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# Carbon nanotubes supported cerium dioxide and platinum nanohybrids: Layer-by-layer synthesis and enhanced electrocatalytic activity for methanol oxidation

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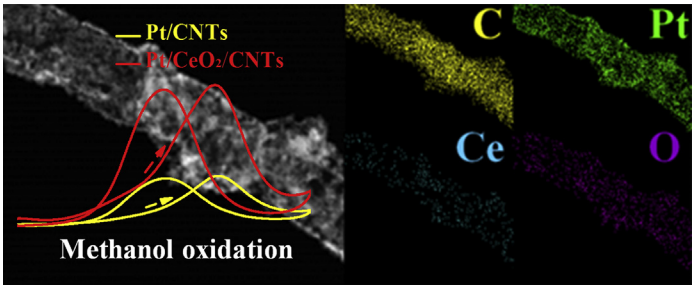
## HIGHLIGHTS

- High-quality Pt/$CeO_2$/CNTs nanohybrids are synthesized via layer-by-layer assembly.
- Pt and $CeO_2$ nanoparticles are homogenously deposited on the CNTs surface.
- Pt/$CeO_2$/CNTs exhibit enhanced electrocatalytic activity for methanol oxidation.

## GRAPHICAL ABSTRACT

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## ABSTRACT

We successfully synthesize carbon nanotubes (CNTs) supported cerium dioxide and platinum (Pt/$CeO_2$/CNTs) nanohybrids via layer-by-layer assembly. The composition, morphology and structure of the as-prepared Pt/$CeO_2$/CNTs nanohybrids are characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectrometer (EDX), selected-area electron diffraction (SAED), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and inductively coupled plasma atomic emission spectrometry (ICP-AES). By comparison of the electrocatalytic properties of the Pt/$CeO_2$/CNTs with the Pt/CNTs, we systematically investigate the promotion effect of $CeO_2$ on the Pt/$CeO_2$/CNTs catalysts towards methanol oxidation. It is found that the introduction of $CeO_2$ not only enhances the electrocatalytic activity and stability of the Pt/$CeO_2$/CNTs catalyst for methanol oxidation but also minimizes the CO poisoning, probably accounting for the good oxygen carrying capacity of $CeO_2$ and its high stability in acidic solution.



## 1. Introduction

Recently, direct methanol fuel cells (DMFCs) are actively pursued as an alternative power source for portable electronic devices due to their excellent efficiency, system simplicity, and environmental friendliness [1–6]. Pt-based electrocatalysts are regarded as the most popular and effective anodic electrocatalysts for DMFCs [3,7–12], which usually are well-dispersed on a suitable carbon supporting material, such as carbon black, carbon nanotubes (CNTs), carbon nanofibers, etc. The addition of the matrix is to maximize the electrocatalytic activity of the Pt electrocatalysts and to lower the usage of precious Pt [13–23]. In particular, CNTs is reported as an attractive support to load metal nanoparticles for the electrocatalytic applications, due to its unique properties, such as

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high electronic conductivity, huge surface area, mechanical and thermal stability and durability [24–27]. Much efforts have been made to prepare CNT-supported Pt-based catalysts in different shape and structure for methanol oxidation towards DMFCs application. For example, Wang et al. prepared boron-doped carbon nanotube-supported Pt nanoparticles with improved CO tolerance for methanol oxidation [28]. Hsieh et al. synthesized Pt–Sn nanoparticles decorated CNTs as the electrocatalysts applied in methanol oxidation [3].

However, the electrocatalytic stability of the prepared carbon supported Pt-based catalysts for methanol oxidation is still not satisfying, owing to strong poisoning of $CO_{ads}$ intermediate [29,30]. Recently, it is demonstrated that when $MnO_2$ [31], $TiO_2$ [32], $SnO_2$ [33], $IrO_2$ [34], and $CeO_2$ [35–39] are incorporated, the prepared core–shell typed Pt-based electrocatalysts show improved electrocatalytic activity and stability, probably attributing to the synergistic interactions between the Pt nanoparticles and the nanooxides. For example, Liu et al. reported that $TiO_2$ supported Pt was a catalyst with high electrocatalytic performance for methanol oxidation [40]. It is worth noticing that, among the inert inorganic oxidates, $CeO_2$ has received considerable attention due to their high stability under acidic conditions and the good oxygen carrying capacity. It is reported that Ce can undergo a redox process reversibly between $Ce^{4+}$ and $Ce^{3+}$ that enables the storage and release of oxygen at low potential [33,41,42]. Shipra et al. recently presented the successful fabrication of nanostructured Pt-loaded cerium oxide nanowire for methanol oxidation [43]. Although $CeO_2$ is desirable for the electrocatalytic improvement of the anchored Pt nanocatalysts, the poor intrinsic electronic conductivity will result in low rate anode performance in DMFCs.

To integrate the properties of these two supporting components of CNTs and $CeO_2$ in some mode at Pt-based composite catalysts, we present here in this work, the successful synthesis of high-quality Pt/$CeO_2$/CNTs nanohybrids in high yield via layer-by-layer self-assembly method. Compared to the most used routes for CNTs-supported metal hybrid nanomaterials by electrochemical deposition or chemical-wet approach, the protocol we proposed is scalable and more effective with high reproducibility. The prepared Pt/$CeO_2$/CNTs nanohybrids show excellent electrocatalytic performance for methanol oxidation due to the proper amount of $CeO_2$ introduced with even distribution.

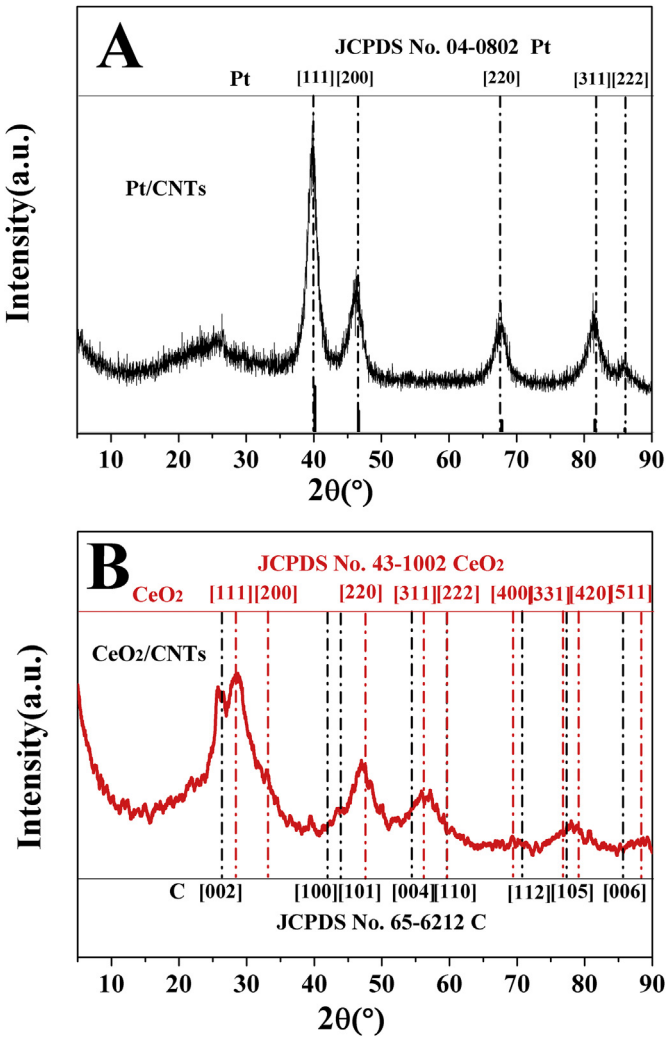
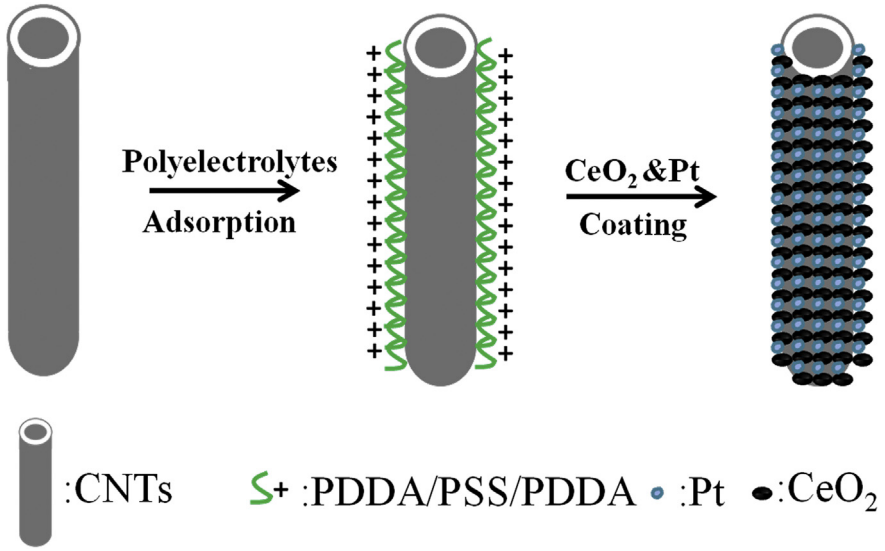



**Fig. 1.** XRD patterns of (A) the Pt/CNTs and (B) the $CeO_2$/CNTs nanohybrids.




**Scheme 1.** Schematic illustration for the formation of the Pt/$CeO_2$/CNTs nanohybrids.