

crystal structure, with angle equal to $175.734(7)^\circ$. This angle differs from that of a commercial fluoride phosphor, such as $K_2SiF_6:Mn^{4+}$ (KSF) that has an F–Si–F angle equal to 180° with point group O_h of the SiF_6^{2-} site. Consequently, once the MnF_6^{2-} activator becomes doped into RbGF in the GeF_6^{2-} site, the MnF_6^{2-} geometry might also become distorted; the MnF_6^{2-} point group might alter to C_3 , which would directly affect the RbGF spectra.

In summary, the authors synthesized a fluoride phosphor (RbGF) of a new chemical composition that exhibits a ZPL and high quantum efficiency (external quantum efficiency = 58%) that is almost equal to that of the commercial phosphor (KSF). The mechanism of the ZPL formation, and the relation between the ZPL and its sideband, were studied under various conditions such as low temperature and high pres-

sure. This new fluoride phosphor might be a critical material in revolutionizing WLED. (Reported by Yan-Gu Lin)

*This report features the work of Ru-Shi Liu and his co-workers published in Chem. Mater. **29**, 935 (2017).*

TPS 09A Temporally Coherent X-ray Diffraction

- XRD
- Material Science, Surface, Interface and Thin Films, Condensed Matter Physics

Reference

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Dual Doping Strengthens Metal-Support Interactions

Dual-doped TiO_2 provides an enhanced electron conductivity and improved activities in fuel cells.

As a proton-exchange-membrane fuel-cell catalyst, platinum (Pt) has the best performance among catalytic metals, but its great cost and the small rate of reaction at the cathode, which is the site of the oxygen reduction reaction (ORR), limit the widespread use of proton-exchange-membrane fuel cells. Moreover, Pt sintering and support degradation remain unresolved problems in acidic solutions. The most commonly used support (as a Pt carrier) is TiO_2 , because of its electrochemical stability and its resistance to dissolution in acidic media, as found in working fuel cells. Although TiO_2 allows for some degree of electron transfer from Pt to the electrode, its conductivity is much less than that of carbon. This decreased conductivity effectively limits the activity of a Pt/ TiO_2 catalyst, such that it is not comparable to a Pt/C catalyst. One common approach to enhance the conductivity of TiO_2 , and thus to increase the activity of the catalyst, is to dope other elements (cationic or anionic) into the TiO_2 lattice. In addition to single-ion doping, the TiO_2 lattice can simultaneously accommodate both cationic and anionic dopants. An intriguing question naturally arises as to the utility, application and activity of dual-doped supports for Pt catalysts in fuel-cell applications.

In the study¹ conducted by Bing-Joe Hwang (National

Taiwan University of Science and Technology) and his team, electrochemical and spectral data together with ORR activity studies indicated that $Ti_{0.9}Nb_{0.1}N_xO_y$ and $Ti_{0.8}W_{0.2}N_xO_y$ synthesized as dual-doped catalytic supports for Pt nanoparticles offer considerable promise as a new class of catalytic support for use in fuel cells. The authors recorded synchrotron-based X-ray absorption spectra (XAS) at **TLS 17C1** to demonstrate how the defect formation affects the interactions between Pt and the singly or doubly doped TiO_2 supports, and manipulates the physical and chemical properties of the resulting catalysts.

To investigate the electronic properties of Pt nanoparticles on $Ti_{0.9}Nb_{0.1}N_xO_y$ and to verify the strong metal-support interaction (SMSI) state, Pt L_{3-} edge X-ray absorption near-edge structure (XANES) spectra were recorded. The spectrum was plotted and compared with those of the Pt/ TiN_xO_y and Pt/ $Ti_{0.9}Nb_{0.1}O_y$ catalysts; Pt foil and Pt/C were measured as references (**Fig. 1(a)**). In XANES spectra, the intensity of the white line is a direct measure of the d-band vacancy. The decrease in the white-line intensity can be attributed to SMSI that in turn lead to an electron transfer from the support to Pt. Additionally, the SMSI decrease the adsorption strength of the oxygen intermediates that are formed during

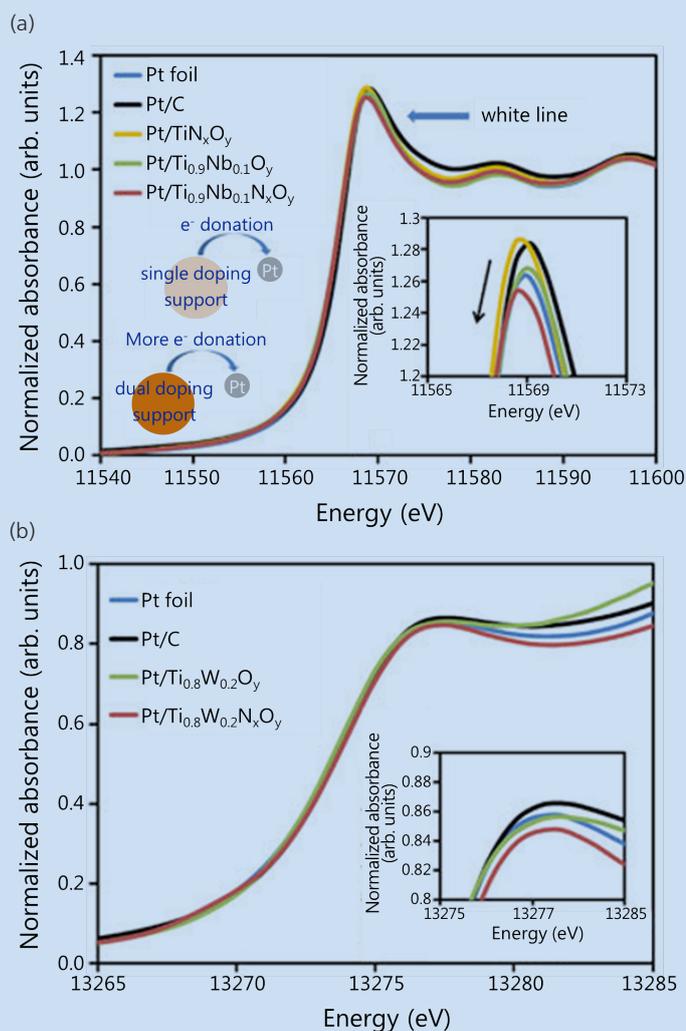


Fig. 1: (a) Pt L_3 -edge XANES spectra of Pt/TiN_xO_y, Pt/Ti_{0.9}Nb_{0.1}O_y and Pt/Ti_{0.9}Nb_{0.1}N_xO_y. Pt foil and Pt/C served as references. (Inset) Enlarged regions of the maxima of the Pt L_3 -edge XANES white line. (b) Pt L_2 -edge XANES spectra of Pt/Ti_{0.8}W_{0.2}O_y and Pt/Ti_{0.8}W_{0.2}N_xO_y. Pt foil and Pt/C served as references. (Inset) Enlarged region of the maxima of the Pt L_2 -edge. [Reproduced from Ref. 1]

the ORR on the Pt surface in the rate-determining step, thus leading to a more rapid reaction of oxygen reduction. Another important effect of the SMSI is an enhancement of the bonding strength between Pt and the metal-oxide support that prevents the migration and aggregation of Pt on the surface of the support in tests of long-term stability. Unexpectedly, the white-line intensity decreased in the following order: Pt/TiN_xO_y > Pt/C > Pt/Ti_{0.9}Nb_{0.1}O_y > Pt foil > Pt/Ti_{0.9}Nb_{0.1}N_xO_y. Here, Pt/Ti_{0.9}Nb_{0.1}N_xO_y represents the least white-line intensity, thus indicating that dual-doped TiO₂ has a stronger metal-support interaction with Pt nanoparticles, thereby leading to increased activity and stability during electrochemical testing. Pt/Ti_{0.8}W_{0.2}N_xO_y was also compared with singly doped TiO₂. Because of the Pt L_3 -edge overlap with the W L_2 -edge, only the Pt L_2 -edge of the Pt foil,

Pt/C, Pt/Ti_{0.8}W_{0.2}O_y and Pt/Ti_{0.8}W_{0.2}N_xO_y was measured (Fig. 1(b)).

Pt/Ti_{0.8}W_{0.2}N_xO_y showed the least intensity of the Pt L_2 -edge, thus indicating a strong driving force for electron transfer from the support to Pt because of the SMSI. Compared with Pt/C, both Pt/Ti_{0.9}Nb_{0.1}O_y and Pt/Ti_{0.8}W_{0.2}O_y demonstrated a donation of electrons from the support to Pt, unlike Pt/TiN_xO_y. Defects played an important role and significantly altered the properties of the deposited Pt. From the XAS results, the decreased intensity of the white line indicated that Pt was deposited at defect sites rather than at defect-free sites.

In summary, dual-doped TiO₂-supported Pt catalysts, which were readily prepared and showed excellent activity and stability for oxygen reduction reactions, were developed. Dual doping not only enhances the electron conductivity but also alters the electronic state of Pt on the support materials, thus allowing for more active and stable catalysts. XAS were recorded to identify the electronic properties of Pt on the Ti_{0.9}Nb_{0.1}N_xO_y and Pt/Ti_{0.8}W_{0.2}N_xO_y supports. This work opens a new path toward the development of novel catalysts for fuel-cell applications. (Reported by Yan-Gu Lin)

This report features the work of Bing-Joe Hwang and his co-workers published in NPG Asia Mater. 9, e403 (2017).

TLS 17C1 W200 – EXAFS

- XANES, EXAFS
- Material Science, Chemistry, Condensed Matter Physics, Environmental and Earth Science

Reference

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