PHOTOPHYSICS AND PHOTOCHEMISTRY OF $Cd(OH)_2$ COATED QUANTIZED CdS AND COLLOIDAL CdS -TiO_2 SEMICONDUCTORS - STUDY OF CERTAIN REDOX REACTIONS AT THEIR INTERFACE

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Abstract

Coating of $Cd(OH)_2$ on CdS particles enhances their photostability, luminescing efficiency and emission lifetime .These particles were found to be inactive as sensitizer for most of the redox couples. It, however, initiated the photochemical reactions of tryptophan and indole-3-acetic acid like substrates . In case of tryptophan ,the photogenerated hole on the particle was intercepted by the bulk substrate ($\phi_{-tryp} = 0.22$) to produce 5- hydroxytryptophan ($\phi_{0H-\ tryp} = 0.08$) as one of the main products of oxidation .The presence of tryptophan quenches the bandgap emission of CdS and reduces its emission lifetime. Emission experiments indicated the nature of reactive hole in stoichiometric Q-CdS to be different to that of $Cd(OH)_2$ coated Q-CdS . Shallowly trapped hole has been assigned to participate in the oxidation via hydrogen bonding interaction involving the surface of the particle and the substrate.

The coupling of $Cd(OH)_2$ coated Q-CdS with colloidal TiO_2 causes the quenching of the bandgap emission of CdS but the red emission is not affected appreciably . For a typical $2x10^{-4}$ mol dm^{-3} of TiO_2 , the average emission lifetime is reduced from 26.4 ns to 6.8 ns . The extent of charge separation in the photocatalyst is affected by concentration of both TiO_2 and the redox couple. Charge carriers trapped in shallow traps are efficiently scavenged by the indole-O_2 redox couple to produce indigo with a quantum efficiency of 0.08 . Doping of Ag^+($3.5x10^{-7}$ mol dm^{-3}) to TiO_2 prior to coupling with $Cd(OH)_2$ coated Q-CdS enhances the ϕ_{indigo} to 0.15 whereas about three fold higher silver (9×10^{-6} mol dm^{-3}) was needed to be doped to the $Cd(OH)_2$ coated Q-CdS to cause the catalytic effect of similar magnitude . For Ag^+, Cu^{2+} and Mn^{2+}, the order of catalytic activity was found to be $Ag^+ > Cu^{2+} > Mn^{2+}$. Higher catalytic action of Ag^+ is understood in terms of the positive redox potential of the Ag^+/Ag couple which intercepts the conduction band electrons and reduces the $e^- - h^+$ recombination . Mechanism of the studied reactions will be discussed .