Ru^{III}(edta)] (edta^{4-} = ethylenediaminetetraacetate) mediates photocatalytic conversion of bicarbonate to formate over visible light irradiated non-metal doped TiO₂ semiconductor photocatalysts

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S1. Surface modification of TiO₂ semiconductor particles with [Ru^{III}(edta)] catalyst complex

Surface modification of TiO₂ semiconductor particles with [Ru^{III}(edta)] catalyst complex was achieved by the following procedure. TiO₂ powder (500 mg) was added into an aqueous solution of [Ru^{III}(edta)] complex (1.0 mM). The resulting solution was stirred magnetically for over 5 h, to allow the complex to adsorb onto the TiO₂. The pH of the mixture was kept at 5.0 (by using 0.1M HCl / 0.1M NaOH). It was then filtered, washed twice with distilled water and dried at room temperature. The uptake of the [Ru^{III}(edta)] complex by the surface of TiO₂ was estimated spectrophotometrically by measuring the difference in absorbance of free [Ru^{III}(edta)] complex in aqueous solution with that of the supernatant liquid obtained after filtration, which was found to be 3.20 µmol/g. For C-TiO₂, N-TiO₂ and S-TiO₂ samples, the values of [Ru^{III}(edta)] uptake are 3.11 µmol/g, 3.17 µmol/g and 3.22 µmol/g, respectively.

Fig. S1 IR Spectra of (↑) Ru(edta) complex and (↓) Ru(edta) adsorbed in TiO₂ surface
Fig.S2. Diffuse reflectance spectra of the catalyst sample collected (by filtration) after the completion of the catalytic reaction.

Fig.S3. Diffuse reflectance spectra of (a) [Ru^{III}(edta)pz)] surface adsorbed TiO$_2$ and (b) [Ru^{II}(edta)pz)] surface adsorbed TiO$_2$ semiconductor photocatalysts.