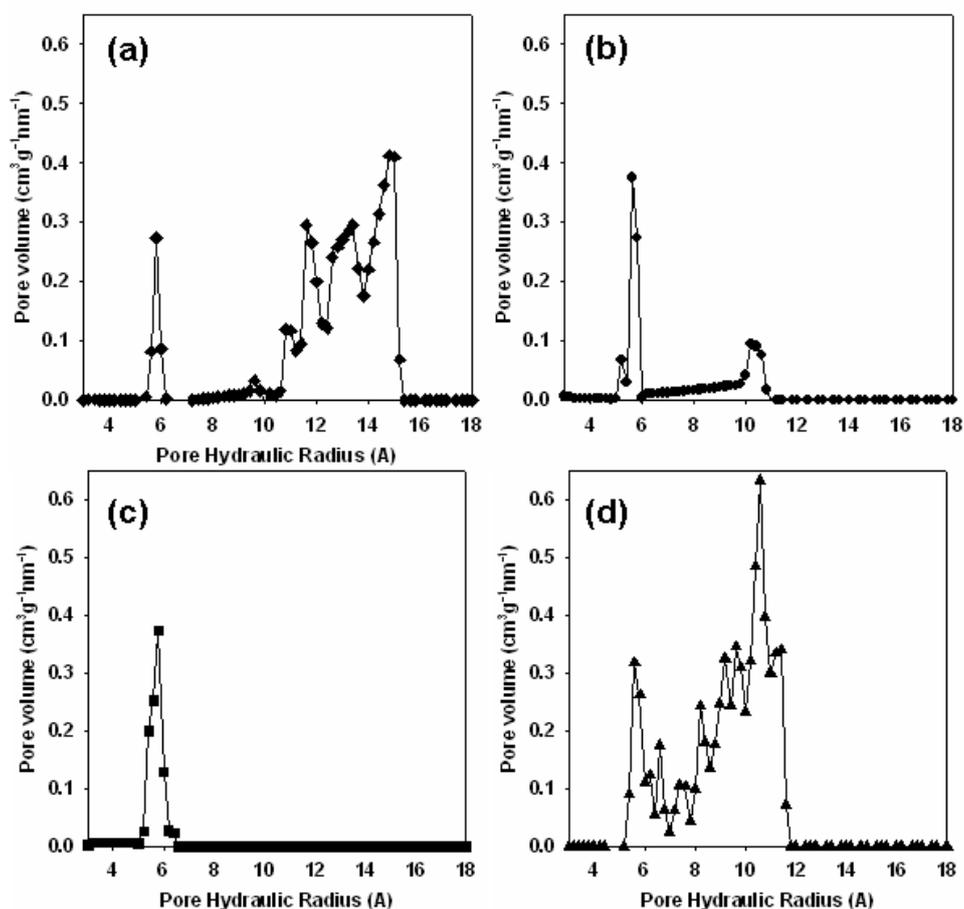
: The size distribution of Pt particles in the Pt–RGO–layered titanate nanocomposites is estimated from the TEM data. As plotted in **Fig. S1**, all the present nanocomposite materials display a monomodal distribution of the Pt particle size with the average size of ~4.8–5.8 nm. The decrease of Pt particle size with the increase of titanate content is obviously observed from these data.

Fig. S2. Mesopore size distribution curves of the Pt–RGO–layered titanate nanocomposites of **PGT1** (diamonds), **PGT2** (circles), **PGT3** (squares), and **PGT4** (triangles).



: The mesopore size distribution of the present Pt–RGO–layered titanate nanocomposites is estimated on the basis of Barrett–Joyner–Halender (BJH) method. As plotted in **Fig. S2**, all of the Pt–RGO–layered titanate nanocomposites possess mesopores with the average pore size of ~3.5–4.0 nm.

Fig. S3. Nanopore size distribution curves of the Pt–RGO–layered titanate nanocomposites of (a) **PGT1**, (b) **PGT2**, (c) **PGT3**, and (d) **PGT4**.



: Micropore size (MP) analysis using the adsorption isotherm data is carried out to estimate the nanopore size distribution of the present Pt–RGO–layered titanate nanocomposites. All of the present Pt–RGO–layered titanate materials possess nanopores with the size of ~0.5–1.5 nm. Among the present materials, the **PGT3** nanocomposite shows the narrowest size distribution of micropores. Taking into account the fact that this **PGT3** material shows the best performance as ORR catalyst, the results of MP calculation provide strong evidence for the important role of nanoporous structure of the present nanocomposite materials for their excellent ORR catalyst performance.

- Determination method of Geometric Surface Area (GSA)

: To estimate the GSA of the electrodes, chronocoulometry (CC) is performed in a 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution containing 0.1 M KCl. The GSAs are estimated from the slopes of the linear plot of the measured charge (Q) vs. time^{1/2}, according to equation (1).¹ The determined GSAs are greater (ca. 0.081 ~ 0.101 cm² depending on the catalyst loading) than that of the substrate GC electrode (0.071 cm²). This suggests that the Pt-RGO-layered titanate nanocomposite catalysts are loaded, even over the insulator of the GC electrode, resulting in an enlarged GSA. To avoid any possible contamination of the catalysts, the GSAs are determined by CC after the ORR activity characterization.

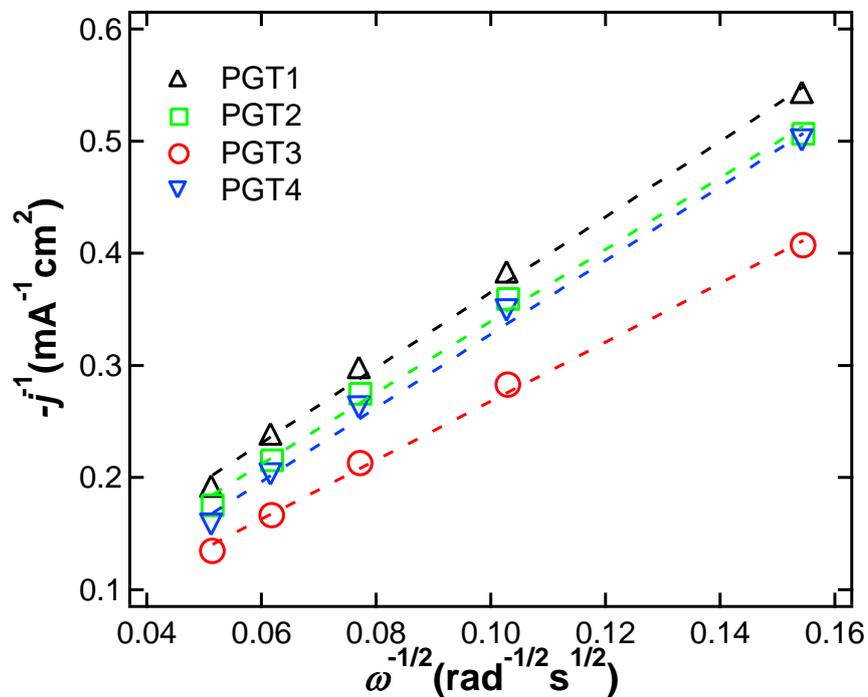
$$Q = \frac{2nFAD_{\text{Fe}}C_{\text{Fe}}t^{1/2}}{\pi^{1/2}} + Q_{\text{dl}} \quad (1)$$

where, Q is the charge passed, n is the number of electrons transferred (i.e., $n = 1$ in the case of the $\text{Fe}(\text{CN})_6^{3-}$ reduction), F is the Faraday constant, C_{Fe} is the concentration, D_{Fe} is the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$, t is the time passed, and Q_{dl} is the capacitive charge.

Notes and references

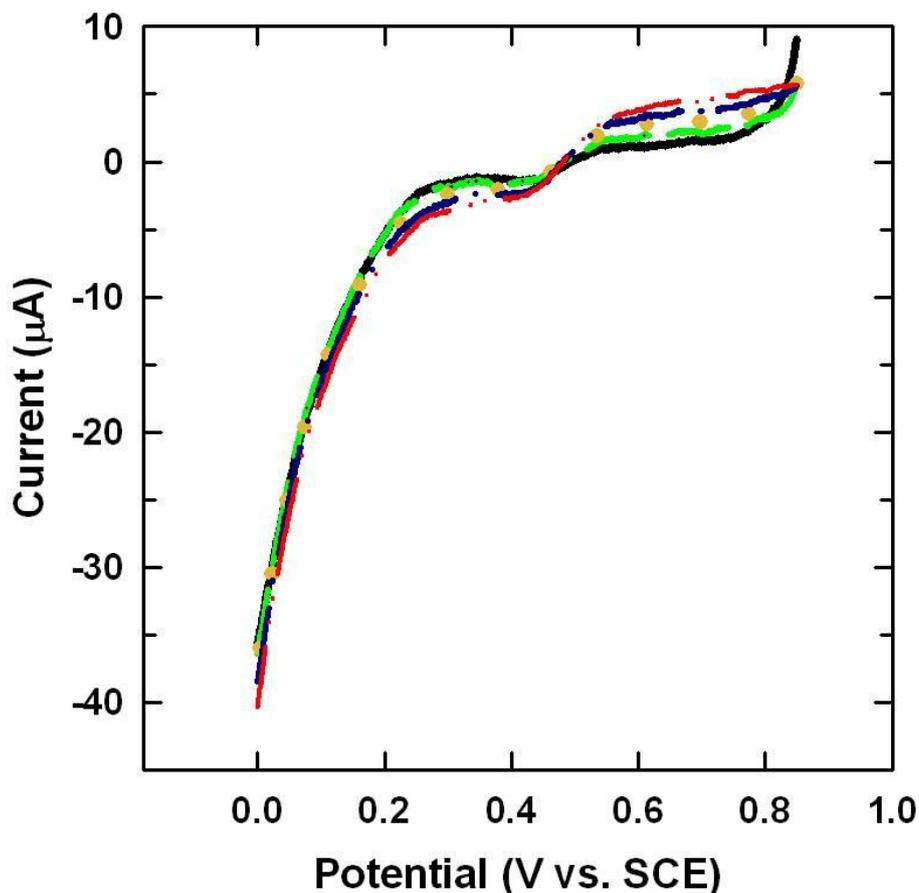
1. F. C. Anson, *Anal. Chem.* 1966, **38**, 54.

Fig. S4 Koutecky–Levich plots for the oxygen reduction at the Pt–RGO–layered titanate nanocomposites obtained from the RDE data presented in Fig. 9.



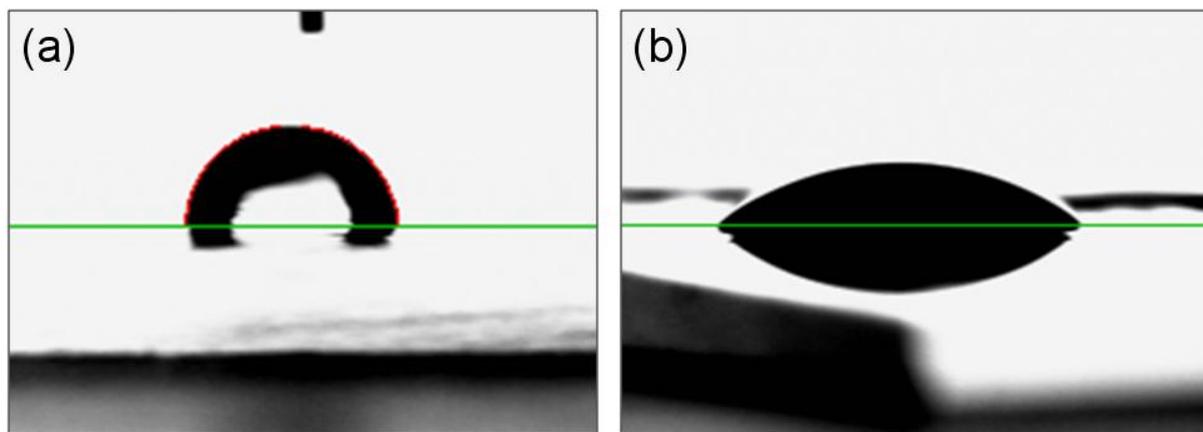
: The number of electrons transferred (n) during the ORR is estimated from the slopes of the Koutecky–Levich (K–L) plots using the RDE results obtained at various electrode rotation speeds, on the basis of the K–L equation. As presented in **Fig. S4**, the incorporation of the layered titanate nanosheets leads to a notable change of the slope of K–L plots (j_d^{-1} vs. $\omega^{-1/2}$). From these data, the n values are calculated to be 2.97, 3.12, 3.80, and 3.04 for **PGT1**, **PGT2**, **PGT3**, and **PGT4**, respectively.

Fig. S5 Rotation disc electrode (RDE) polarization curves of the Pt-free reference of layered titanate–RGO nanocomposite measured in O₂-saturated 0.1 M HClO₄ solution at various rotating speeds of 400 (solid lines), 900 (dashed lines), 1600 (dotted lines), 2500 (dot-dashed lines), and 3600 rpm (dot-dot-dashed lines) at a sweep rate of 5 mV s⁻¹.



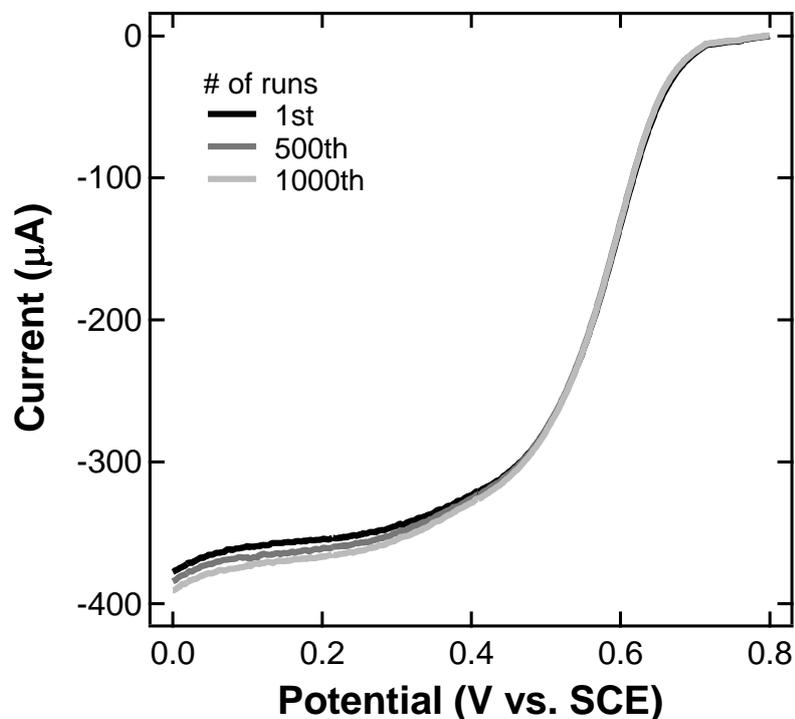
: To identify a component mainly contributing to the excellent ORR activity of the Pt–RGO–layered titanate nanocomposites, the Pt-free nanocomposite of layered titanate–RGO is synthesized as reference and its ORR electrocatalytic activity is tested by measuring the RDE polarization curves. As plotted in **Fig. S5**, this material shows only a negligible activity as ORR catalyst, which is much poorer than that of the Pt–RGO nanocomposite. This result clearly demonstrates that the Pt particles are mainly responsible for the observed excellent ORR catalytic activity of the Pt–RGO–layered titanate nanocomposites and the addition of layered titanate nanosheets helps to enhance the catalytic activity of Pt nanoparticles.

Fig. S6 Photoimages of the contact angle measurement for the precipitated materials restored from (a) the pure suspension of RGO and (b) the mixture suspension of RGO and layered titanate nanosheets.



: The effect of the incorporation of layered titanate nanosheets on the hydrophilicity of RGO nanocomposite is examined by the contact angle measurements for the materials restored from the pure suspension of RGO and from the mixture suspension of RGO and layered titanate nanosheets. As illustrated in **Fig. S6**, the incorporation of layered titanate nanosheets induces the remarkable enhancement of surface hydrophilicity, as evidenced by the decrease of contact angle.

Fig. S7 RDE polarization curves for repetitive 1000 runs obtained with **PGT3**-doped GC electrode (diameter, 3 mm) in an O₂-saturated 0.1 M HClO₄ solution at a rotation rate of 2500 rpm. All the other conditions are the same as in Fig. 9.



: The stability of the Pt-RGO-layered titanate composite catalysts is examined by repetitive RDE polarization experiments in an O₂-saturated 0.1 M HClO₄ solution at a rotation rate of 2500 rpm. As plotted in **Fig. S7**, the repeated RDE runs performed 1000 times result in nearly identical RDE curves in terms of the ORR onset potential, and curve shape, indicating the reasonable stability of the catalyst.