Structural Analysis of Platinum Nanoclusters Accumulated by Photosystem I Photo-reduction via the X-Ray Scattering Techniques

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Photosystem I (PSI) is one of the major protein complexes sustaining the photoinduced electron transfer reactions in the conversion of the energy of solar electromagnetic radiation to the energy of chemical bonds in the process of photosynthesis. The accumulated under the influence of light potential for reduction reaction in this protein-cofactor assembly can be redirected from natural electron carriers to alternative acceptors. Such deviation, while retaining the exceptional ability for electron transfer, imparts novel functionality to photosynthetic complexes. One of the most inspiring applications of the reducing ability of PSI is the photo-precipitation of metallic platinum from its solution and thus functionalization of this protein by a nanocluster complex capable of catalyzing the consequent hydrogen evolution reaction. After first demonstrated about 50 years ago [Elias Greenbaum, Platinized Chloroplast: A novel photocatalytic material. Science 1985, 230, 1373-1375], this approach has been further corroborated in succeeding works, and the utilizing it systems were found to be stable and viable.

While the light-induced effect of platinization was known and utilized for the catalysis of subsequent hydrogen evolution reactions, the atomic structure of formed abiotic clusters certainly needed investigation for innovative implementations. Since photo-reduction was expected to produce the non-crystalline or semi-crystalline substance in solution, its structural characterization by application of traditional diffraction methods, where a periodic arrangement of elements is the prerequisite for analysis, was very challenging and the rational explanation for the lack of atomic structural investigations up to now.

The development of X-ray total scattering and corresponding Pair Distribution Function analysis made a structural study of materials in solution feasible and they become powerful techniques for the atomic structure characterization of nanomaterials, including amorphous clusters. The application of this approach for the examination of Pt nanoclusters accumulated by photo-reaction provided adequate information for elucidation of the internal structure of produced nanodiscs and for the modeling to be carried out. The investigation of the photo-precipitation of platinum using X-ray scattering complemented by High-angle annular dark-field scanning transmission electron microscopy and Energy dispersive X-ray spectroscopy facilitated the search for insight into the bio-inorganic interfaces on which this reaction is taking place, the sites for reductive electron transfer chemistry on the PSI surface.