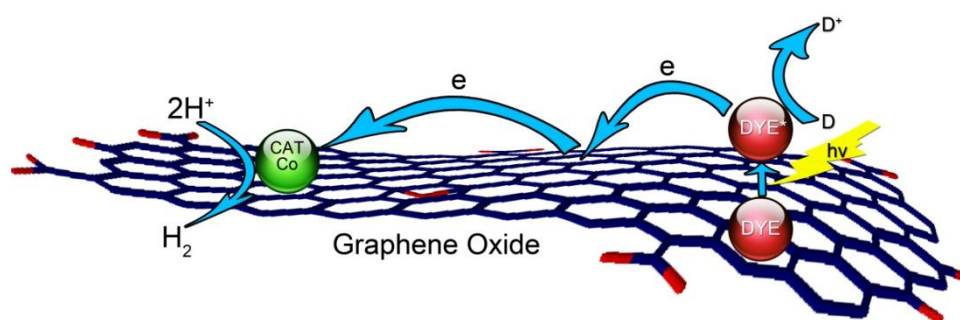


The conversion of solar energy into fuels through photochemical water splitting is considered to be a viable solution to global energy problems. Basically, the water splitting reaction can be divided into two half reactions: water oxidation ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) and water reduction ( $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$ ). Hydrogen is considered to be fuel of the future because chemical energy stored in the H–H bond is easily released when it reacts with oxygen, producing only water. The photochemical production of  $\text{H}_2$  by water splitting has been eagerly pursued by many scientists for decades. The photoinduced hydrogen generation from aqueous protons can be accomplished by systems containing a photosensitizer, an electron relay, a sacrificial electron donor and a heterogeneous or homogeneous catalyst. The important problem for large-scale  $\text{H}_2$  production is to produce high-efficiency, low cost, and robust catalytic systems. The photo-to-energy conversion efficiency is also low owing to the poor electron transport between the dye and the catalyst. **To address those setbacks we intend in this project to investigate hydrogen generation in multicomponent hybrid nanomaterials (dye/graphene oxide/Co catalyst) derived entirely from earth-abundant materials.** By binding dye molecules and catalysts with graphene sheets, we intend to obtain novel graphene-based nanomaterials with the needed charge-separation properties and, thereby, enhance the activity toward hydrogen production. In general, the functionalization of graphene sheets with molecules (dye or catalyst) will be performed by both non-covalent and covalent interactions. The innovative element of this proposal is applying molecular cobalt complexes as catalysts instead of expensive Pt nanoparticles. It will be advantageous in the elucidation of detailed catalytic mechanisms including the detection of active intermediates for water reduction. It is of great interest to explore the detailed mechanistic picture for hydrogen generation and to identify the factors that limit the efficiency and stability of the prepared nanomaterials. A broader knowledge about the interactions and kinetic processes of electron injection from photoexcited sensitizers to graphene oxide will give us a chance to determine graphene's role in these systems.



*Fig. Schematic hydrogen evolution over dye/graphene oxide/Co cat. under visible light irradiation; D - sacrificial electron donor.*

For the achievement of the goals in the proposed project, we plan to employ: UV-vis absorption and fluorescence measurements, femto- and nanosecond time-resolved spectroscopy, spectro- and photoelectrochemical measurements, steady-state irradiation followed by product analyses with gas chromatographic and structural analyses of the prepared samples (X-ray photoelectron and Fourier Transform Infrared Spectroscopy; Atomic Force, Raman and Scanning Electron Microscopy).

Studies that we are going to undertake can make an interesting contribution to the fundamental research on graphene oxide's role in photocatalytic water splitting. We strongly believe that a complete mechanistic understanding will pave the way to efficient and stable designs for photocatalytic water splitting. Furthermore these studies will facilitate the identification of crucial factors that limit the efficiency of the overall system and provide promising results for future applications. From a practical standpoint, the development of a noble-metal-free system for hydrogen production is still a great challenge to be met, and thus this is a highly significant and important research topic. Thus our concept will further advance the state-of-the-art in the field. With this as background, the development of novel graphene-based photocatalytic materials, if successful, will be very useful especially in the context of the possible number of practical applications.