# **Engineering High Surface Area Catalysts for Clean Tech Applications**

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## ABSTRACT

Catalysts are central to energy conversion and play a key role in chemical synthesis and processes for the hydrogen economy. Since catalytic performance is a limiting factor for many essential elements of the hydrogen economy (including fuel cell efficiency, storage kinetics, and production capacity), the need for improved catalysts is great. One-dimensional (1D) nanomaterials are ideal for catalyst applications because of their large surface area to volume ratio, which results in orders of magnitude more reactive sites than thin films or bulk materials. They are often reusable and in some cases are more environmentally friendly than traditional catalyst materials. The ability to engineer the surface of 1D nanomaterials allows catalysts to be created that have, in addition to enhanced kinetics, specificity for certain reactions. The process used to produce a range of surface engineered nanostructured catalysts is described and the resultant microstructures are related to specific reactions that can be enhanced.

*Keywords*: catalyst, nanomaterial, Nanospring<sup>TM</sup>, surface area, silica

## **1 INTRODUCTION**

One-dimensional ceramic nanostructures offer desirable alternatives to conventional catalysts for a number of different reactions, as summarized in Table 1 [see e.g., 1]. One of the main advantages of using 1D ceramic nanostructures is that they are more active at low temperatures relative to thin films; TiO<sub>2</sub> nanotubes with Au nanoparticles are almost five times as catalytically active as conventional Au/Al<sub>2</sub>O<sub>3</sub> catalysts for the oxidation of CO at 300°C [2]. This reaction is essential for the operation of hydrogen fuel cells. Ceramic nanostructures also offer stability in harsh environments. For example, reduction of  $NO_x$  gas species to  $N_2$  and  $O_2$  is an important reaction for environmental health because of the fact that NO<sub>x</sub> gases are a primary cause of acid rain, a common by-product of the combustion of fuels in automobiles. Mats of ZnAl<sub>2</sub>O<sub>4</sub> nanowires were found to effectively catalyze the reduction of NO<sub>x</sub> vapors in typical automotive conditions and were thermally stable in these environments unlike traditional zeolite-based catalysts [3].

Catalyst	Form	Reaction
SnO <sub>2</sub>	Nanowire	Oxidation of CO
TiO <sub>2</sub>	Au-decorated nanotube	Oxidation of CO
ZnO	Nanobelt	Synthesis of 1H-
		tetrazoles
CeO <sub>2</sub>	Nanowire	H <sub>2</sub> generation
С	Nanotube	Reduction of NH <sub>3</sub>
MnO <sub>2</sub>	Ag-decorated nanowire	Oxidation of CO
$ZnAl_2O_4$	Nanowire	Reduction of NO
		complexes
GaN	Au-decorated nanowires	Water-gas shift reaction

Table 1: Catalysts using 1D nanostructures.

Nanowire-based catalysts also provide a level of control of the catalytic process, which is very desirable for commercial processing. Tin oxide nanowire catalysts have been used in FET devices in the same manner as  $SnO_2$ sensors [4]. The advantage of using the nanowire catalyst in this case is the ability to start and stop the reaction by controlling the gate voltage. The gate voltage affects the amount of  $O_2$  adsorbed on the nanowire surface. At negative gate voltages there are few electrons available in the n-type nanowires, which results in the adsorption of very few oxygen molecules. The lack of oxygen molecules essentially stops the oxidation of CO [4].

Simple metal oxides form the majority of 1D ceramic nanostructures studied for catalysis. These materials were studied because of their ease of synthesis, low cost, and known functionality (at least in bulk form). There remains a vast amount of research to be done using nanowires of more complex ceramics, which may actually function better than many of the materials listed in Table 1. For example, one study has shown that the lanthanide hydroxide ceramics, e.g., Pr(OH)<sub>3</sub>, Nd(OH)<sub>3</sub>, and Yb(OH)<sub>3</sub>, can be predictably synthesized as nanowires using a solvent growth method and have potential as catalysts due to the many possible transitions within their 4f subshells [5].

An important reaction for hydrogen generation is the water-gas shift reaction (WGSR) where carbon monoxide is reformed with water. While ferrochrome catalysts are used extensively for the high-temperature shift reaction, the hexavalent chromium presents a severe toxicological hazard. There are a number of developments underway to

create alternative water-gas shift catalysts. One approach that we have investigated is to use gallium nitride (GaN) nanowires decorated with gold (Au) nanoparticles [6]. Normally an unreactive metal, gold at nanometer sizes becomes a potent catalyst and the activity and selectivity of gold nanoparticle catalysts can be enhanced through interaction with the support material [e.g., 7]. Preliminary results show that the GaN-Au system (shown in Figure 1) can catalyze the WGSR at ambient temperature and pressure. The disordered mat of GaN nanowires provides many open pathways and reaction sites.



Figure 1: Low magnification secondary electron image of a mat of GaN nanowires decorated with Au nanoparticles.

Several 1D ceramic nanostructures including  $TiO_2$  and  $MnO_2$  have shown promise as catalysts for hydrogen generation reactions. One-dimensional ceramic nanostructures that have been identified as potential catalysts for the oxidation of CO or other possible fuel cell energy sources include  $SnO_2$  [4] and  $CeO_2$  [8] nanowires. Although these systems have proven to be efficient catalysts, huge opportunities remain for the development of low temperature, inexpensive, efficient catalysts in the fuel cell industry. The most promising materials will be compatible with high-volume manufacturability, which is required for economical catalyst production.

We have developed a low cost process to produce very large area mats of silica Nanosprings<sup>TM</sup> that provide a thermally and chemically stable catalyst support [9]. The Nanosprings<sup>TM</sup> can be formed at temperatures as low as 300°C and can then be further functionalized by the application of nanocrystalline oxides (e.g., ZnO, TiO<sub>2</sub>, CuO) and/or metal nanoparticles (e.g., Au, Pt, Pd). This process creates hierarchical nanostructures that can be engineered for specific catalyst applications.

## **2** EXPERIMENTAL METHOD

The Nanospring<sup>TM</sup> mats can be grown on a variety of substrates depending upon the specific application requirements. The range of substrates includes glass,

sapphire, silicon, aluminum foil, and high T<sub>g</sub> polymers such as the polyimides. The growth process for the Nanospring<sup>TM</sup> mats follows that developed by Wang et al. and McIlroy et al., which is described in detail elsewhere [9, 10]. Figure 2 shows an uncoated Nanospring<sup>TM</sup> mat on an aluminum foil substrate. Optimization of the growth procedure allows dimensional control of the Nanosprings<sup>TM</sup> and the density of the Nanospring<sup>TM</sup> mats, which translates to increased strength and/or higher surface area. The Nanosprings<sup>TM</sup> can be conformally coated with different metals, metal oxides and/or nanoparticles using a variety of different physical and chemical deposition techniques.



Figure 2: Aluminum foil coated with Nanosprings<sup>TM</sup>.

Atomic layer deposition (ALD), plasma enhanced chemical vapor deposition (PECVD) and wet chemistry are some of the processes we have employed for coating Nanospring<sup>TM</sup> mats. In particular, ALD offers a number of advantages including: conformal coating, ultra thin films, stoichiometry control, and scalability [11-13]. Known procedures for different metal oxides, such as  $Al_2O_3$ , ZnO, and TiO<sub>2</sub> [14-16], have been used as an initial reference point and subsequently optimized for coating the Nanospring<sup>TM</sup> mats. PECVD and wet chemistry have been used to produce nanoparticles of different metals, including those well known for their high catalytic potential such as Au, Pt, Pd, Cu and Ag [17,18]. Metal nanoparticles can be deposited on both coated Nanospring<sup>TM</sup> mats.

### **3 RESULTS AND DISCUSSION**

The flexibility of the synthesis and coating processes has allowed us to engineer the Nanospring<sup>TM</sup> mats to meet the specific requirements for given catalytic reactions. Reactions such as the destruction of amine odor causing compounds, dechlorination reactions, and propylene epoxidation can be performed with Au-coated Nanospring<sup>TM</sup> mats similar to the one shown on Fig. 3 [17, 18].



Figure 3: Backscattered (left) and secondary (right) electron images of surface coated SiO<sub>2</sub> Nanosprings<sup>™</sup> decorated with gold nanoparticles.



Figure 4: Secondary electron images of a) a mat of silica Nanosprings<sup>TM</sup> coated with nanocrystalline ZnO, b) a mat of silica Nanosprings<sup>TM</sup> coated with nanocrystalline TiO<sub>2</sub> (anatase phase).

Palladium nanoparticles are commonly used in pharmaceutical synthesis and can easily be deposited onto the Nanosprings<sup>TM</sup>. Silver nanoparticle coated Nanosprings<sup>TM</sup> can be used in catalytic reactions such as redox catalysis and conversion of aromatic nitro

compounds to amino compounds [19, 20]. Platinum is a common catalyst in catalytic converters for the reduction of car emissions [21] and in fuel cell electrodes [22]. Platinum nanoparticles with an average size of 3nm and very narrow size distribution have been formed using PECVD with dimethyl(1,5-cyclooctadiene)platinum (II) as the source compound.



Figure 5: Crystalline ZnO coated silica Nanosprings<sup>TM</sup> decorated with copper nanoparticles.

The strong bond between the Nanosprings<sup>TM</sup> and the substrate not only provides a durable and resilient support for gas-to-gas catalytic reactions, but also enhances efficiency due to the large accessible surface area provided by the Nanosprings<sup>TM</sup>. In addition, the strong bond dramatically decreases the amount of nanoparticles transferred to the reaction products, compared with slurries or nanoparticles in solution. This, in turn, translates to less of the noble metal being removed and longer life of the catalyst.

Figure 4 shows two of the most active photocatalytic materials ZnO and anatase TiO<sub>2</sub> [23,24]. Nanocrystals of ZnO, shown on Fig. 4(a), are excited at a wavelength of 388nm and can be used in the recovery of noble metals from plating industries [25]. Nanocrystalline TiO<sub>2</sub> in the anatase phase, shown on Fig. 4(b), is a highly desirable photocatalyst with numerous applications that range from water treatments [26] to methanol synthesis from carbon dioxide [27]. The open three-dimensional structure of the Nanospring<sup>TM</sup> mat substantially increases the amount of accessible surface area and therefore the efficiency of these reactions.

Copper supported on zinc oxide, shown on Fig. 5, is a widely used catalyst for the WGSR and for methanol synthesis. In addition, this materials combination is used for hydrogenation/dehydrogenation reactions and can also be used as a catalyst for room temperature oxidation of carbon monoxide [28].

#### 4 CONCLUSIONS

Surface engineered silica Nanospring<sup>™</sup> mats offer a number of significant advantages as advanced materials for catalysis. The mats provide very high accessible surface area and can be conformally coated with a range of different oxides. Through judicious process control it is possible to obtain the desired phase for a material that exists in different polymorphs. For example. nanocrystalline TiO<sub>2</sub> coatings can be produced in the anatase phase (rather than rutile), which is the one most suited to photocatalyst applications. Metal nanoparticles can be subsequently deposited on the oxide coatings to create hierarchical nanostructures tailored for specific applications. The size of the nanoparticles can be tightly controlled to maximize their efficiency for certain catalytic reactions.

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