Tetracyanoquinodimethane and Dawson-Type Polyoxometalates as Catalysts for Water Oxidation in Ionic Liquid Media

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The synthesis of exceptionally long semiconducting silver tetracyanoquinodimethane (AgTCNQ) nanowires has been achieved in the room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) by photochemical reduction of TCNQ to TCNQ⁻. The presence of Ag(I) in the ionic liquid allows formation of mm length AgTCNQ nanowires onto both conducting and insulating surfaces, via a nucleation and diffusion-controlled growth mechanism. Remarkably, photocrystallization is achieved using adventitious water present in the ionic liquid as the sacrificial electron donor. Oxidation of water produces O₂ as the counter reaction in the photoreduction of TCNQ. In contrast, irradiation in “dried” ionic liquids fails to induce any detectable photochemistry. Molecular structural differences, relative to the situation encountered in more conventional solvent media, are believed to account for the more favorable kinetics available for oxidization of water in ionic liquids.

Many polyoxometalates also photoactive and rich in their redox chemistry. We now show that photoreduction of [S₂Mo₁₈O₆₂⁻]⁴⁻ can be achieved in molecular solvents or ionic liquids, with adventitious or deliberately added water present in the solvent acting as an electron donor:

\[
[S₂Mo₁₈O₆₂]^{4⁻} + h\nu \rightarrow [S₂Mo₁₈O₆₂]^{5⁻}
\]

\[
2[S₂Mo₁₈O₆₂]^{4⁻} + H₂O \rightarrow 2[S₂Mo₁₈O₆₂]^{5⁻} + \frac{1}{2} O₂ + 2H^+
\]

Photoreduction of [S₂Mo₁₈O₆₂]^{4⁻} to [S₂Mo₁₈O₆₂]^{5⁻} was confirmed by rotating disk electrode voltammograms and visually by colour change, while the Clark-type electrode conferred the evolution of oxygen. In contrast, photoreduction of other Dawson-type polyoxometalates of interest in this study, [P₂W₁₈O₆₂]⁶⁻ and [S₂W₁₈O₆₂]⁴⁻, does not occur in neat water or when water is present in an organic solvent. However, it does occur when these polyoxometalates are dissolved in either protic or aprotic room temperature ionic liquids containing water.

These studies highlights the significant role that water present as an adventitious impurity may play in photochemical studies in ionic liquids, and also suggest that ionic liquids may provide a favorable environment for photochemically based water splitting.