Researchers in the Shen group have collaborated with the Mazur group at Harvard to discover a method of fabricating micro- and nanometer sized structures on a variety of substrates.[1] The substrates used in this research include silicon wafers, various transition metals (Co, Fe, Ti, Cu), and also some semiconductors like GaAs. They are able to achieve this by using femtosecond pulsed laser irradiation. This method is able to form nano structures through the use of capillary waves propagating through a molten layer of substrate that forms after the interaction of the laser pulse and substrate. In the case of a silicon wafer, a 400nm laser pulse is mostly absorbed by a layer of silicon a few nanometers thick by the silicon/water interface. As a result of intense light being absorbed by such a thin layer of silicon, a plasma is formed at the silicon/water interface. Once this plasma equilibrates with its surroundings, it leaves a molten layer as mentioned above. When the molten layer cools and solidifies the capillary waves are trapped on the surface of the substrate. As more pulses are absorbed more capillary waves are formed. Therefore, the formation of the nano features that result from femtosecond pulsed laser irradiation are due to the interference of the capillary waves with one another[1]. With most of the substrates used in this research the resulting nano features are spikes on the surface, one exception to this is cobalt which will be mentioned later.

The characteristics of the nano spikes can be controlled by adjusting the experimental conditions. The fabrication of the spikes is dependent on the wavelength of the pulsed laser irradiation. When 400 nm wavelength light is used to irradiate the substrate the nano spikes form, but when the same substrate is irradiated with 800 nm wavelength light the nano spikes do not form. Another important aspect that controls the morphology of the nano features is the fluency of the laser. At 800 nm high fluency (>10 kJ/m^2), micrometer sized structures and nanometer sized holes form. When the fluency of the laser is between 4-10 kJ/m2 straight ripples form with a spacing equal to the laser wavelength. At lower fluence, 2-4 kJ/m^2, straight nano-ripples form with a spacing of about 120 nm. In both cases, the ripples form perpendicular to the polarization of the laser pulse. Lastly, when the fluence of the laser is below 2 kJ/m^2, no structure is observed on the surface. For cobalt, instead of forming nano-ripples it forms nano-grasses (1 kJ/m^2) and nano-flakes (5 kJ/m^2) which is also fluence dependent[2]. Another factor that effects the formation of the structures on the surface is the medium in which the substrate is irradiated in. For example, irradiation of the substrate in a medium filled with SF_6 gas or in a vacuum will lead to structures that differ in shape and size when compared to the substrate being irradiated in a liquid such as water. The reason for these differences relates back to the molten layer and the heat exchange dynamics of the substrate and the medium it is in[1].

Due the large number of substrates that form nano structures from the femtosecond pulsed laser irradiation, there are many applications that the irradiated substrates can serve. One application is to use nano-spikes to enhance the roughness of a titanium surface which can be used to accelerate the growth of bone cells[2]. Another application of the nano structured substrates is to act as a master for nanolithography to mass produce SERS sensors[3]. Of all the applications, arguably the most interesting is the use of nano structured cobalt microparticles for an artificial photosynthesis process.

As stated earlier, when cobalt is subjected to femtosecond pulsed laser irradiation it forms nano flakes or grasses on the surface depending on the fluency of the laser. These nano structures are much thinner than 100 nm and occupy about 1% of the particle, greatly increasing the surface area. When the cobalt microparticles are submerged under a thin layer of water in a cell pressurized with CO_2 then exposed to sunlight, a thin film of waxy/oily hydrocarbons will form on top of the water.

The water, the gas inside the container, and the solid hydrocarbon film were all analyzed by HNMR, GS-MS, and GC-TCD. The analysis of the wax/oil showed that various types of hydrocarbons are formed including alkanes, olefins, alcohols, and branched paraffins. Production rate of solid and liquid hydrocarbons is 50 mL per gram of cobalt per hour, which is 60 times higher than previously reported works. Additionally, those production rates reported by previous research are mostly for gaseous hydrocarbons[4].

Fabrication of nano structures on the metal substrate surface induces a surface enhanced Raman scattering (SERS) effect which is integral to the artificial photosynthesis process. The observation of SERS indicates that the nano structures can act as a nano lens that focuses light and increases the intensity of the light around the "tips" of the nano structures. The increased intensity around the tips gives the light enough energy to photodissociate CO_2 and H_2O molecules on the surface of the cobalt. However, it is not yet known if this photodissociation is single photon or multiple photon process. As a control experiment, silver nano structures were fabricated because of silvers well known ability for SERS. The researchers found that the silver was able to photodissociate H_2O and CO_2, but there was no formation of hydrocarbons. This alludes to the fact that silver is a poor catalyst for hydrocarbon formation, where as cobalt has been known to be a good catalyst for hydrocarbon formation and has demonstrated this in the Fischer-Tropsch process[5].

By optimizing the artificial photosynthesis process the researchers have discovered a way to efficiently store energy from sunlight in the form of hydrocarbons. This is achieved by using catalytic cobalt microparticles that have been subjected to femtosecond pulsed laser irradiation. Upon irradiation, nano structures are formed on the surface of the cobalt which increases its surface area and induces a SERS effect. Because of the enhanced intensity of light at the tips of the nano structures, the microparticles are able to photodissociate CO_2 and H_2O. The dissociated atoms recombine to form hydrocarbons.

Sources:

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