

Progress in Ruthenium Complexes for Dye Sensitised Solar Cells

The need to move towards a low carbon economy has led to unprecedented interest in renewable energy sources, including solar power. One type of solar cell, the dye sensitised solar cell (DSSC), first reported in 1991 by Michael Grätzel and coworkers at the Ecole Polytechnique Fédérale de Lausanne (1), is a photoelectrochemical device which contains ruthenium in the photoanode and platinum in the counter electrode. It therefore represents another example of a platinum group metal-based sustainable technology. In this review, DSSC technology is briefly discussed to provide some context for selected examples of recent patent activity.

Background

Historically, conventional solar cells have relied on a solid semiconductor to perform the dual function of light absorption and charge conduction, imposing strict requirements on the composition and purity of materials used (2). DSSCs, by contrast, use a monolayer of photosensitive ruthenium-based dye adsorbed on a thin layer of nanocrystalline titanium dioxide (TiO_2) to harvest light and, as a result, have comparatively low manufacturing costs. They can take the form of thin, flexible and transparent sheets, making them useful in applications such as building-integrated power sources (3). Furthermore, they perform effectively in dim and diffuse light (1), allowing for use indoors and in mobile electronic devices.

These advantages largely offset the lower efficiency of DSSCs, which stands at a record of 10% to 11% (3–5) – significantly lower than the 15% to 18% achieved by the widely-used polycrystalline silicon cell (6). Efforts are continually being undertaken to improve the efficiency and hence the competitiveness of the technology.

Overall cell efficiency is subject to a number of factors, but fundamental considerations relating to the dye are: firstly, how efficiently the molecules absorb incident photons; secondly, how efficiently these photons are converted to electron-hole pairs;

and thirdly, how effectively charge separation and collection occurs (2). The most efficient DSSCs demonstrated to date have all been based on ruthenium dyes developed by the Grätzel group: the N3, N719 and ‘black’ dyes (4) (Figure 1 (4, 7)). As well as superior light harvesting properties and durability, a considerable advantage of these dyes lies in the metal-ligand charge transfer (MLCT) transition, through which the photoelectric charge is injected into the TiO_2 . For these ruthenium complexes, this transfer takes place at a much faster rate than the back reaction, in which the electron recombines with the oxidised dye molecule rather than flowing through the circuit and performing work (2).

Conversion efficiency of absorbed photons is also very high, and offers little room for improvement (2, 8). Therefore, continued research efforts are largely focused on improving the absorption of incident light. This can be achieved by manipulating the dye’s molecular structure to either increase the degree of absorption of photons in the functional wavelength range (as measured by the molar extinction coefficient, ϵ), or to extend the functional range – ideally, to within the near infrared (N-IR) region (9). Here, we have selected three patents, all claiming novel ruthenium complexes for application to DSSCs, to demonstrate strategies currently being investigated in this area.

Novel Ruthenium Dye Complexes

The first example, filed by Dongjin Semichem Co, Ltd, South Korea (7), claims a number of new complexes based on the N3 structure. The structure has been altered by replacing one or both of the COOH groups on at least one of the bipyridyl ligands with a range of more highly π -conjugated moieties. The absorption spectra of six examples of the new complexes are presented, and the values of ϵ for three of the new dyes indicate a significant improvement in absorption: in one embodiment $\epsilon = 22,640 \text{ M}^{-1} \text{ cm}^{-1}$ at 533 nm, compared to values of between $14,000 \text{ M}^{-1} \text{ cm}^{-1}$ and $15,000 \text{ M}^{-1} \text{ cm}^{-1}$ for

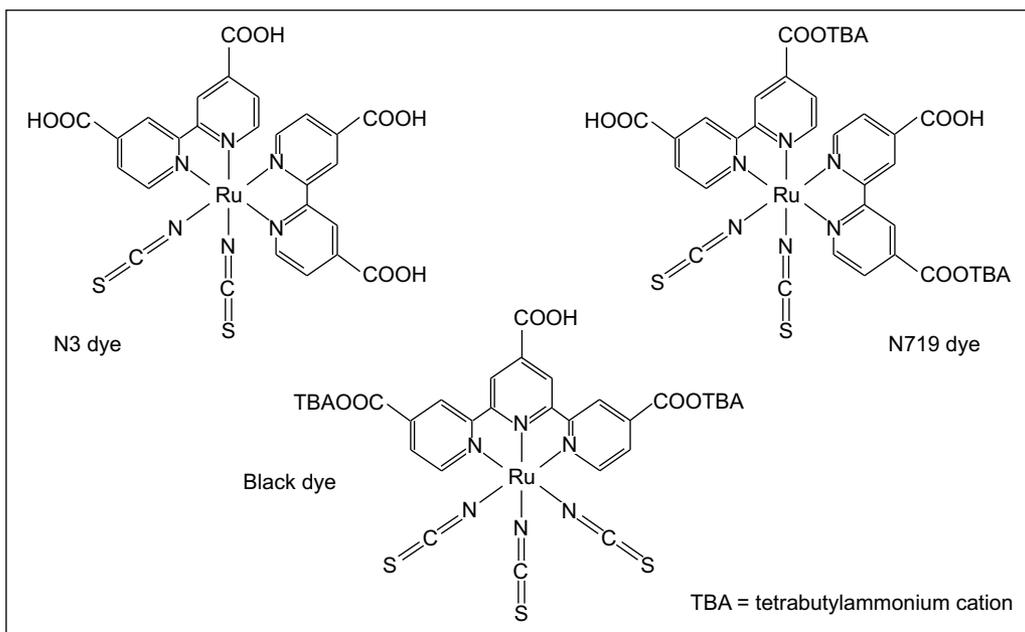


Fig. 1 Structures of the ruthenium-based dyes N3, N719 and 'black dye' developed by the Grätzel group (4, 7)

N3 and N719 at ~ 535 nm (8, 10). In two other embodiments, ϵ values of $\sim 21,000 \text{ M}^{-1} \text{ cm}^{-1}$ to $22,500 \text{ M}^{-1} \text{ cm}^{-1}$ are achieved at wavelengths longer than 550 nm, indicating a shift towards longer wavelengths. These improvements do not appear to translate into increased cell efficiency and values given for short-circuit current density (J_{sc}) and open circuit voltage (V_{oc}) are lower than for the established dye. However, an interesting point to note is the possibility of using a combination of dyes, an approach which may allow greater flexibility in optimising both absorption and range.

An application filed by Türkiye Sise ve Cam Fabrikalari AS, Turkey (11), aims in one embodi-

ment to increase ϵ through extended π -conjugation and a double core. A ruthenium dimer structure is claimed, designated K20 (Figure 2) and described as having $\epsilon = 22,000 \text{ M}^{-1} \text{ cm}^{-1}$. The wavelength at which this measurement is taken is not given, although elsewhere the authors show that the longest-wavelength absorption peak occurs at 520 nm. This ϵ value is again higher than values for N3 and N719 at similar wavelengths. Overall efficiency is also good, being comparable to the existing dyes.

The technique of increasing conjugation through the use of larger and more complex ligands is again demonstrated by a patent granted in 2009 to inventors from Everlight Chemical

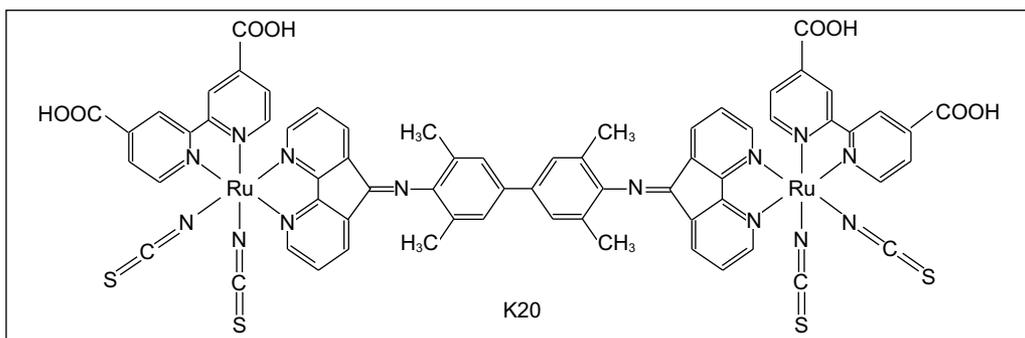


Fig. 2 Structure of a novel ruthenium dimer dye complex (11)

Industrial Corp (U.S.A.) and Academia Sinica in Taiwan (12). The complexes claimed here are also based on N3, with one of the ligands modified to a structure with additional aromatic rings and, in some embodiments, containing alkyl chains. The inventors present the results of comparative tests of one of the complexes (shown in Figure 3) against N719: at the longest peak wavelength (~ 530 nm), ϵ is increased to $14,007 \text{ M}^{-1} \text{ cm}^{-1}$ (from $12,617 \text{ M}^{-1} \text{ cm}^{-1}$ quoted for N719) and a slight redshift in the absorption spectrum is seen. The values claimed for J_{sc} and V_{oc} are very similar to those achieved using N719, and the overall cell efficiency is also comparable to the existing dyes.

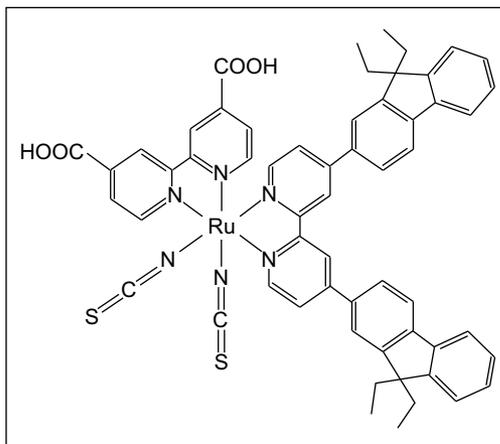


Fig. 3 A modified complex based on the ruthenium dye N3 (12)

Concluding Remarks

It is clear that research into dyes for DSSCs is progressing and new ruthenium-based structures continue to be reported. Although alternative dyes have been developed, including non-metal organic dyes (13) and dyes based on iron and zinc (14, 15), these have so far proved inferior to the ruthenium dyes (4). Dyes formulated from platinum and iridium complexes are also showing some promise (16, 17), but this research is still in the early stages. With this in mind, the most promising current strategy is to increase the efficiency of light absorption at the molecular level by modifying or enhancing the established ruthenium-based dyes, which still hold their place at the forefront of the technology. The improved light absorption

achieved in the patents discussed here holds promise for increased cell efficiency, which may be realised with further refinements. With DSSCs now at the pilot scale and seeing increasing commercial investment (18–21), developments in this area will be watched with interest.

M. RYAN

References

- 1 B. O'Regan and M. Grätzel, *Nature*, 1991, 353, (6346), 737
- 2 M. Grätzel, *Platinum Metals Rev.*, 1994, 38, (4), 151
- 3 M. Grätzel, *Innovation*, 2007, 7, (3), cover story
- 4 Z. Jin, H. Masuda, N. Yamanaka, M. Minami, T. Nakamura and Y. Nishikitani, *J. Phys. Chem. C*, 2009, 113, (6), 2618
- 5 Md. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, 123, (8), 1613
- 6 K. Bullis, 'More Efficient, and Cheaper, Solar Cells', Technology Review, MIT, U.S.A., 14th September 2009: <http://www.technologyreview.com/energy/23459/>
- 7 H. Bae, C. Lee, J. Baek and H. Yang, Dongjin Semichem Co Ltd, 'Novel Ru-Type Sensitizers and Method of Preparing the Same', *World Appl.* 2009/082,163
- 8 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, 115, (14), 6382
- 9 Y. Liu, H. Shen and Y. Deng, *Front. Mater. Sci. China*, 2007, 1, (3), 293
- 10 Md. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer and M. Grätzel, *Inorg. Chem.*, 1999, 38, (26), 6298
- 11 S. Icli, C. Zafer, K. Ocakoglu, C. Karapire, B. Yoldas, Y. Teoman and B. Kuban, Türkiye Sise ve Cam Fabrikalari AS, 'Novel Ruthenium Complex Photosensitizers for Dye Sensitized Solar Cells', *World Appl.* 2009/078,823
- 12 J.-T. Lin, Y.-C. Hsu, Y.-S. Yen and T.-C. Yin, Everlight USA, Inc and Academia Sinica, 'Ruthenium Complex', *U.S. Patent* 7,538,217; 2009
- 13 K.-J. Jiang, K. Manseki, Y. Yu, N. Masaki, J.-B. Xia, L.-M. Yang, Y. Song and S. Yanagida, *New J. Chem.*, 2009, 33, (9), 1973
- 14 S. Ferrere, *Inorg. Chim. Acta*, 2002, 329, (1), 79
- 15 Q. Wang, W. M. Campbell, E. E. Bonfantani, K. W. Jolley, D. L. Officer, P. J. Walsh, K. Gordon, R. Humphry-Baker, Md. K. Nazeeruddin and M. Grätzel, *J. Phys. Chem. B*, 2005, 109, (32), 15397
- 16 E. A. M. Geary, L. J. Yellowlees, L. A. Jack, I. D. H. Oswald, S. Parsons, N. Hirata, J. R. Durrant and N. Robertson, *Inorg. Chem.*, 2005, 44, (2), 242
- 17 E. Baranoff, J.-H. Yum, M. Grätzel and Md. K. Nazeeruddin, *J. Organomet. Chem.*, 2009, 694, (17), 2661
- 18 Dyesol: <http://www.dyesol.com/>
- 19 G24 Innovations: <http://www.g24i.com/>
- 20 3GSolar Ltd, Solar Energy Modules: <http://3gsolar.com/>
- 21 Solaronix SA: <http://www.solaronix.com/>