

3. Injected electrons in the conduction band of TiO_2 are transported between TiO_2 nanoparticles with diffusion toward the back contact (TCO) and consequently reach the counter electrode through the external load and wiring.
4. The oxidized photosensitizer (S^+) accepts electrons from the I^- ion redox mediator, regenerating the ground state (S), and I^- is oxidized to the oxidized state, I_3^- .



5. The oxidized redox mediator, I_3^- , diffuses toward the counter electrode and is re-reduced to I^- ions.



Overall, electric power is generated without permanent chemical transformation.

The performance of a DSSC is predominantly based on four energy levels of the component: the excited state (approximately LUMO) and the ground state (HOMO) of the photosensitizer, the Fermi level of the TiO_2 electrode, which is located near the conduction-band level, and the redox potential of the mediator (I^-/I_3^-) in the electrolyte. The photocurrent obtained from a DSSC is determined by the energy difference between the HOMO and the LUMO of the photosensitizer, analogous to the band gap, E_g , for inorganic semiconductor materials. The smaller the HOMO–LUMO energy gap, the larger the photocurrent will be because of the utilization of the long-wavelength region in the solar spectrum. The energy gap between the LUMO level and the conduction-band level of TiO_2 , ΔE_1 , is important, and the energy level of the LUMO must be sufficiently negative with respect to the conduction band of TiO_2 to inject electrons effectively. In addition, substantial electronic coupling between the LUMO and the conduction band of TiO_2 also leads to effective electron injection. The HOMO level of the complex must be sufficiently more positive than the redox potential of the I^-/I_3^- redox mediator to accept electrons effectively (ΔE_2). The energy gaps, ΔE_1 and ΔE_2 , must be larger than approximately 200 mV as driving force for each of the electron-transfer reactions to take place with optimal efficiency [16].

In the case of solid–liquid junction solar cells, PSCs, the voltage is attributed to the energy gap between the Fermi level (near conduction-band level for *n*-type semiconductor) of the semiconductor electrode and the redox potential of the mediator in the electrolyte. As shown in Figure 15.6, the voltage in the DSSC is developed by the energy gap between the Fermi level of a TiO_2 electrode and the redox potential of the I^-/I_3^- in the electrolyte. The conduction-band level of the TiO_2 electrode and the redox potential of I^-/I_3^- were estimated to be -0.5 V versus normal hydrogen electrode (NHE) and 0.4 V versus NHE, respectively, as shown in Figure 15.6 [18] (or -0.7 V versus saturated calomel electrode (SCE) and 0.2 V versus SCE, respectively [12, 16]). Thus, in the case of a DSSC using a TiO_2 electrode and I^-/I_3^- redox mediator, the maximum voltage is expected to be approximately 0.9 V, depending on the electrolyte component because the Fermi level of the TiO_2 electrode depends on the electrolyte components and their concentrations.

In contrast to a conventional *p-n*-type solar cell, the mechanism of a DSSC does not involve a charge-recombination process between electrons and holes because electrons are only injected from the photosensitizer into the semiconductor and a hole is not formed in the valence band of the semiconductor. In addition, charge transport