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A general route for RuO₂ deposition on metal oxides from RuO₄†Alan Kleiman-Shwarsstein,^a Anders B. Laursen,^a Filippo Cavalca,^b Wei Tang,^a Søren Dahl^a and Ib Chorkendorff^{*a}

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A novel method for the deposition of RuO₂ from RuO₄(g) on diverse metal oxides has been developed by grafting dopamine onto the otherwise un-reactive metal oxide surface. Oxygen evolution reaction on TiO₂ and the photoelectrochemical improvement of WO₃ by deposition of RuO₂ are just a few examples where this novel deposition method can be used.

Ruthenium dioxide (and metallic Ru) is widely used, for heterogeneous catalysis including oxidation reactions, reduction/hydrogenation reactions and ammonia synthesis; electrochemical/photoelectrochemical reactions including Oxygen Evolution¹ (OER), Hydrogen Evolution (HER), Oxygen Reduction (ORR, combined with Pt or Ir)² as well as the chloro-alkali process to produce Cl₂ and NaOH. Other applications of Ru and RuO₂ are in electronic materials where the high conductivity can be exploited for usage in DRAM capacitors, and battery materials.³ RuO₂ is especially regarded as being amongst the most promising electrode materials for super-capacitor⁴ applications.

Although there are many uses for Ru and RuO₂ the incorporation, of this high-performance material, into industrial applications, is very limited due to the high cost of Ru. In many cases the overall cost of utilizing RuO₂ could be decreased if an economically feasible method, which provides high stability and increased surface area, could be achieved. Furthermore, due to the great chemical resistance of RuO₂ it is desirable to make thin coatings that can prevent the support material from being in contact with the chemical environment. Advances in chemical synthesis^{5,6} have provided mesoporous RuO₂ materials, which provide an increased accessible surface area. In addition, conformal RuO₂ coating can be achieved by atomic layer deposition (ALD). However, this requires expensive setups and in many cases exotic organic Ru complexes which need to be tailored depending on the metal oxide support that is being used.

Until now there was no general synthesis route in which RuO₂ can be deposited from RuO₄(g) onto a metal oxide, producing a thin semi-continuous, conformal or thin particulate coating that can be applied to any geometry and type of substrate

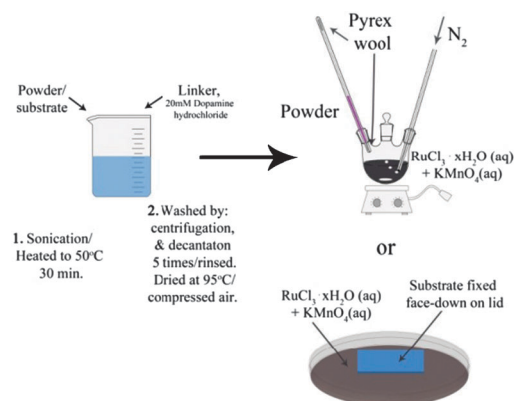
in an economical and easy way. Herein, we describe a 3 step method that is generally applicable to most metal oxides: (1) functionalization of the metal oxide host with a grafting agent, (2) reaction of the functionalized group with gas phase RuO₄ and (3) post-treatment of the metal-oxide–RuO₂ composite to obtain the required properties. This method is flexible, since the modification of these 3 steps could be used to include other families of support materials by changing the grafting molecule or the post-treatment conditions after deposition of RuO₂.

Titanium dioxide (P25 or Degusa Vp Disp “W2730X” on fluorine doped tin oxide (FTO)) and tungsten trioxide (electrodeposited on FTO) were chosen as examples of metal oxide supports to show how this general RuO₂ deposition method works. Many other metal oxides can also be functionalized with RuO₂ and are shown in Table 1 as a reference. The functionalization (step 1, Scheme 1) of the metal oxide consists of the grafting of 20 mM dopamine hydrochloride ((HO)₂C₆H₃CH₂CH₂NH₂HCl) onto the metal oxide, followed by washing of the metal oxide to remove non-grafted dopamine (see ESI† for full details on the grafting procedure).

X-Ray photoelectron spectroscopy of the N1s region for a dopamine functionalized TiO₂ sample (Fig. S4a, ESI†) shows two peaks at binding energies of 399.8 and 401.7 eV. The peak

Table 1 List of metal oxides that have been tested for RuO₂ deposition

RuO ₂ deposition	TiO ₂ , SrTiO ₃ , WO ₃ , Cu ₂ O, α-Fe ₂ O ₃ , Al ₂ O ₃ , Li ₄ Ti ₅ O ₁₂ , MgAlO, GaN : ZnO
No RuO ₂ deposition	SiO ₂ , FTO



Scheme 1 Deposition process of RuO₂ for powders and thin film metal oxides.

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at 399.8 eV can be ascribed to the NH_2 group of dopamine⁷ while the peak at 401.7 eV could be related to NH_3^+ species.^{7,8} The pristine TiO_2 and the TiO_2 with RuO_2 before calcination (R0 and R1) show a peak at 400.1 eV and after calcination (R3) at 400.4 eV, this peak could be related to adsorbed molecular N_2 ⁹ and does not correspond to the binding energy reported for N-doped TiO_2 . The XPS spectra is a clear indication that the dopamine is attached in a chelating bidentate structure *via* the diol groups to the uncoordinated titanium atoms at the surface of titanium dioxide, which is consistent with DFT calculations.^{7,10} The absorption of the dopamine on the TiO_2 results in a slight color change as shown by the UV-Vis absorption properties (Fig. S5, ESI[†]), in which the bandgap of TiO_2 is decreased from 3.2 eV to 3. Changes in the absorption properties of TiO_2 are due to the removal of band gap states in the TiO_2 valence band⁷ caused by adsorption of dopamine.

Deposition of RuO_2 on the metal oxides is done by a new method, in which gas phase *in situ* generated RuO_4 is reacted with the dopamine functionalized metal oxide; this methodology has never been reported in literature before. Previous work in this area was limited to biological samples,¹¹ polymers¹² and etched metal surfaces¹² since most metal oxides will not reduce RuO_4 to RuO_2 and therefore the RuO_2 will not be deposited (see ESI[†]). RuO_4 was synthesized by *in situ* oxidation¹² of RuCl_3 with KMnO_4 in a closed container, such that the toxic RuO_4 gas evolves from the reaction mixture and reacts with the functionalized metal oxide.

Consideration of the type of support must be taken into account when delivering the gas phase RuO_4 , so that there are no gas diffusion limitations to the surface in order to ensure a homogeneous distribution of the RuO_2 on the sample. Thin film substrates used were attached to the lid of a pyrex crystallizer (coating by convection of $\text{RuO}_4(\text{g})$), while powders were packed in a pressurized glass tube flow reactor (forced flow, due to mass transport limitations). The loading of RuO_2 can be controlled by the amount of $\text{RuO}_4(\text{g})$ that is generated *in situ* by controlling the amount of RuCl_3 and KMnO_4 used or by repeating the deposition process several times (safety precautions and deposition details given in ESI[†]). RuO_4 in the gas phase will react with organics such as Kapton[®], phenol and paraffin, but will not be reactive to most metal oxides. This is clear from control experiments, which we have performed—in which *no* RuO_2 is observed on the non-functionalized TiO_2 and WO_3 samples; results that were also observed by Rolison *et al.*¹² However in the case when dopamine is grafted to a great variety of metal oxides, which can be coated with hydrated RuO_2 (Table 1), SiO_2 and FTO could not be coated with RuO_2 since dopamine adsorbs weakly on these substrates, however by using a different grafting agent they could be functionalized.

After deposition of RuO_2 on the functionalized metal oxides, a distinct color change is observed, indicative of the deposition of Ru/RuO_x (see photography S1, and UV-VIS S5, ESI[†]). STEM HAADF imaging (Fig. 1a) shows a P25-Dopamine particle that has been reacted with $\text{RuO}_4(\text{g})$; STEM EDX mapping shows the ruthenium distribution on the TiO_2 particle: the brighter contrast in the image corresponds to that of Ru nanoclusters covering the darker TiO_2 particle. X-Ray diffraction patterns of TiO_2 can only be indexed to anatase and rutile phases (S2) indicating that the Ru deposit is not crystalline or/and is

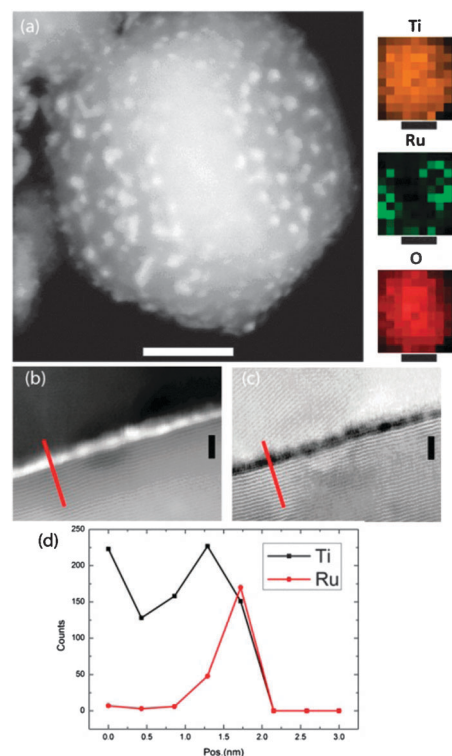


Fig. 1 (a) STEM HAADF image of P25 TiO_2 with RuO_2 deposition and EDX elemental map, prior to calcination, scale bar 5 nm. (b–c) STEM HAADF and bright field of a RuO_2 layer on a (123) anatase TiO_2 surface after 450 °C calcination, scale bar 1 nm; and (d) EDX spectrum profile acquired along the red line in (b–c).

present in minute amounts or as small particles. Once the sample is calcined at 450 °C in air, STEM (Fig. 1b) reveals that RuO_2 predominantly covers the surface of the TiO_2 nanoparticle and is sintered into large homogeneous amorphous ~ 1 nm thick layers. The predominantly small cluster from the uncalcined sample disappears leaving behind an empty TiO_2 surface and a very sharp interface where RuO_2 is present. Due to the higher Z number, Ru appears brighter in the HAADF image and darker in the corresponding BF image. Lattice fringes on the lower side of Fig. 1b and c relate to the TiO_2 particle where RuO_2 is deposited, while the ones appearing on the uppermost side come from another particle at a different height. STEM EDX line scans performed on the calcined sample show that all of the RuO_2 is present at the TiO_2 grain boundaries. X-Ray diffraction patterns of the sample calcined at 450 °C do not show any RuO_2 features but show a decreased crystallinity of the TiO_2 .

XPS spectra (Fig. S4d, e R2, further details in ESI[†]) of the C 1s–Ru 3d XPS region show two peaks at 281.2 and 282.5 eV in the Ru 3d_{5/2} region and the corresponding peaks in the Ru 3d_{3/2} at 285.7, and 287 eV corresponding to Ru^{3+} or hydrated RuO_2 ,¹³ and Ru^{6+} respectively;^{14,15} the C 1s region shows two peaks at 284.9 eV (advantageous carbon) and a second carbon peak at 288.8 eV.¹⁴ Upon calcination at 250 °C (Fig. S4d, f R3, ESI[†]) the XPS spectra show peaks at 280.2 and 281.3 eV for the Ru 3d_{5/2} and 284.7 and 285.9 eV for Ru 3d_{3/2} corresponding to Ru^{4+} and Ru^{3+} or hydrated RuO_2 ¹³ respectively. The C 1s region has the advantageous carbon peak at 285.3 eV and a second carbon peak at 288.7 eV.

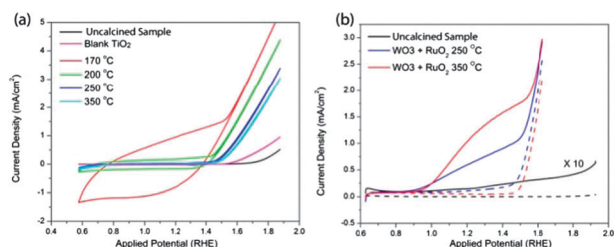


Fig. 2 (a) Cyclic Voltammogram of TiO₂ on the FTO substrate with and without RuO₂ in 1 M NaOH, (b) cyclic voltammogram of electrodeposited WO₃ on FTO with RuO₂ calcined at 250 °C (blue) and 350 °C (red) and without RuO₂ (black) in 1 M HClO₄. Dashed lines show the response in the dark, while continuous lines show the photoresponse. Photocurrent of WO₃ without RuO₂ (black) has been scaled to 10 times its original value.

As one of the many potential applications for this RuO₂ coating, the electrochemical performance towards OER was tested using spin coated TiO₂ electrodes on FTO as a function of calcination temperature (see ESI†). From Fig. 2a it can be seen that activity for OER is negligible for the uncalcined sample at 100 °C (data not shown). At 170 °C the sample has the highest OER activity and also shows hysteresis, which is indicative of proton intercalation into the RuO₂.⁴ However, at higher calcination temperatures the intercalation is decreased and the OER performance decreases due to a reduction in the electrochemical active¹² area due to sintering of the RuO₂. The latter is verified by observations from the TEM studies (Fig. 1). The overpotentials at 1 mA cm⁻² and 0.1 mA cm⁻² observed for OER are ~250 mV and ~220 mV, respectively, which is the range of that reported for RuO₂ and RuO₂ alloys^{16–19} (160–280 mV¹²).

The photocatalytic performance of WO₃ with and without RuO₂ was tested as another example of the application of the RuO₂ deposition method being applicable to photocatalysts (see ESI†). From Fig. 2b it can be observed that the OER performance of WO₃ in the dark (black dashed lines) is negligible, this is due in part to the poor OER kinetics on WO₃²⁰ as well as to the lack of holes in tungsten trioxide in the dark. Once RuO₂ is deposited (dashed blue and red lines), an increase in current in the dark is observed, which is indicative of an increased OER activity in the dark due to the RuO₂. This behavior would most probably be indicative of deposition of the RuO₂ near the back contact where there is a lower resistance for OER due to pinholes in the WO₃, since light would be needed for photoconduction of carriers through the WO₃. In the case of the photoactivity of the WO₃, the addition of RuO₂ increased the PEC performance (blue and red curves) as compared to the WO₃ sample without RuO₂ (black curve, magnified 10 times). We can observe that the photocurrent onset potential of the samples with RuO₂ is ~1.0 V vs. RHE as compared to ~1.2 V vs. RHE for the WO₃ sample with no RuO₂. This reduction in the onset potential for photocurrent is indicative that the OER reaction is being efficiently catalyzed when RuO₂ is deposited on the photocatalyst.

A general route for RuO₂ deposition on metal oxides from gas phase RuO₄ has been developed by a simple 3 step process,

in which a reactive moiety such as dopamine is grafted to the metal oxide and afterwards reacted with RuO₄(g) to form RuO₂. This application of the deposition process to synthesize supported RuO₂ is of great interest for many catalysis and energy storage applications. Two examples have been showcased to demonstrate some of the potential applications that this method has. (1) The deposition of RuO₂ on TiO₂ as an OER catalyst has been shown to give similar results to those found in the literature and TEM microscopy has shown that small RuO₂ clusters with a very homogenous coverage can be deposited utilizing this method. (2) The application of RuO₂ as an OER catalyst in combination with WO₃ as a photocatalyst has shown a superb improvement in performance by the deposition of RuO₂. These two examples show just how versatile and universal the deposition method of RuO₂ described in this communication is and some of the possible applications for catalysis in the renewable energy area.

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