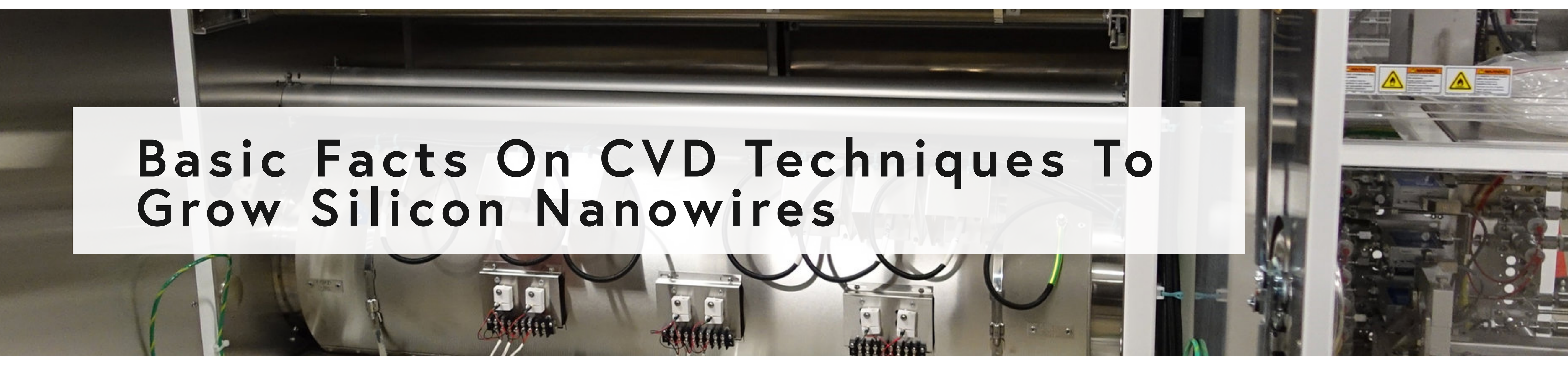
OneD BATTERY SCIENCES

SINANODE. SILICON NANOWIRE MOBILITY



Basic Facts On CVD Techniques To Grow Silicon Nanowires

Techniques to grow silicon nanostructures by decomposition of silane gas (SiH_4) into polycrystalline silicon nanowires ("Si NWs") and hydrogen (H_2) using CVD equipment are not new and were first described more than two decades ago. Yet, most of the scientific literature describes the CVD growth of Si NWs on planar substrates, such as silicon wafers or directly on electrode foils, in small quantities and at a high cost.

More than a decade ago, Nanosys pioneered the CVD growth of Si NWs on various carbon-based powders. A team led by Dr. Yimin Zhu perfected the equipment and processes during over a decade of intense R&D work, first at Nanosys and later at OneD Material ("OneD"), after OneD acquired all of the IP assets (hundreds of patents) and R&D facility from Nanosys in 2013.

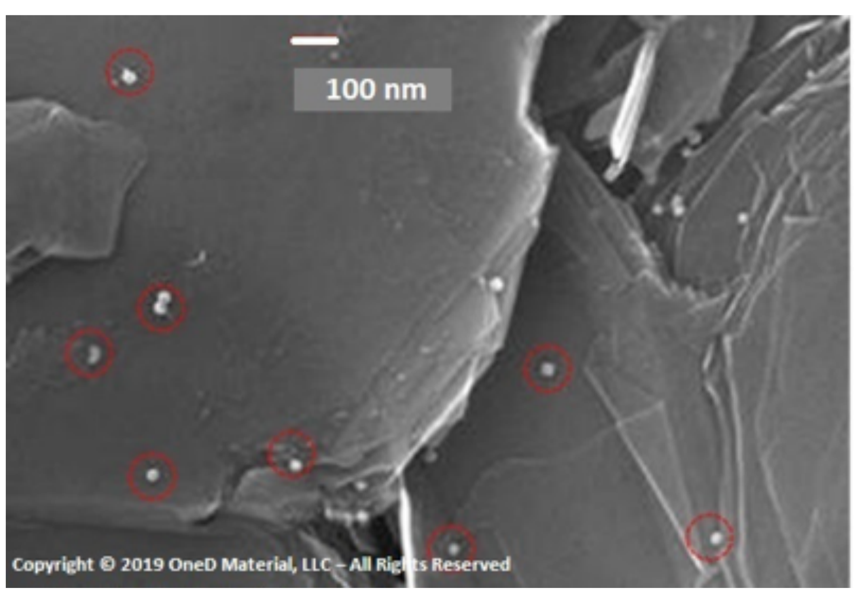
Dr. Yimin Zhu and his team focused on growing silicon nanowires directly onto the graphite particles of commercial graphite powders used by battery makers to coat the anode electrodes of lithium ion batteries. This pioneering work culminated in the ability to manufacture SINANODE® materials in large quantities (i.e. hundreds or thousands of tons per year), with high performance (greater specific capacity and longer reversible capacity retention than current SiOx-Graphite anodes), at an attractive cost (higher Ah/$). This work also resulted in many inventions and patent applications, including a patent application filed in 2011 and issued as US patent **10,243,207** on 26th of March 2019.

The lithium ion battery makers use very large quantities of graphite (well over 150,000 tons per year), which are produced from natural ore (natural graphite) or from the graphitization of petroleum coke (artificial or synthetic graphite). Since the commercial introduction of lithium ion batteries in 1992, the manufacturing of graphite powders has improved greatly, progressively increasing performance and decreasing costs. The leading suppliers each produce and sell annually well over 30,000 tons of synthetic graphite at less than $10/Kg.

The key performance metrics for high quality graphite are the specific capacity (measured in Ah/Kg or mAh/g) and the reversible capacity retention over 600 to 1000 cycles, even at higher charge-discharge rates. Over the last two decades, the specific capacity of high-performance commercial graphite active materials has improved by about 5% per year, reaching approximately 357 mAh/g a few years ago (the graphite theoretical maximum specific capacity is 372 mAh/g corresponding to the intercalation of 1 lithium ion per 6 of carbon, LiC_6).

To further increase the anode energy density, Dr. Yimin Zhu, Chief Technology Officer of OneD Material, started with a basic assumption: the SINANODE® manufacturing processes would leverage the best existing graphite active materials already in commercial use. Growing silicon nanowires directly onto the particles of these powders has two immediate advantages: *(1)* the resulting silicon-graphite composite builds upon all of the known performance characteristics of the graphite substrate and *(2)* the production and use of SINANODE® leverages existing large volume manufacturing, lowering material and adoption costs. Thus, OneD Material purchased and perfected the CVD growth of silicon nanowires directly on the particles of commercial graphite powders from leading global suppliers.

The first step in growing nanowires requires the synthesis and deposition of catalyst nanoparticles onto the surface of the graphite particles. The size of the nanoparticles determines the diameter of the nanowires and the surface density of the nanoparticles determines the density of nanowires grown on each graphite particle. A high quality SINANODE® material requires a narrow distribution of nanowire diameters and uniform distribution onto the particles in the graphite powder. A scalable process must achieve these goals for billions of graphite particles per Kg of graphite and over hundred billion nanowires per milligram of silicon, at low cost.



Cu nanoparticles deposited on the surface of a grpaphite particle

To reduce cost, OneD Material developed how to use copper catalyst nanoparticles in lieu of the gold catalyst nanoparticles traditionally used for growing silicon nanowires. The synthesis of copper nanoparticles uses inexpensive and safe ingredients (copper sulfate; potassium sodium tartrate; and sodium ascorbate) in a aqueous colloidal solution. The deposition mixes the colloidal solution with the graphite powder, quickly resulting in hundreds of billions of uniform copper nanoparticles disposed on the surfaces of billions of graphite particles. After drying, the graphite with the copper catalysts deposited thereon can be stored for weeks before being processed to grow nanowires using CVD processing. The novel deposition and synthesis processes are simple, cost effective and safe (for more details see US patent **10,243,207**).

After completing the catalyst deposition, the copper-catalyzed graphite powder is loaded into special reactors designed and optimized by OneD after years of experimentation, (for more details see **WO 2018/013991**) which reactors are then loaded into commercially available CVD furnaces.

Many people have incorrectly assumed that a CVD process is too expensive to produce cost-competitive battery materials. It is worth mentioning some of the key reasons why this is not the case.

OneD proprietary design reactor are designed to fit into commercially available CVD furnaces which have standardized tube dimensions and are designed and built by multiple vendors; These furnaces have been in use extensively for decades in the solar cell and semiconductor industries, making them safe and cost effective. The reactor designed by OneD incorporates a robust metallic cylindrical tube, which rotates to mix the copper-catalyzed graphite powder with a reactant gas (e.g. Silane SiH_4) and an inert gas (e.g. Nitrogen) at a stable temperature below 600 °C and a pressure below 1 atm. All parameters throughout the CVD growing process are precisely-controlled using software automation. Thus, fixed costs (equipment and labor) for the growing process are minimized.

Variable costs for SINANODE® are driven by the cost of raw materials, mainly graphite, silane and nitrogen, the cost of energy, and other minor costs for product handling and packaging. The cost of graphite benefits from the large existing production volumes. The cost of nitrogen is negligible. Energy cost, mainly the electricity used to heat the CVD furnaces, has a minor impact on the overall variable costs. Regarding the silane gas (SiH_4), today's worldwide silane production is well established and supplies the semiconductor and the solar cell industries. The world's largest silane gas producer, REC Silicon, has available capacity exceeding 20,000 tons per year and produces silane gas at 99.9999% purity. Therefore, silane cost and availability are not expected to be a limiting factor for SINANODE® large scale production and overall unit cost.

SINANODE® CVD manufacturing process requires silane gas (SiH_4) to react with copper nanoparticles (Cu_2O) to grow silicon nanowires. A manifold distributes the reactant gas throughout the full load of copper-catalyzed graphite particles into the rotating reactor to ensure product uniformity and quality.

The growth rate of the silicon nanowires is proportional to the pressure of silane in the reactor. Hence, by supplying enough silane at a pressure which is higher than in conventional techniques, the growth process starts at once on billions of graphite particles and the nanowires reach their final length faster. Minimizing the duration of the growth process is critical to optimize the use and maximize the yield of the furnaces: less processing time turns into greater SINANODE® production per unit of time for each CVD furnace. For example, a single commercial furnace ("stack") with four process tubes, each with one reactor, can produce 100 tons per year of SINANODE® (note that having multiple reactors in each process tube multiplies this capacity, as described in the PCT patent application mentioned above).

Another key metric is the "silane utilization", i.e. the percentage of the silane gas converted into silicon nanowires. When silane (SiH_4) decomposes into silicon (Si) and hydrogen (H_2), each mole of silane creates two moles of hydrogen gas, which must be exhausted from the reactor, along with the inert nitrogen. The exhaust gases are pumped out (using a vacuum pump) from the reactor thru micronized meshes at each end of the reactor metallic tube, and flow thru the CVD process tube to an exhaust and abatement system. The gas distribution manifold, the reactor and end-cap mesh dimensions, the silane partial pressure inside the reactor and the vacuum outside the reactor are all carefully designed to ensure that 99% of the silane decomposes into silicon and less than 1% of it escapes into the exhaust system before reacting with the catalyst copper nanoparticles on the graphite.

The high yield of silane utilization minimizes wasting reactant gas and is critical for SINANODE® to be cost competitive. The ratio of silicon and graphite (Si/C wt. %) in 1 Kg of SINANODE® powder can be adjusted by controlling the density and length of the nanowires grown on the graphite powder. For example, at 10% Si/C, 1 Kg of SINANODE® comprises 900 g of graphite and 100 g of silicon and, at 20% Si/C, 1Kg of SINANODE® comprises 800 g of graphite and 200 g of silicon.

The cost and the "value" of the graphite are well known: for example, at a cost of $8/Kg for a specific capacity close to 357 Ah/Kg, i.e. the "value" of graphite is V_g = 357/8 = 45 Ah/$. Taking into account, for example, a 90% initial coulombic efficiency ("ICE"), this "value" corresponds to approximately $7/kWh cost contribution to a lithium ion battery with a nominal voltage rating of 3.6V.

Unlike silicon oxide additives where the oxygen atoms add to the weight and decrease the silicon capacity, the charge capacity of the silicon in SINANODE® is close to 3570 Ah/Kg, i.e. ten times greater than graphite, while the cost of the silane used is less than twice that of the graphite (at large volume). For example, assuming for simplicity a cost of silane of $16/Kg, converted in Si NWs in 20% Si/C SINANODE®, the "value" of the combined graphite and silicon nanowires SINANODE® composite material can be estimated by:

$$V_{SINANODE} = [80\% \times 357 + 20\% \times 3570] / [80\% \times 8 + 20\% \times 16] = [286 + 714] / [6.4 + 3.2] = 104 \text{ Ah/\$}$$

SINANODE® anodes can also achieve 90% ICE (or better) in cells with NCA or NMC cathodes, and this "value" corresponds to a $3/kWh cost contribution. This estimate only includes the two key inputs and does not include the other manufacturing costs. However, at large production volumes, the capital equipment depreciation and labor costs become less important than the cost of the key raw materials.

Thus, SINANODE® active materials not only enable lighter, slimmer batteries which can be sold at a premium, but the SINANODE® manufacturing processes are simple, scalable and cost effective.