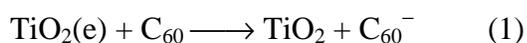


**C₆₀/C₆₀⁻ Redox couple as a probe in the
Determination of Fermi Level of
Semiconductor Nanoparticles**

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Oxide semiconductor colloids (TiO₂, and WO₃) are capable of undergoing charge storage under UV-irradiation. The accumulation of electrons dictate the Fermi level of the semiconductor nanoparticle. These stored electrons can be titrated using C₆₀. With increasing addition of C₆₀ solution to UV-irradiated TiO₂ colloids, we observe a decrease in the absorption at 700 nm with simultaneous appearance of C₆₀⁻ absorption at 1075 nm.



At higher concentration of C₆₀, the reduction ceases as C₆₀/C₆₀⁻ redox couple attains equilibrium with the electrons stored within the TiO₂ particles.

By employing C₆₀/C₆₀⁻ as a redox couple we were able to probe the apparent Fermi level of TiO₂ and TiO₂/Au nanoparticles. Under equilibrium conditions the Fermi level of the semiconductor particle can be related to the ratio of the [C₆₀]/[C₆₀⁻] by the expression (2),

$$E_{\text{F}}(\text{TiO}_2(\text{e})) = E_{\text{fb}} = E^0(\text{C}_{60}/\text{C}_{60}^-) + 0.059 \log [\text{C}_{60}]/[\text{C}_{60}^-] \quad (2)$$

By substituting the values of [C₆₀⁻] and [C₆₀] and E⁰(C₆₀/C₆₀⁻) as -0.25 V vs. NHE, we obtained the values of E_F for TiO₂ and TiO₂-Au systems. The E_F for TiO₂ was determined to be -0.192 V vs. NHE. In the presence of gold nanoparticles, E_F shifts to more negative potentials -0.215 V.

In the case of TiO₂-Au system the efficiency of charge separation improves as the electrons are distributed between TiO₂ and Au nanoparticles. As the electrons are transferred to gold nanoparticles, the Fermi level of the composite shifts to more negative potential ultimately equilibrating with that of TiO₂ nanoparticle. The E_F value determined for TiO₂-Au composite is about 22 mV more negative than that of TiO₂. This negative shift in Fermi level implies higher degree of electron accumulation in the Au-TiO₂ composite. Such a higher degree of electron accumulation in turn elucidates the indirect role of noble metals towards improving the charge separation as well

as promoting the interfacial charge transfer kinetics in semiconductor photocatalysis.

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