catalysts

MDPI

Supporting Information

IrO_x Supported on Submicron-sized Anatase TiO_2 as a Catalyst for the Oxygen Evolution Reaction

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Raman spectra and XRD patterns of the titania supports

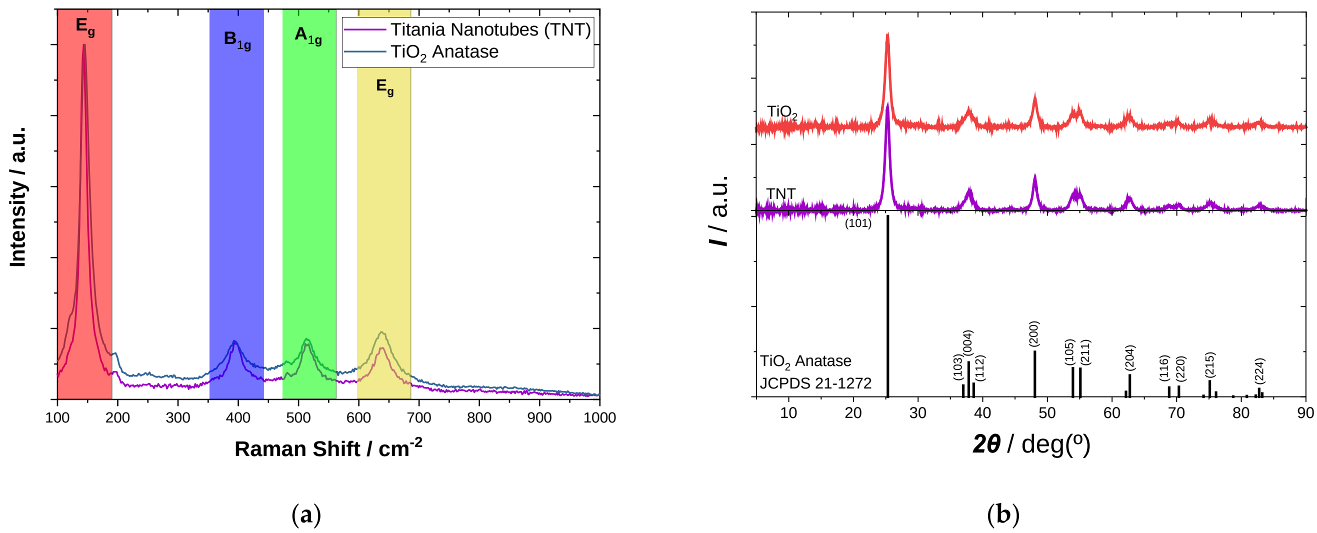


Figure S1. (a) Raman Spectra and (b) XRD patterns of the synthesized titania nanotubes (TNTs) and of the commercial anatase TiO_2 used as supports. The peaks at 2θ = 25.3 deg(º), presenting β values (in 2θ deg(º)) of 0.256 and 0.128 for TNTs and TiO_2, respectively, were taken to determine the crystallite sizes through the Scherrer equation.

TEM image of commercial Ir Black

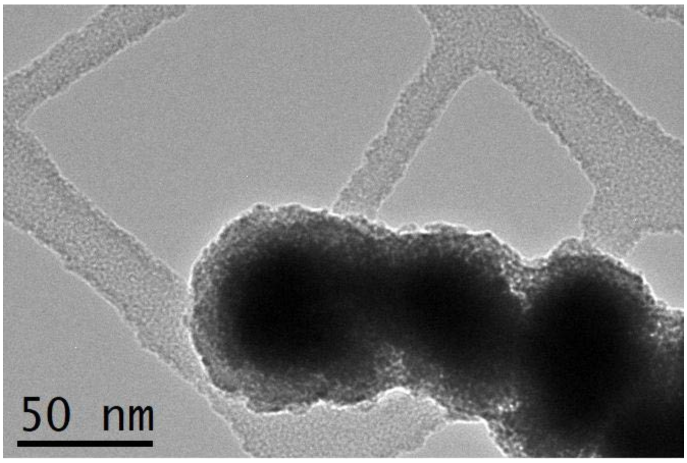


Figure S2. TEM image of the commercial Ir Black catalyst.

Estimation of the maximum Ir loading on the catalysts

To estimate the maximum iridium load for complete coverage in each TiO_2 nanostructure, we have assumed that the commercial TiO_2 nanoparticles are spheres of a given diameter, from which it is possible to calculate the available area of the spherical particle. In the case of nanotubes, we consider only the lateral area of the cylinder. In both cases, based on the hypothesis of a sphere or cylinder, the weight of TiO_2 can be calculated by knowing the volume and the anatase density (3.9 g cm^{-3}), which may be lower in the case of nanotubes.

Once the available area is known, it is possible to calculate the maximum iridium loading by considering spherical Ir nanoparticles (ρ=22.59 g cm^{-3}) of a given diameter (d_{Ir}) that completely cover the available TiO_2 surface in a hexagonal compact distribution. In this arrangement, the TiO_2 area that is covered by each spherical Ir particle is given by Eq. S1.

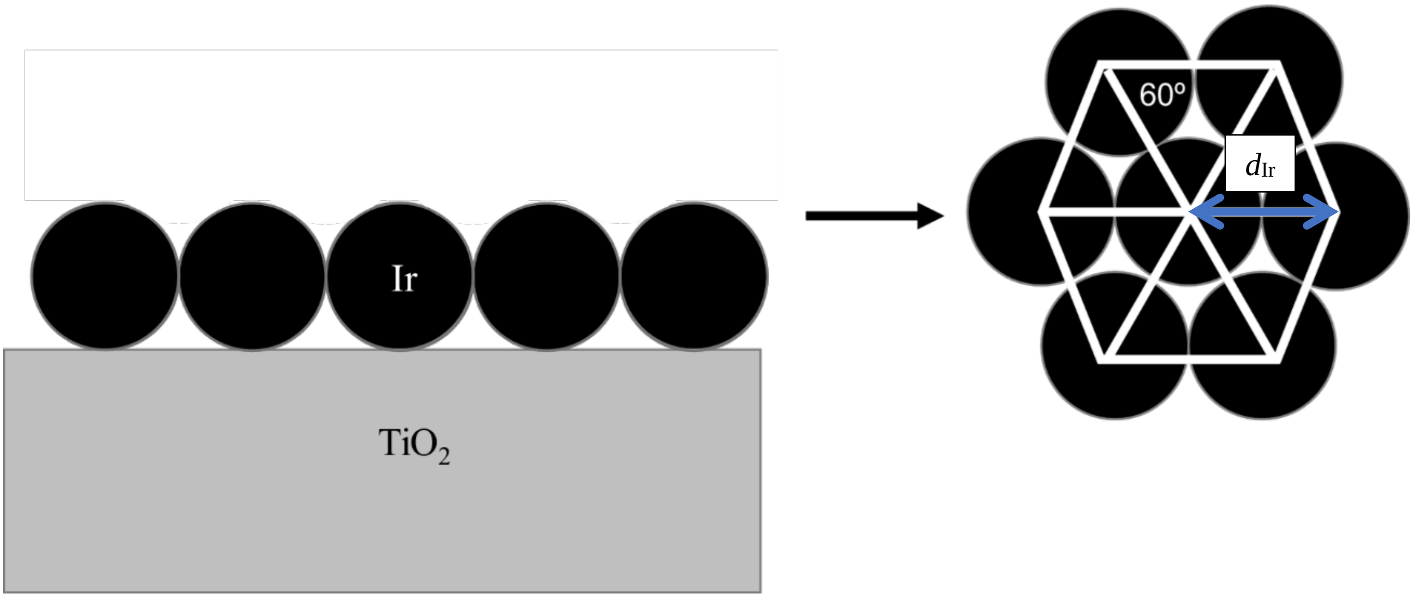


Figure S3. Model to estimate the TiO_2 available area to immobilize the Ir nanoparticles

$$Area/_{Ir\ NP} = \frac{2}{\sqrt{2}} d_{Ir}^2 \qquad \text{(S1)}$$

Finally, based on the above calculation of the available area per weight of TiO_2 support and Eq. S1, the amount of iridium required to completely cover the support can be known, from which the maximum iridium loading can be estimated. The results of different geometries based on TEM images are shown in Table S1. As can be seen, due to the low surface to volume ratio of commercial TiO_2 nanoparticles, with particle diameters in the range of 80 to 120 nm, the 40 wt.% Ir load far exceeds the amount needed for a complete TiO_2 coverage with the consequent formation of aggregates in certain areas and probable losses, being the main reason of the differences between the nominal values of the precursors and the synthetized catalysts. In agreement with the TEM images, 20 wt.% Ir loading corresponds to an almost completely covered surface with nanoparticles of an average size of 2 nm. In the case of nanotubes, the surface to volume ratio is significantly increased and consequently it is possible to synthesize electrocatalysts with the nominal 40 wt.% Ir loading with still uncovered surface areas.

Table S1. Estimation of the maximum iridium loading on the TiO_2 anatase and TNTs.

Maximum iridium loading (wt.%)		**TiO_2 support shape**					
		Spheric Φ=80 nm	**Spheric Φ=120 nm**	**Nanotube[a] Φ=8.5 nm, L= 55 nm**	**Nanotube[a] Φ=9 nm, L= 60 nm**	**Nanotube[b] Φ=8.5 nm, L= 55 nm**	**Nanotube[b] Φ=9 nm, L= 60 nm**
Ir NP	1 nm	14 %	10 %	50 %	49 %	67 %	66 %
	2 nm	24 %	18 %	67 %	66 %	80 %	79 %
	3 nm	33 %	24 %	75 %	74 %	86 %	85 %

[a]dense TiO_2 nanotube (ρ=3.9 g cm^{-3}), [b]low-density TiO_2 nanotube (ρ=1.95 g cm^{-3})

Cyclic voltammograms at different scan rates

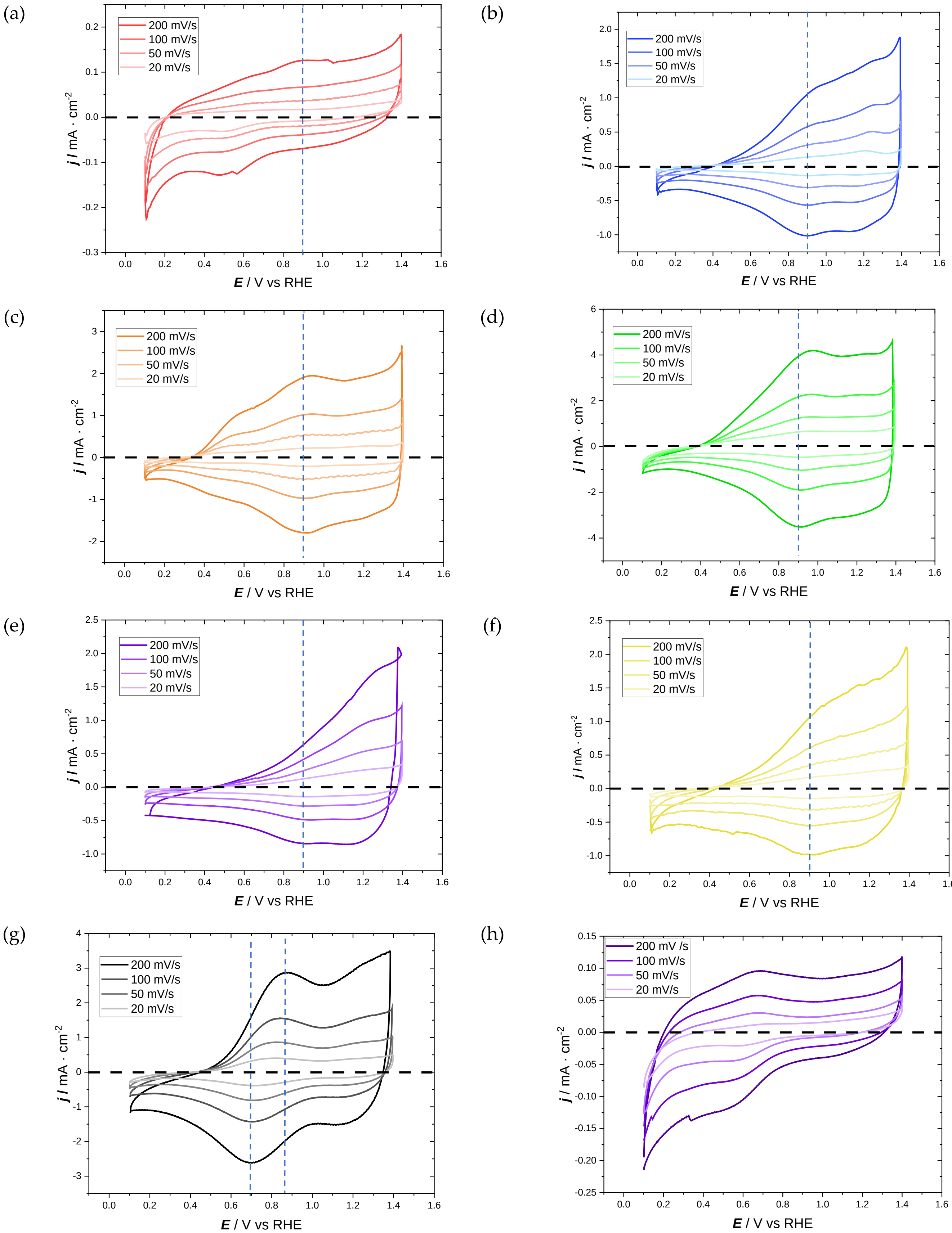
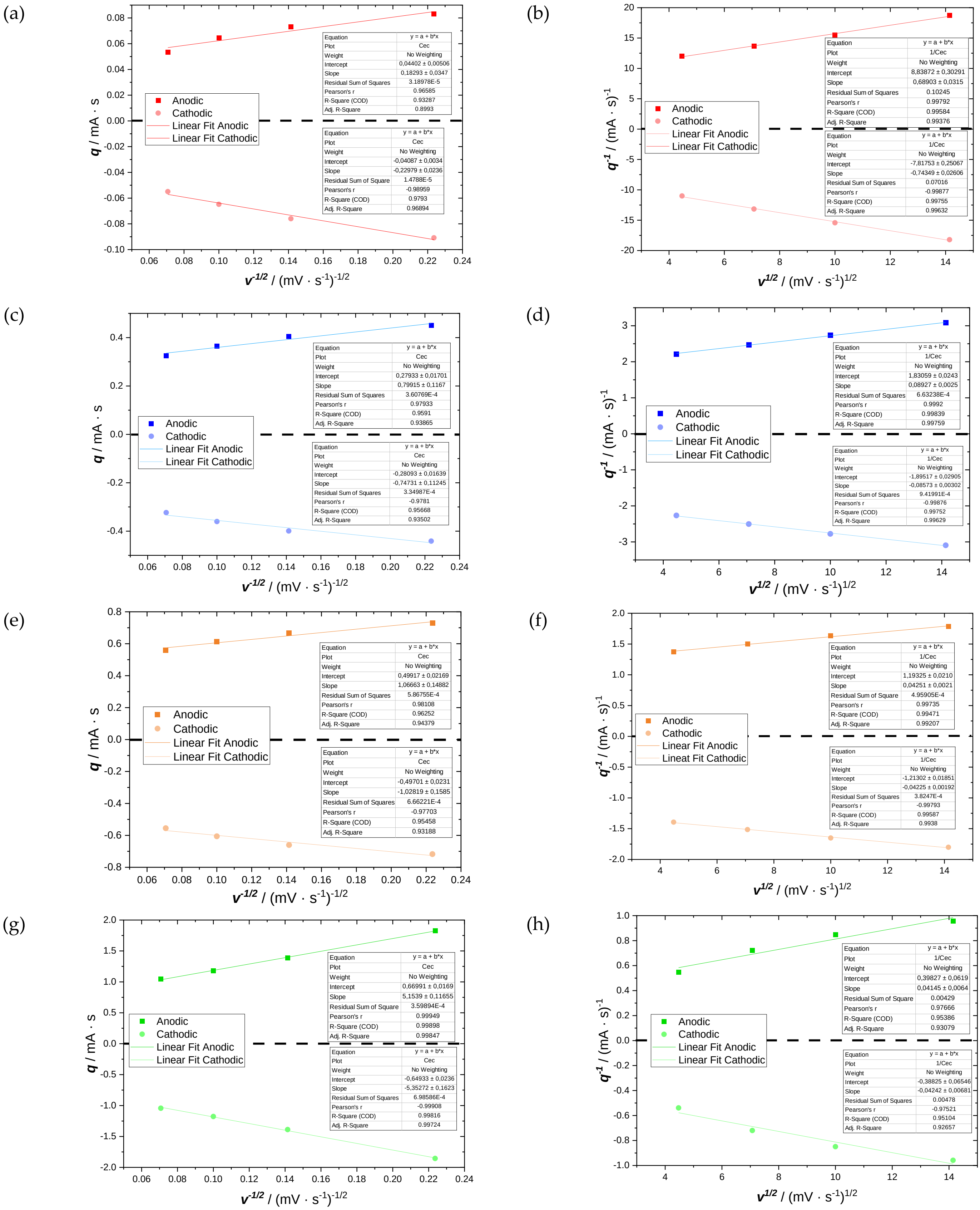


Figure S4. Cyclic voltammograms of the catalysts at different scan rates: (a) Ir/TiO_2(05:95), (b) Ir/TiO_2(10:90), (c) Ir/TiO_2(20:80), (d) Ir/TiO_2(40:60), (e) Ir/TNT(40:60), (f) Ir NPs, (g) Ir Black, and (h) TiO_2 support.

Linear regression to determine the catalyst accessibility



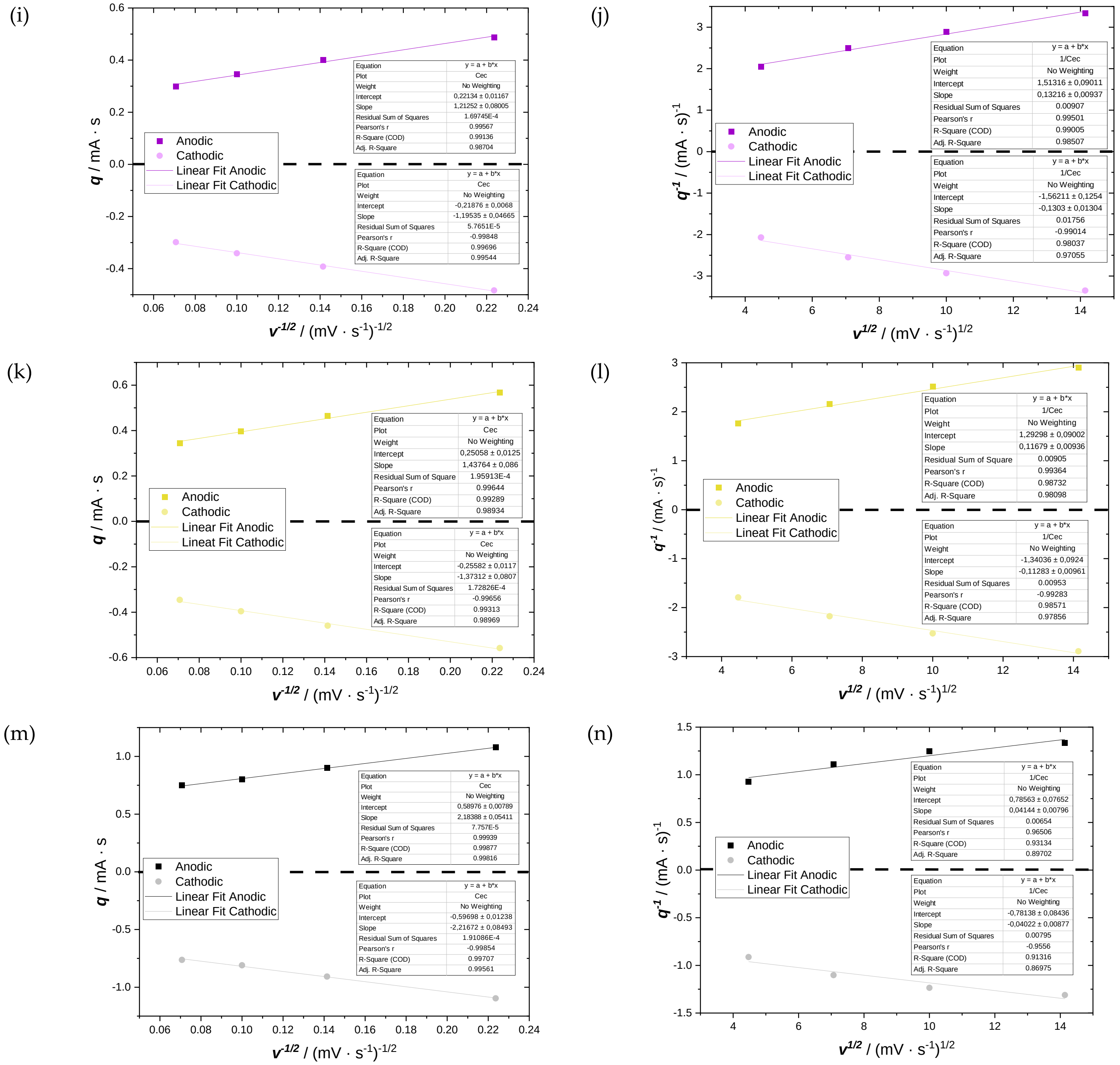


Figure S5. Linear plots to determine q_{outer}: (a) Ir/TiO_2(05:95), (c) Ir/TiO_2(10:90), (e) Ir/TiO_2(20:80), (g) Ir/TiO_2(40:60), (i) Ir/TNT(40:60), (k) Ir NPs and (m) Ir Black and q_{total}: (b) Ir/TiO_2(05:95), (d) Ir/TiO_2(10:90), (f) Ir/TiO_2 (20:80), (h) Ir/TiO_2(40:60), (j) Ir/TNT(40:60), (l) Ir NPs and (n) Ir Black.

Linear regression to determine the C_{dl} and the ECSAs

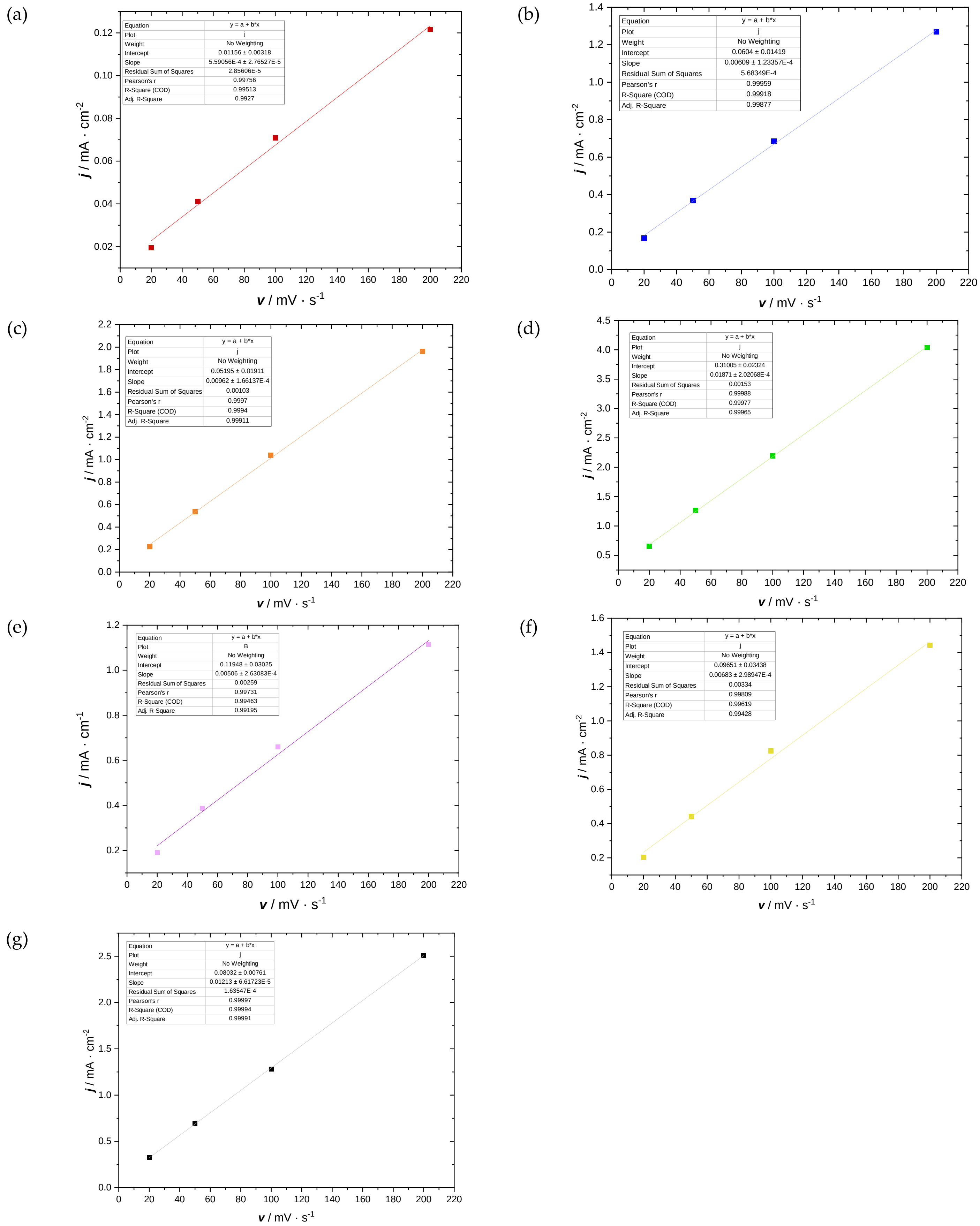


Figure S6. Linear plots to determine C_{dl} to obtain the ECSAs: (a) Ir/TiO_2(05:95), (b) Ir/TiO_2(10:90), (c) Ir/TiO_2(20:80), (d) Ir/TiO_2(40:60), (e) Ir/TNT(40:60), (f) Ir NPs and (g) Ir Black.