level of the semiconductor. For example, the rate constant for electron injection, k_{inj}, is given by Fermi's golden rule expression

$$k_{\text{inj}} = \left(\frac{4\pi^2}{h}\right)|V|^2\rho(E) \tag{15.5}$$

where V is the electronic coupling between the photosensitizer and the semiconductor, $\rho(E)$ is the density-of-states of the conduction band, and h is the Planck constant. The value of V is attributed to overlap between the wavefunction of the excited states of the photosensitizer and the conduction band, and it depends largely on the distance between the adsorbed photosensitizer material and the semiconductor surface. In a DSSC, the photosensitizer is strongly adsorbed on the semiconductor surface with carboxyl groups as the anchor, resulting in a very large V between the π^* orbital of the excited state of the photosensitizer and the conduction band of TiO_2, which consists of the unoccupied 3d orbital of Ti^{4+}. In addition, the conduction band of the semiconductor has a continuous and relatively large density-of-states. Thus, electron injection from the photosensitizer to the semiconductor occurs at a higher rate than does the relaxation from the excited state to the ground state (i.e. relaxation via the emission lifetime). For example, it has been observed that electron injection from N3 dye into TiO_2 occurs on the order of femtoseconds as measured by the time-resolved laser spectroscopy [28, 32]. This ultrafast rate of electron injection contributes to the high energy-conversion efficiencies of the DSSC.

In addition, the rate constant for electron injection depends largely on the semiconductor materials employed. A slower electron injection rate was observed with coumarin dyes and N3 dye injected into ZnO compared to the TiO_2 system [35, 37, 45]. The different rate constant may be caused by the difference in the electronic coupling between the π^* orbital of the dye and the accepting orbitals in ZnO and TiO_2 and/or their density-of-states. The states near the conduction-band edge of ZnO consist of the 4s orbitals of Zn^{2+}, while those of TiO_2 consist of the 3d orbitals of Ti^{4+}, which may result in the observed difference in their electronic coupling with the π^* orbital of the dye.

15.1.4.2 Charge recombination

The charge-recombination process (Figure 15.9) between injected electrons and oxidized dyes must be much slower than electron injection and electron transfer from I^- ion into oxidized dyes (i.e. regeneration of dyes) to accomplish effective charge separation. It was reported that charge recombination between injected electrons on TiO_2 and cations of N3 dye occurs on the order of microseconds to milliseconds, in contrast with ultrafast electron injection [28, 39, 40, 48–50]. The much slower charge recombination compared to electron injection leads to effective charge separation and consequently high cell performance. Charge recombination in the N3 dye/TiO_2 system is derived from electron transfer from TiO_2 to Ru(III), while electron injection occurs because of electron transfer from the bipyridyl ligand to TiO_2. Thus, it is considered that long-distance electron transfer from TiO_2 to the Ru metal center leads to a much smaller electron-transfer rate.