Ruthenium

Ellen Järvinen & Emma Verkama
30.9.2022

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  - Dye-sensitized solar cells

1 https://onlinelibrary.wiley.com/doi/10.1002/9783527306732.a21_075.pub2

Ullmann's encyclopedia of industrial chemistry: täältä löytyy paljon "perusasioita", tietoa yhdisteistä jne (ja on lisäksi oikein arvostettu viite)

Emma Verkama; 26.9.2022

Element – history

- Discovery attributed to Karl Claus, Kazan State University (1844)
    - First observed by Sniadecki (1808), from South American platinum ores
    - Identified and named Ruthenium by Osann (1825) from Ural ores
    - Extracted, purified and confirmed by Claus
- Named in the honor or Russia

Image reference: By Alchemist-hp (talk) (www.pse-mendelejew.de) - Own work, FAL, https://commons.wikimedia.org/w/index.php?curid=9915539, accessed 26.9.2022

https://www.rsc.org/periodic-table/element/44/ruthenium, accessed 28.9.2022

Ruthenium in *Encyclopedia Britannica*, https://www.britannica.com/science/ruthenium, accessed 26.9.2022

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018 https://doi.org/10.1002/9783527306732.a21_075.pub2

Element – abundancy and world production

- Crustal abundance ~0.001 ppm
  - Mined together with other platinum group metals
  - Encountered both as elemental and sulfide
- Production ~35 t/a
  - (Pt: ~180 t/a)
- Applications: thick film resistors, electrical contacts, alloying with other platinum group metals, catalysis

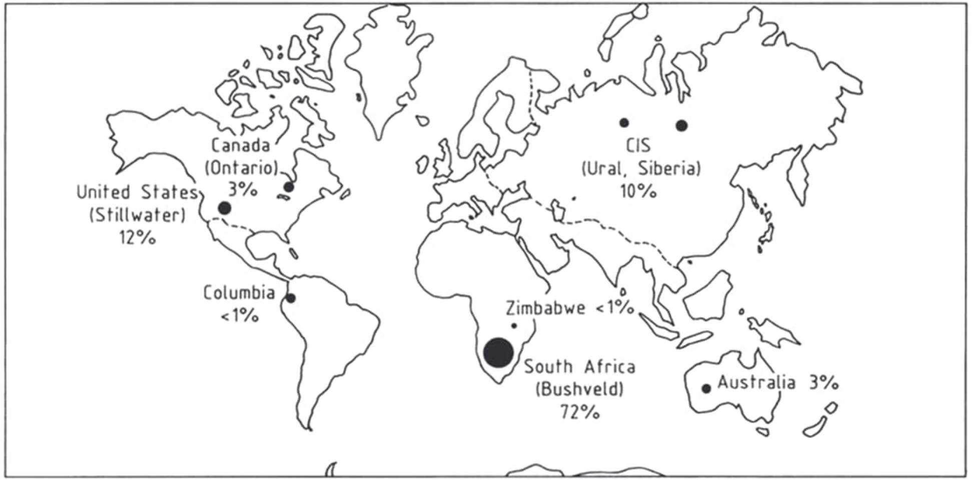


Figure 4. World platinum group metal reserves (total 69 000 t)

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2

https://www.statista.com/statistics/1170691/mine-production-of-platinum-worldwide/, accessed 28.9.2022

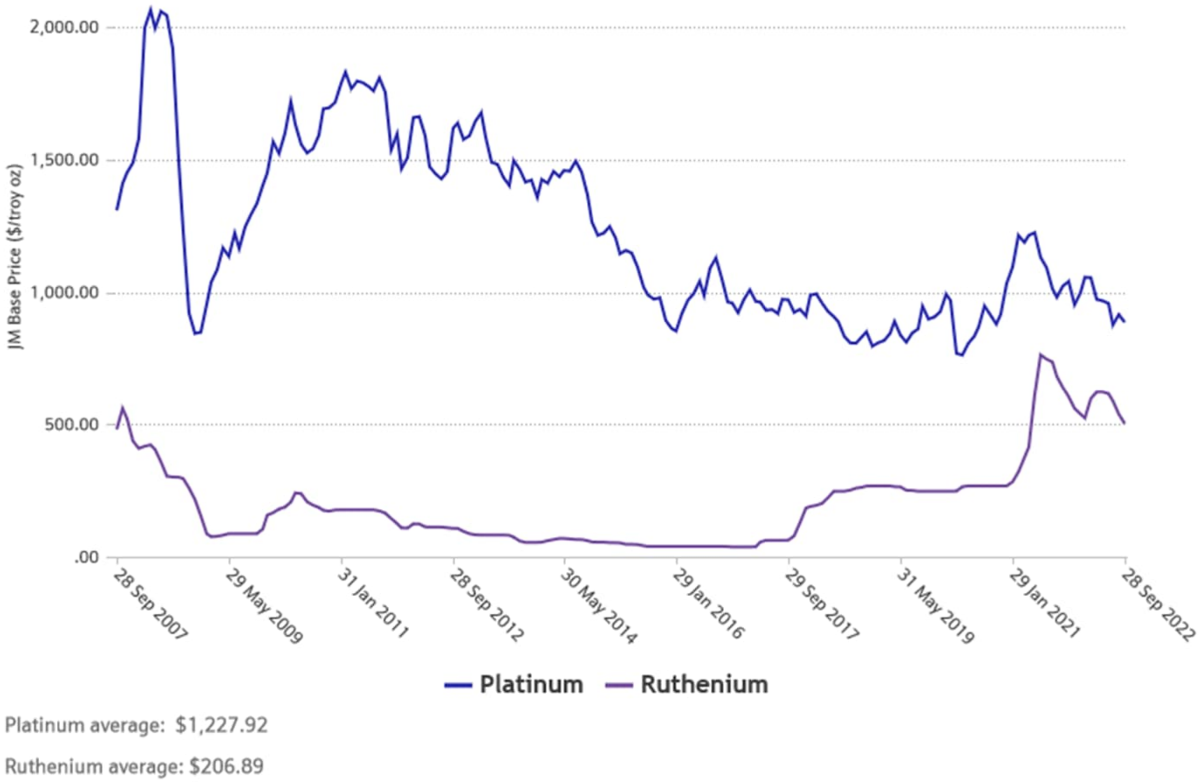
Abundancy relative to other platinum group metals

Table 4. Relative proportions of platinum group metals in selected deposits, and their grades

	Bushveld complex							
	Merensky Reef	UG 2 Reef	South Africa, Plat Reef	Sudbury, Canada	Noril’sk, CIS	Colombia	Stillwater, USA	Average
Platinum, %	59	42	42	38	25	93	19	45
Palladium, %	25	35	46	40	71	1	66.5	30
Ruthenium, %	8	12	4	2.9	1		4.0	5
Rhodium, %	3	8	3	3.3	3	2	7.6	4
Iridium, %	1	2.3	0.8	1.2		3	2.4	1
Osmium, %	0.8		0.6	1.2		1		<1
Gold, %	3.2	0.7	3.4	13.5			0.5	
Grade, g/t	8.1	8.71	7–27	0.9	3.8		22.3	

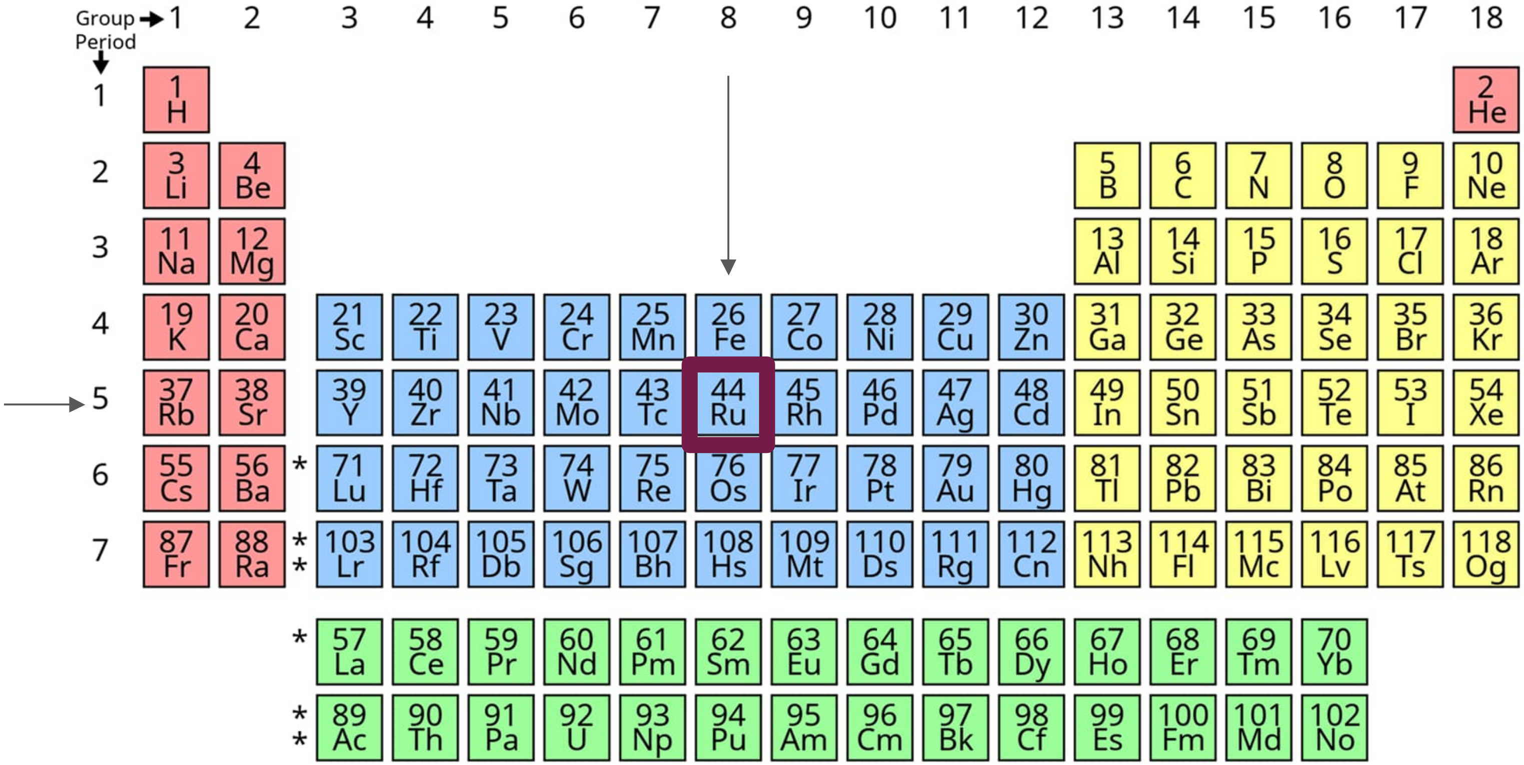
Renner et al., Platinum group metals and compounds in *Ullmann’s Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2

Prize development



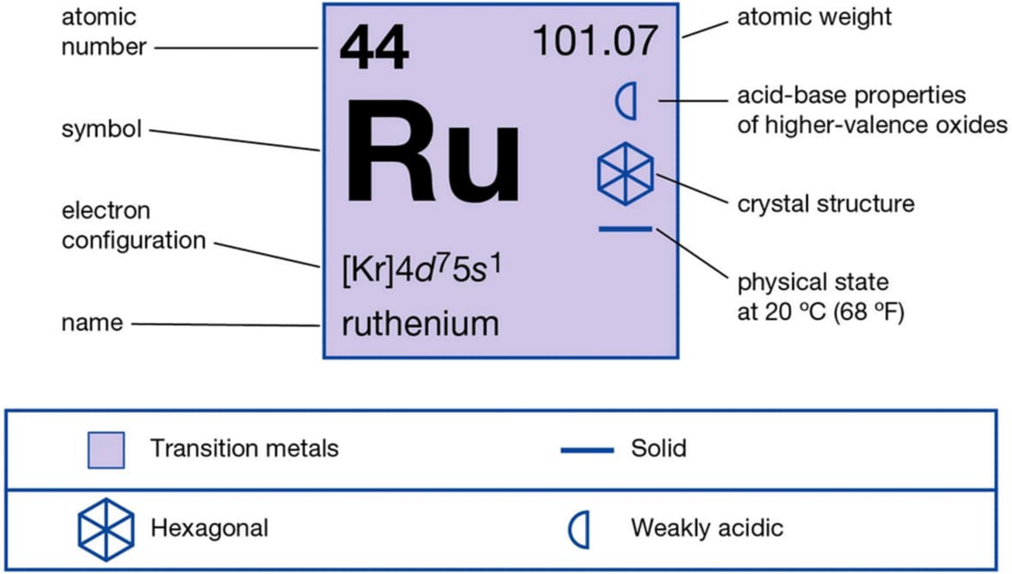
https://matthey.com/products-and-markets/pgms-and-circularity/pgm-management/, accessed 28.9.2022

Chemistry – location in the periodic table



Chemistry

- In general: similarities with other platinum group metals
- A shiny, hard, brittle and silvery
- Melting point 2334 °C
- Size
  - Atomic radius 2.13Å
  - Covalent radius 1.36Å
- Electron configuration
  - $1s^2 2s^2 2p^6 3s^2 3d^{10} 4s^2 4p^6 4d^7 5s^1$
- Oxidation states -2 to +8
  - +3 and +4 most important
  - Attributed to small energy differences in valence shells
- Electronegativity 2.2



https://www.rsc.org/periodic-table/element/44/ruthenium, accessed 28.9.2022

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Figure reference: Ruthenium in *Encyclopedia Britannica*, https://www.britannica.com/science/ruthenium, accessed 26.9.2022

2 Note this. Just as with the neighboring elements Nb, Rh and Mo

Emma Verkama; 28.9.2022

3 Although there are some differences per row and per period - also reflected in catalytic activity

Emma Verkama; 28.9.2022

Chemistry – reactivity

- Chemically resistant
    - Oxidizes at temperatures above 800 °C
    - Resistant to strong acids (even aqua regia)
    - Dissolves in sodium hypochlorite (NaClO)
- Treatment with KOH-KNO_3 to water-soluble $K_2[RuO_4]$
- Dissolution by alkaline flux fusion possible (e.g. Na_2O_2)
- RuO_4 is volatile
    - Ru is industrially separated from other (platinum group) metals by distillation of RuO_4

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2

Compounds – oxides

Ruthenium(IV) oxide, $\mathbf{RuO_2}$

- Blue-black solid, rutile structure
  - Color potentially from mixed valency
- Used in mixed metal oxide electrodes, catalyst for oxygen evolution reaction

Ruthenium(VIII) oxide, $\mathbf{RuO_4}$

- Melting point 25.5 °C, tetrahedral molecule
- Aggressive oxidant
  - Similar to OsO_4, though Ru(VIII) less stable than Os(VIII)

Greenwood and Earnshaw, Chemistry of the Elements (2nd edition), Elsevier, 1997 https://doi.org/10.1016/C2009-0-30414-6

Seymour and O'Farrelly, Platinum-Group Metals in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-VCH, 2012 https://doi.org/10.1002/0471238961.1612012019052513.a01.pub3

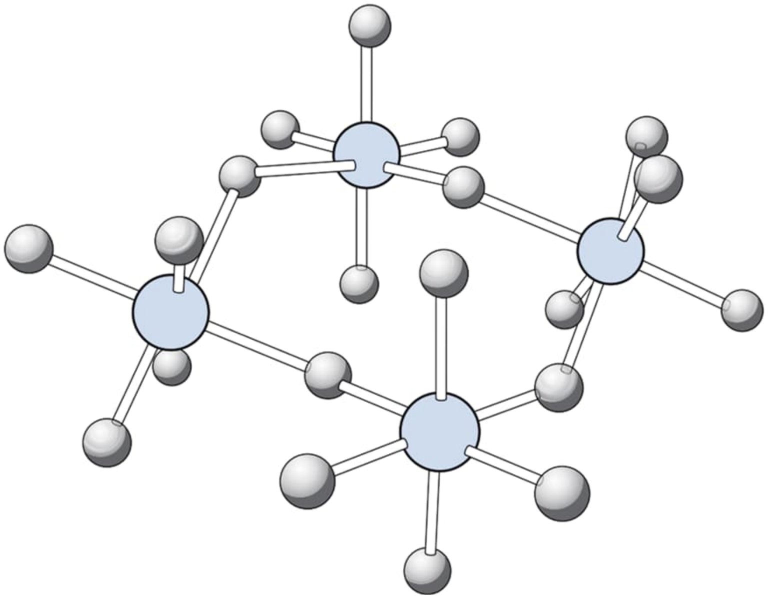
Rao et al., Operando identification of site-dependent water oxidation activity on ruthenium dioxide single-crystal surfaces, *Nature Catalysis*, 2020 https://doi.org/10.1038/s41929-020-0457-6

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018 https://doi.org/10.1002/9783527306732.a21_075.pub2

Compounds – binary inorganic

Ruthenium(V) fluoride, **RuF_5**

- Tetramer, **Ru_4F_{20}**
  - Corner-sharing octahedral units
  - Common for other 4d and 5d metals in groups 8, 9, and 10



Text
Rayner-Canham and Overton, Descriptive Inorganic Chemistry (5th edition), W.H. Freeman and Company, 2010

Greenwood and Earnshaw, Chemistry of the Elements (2nd edition), Elsevier, 1997 https://doi.org/10.1016/C2009-0-30414-6

Figure
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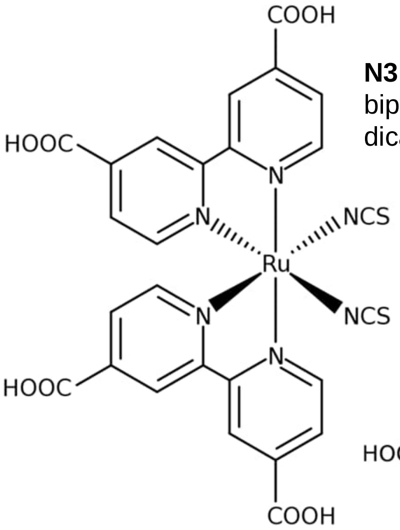
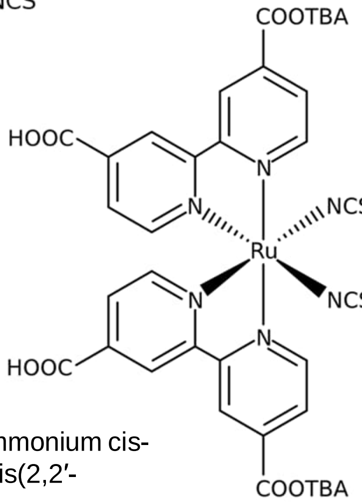
Compounds – complexes

Organometallic Ru(II) dyes

- Various options, e.g. N3 and N719
- Combined to a wide band gap semiconductor in dye-sensitized solar cells



N3 Cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)



N719 Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)

Text

Rhee and Kwon, Key technological elements in dye-sensitized solar cells (DSC), *Korean Journal of Chemical Engineering*, 2011 https://doi.org/10.1007/s11814-011-0148-8

Gurunathan, Maruthamuthu, and Sastri, Photocatalytic hydrogen production by dye-sensitized Pt/SnO_2 and Pt/SnO_2/RuO_2 in aqueous methyl viologen solution, *International Journal of Hydrogen Energy*, 1997 https://doi.org/10.1016/S0360-3199(96)00075-4

Figures

https://commons.wikimedia.org/wiki/File:N3_Dye_01.svg [accessed 28.9.2022]
https://commons.wikimedia.org/wiki/File:N719_Dye_01.svg [accessed 28.9.2022]

Applications – heterogeneous catalysis (1/2)

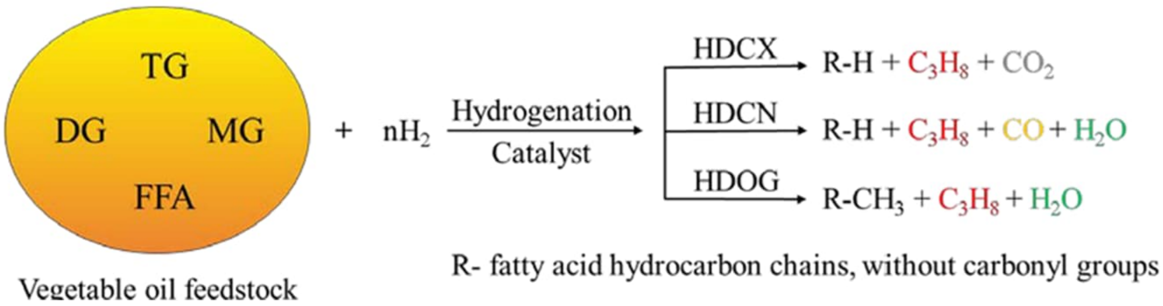
- Ru displays catalytic activity in several industrially relevant reactions - especially those related to **hydrogenation**
  - Ammonia synthesis
  - Methanation
  - Fischer-Tropsch synthesis
  - HDO, HDN..
- Active Ru phases: **reduced**, oxide, sulfide…
- Typically paired with a catalyst support (e.g. Al_2O_3, ZrO_2…) to decrease the prize, improve the dispersion and introduce bifunctionality
- Major drawback: prize, prone to deactivation
- (In practice used less than Pt and Pd)

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2

Applications – heterogeneous catalysis (2/2)

- Hydrodeoxygenation (HDO) of vegetable oils and fatty acids to paraffinic renewable diesel
  - Commercial process (e.g. Neste) uses transition metal sulfide catalysts → require external sulfur additions to maintain activity in the hydrotreatment of renewable, sulfur free fuels
  - Ru (and other PGM) are active in their reduced state and at lower temperatures → improved process safety, milder operating conditions possible

- Supported Ru catalysts are active in oxygen removal, and selective for the formation of C_{n-1} *n*-paraffins through decarbonylation (HDCN) and decarboxylation (HDCX) pathways



Malins, K., Synthesis of renewable hydrocarbons from vegetable oil feedstock by hydrotreatment over selective sulfur-free SiO_2-Al_2O_3 supported monometallic Pd, Pt, Ru, Ni, Mo and bimetallic NiMo catalysts, *Fuel* **285** (2021) 119129, https://doi.org/10.1016/j.fuel.2020.119129

Applications – dye-sensitized solar cells

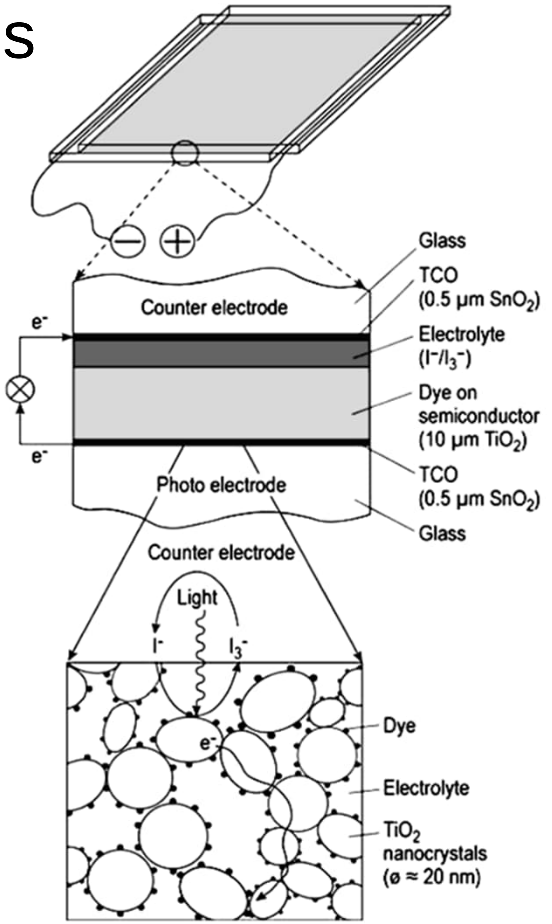
Third-generation photovoltaic cells

First-generation systems

- Crystalline silicon
- Low tolerance of defects → high purity requirements → expensive

DSSC

- Wide band gap semiconductor sensitized with, e.g., Ru based dye
- Potential for lower manufacturing costs

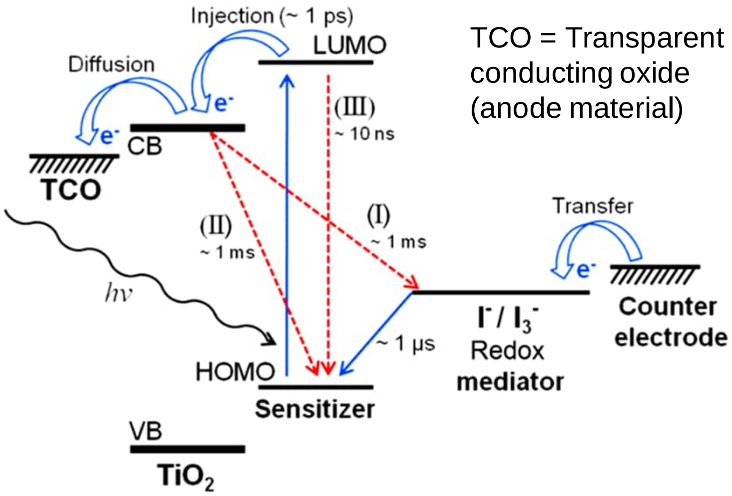


Text
Grätzel, Highly Efficient Nanocrystalline Photovoltaic Devices, *Platinum Metals Review*, 1994
Rhee and Kwon, Key technological elements in dye-sensitized solar cells (DSC), *Korean Journal of Chemical Engineering*, 2011
https://doi.org/10.1007/s11814-011-0148-8

Figure
Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2, originally published in Grätzel, Highly Efficient Nanocrystalline Photovoltaic Devices, *Platinum Metals Review*, 1994

Applications – dye-sensitized solar cells

- Dye absorbs incident light, excitation from HOMO to LUMO
- Electrons injected from excited dye to the TiO_2 conduction band
- Diffusion of electrons to anode
- Electrons donated by electrolyte to dye, dye reduced to initial state
- Electrolyte reduced back at counter electrode



TCO = Transparent conducting oxide (anode material)

Text and figure
Rhee and Kwon, Key technological elements in dye-sensitized solar cells (DSC), *Korean Journal of Chemical Engineering*, 2011
https://doi.org/10.1007/s11814-011-0148-8

Applications – dye-sensitized photovoltaics for hydrogen production

The photovoltage produced with a dye-sensitized system can be utilized directly for hydrogen production

Combination of two photo-systems

- Nanocrystalline WO_3 film
  - Band gap excitation creates valence band holes → water oxidation
- Dye-sensitized, nanocrystalline TiO_2 film
  - Photovoltage production → hydrogen formation

Renner et al., Platinum group metals and compounds in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH, 2018
https://doi.org/10.1002/9783527306732.a21_075.pub2

Thank you!