

Innovative development of bottom-up Nanotechnology-based value-added products for enhancing competitiveness in the Asia-Pacific



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**Asian and Pacific Centre for Transfer of Technology
of the United Nations – Economic and Social
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By

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Innovative Development of Bottom-Up Nanotechnology-Based Value-Added Products for Enhancing Competitiveness in the Asia-Pacific

1. Prologue

The roles of UNESCAP (United Nations Economic and Social Commission for Asia and the Pacific) and specifically that of APCTT (Asian and Pacific Centre for Transfer of Technology) are vital in directing, promoting and supporting the development of new technologies in the Asia-Pacific region from the top-down. Nanotechnology, for example, is a proven driver of commercialization, R&D, training, education and job creation worldwide. To become a competitive global partner in this field, strong partnerships among academia, business and government and regional coordinating bodies in the Asia-Pacific region – e.g. UNESCAP-APCTT– need to be in place. The topic of this EGM (Experts Group Meeting) is “Networking of R&D Institutions in the Asia-Pacific to Strengthen Capacity of R&D Management and Innovation in the Field of Nanotechnology”. The importance of identifying, organizing and promoting bottom-up strategies for synthesis and manufacturing, local association and bottom-up collaboration and business development with maximum incentive are presented and discussed.

This report focuses on bottom-up synthesis of nanomaterials from the ‘poor man’s nanotechnology’ or ‘low-tech nanotech’ point of view– ‘poor man’ and ‘low tech’ in the sense of limited resources available to conduct cutting-edge nanotechnology research and development. At the Asian Institute of Technology in Bangkok (AIT), Thailand, for example, nanotechnology research was conducted on a shoestring budget and the program was built from there. However, if enough bottom-up potential is marshaled and integrated properly, the high entry barrier to nanotechnology can be mitigated. This can only happen if serious and deliberate attention, incentive and funds are paid to bottom-up elements of developing nanotechnology infrastructure concomitant with complementary strategic partnerships. The “Top-Down” organizations of all participating nations in this chapter of the UNESCAP project were all impressive in their scope and strategy. The bottom-line understanding by all nations that nanotechnology is and can be a significant driver for economic sustainability was equally impressive.

2. Introduction

This report does not serve the purpose of an in depth survey, but rather addresses a few general strategies that support the theme given above. There are many excellent reports that provide surveys

and summaries of nanotechnology and its development in Asia. There is no need to repeat those results here. Everyone is aware of them and they are quite good and informative.

2.1 Perspectives

2.1.1. Top-Down / Bottom-Up perspectives

Both Top-Down and Bottom-Up drivers are necessary to successfully promote the development of nanotechnology. Top-down components consist of governments and national, regional and international organizations, e.g. UNESCAP. Bottom-up components consist of energy non-intensive/high throughput molecular-scale synthesis and societal elements driven by local association, individual collaboration, and small business. Bottom-up processes occur quite naturally (and in analogy to chemical synthesis, quite spontaneously). The endorsement of programs that promote bottom-up methods and philosophy should be able to run parallel to those that involve institutional collaboration, big business and top-down synthesis and manufacturing.

Products can be enhanced by addition of nanomaterials made from the bottom-up (atoms and/or molecules). For example, zinc oxide (ZnO) based sunscreen was made better by making the ZnO nanoscale– the product was rendered clear with better UV-absorbing properties. Bottom-up synthetic methods of most nanomaterials are affordable and energy non-intensive. Bottom-up technologies are relatively simple, require shorter lead-time and do not require sophisticated equipment during manufacturing. Throughput of bottom-up processes is limited only by manufacturing capacity and availability of raw materials. Ideally and obviously, the cost of products enhanced with bottom-up nanotechnologies should provide competitive advantages. From the societal perspective, local associations spread concepts and promises of nanotechnology to provinces and regions. Creation and support of such associations bring awareness, education and eventual business to communities. Bottom-up collaboration, already worldwide, can be enhanced by providing more venues- e.g. conferences and workshops. Lastly, support for emerging businesses (with fewer strings attached) and technology transfer reform would lead to a culture of diversity.

The powers that be, existing at the top, need to understand that it is good to form ‘global networks’ and ‘regional networks’, but serious and fundamental efforts need to be placed on the bottom-up elements of association, collaboration and business development and, to promote and enhance bottom-synthesis methods to get products to the marketplace quicker.

2.1.2 Target audience

The target audience of this report consists of individuals and groups associated with government,

academic and industry sectors– with or without previous understanding of nanotechnology and its promise.

2.1.3 What is nanotechnology- Part I?

Nanotechnology involves the use of nanoscale materials that are generally between a few nanometers (1 nm = one-billionth of a meter) and ca. 100 nm along any or all dimensions. Nanotechnology, like microtechnology (1 μm = one millionth of a meter), involves materials defined by a size scale, but unlike micromaterials, nanomaterials are capable of possessing remarkable properties– properties that deviate dramatically from the bulk parent material. On the other hand, the properties of micromaterials are fundamentally the same as those of the bulk phase. A human hair is roughly 100 μm in diameter. 1 nm is 1/100,000th as thin.

Nanoscience and nanotechnology are considered to be horizontal in nature. In other words, they cut across all academic disciplines and all vertical industrial sectors. Nanotechnology is a platform upon which many kinds of science and technology dwell (Figure 1).

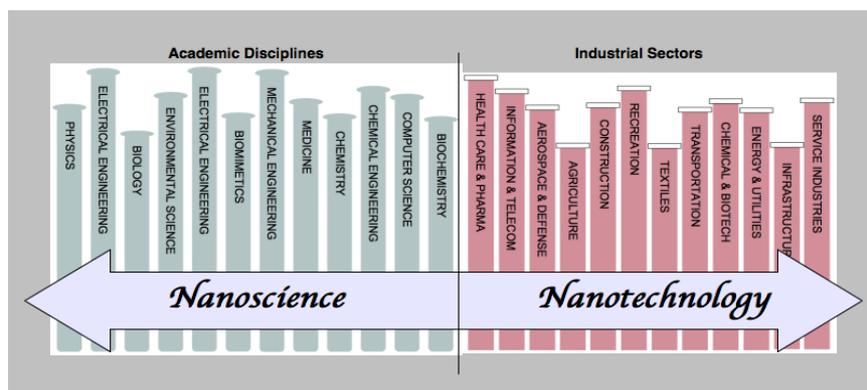


Figure 1: Horizontal and vertical linkages of nanoscience and nanotechnology

It is in many ways everything that comes with a new industrial revolution, but it is also viewed by others as nothing special- a consequence of the natural evolution of miniaturization. Whether it is part of a new revolution or not is actually unimportant, and that debate, therefore, is left best for pundits to sort. What is real is the perception of nanotechnology, and that real world properties of nanoscale materials do indeed add value to new and previously existing products. In its most simplistic sense, nanotechnology, for the sake of this report, involves the study and development of nanoscale materials and their ultimate incorporation into commercialized products with enhanced properties and performance. Nanotechnology, however, is simultaneously remarkable and mundane. Apart from well-known miracle materials that can potentially cure cancer, reach to geosynchronous orbit or deliver 700% efficient solar cells, nanotechnology gives us materials that simply make products

better– products that seem to slide under the radar of exotic headlines. Examples include use of nanoscale zinc oxide (ZnO) in sunscreens for enhanced absorbance and transparency, teflon nanoparticles in stain-free pants, silver nanoparticles in odorless socks and carbon nanotubes in tennis racquets for added strength and flexibility. Most of nanotechnology therefore falls in the category of non-remarkable, non-sensational.

2.1.4 World Science Forum Declarations

How can countries in the Asia-Pacific Rim identify which products to develop, manufacture and commercialize? In particular, how do countries with developing nanotechnology programs develop strategies that rely on nanotechnology to add value to products and, subsequently, enhance competitiveness in the Asia-Pacific region- e.g. the prime directive of this experts meeting group. There are several factors to consider. First, there is the unabated rise of the ‘global science and technology community’. Evidence of its relevance, and inevitability, was proclaimed over and over at the World Science Forum (WSF) in Budapest, Hungary from November 16 – 19, 2011. The title of the conference was “The Changing Landscape of Science: Challenges and Opportunities”. Participants included members from the United Nations Education, Scientific and Cultural Organization (UNESCO); the International Council for Science (ICSU); and the American Association for the Advancement of Science (AAAS), among many other organizations. A summary document titled “Declaration on a New Era of Global Science” was released and read at the Hungarian Parliament on the final day of the conference. Recommendations listed in the summary focused on the promotion of international collaboration and capacity building on a global scale. From the point of view of this observer, Asian-Pacific countries (specifically Thailand, Malaysia, Indonesia, the Philippines, Cambodia, Viet Nam, Sri Lanka, Bangladesh, etc.) need to participate on a larger scale in the next WSF to be held in Rio de Janeiro in 2013 (www.sciforum.org). The attendance of UNESCAP and APCTT is encouraged. The WSF conference is an indicator of changing times and the Asia-Pacific region needs to keep pace by forming strong regional top-down organizations. Therefore, individual member countries must consider the scope of regional inputs, outputs and outcomes in strategic planning to prepare. In other words, how can these countries take advantage of bottom-up approaches listed above to build capacity and market presence?

2.2 Orientation

Four levels of orientation are presented below. Business, academia and government are inherently represented in all categories:

1. Representation and organization
2. Niches, needs and opportunities
3. Collaboration

4. Synthesis and manufacturing practices.

Each is influenced to some degree by top-down and bottom-up philosophy. Looking at the two extremes, top-down skewed infrastructures would favor big laboratories, big names, big industries, big international projects (e.g. ‘rich get richer’) and the well connected. With increased globalization of science and technology (as per the WSF), more centralized order, direction and control are inevitable. Such centralization is a natural societal process similar to the phenomenon of Ostwald ripening in chemistry where big clusters grow at the expense of little ones. On the other hand, bottom-up skewed infrastructure, albeit diverse, would have limited regional and international presence and perhaps limited interaction between and among academia, government and industry. Both approaches are necessary, but how a balance is achieved – a balance that serves to promote nanotechnology product development with the aim of developing competitive presence in the Asia-Pacific region.

2.2.1 Representation and organization

The genre of strategic goals derived at the WSF are considered to be ‘top-down’ in character- e.g. concerted movement towards globalization of science and technology directed by larger and larger international coordinating organizations and funding bodies. Eventually the formation of working global scientific funding agencies and, as was stated there, ‘global fora’ are inevitable. Governments, academic and business leaders and international organizations like UNESCAP are best suited to develop regional and global strategy.

2.2.2 Niches, opportunities and needs

It is up to individual countries to define inherent needs, opportunities and practical niches for nanotechnology products. It is up to regional bodies to advise how they are managed and distributed. Needs, opportunities and practical niches arise naturally from the bottom-up as people exploit materials at hand to develop products. Subsequently, market forces test the viability of those products. Is there a need for national and regional coordination and planning in order to better define niches so that redundancies and detrimental competition (in which competing parties knock each other out) are eliminated and outcomes optimized? In these cases, oversight from the top-down can increase the efficiency of commercialization by forming agreements with other nations in the region.

2.2.3 Collaboration

Collaboration occurs most naturally from the bottom-up without the aid of strategic plans or the necessity of top-down influence. The simple process of exchanging business cards at conferences usually leads to international cooperation and eventually perhaps, product development. Collaboration of course can be and is enhanced from the top-down. Collaboration, specifically of the international flavor, is required to succeed nowadays (e.g. more papers, more citations). Both approaches are

necessary especially if the collaboration proves to be fruitful and proceeds to the next levels – e.g. proof of concept, patent application and filing, prototype development, company establishment, licensing and/or production. Is there a need for national and regional coordination and planning in order to better aid collaborative venues and databases? In these cases, organization and incentives provided from the top-down can increase the efficiency of collaboration. Dr. K. Ramanathan of APCTT suggested the creation of interactive scientist, engineer and company databases to provide an environment for scientists and engineers to collaborate independently without the direction of regional or global motivation.

2.2.4 Bottom-up synthesis and manufacturing

The last category addresses synthesis and manufacture of products enhanced by nanomaterials– the topic of special focus in this section of the report. Once again, like defining needs, niches, and collaborations, synthesis also proceeds in natural ways. People know what their capabilities are and what they can make and how to make it. The purpose of this section is to shine a stronger light on bottom-up synthesis processes of nanomaterials, their incorporation into products and their importance in defining regional strategy. Awareness, training, promotion and funding from the top-down position based on strategic and tactical goals should be able to maximize the potential of bottom-up synthesis processes. The perspective of ‘low-tech-nano-tech’ (LTNT) - or as others have phrased, ‘poor man’s nanotechnology’ (PMNT)¹ – is elaborated upon in this section. The acronym LTNT is adopted in the following text. Figure 2 summarizes subjectively the relationships presented. Top-down drivers need to define strategy and organize accordingly. They also need to define and incorporate niches. Bottom-up drivers need incentives and funding in order to collaborate, conduct research, patent processes and develop businesses. Bottom-up synthesis, of course, offers the least expensive way to achieve marketing goals and competitive status.

¹ Nanotechnology and Global Sustainability, Donald Maclurcan and Natalia Radywyl, editors, CRC Press, Boca Raton, 2012

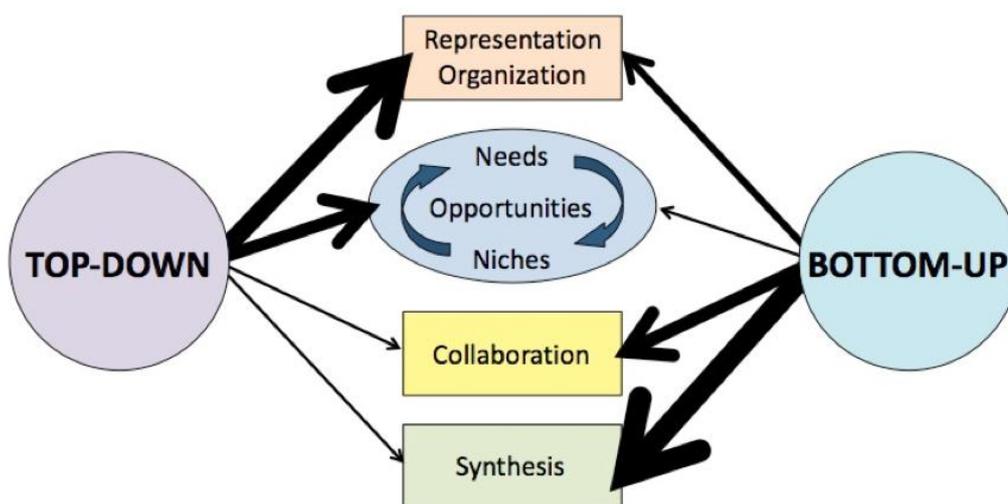


Figure 2: Representation of the relationships between ‘top-down’ and ‘bottom-up’ orientation

Figure 2 illustrates the relationships between ‘top-down’ and ‘bottom-up’ orientation philosophies to capacity building and strategic planning is shown. Greater arrows represent greater participation, influence and action. Lesser arrows represent input, guidance and opinion. Representation & Organization require significant top-down activity. In order to keep pace with globalization and other top-down organizations, the Asia-Pacific region must form its own strong representative body. Identification of needs/ opportunities/ & niches is also best served from the top-down as the regional landscape is best viewed from the top. Collaboration can be enhanced by the formation of a science/ engineering database. This tool will enable scientists and engineers to collaborate more efficiently. Synthesis by the most inexpensive of means arises from the bottom-up synthesis. Top-down assistance, however, is still required to provide venues and instrumentation for characterization.

3. Background

3.1 Opening remarks

‘Innovative development of nanotechnology-based value-added products for enhancing competitiveness in the Asia-Pacific region’ is the theme of this report. The report, as mentioned previously, describes a fundamental strategy based on ‘bottom-up’ synthesis methodologies and enhanced ‘bottom-up’ collaboration that, if adopted by developing nations with incipient or emerging nanotechnology programs, should provide an affordable and hence competitive platforms for product development, competitive markets and government aid programs with lower associated costs. The Asian regions of the South and Southeast in particular are currently well positioned to take advantage and develop the so-called LTNT or PMNT with the singular intent of manufacturing inexpensive products based on materials developed from the bottom-up that are inserted into products during

straightforward manufacturing processes. Evidence of the success of bottom-up inexpensive technologies is found in products of cosmetic, textile, agriculture, recreation, construction materials, office supplies (printers) and food packaging industries. There are many more examples available.

3.2 Overview of R&D in the Asia-Pacific region

3.2.1 2009 UNESCAP-APCTT Report²

UNESCAP has membership from over the world including the United States, the Russian Federation, European countries and middle-eastern nations along with the respected nations that comprise the Asian-Pacific region. The countries represented in this year's 2011 working group consisted of countries in the Pacific and South Asian region: Thailand, Sri Lanka, China, Pakistan, Indonesia, India, Islamic Republic of Iran, and the Philippines. In 2009, Republic of Korea, Malaysia, Nepal, and Bangladesh attended in addition to the previous list. The report from the 2009 meeting in Sri Lanka is titled "Innovation in Nanotechnology: An Asia-Pacific Perspective". Prof. Tissa Vitharana mentioned in his keynote address at the 2009 meeting that 'emerging nations with high populations of poor people needed to ensure that top cutting-edge technology is properly applied in industries if they wished to emerge from poverty'. However, the term 'cutting-edge' implies high technology solutions. The Republic of Korea and China's economies were driven by microelectronics (and hence nanoelectronics) for the development of information and communication technologies. However, emerging economies cannot compete in those arenas without the assistance and resources from developed nations. Prof. Vitharana concluded that 'countries should learn from each other and march together harnessing a new technology to their advantage'. The question that begs asking is which technology (technologies) to harvest? Dr. K. Ramanathan of APCTT in the 2009 report stated 'that generation of cutting-edge technology R&D is expensive and that collaborative efforts with developed nations like the Republic of Korea (North-South) would be necessary, but also launching of South-South initiatives running parallel needs to be accomplished'.

3.2.2 Low-Tech Nanotech (LTNT)

Are there readily available LTNT solutions to make the South-South initiatives competitive? For example, without the need for assistance from advanced countries? Should focus be placed on pooling resources and regional cooperation to develop, in a significant way, LTNT pathways to product development? The good news is that the 'Nanoscience and Technology Wave', as stated in the 2009 report, is upon us, and many LTNT routes are already well developed. Bangladesh's nanotechnology program at Materials Science Division of the Atomic Energy Centre in Dhaka, although considered to be emerging, is producing basic nanoparticles by chemical (bottom-up) methods: Ag, Fe₂O₃ and ceramic oxides. Nanotech research in Bangladesh is limited in scope because of the lack of tools and

² Innovation in Nanotechnology: An Asia-Pacific Perspective (2010), APCTT-ESCAP, New Delhi, India

equipment and an inadequate number of R&D personnel³. Industries in India are manufacturing nanotechnology enhanced water filters, biomedical products, chemicals, cosmetics and paints². Nepal, possessing perhaps the least developed of nanotechnology programs, needs inexpensive applications to enhance soil fertility and crop production. Applications of nanotechnology to water purification and food packaging to prolong freshness are desperately needed in Nepal⁴. Rubber and agricultural resources are strong sectors in Sri Lanka as are production of textile products. Sri Lanka also exports ca. 40,000 t of TiO₂ per year. Nanoporous silica products are made from inexpensive inorganic silicates in Iran that serve as precursor materials in bioadsorption and separation technologies. Silver nanoparticles, metallic nanoparticles for catalytic and biological applications, magnetic nanoparticle, and plastics made from nanopolymeric materials are all produced from the bottom-up, and assumingly, rather inexpensively in Iran.

Other countries in the region are better developed. The Philippines already has a well-developed semiconductor industry and its nanotechnology roadmap includes a wide array of nanotechnology programs and materials ranging from LTNT to high-tech programs. Thailand also possesses an impressive infrastructure with a majority of application-focused nanotechnology programs. Pakistan as well is very capable of conducting high-tech cutting-edge research. Korea invests 35% of its nanotech fund into basic research, 42% into developmental research and 23% into applied research². The capability to conduct basic research is an indicator of an advanced program.

3.2.3 Summary of current nanotech product lines

Table 1 summarizes the capabilities in terms of nanomaterials/ devices of nations present at the 2011 EGM. The table represents but a partial list of nanomaterials made in the region. It is by no means completely representative of any country or of all products. The template information page proposed by Dr. Ramanathan should provide a comprehensive picture of R&D and manufacturing characteristic of the region. The need for such a resource is apparent. The information was gleaned from materials provided by participating nations.

Table 1: Nanotechnology applications

| Sector/ Nanomaterial | Country involvement [‡] | Level of technology | Applications |
|---|----------------------------------|------------------------------|--------------------------------|
| Health | | | |
| Hydroxyapatite | Pakistan, Sri Lanka | Made from eggshells or mined | Bone technology |
| Drug Delivery Systems | Iran, China* | Bottom-Up, high-tech | Anti-cancer therapeutics |
| Nanoencapsulated Nutraceuticals/ Natural Products: Vitamin A, Curcuma, Purwaceng, Mangosteen, | Indonesia, Thailand | Bottom-Up | Anti-aging, health supplements |

³ *Ibid*

⁴ *Ibid*

| | | | |
|---|---|--|---|
| etc. | | | |
| Nanoencapsulated Insulin | Indonesia | Bottom-Up | Oral insulin |
| ZnO | Indonesia, Sri Lanka, Thailand | Bottom-Up | Dental cement, antibacterial |
| Instrumentation | China | High-tech | Nano devices, imaging, diagnostics |
| Nanoencapsulated Oils | Thailand | Bottom-Up | Aroma therapy |
| Nano-Cellulose | Iran | Bottom-Up, surface modification, high-tech | Drug carriers |
| Agriculture | | | |
| Encapsulated fertilizer: SiO ₂ , MgO, CuO, CaCO ₃ , ZnO | Indonesia, Thailand | Bottom-Up | Fertilizers, control release for industry crops |
| Encapsulated Pesticides | Indonesia | Bottom-Up | Crop control |
| Impregnated insecticide | Thailand | Bottom-Up | Vector control lotion |
| Biochar, Carbonaceous Soil | Thailand | Bottom-Up | Smart soil |
| Environment | | | |
| Nanomembranes/ Particles | Thailand | Bottom-Up | Clean water polluted with heavy metals and fertilizers |
| Glutathione-Capped Au NPs | Philippines | Bottom-Up | Optical sensor for Cd ²⁺ heavy metal |
| Nanomaterials/ Indigenous | Philippines | Harvested | Multiple uses |
| Capacitive Membranes | Indonesia, Thailand | Bottom-Up, high tech | Water desalination |
| ZnO, Catalysts | Sri Lanka, Thailand, Pakistan | Bottom-Up | Photocatalytic purification of water |
| Activated Carbon | Sri Lanka | Top-Down, low-tech | Filters |
| Energy | | | |
| Nanoscale Catalysts | Indonesia, Thailand | Bottom-Up | Fuel cells, hydrogen production |
| ZnO, TiO ₂ | Indonesia, Thailand, Sri Lanka, Philippines | Bottom-Up | Dye-sensitized solar cells (DSSC) |
| Battery Technology | China | Bottom-Up | Storage cells |
| Graphene Modification | Philippines | High technology, high risk | Nanostructured photovoltaic cells |
| ZnO, Catalysts | Thailand | Bottom-Up | Hydrogen production |
| Health & Food Safety | | | |
| ZnO, Ag Nanoparticles | Indonesia, Thailand | Bottom-Up | Antibacterial materials, packaging. nylon fiber, paints |
| Biodegradable Starches and Clays | Philippines | Bottom-Up | Advanced food packaging |
| Nanostructured Inorganic Materials | Philippines | Bottom-Up | Fire retardant materials |
| Cosmeceuticals | | | |
| Nanoencapsulated Chitosan, Vitamin A, ZnO | Thailand, Indonesia | Bottom-Up but ZnO produced with arc-plasma | Skin protection, anti-oxidants, anti-aging |
| Materials Industry | | | |
| TiO ₂ Nanoparticles | Indonesia | Bottom-Up | Ceramics, self-cleaning |
| CaCO ₃ | Indonesia | High energy ball milling (Top-Down) | Nanocomposites |
| TiO ₂ | India, Sri Lanka, | Bottom-Up | Paints |

| | | | |
|---|------------------------|---|--|
| | Thailand | | |
| ZnO | Thailand | Bottom-Up | Antibacterial, photocatalysis, water purification |
| Nanosilica | Philippines | Top-Down from local silica source | High performance concrete |
| TiO ₂ Coatings | Sri Lanka | Bottom-Up | Self-cleaning tiles |
| TiN, Ti ₂ N, TiCN, CrN, Si ₃ N ₄ , AlTiN, and More | Pakistan | Bottom-Up, high tech | Specialty nanocomposite coatings, hard high-performance coatings |
| Diamond-Like Materials | Pakistan | Bottom-Up, high-tech | Tools & dyes |
| Zeolites | Iran | Bottom-Up natural/ laboratory synthesis | Catalysts, ion exchange, molecular sieve, mesoporous materials |
| Electronics/ Semiconductors | | | |
| Electronic Components | China, Philippines | Top-Down/ Bottom-up, high-tech | Printed electronics, MEMs, Instruments |
| Textiles | | | |
| ZnO Nanorods | Thailand | Bottom-Up | Superhydrophobic clothing, photocatalytic antibacterial power |
| Ag Nanoparticles | Iran, India, Sri Lanka | Bottom-Up | Anti-bacterial textiles/ automotive industry |
| Hydrophobic Nanoparticles | Iran | Bottom-Up | Anti-staining, water resistant technology |
| Transportation | | | |
| Fluid Coolant Materials | Iran | Bottom-Up, additives | Engine temperature control |
| Nanopolymers and Particles | Sri Lanka | Bottom-Up, additives | Rubber tires |

‡ The purpose of the table is to show and compare kinds of Bottom-Up products. It is not complete by any means. National programs should not feel slighted if the table is not complete.

* Please note that the scope of China's nanotechnology programs is vast, cutting-edge and, with our apologies, is underrepresented in this table.

3.2.4 LTNT and PMNT

LTNT is technology type. Poor Man's Nanotechnology also involves societal elements. This report describes the strategy of 'bottom-up' chemical synthesis leading to the 'Poor Man's Nanotechnology' (PMNT) and, with less fanfare, the strategy of investing more in bottom-up drivers. PMNT is actually a contradictory statement in that in truth, nanotechnology is never the game for the underfunded. Expensive equipment is always required during, *per se*, the analytical leg of research (although recent developments are driving those costs downward as well). PMNT refers to sophisticated nanotechnology that can be accomplished relatively inexpensively- done of course through the bottom-up synthesis that lies within the domain of chemistry. All PMNT is accomplished in old-fashioned glass beakers and Erlenmeyer flasks found in any chemical laboratory in the world.

3.3 Nanotechnology products

According to Project on Emerging Nanotechnologies (PEN) director David Rejeski, consumer products based on nanotechnology keep growing consistently. He stated that in 2006, there were

merely 212 products on the market. Now the PEN director states that if this trend continues, about 3,400 products will be on the market by 2020⁵. Interestingly, more products use nanosilver (over 300) than any other nanomaterial⁶. For a comprehensive list, please consult the PEN website at: <http://www.nanotechproject.org/inventories/consumer/>.

3.3.1 Nanotechnology product data

According to information provided by PEN in 2011, nanotechnology products are distributed in the following ways:

1. Nanoproducts by Region of Origin

| | |
|-----------|-----|
| U.S.A. | 54% |
| East Asia | 24% |
| Europe | 15% |
| Other | 7% |

2. Nanomaterials in Most Demand

| | |
|-------------------|-----|
| Silver | 54% |
| Carbon | 17% |
| Titanium | 10% |
| Silicon/ Silicate | 7% |
| Zinc | 6% |
| Gold | 6% |

3. Nanoproducts According to Industry Sector

| | |
|------------------|-----|
| Health & Fitness | 55% |
| Home & Garden | 14% |
| Food & Beverage | 9% |
| Automotive | 6% |
| Electronics | 5% |
| Other | 10% |

What kinds of bottom-up technologies fit into the last two categories listed above? Furthermore, which nations in the Asia-Pacific region can best adapt certain product lines and make them competitive in the marketplace? In accordance with niches and needs, agriculture, food & beverage, textiles, raw materials, cosmeceuticals, environmental and construction are sectors that can serve to benefit significantly from R&D from emerging nanotechnology programs.

3.3.2 Nanotechnology products

A list of nanotechnology products is provided below. Some are the result of bottom-up LTNT, others are quite sophisticated— you be the judge. The list is by no means a complete one.

1. Automotive Industry

- Bumpers, paints, coatings, glare reduction, catalytic converters

⁵ Nanotech Enabled Consumer Products Continue to Rise, Science News, ScienceDaily, March 10, 2011.

⁶ *Ibid*

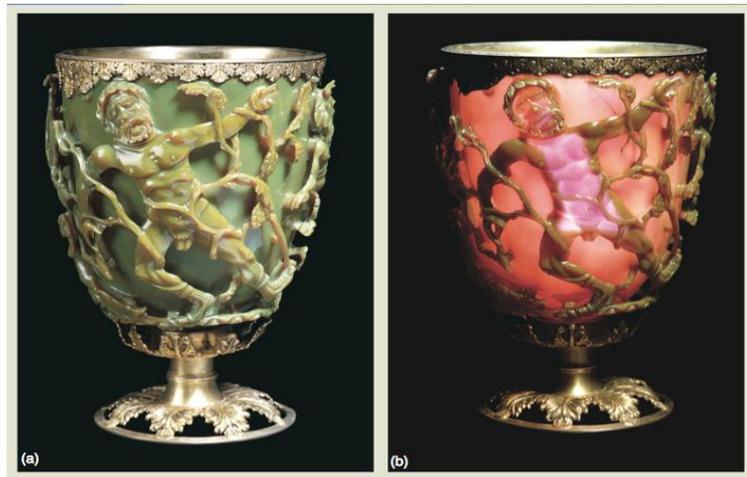
- Cooling chips to replace compressors with no moving parts
2. Recreation
 - Lighter stronger tennis racquets, long-lasting tennis balls, smart golf balls
 - Nanotube reinforced masts for sailboats, new materials for hull and deck
 - Golf shafts, skis, fog eliminators
 - Ski wax
 - Athlete skin care
 3. Personal Use and Food
 - Sunscreens, cosmetics, stain-free clothing
 - Silver nanoparticle food storage containers, cutting boards, pans
 - Nonstick bake ware
 - Umbrella (based on lotus leaf)
 4. Medicine, Therapeutics, and Hygiene
 - Dental-bonding agents, burn and wound dressings
 - Medical imaging with quantum dots
 - Targeted drug delivery and gene therapy
 - Water filters with nanoporous membranes
 - Lab-on-a-chip diagnosis
 - Sanitized toilets– superhydrophobic surfaces
 5. Structural Materials and Industrial Applications
 - Stronger, lighter polymers; enhanced concrete, enhanced steel
 - Wear-resistant, scratch-resistant nanoceramic coatings
 - Catalysts
 - Carbon nanotube-reinforced materials
 - Various nano glues, nanoseal wood, nano-enhanced insulation
 - Self-cleaning glass/ windows
 - Exterior paint
 6. Electronics and Computing
 - Sub-100 nm transistors (old technology)
 - Carbon nanotube triodes
 - Organic LEDs and organic electroluminescent displays
 - Cordless power tool batteries
 - Carbon nanotube displays
 - Protective self-assembling film layers for displays
 - Cellular memory

One company in China, Shanghai Huzheng Nanotechnology Co., Ltd., has on its inventory 400 products that are classified as nanotechnology-based. The list can be accessed from the company's website at <http://hznano.en.made-in-china.com/product-list-15.html>. The diversity in product lines is quite remarkable.

3.4 Nanotechnology & bottom-up synthesis and more

3.4.1 What is nanotechnology? – Part II

Nanotechnology is considered to be a new technology that is growing in importance. Nanomaterials have been around since the dawn of humankind. The color attributed to the Lycurgus Cup (British Museum) is attributed to gold and silver nanoparticles (Figure 3). Quantum dots made of semiconductor materials have been used to color stained glass in medieval cathedrals centuries ago. Photography was founded on the remarkable properties of micron and nanoscale silver chloride particles. Nanotechnology began informally in 1959 with the aftermath of Nobel Laureate Richard Feynman's lecture 'There Is Plenty of Room at the Bottom' delivered at Cal Tech in 1959. Norio Tanaguchi first coined the term 'nanotechnology' in 1972. In 1989, Ron Eigler and his team at IBM Almaden placed 35 xenon atoms to spell 'IBM' and the *nano-age* was formally launched. Although growth has been exponential, nanotechnology is still in its toddler stage.



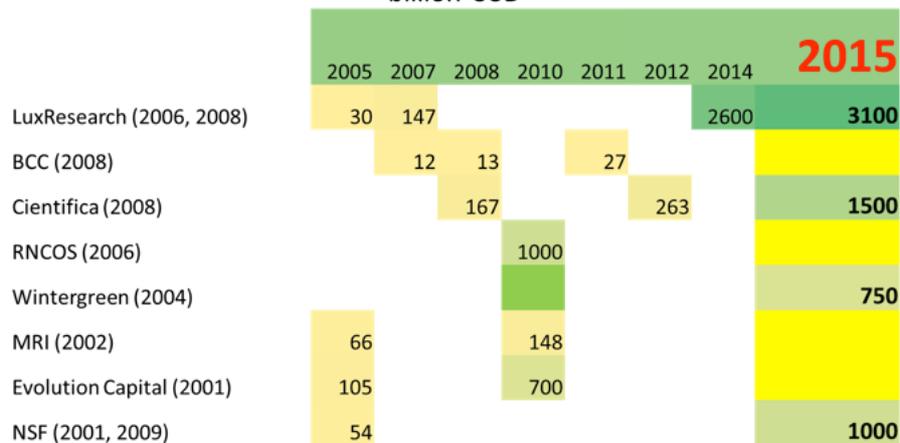
Source: Images reprinted with permission from British Museum Images.

Figure 3: The remarkable dichroism of the Lycurgus Cup is the result of ancient nanotechnology unknowingly practiced by craftsman of the time. Gold and silver nanoparticles are responsible for the red (on transmission of light) and green (on reflection) respectively.

The competition to commercialize products applying nanotechnology is fierce as this 21st century manufacturing technology is expected to generate US \$1.5 trillion for the global GDP by 2015. Other sources claim that the value is closer to US \$3.1 trillion as shown in Table 2. Information technology, biotechnology, nanotechnology and other emerging technologies are being applied for new products and services. Added to this the rapidity with which information is disseminated and assimilated on a global scale, change can come upon us rather quickly. Table 2 shows a typical market forecast.

Table 2: Global market forecasts for nanotechnology

Selection of global market forecasts for nanotech-enabled products,
billion USD



Source: Publicly available information on private market forecasts.

(Adapted from Joydeep Dutta- Course materials Asian Institute of Technology)

Nano is cutting across international borders and conventions without consideration. In this way, nanotechnology has found another way to be horizontal— around the equator and latitudes north and south. In the industrialized countries, governmental agencies, branches and departments all have had some form of involvement with nanotechnology. Nanotechnology also presents high entry barriers for less-resourced countries in the Global South, both in terms of research and development (R&D) and market entry. However, nanotechnology cannot be overlooked as a field of potential in the Global South, for, like any other technology, nanotechnology has the potential to change society. The change may be for the better or for the worse, depending on the orientation of its output and who wields its power. Figure 4 shows global investment behavior into nanotech R&D in 2007.

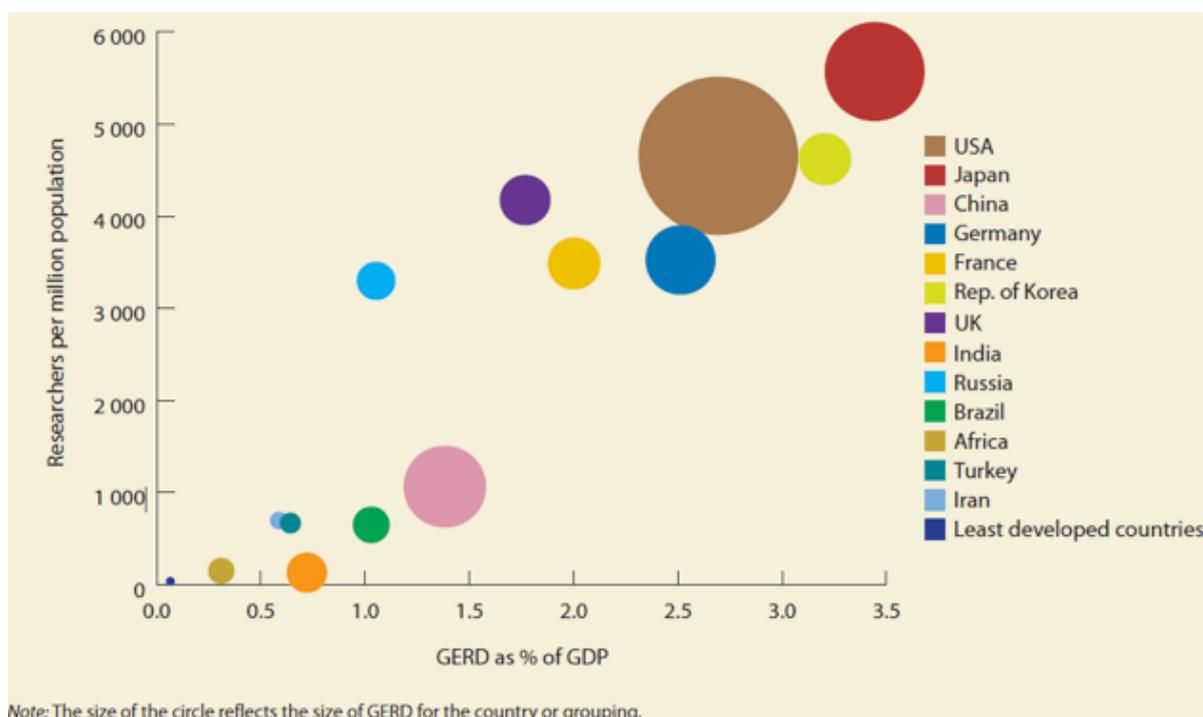


Figure 4: Global investment in R&D in absolute and relative terms, 2007 for selected countries and regions

Source: UNESCO Science Report 2010: *The Current Status of Science around the World*, ISBN: 978-92-3-104132-7

Nanotechnology is the application of nanoscience and is interdisciplinary. In other words, nanoscience cuts across all academic disciplines (basic sciences of chemistry, physics and biology and their offspring) as well as the engineering disciplines (mechanical, chemical, civil and electrical engineering and their crossovers). Nanoscience and nanotechnology are therefore interdisciplinary. More so than ever before, physicists are working with biologists, chemists with engineers and computer scientists with environmental engineers. Flexibility is the name of the game in the workforce of today and new approaches to science education and training are bringing down the walls of the monolithic disciplines to form interdisciplinary platforms. For example, DNA is used as a spring in nano-electromechanical (NEMs) devices. Inorganic materials like cadmium selenide quantum dots are merged with biopolymers and immunological materials to produce targeted-imaging systems. Nanotech and biotech are so involved that it becomes impossible to distinguish them. New labs are designed to accommodate the needs of an interdisciplinary staff. There are many examples. *Nanotechnology is therefore a convergent technology.* Nanotechnology requires a staff of Ph.Ds, trained staff and a veritable stable of multi-million dollar characterization and manufacturing equipment and solid long-term financial commitments— all to bring nano-products and nano-enhanced products to the marketplace.

While nanoscience is often associated with R&D in higher education institutions, industry and commerce, it can also be thought of as the study of nature's nanotechnology. Nature is the master of nanotechnology. Everything in our bodies originates from atoms and molecules first and then from nanomaterials– from the bottom-up. For example, the nanometer domain encompasses the visible spectrum – an important coincidence with living things. The blue color of the *Morpho* genus' butterfly wings is due to interference created by nanostructures (Figure 5).

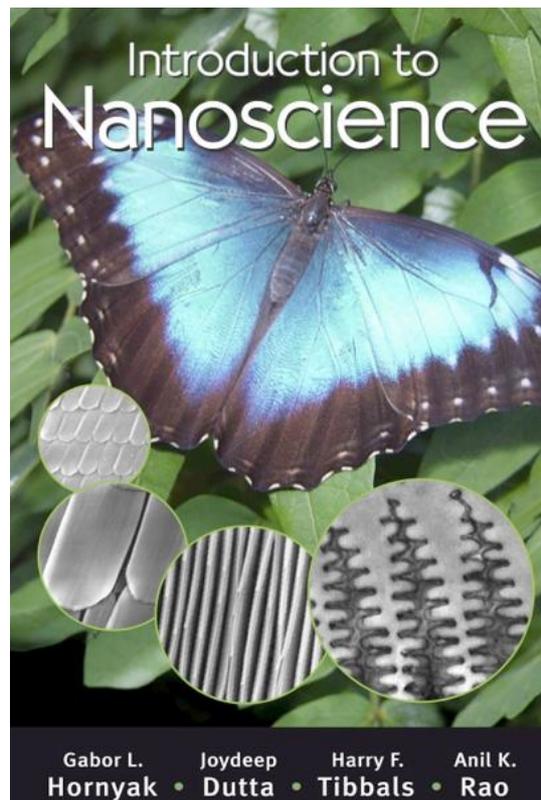


Figure 5: The morpho butterfly's color is due to nanostructured elements in the platelets of its wing structure. Angular dependent interference colors generated by the structures yield the striking blue hues.

The gecko sticks to ceilings due to millions of nanoscale setae on its feet that are approximately 200 nanometers in diameter. The setae take advantage of very weak intermolecular forces called van der Waals forces that collectively bear the weight of this remarkable creature – a force important at the nanoscale. Chromosomes, of course, are also nanomaterials. We recognize that we must listen to nature and learn how to make nanomaterial devices from the 'bottom-up' with minimal raw materials and input of energy.

3.4.2 Top-Down vs. Bottom-Up synthesis

Based on fundamental thermodynamic arguments, breaking bonds and converting a big material into smaller materials requires energy. Conversely, energy is released when small materials combine to

form big materials – also one of the primary reasons that nanomaterials are metastable – nanomaterials inherently want to become larger materials. In nature, biological materials are made exclusively from the bottom-up. It seems to make logical sense that we would copy nature and make our materials in similar ways. We therefore argue that a bottom-up chemical synthesis-strategy is the best way to develop nanotechnology in our lab environment and research development context for the simple fact that top-down fabrication is costly. By definition, ‘top-down’ requires significant input of energy and millions of dollars’ worth of equipment. For example, top-down methods require ultra-high-vacuum and high-energy electron beams for micro and nanolithography. In all cases, parts are checked for quality control by scanning electron microscopes, surface topography scanners like the AFM (atomic force microscopy) and nano-manipulators. For the most part, bottom-up synthesis does not require highly complex and expensive equipment. However, while bottom-up methods are potentially less expensive, with a higher throughput of product, the long-range order of nanostructures is not always apparent– a factor that impacts repeatability, reproducibility and perhaps overall reliability. Both manufacturing philosophies are therefore necessary to make nanotechnology continue its evolution successfully, and both methods are often mixed. During a manufacturing cycle, there may be a top-down application followed by a bottom-up application. Therefore in the short term, purely bottom-up synthesis of electronic products is currently not practical. However, if the goal is to simply make nanomaterials by the ton and monodisperse particles or long-range order are not factors, the bottom-up synthesis is the way to go.

3.4.3 Societal implications

Like any other technology, nanotechnology has the potential to change society– for the better or for the worse depending on which technology is applied and what group wields the power and the money. Therefore, the ‘societal implications and impacts of nanoscience and nanotechnology’ are very serious matters that require serious discussion and eventual regulation. Like never before, societal implications are topics of high priority, and its form is evolving and developing well before most of the products, weapons and services have made it into the boiling geopolitical, economic and societal cauldron. Like never before, governments are trying to get ahead the technology– not an easy task. Nanotechnology is accompanied by complex societal implications.

What then are the implications of poor man’s nanotechnology? We understand very well the first aspect of PMNT – i.e. conducting nanotechnology with limited resources but well aligned partnerships – but at least some of the purpose of PMNT must be directed towards those that can least afford new technologies. For example, can we manufacture cheap solar cells (e.g. DSSCs) so that individuals living in remote rural areas have a means to power laptops? Can we distribute inexpensive photocatalytic water filters to victims of flooded regions? Can we protect food supplies from spoiling

to help multitudes living in areas ravaged by starvation? Yes, most of the answers to these questions will have to be given from those dwelling in the top-down regime of our societal elements. Societal implications transcend all of society– from the Bottom-Up.

4. Bottom-up technologies

Examples of bottom-up technologies are provided to the non-scientist/ engineer for the sake of perspective. Images are provided to help acquire a grasp of the nanoscale and insight into some of the remarkable properties mentioned previously.

4.1 Colloidal nanoparticles

4.1.1 Colloid technology

Synthesis of nanoparticles can be carried out from the bottom-up in liquid phases at moderate temperatures and conditions. Wet-chemical processes can lead to the formation of highly dispersed nanoparticles with consistent crystal structure. Synthesis of metal and semiconductor nanoparticles is carried out by wet chemical methods. Sol-gel processing for the generation of nanoparticles has gained immense popularity due to its simplicity and use of mild conditions. Typical sol-gel processes include hydrothermal growth, precipitation and gelation. Manipulation of the size distribution of metal, semiconductor and metal nanoparticles is achieved by either doping or thermal treatment. Improved size control of quantum-confined semiconductor nanoparticles can be achieved through the use of block copolymers or polymer blends and inverted micelles.

The sol-gel process yields nanoparticles in a dispersion and consequently it is important to stabilize the colloid so that the nanoparticles do not agglomerate and flocculate and settle out of solution. Stabilization can be achieved either through electrostatic repulsion involving the creation of an electrical double layer or through steric hindrance that can be achieved by adsorption of large molecules such as polymers on the surface of the nanoparticles. Both are easy to accomplish bottom-up processes. A transmission electron micrograph (TEM) of electrostatically stabilized Au nanoparticles and ZnS nanoparticles stabilized through steric hindrance by coating with a biopolymer called chitosan are shown in Figure 6.

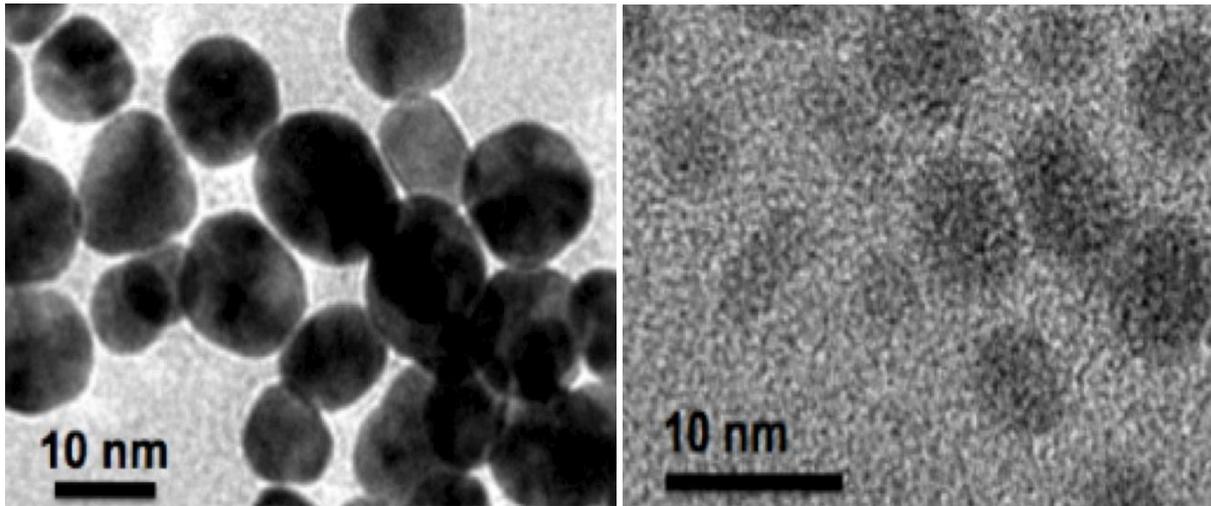


Figure 6: Transmission electron micrographs (TEM) of Au and ZnS nanoparticles electrostatically stabilized through steric hindrance by coating with a biopolymer called chitosan (Image courtesy : Center of Excellence in Nanotechnology, Asian Institute of Technology)

The TEMs are those of easy to synthesize gold (Au) and zinc sulfide (ZnS) nanoparticles stabilized electrostatically or with layer of chitosan respectively. Such bottom-up chemical synthesis can be scaled-up without difficulty.

4.1.2 Colloid technology is scalable technology

Extensive research on the applications of nanoparticles has generated considerable interest in scale up production of nanoparticles. The bottom-up production of ZnO can be scaled up easily— a convenient trait of bottom-up processes. A continuous hydrothermal synthesis can be scaled up for commercial production using a specially designed reactor. The sol-gel process is a simple process using mild conditions and with continuous evolution of different passivation schemes; it seems to be an attractive option for commercial production of different nanoparticles (Figure 7).



Figure 7: Picture of a ZnO mini-factory

Figure 7 shows the picture of a ZnO mini-factory. The process is fundamentally one of chemistry— in other words, it is a process that can be scaled-up easily to industrial proportions. The product formed from this apparatus demonstrated better physical properties than samples made in the laboratory. Image courtesy of the the Center of Excellence in Nanotechnology at the Asian Institute of Technology.

4.2 Zinc oxide nanoparticle technology

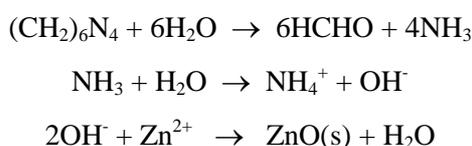
4.2.1 Zinc oxide (ZnO) synthesis— from the bottom-up

Zinc oxide nanostructures can be made cheaply from bottom-up chemical methods. For applications that involve zinc oxide, long-range order is not that critical. Although formation of relatively monodisperse product is desired, the operation of a catalytic water purification system will not be impacted in the slightest if there are, for example, some ZnO nanorods that exist at the threshold of the third standard deviation from the norm. The idea is to make a lot of ZnO, as quickly as possible and as inexpensively as possible with the single governing criterion that the resulting filter operates within the proper parameters.

ZnO is a semiconductor material with a bandgap of 3.37 eV (electron volts). Various morphologies of ZnO can be synthesized following a simple and economical hydrothermal route at temperatures below the boiling point of water. The hydrothermal growth of ZnO nanostructures requires a source of Zn²⁺ ions like Zn(CH₃COO)₂, ZnCl₂, Zn(NO₃)₂, etc. and a source of OH⁻ ions like NaOH, KOH, NH₄OH, etc. ZnO nanostructures form as per the following reaction:



The morphology of the ZnO nanostructures can be controlled through the control of growth parameters like concentrations of reactants, growth temperature, pH of growth solution, etc. Controlled fabrication of ZnO nanorods have been successfully carried out in the CoEN at AIT on different substrates by the thermal decomposition of hexamine and zinc nitrate. To initiate the growth from the substrate, a thin layer of ZnO nanoparticles is grown on the substrate. Hexamethylenetetramine (HMT) or hexamine is a highly water soluble, non-ionic tetradentate cyclic tertiary amine. Thermal degradation of HMT releases hydroxyl ions, which react with Zn²⁺ ions to form ZnO [54]. This can be summarized in the following equations:



The procedure followed for the growth of ZnO nanorods is given in details in Figure 8.

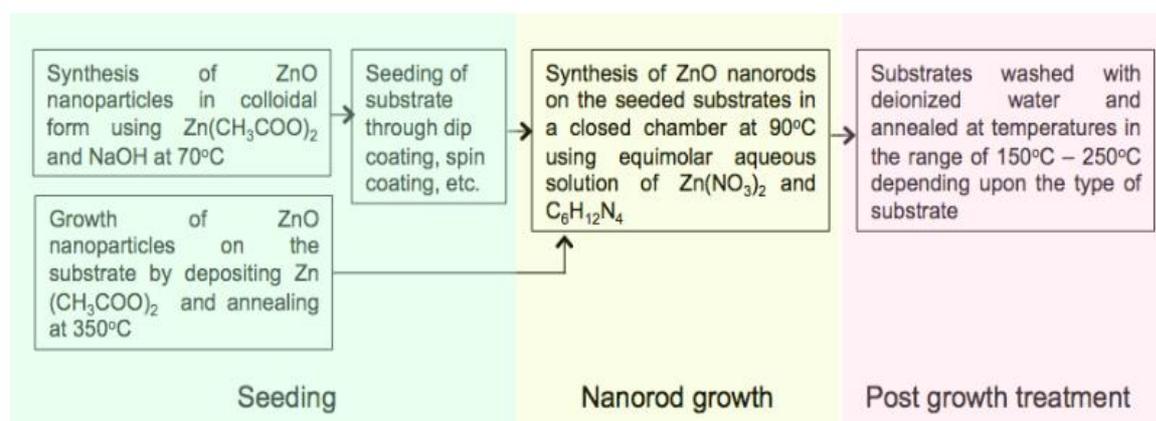


Figure 8: Synthesis of ZnO is straightforward and cost effective– it all depends on chemistry from the bottom-up (Image courtesy: Center of Excellence in Nanotechnology, Asian Institute of Technology)

4.2.2 ZnO applications

Applications of ZnO nanostructures are numerous. They include:

1. Photocatalytic purification of air/water

Photocatalysis: Semiconductors that can accelerate the rate of reactions when exposed to light without undergoing any change themselves are called photocatalysts. A good photocatalyst should have a very wide absorption band preferably in the visible or near UV part of the electromagnetic spectrum. ZnO semiconductor nanoparticles are able to remove organic chemicals from air and water based on the production of active radical species (Figure 9). ZnO is cheap and these filters can be made very inexpensively.

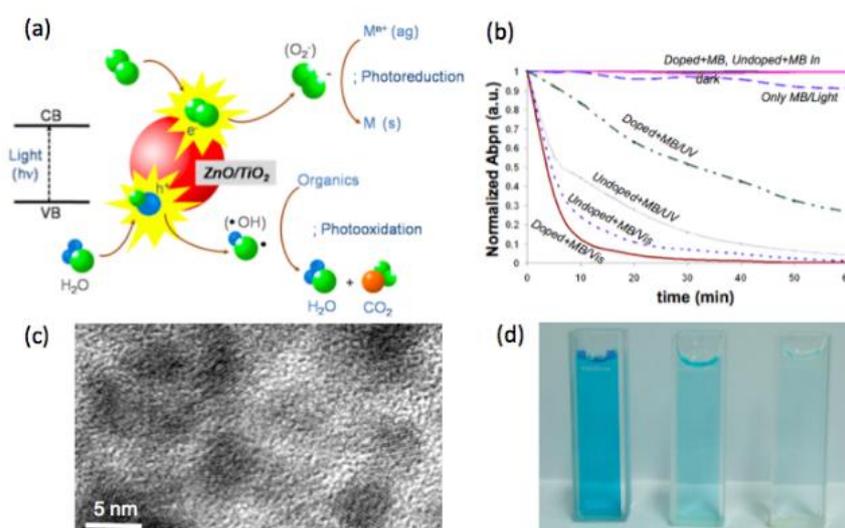


Figure 9: Scheme of reaction of a photocatalytic system based on ZnO

2. Dye-sensitized solar cells

Dye sensitized solar cells (DSSC) can be fabricated cheaply. The fabrication procedure is simple and environmentally friendly. DSSC are made of nanostructured titanium dioxide (TiO₂), zinc oxide (ZnO) or tin dioxide (SnO₂). A schematic representation of a DSSC is shown in Figure 10. Light is absorbed forming an electron-hole pair. This results in charge separation and charge transport. ZnO nanorods based DSSC has been successfully fabricated at the CoEN@AIT with efficiency up to 6.5%.

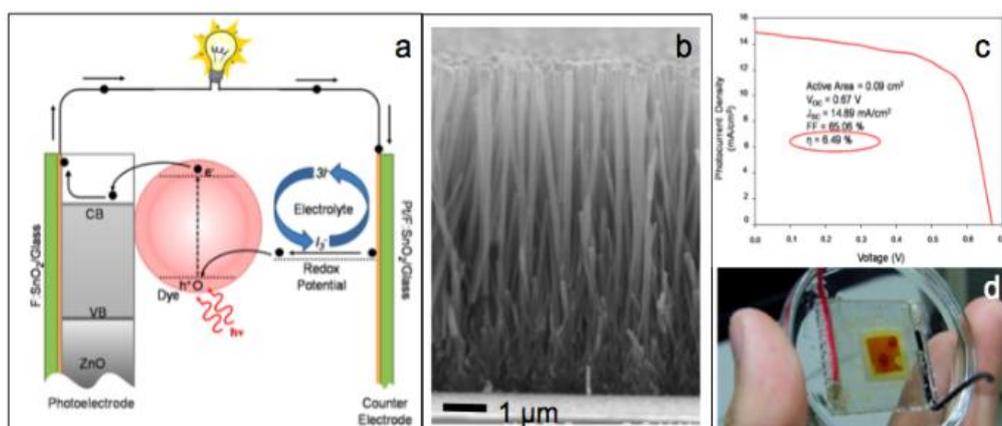


Figure 10: Dye-sensitized solar cells (DSSC). The electron transport scheme is shown in (a). The ZnO nanorods are shown in (b). A sample current-voltage curve is shown in (c). (d) depicts a DSSC.

The dye-sensitized solar cells (DSSC) offer a low-tech pathway to solar energy collection and conversion into electricity. The chromophore (dye)-decorated ZnO nanorods offer high surface area semiconductor substrate for reasonable solar collection. Although not as efficient (efficiency at ca. 12%) as conventional solar cells, DSSC are potent enough to power laptops and other small appliances, and above all are very easy and inexpensive to manufacture. This gives the competitive advantage to any country that can mass produce DSSC devices.

3. Antimicrobial agents

Preserving food and medical salves are just a few applications of antimicrobial systems using nanotechnology. This field is already showing incredible growth worldwide. Antimicrobial systems would be able to fight infections to wounds encountered in the agricultural regions. Silver-based antimicrobial products are sweeping the nanoworld in terms of product diversity and volume however other nanomaterials are also effective. Figure 8 shows the antimicrobial effects of ZnO nanoparticles on paper impregnated with the material.

In addition to health benefits, antimicrobial systems are increasingly more important in the food safety and preservation industry, according to resources, anywhere from 30% to 40% of world food supplies result in a state contamination and spoilage. By storing foods in antimicrobial environments, the

percentage of food efficiency (from harvest to consumption) can be increased. This is indeed an important bottom-up nanotechnology.

The antimicrobial behavior of ZnO-treated paper is shown in Figure 11. The ZnO-treated paper shows antimicrobial properties against the common mold *Aspergillus niger*. The zone of inhibition demonstrates the effectiveness of the antimicrobial paper. Since ZnO is also catalytic in the UV range, more potency is demonstrated in daylight. It is a simple adaptation to treat paper with ZnO and the process has potential for scale-up.

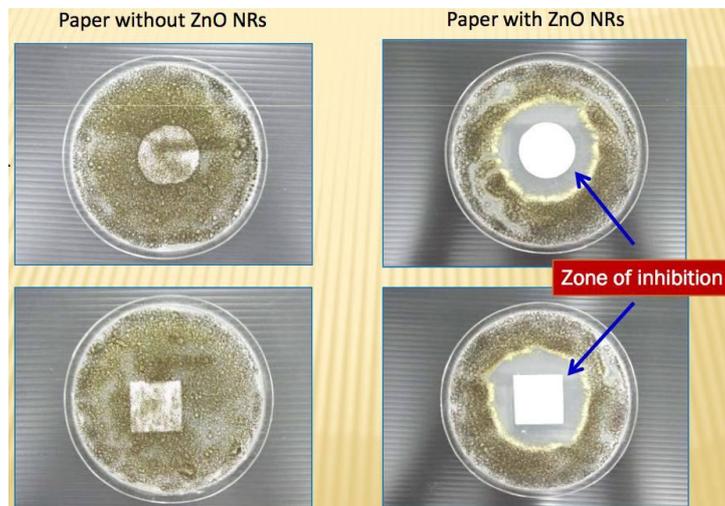


Figure 11: ZnO-treated paper showing antimicrobial properties against the common mold *Aspergillus niger*

4. Gas sensors

Gas sensors are important to environmental monitor systems, home and personal safety, and in industry. ZnO nanostructures were once again the keys to the functioning mechanism of the sensor. The basic principle is based on detection of the change in resistivity of the semiconductor-sensing element when exposed to test gases. Nanostructured noble metal catalysts like Pt are used to enhance the performance of the sensor (Figure 12). Due to the semiconducting behavior of ZnO nanorods, they are well suited to serve as resistors in such a gas sensing device. Selectivity and sensitivity are improved with the use of nanomaterials. The bottom line however is that these sensors are inexpensive.

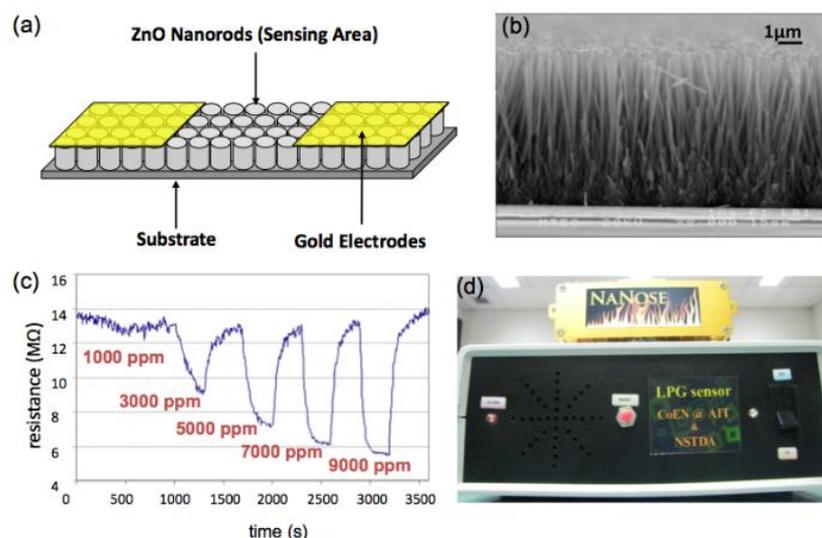


Figure 12: Schematic diagram showing enhanced performance of gas sensor

The gas sensor is very easy to fabricate. The micron-scale inter-digitated electrodes are formed with a homemade revitalized inkjet printer (yes, an aspect of PMNT–II, see below). Then, ZnO crystallite seeds are strewn over the surface. Hydrothermal growth takes place to form the ZnO nanorods. The system is then engaged to an ohmic junction to detect electrical signals via a change in the resistance of the ZnO conduit as a result of contact with a target gas.

The nanosensor is inexpensive to manufacture and the process can be scale-up to industrial proportions. Moreover, such technology in energy and material non-intensive and should be sold for low cost. Such bottom-up technologies will make nanotechnology readily available to those who take advantage of the opportunity.

5. Superhydrophobic surfaces

A superhydrophobic surface repels water efficiently with a water contact angle (WCA) greater than 150°. The lotus leaf is a natural model of a superhydrophobic surface. Superhydrophobicity property is due to an array of micro- and nanostructures protruding from the surface that minimizes the interaction between the drop and the nanostructured surface. An analogy can be made with the famous Fakir effect— a ‘bed of nails’ onto which a person is capable of lie down upon with out injury due to judicious spacing of the nails.

ZnO nanorods on a surface consisting of microbumps are patterned to mimic the lotus leaf (Figure 13). The microbumps were formed with the aid of a rebuilt inkjet printer (true PMNT). The ink used was composed of ZnO seed particles. Depending on the spacing and height of the ZnO nanorods, varying degrees of hydrophobicity were obtained.

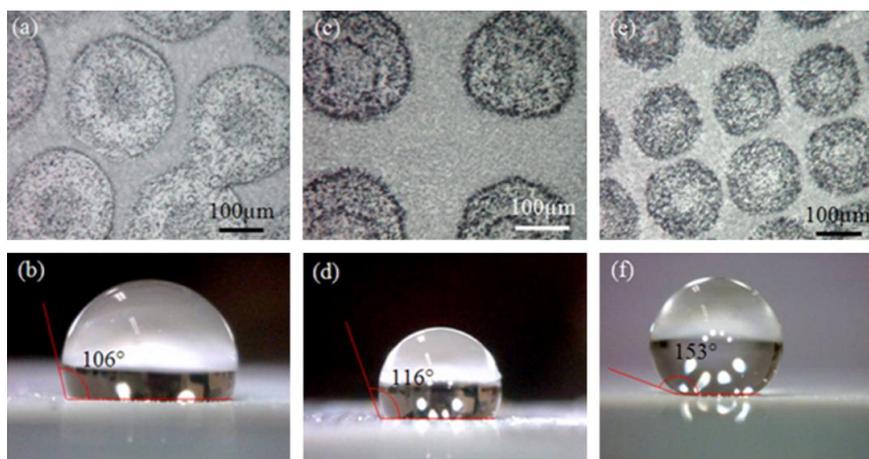


Figure 13: Superhydrophobic surface created by use of ZnO nanorods and other structures. The water contact angle can be affected by control of the spacing of the microbumps and the height of the ZnO rods.

Superhydrophobic surfaces have applications in many sectors. In the textile industry, for example, clothing that is both water repellent and breathable is desired in countries with high humidity. Stain-free and water resistant clothing developed with nanotechnology have been on the market for several years. Essentially, during a standard manufacturing process, a nano-step can be inserted that imparts enhanced properties to the material. Therefore, there is not much to change in the process except to add space for the additional step. Nanotechnology just makes products better— often from the bottom-up.

6. Capacitive Desalination

Desalination of spoiled or salty waters is important in many regions affected by drought or flood conditions. However, current methods of desalination are energy intensive— e.g. distillation, reverse osmosis and filter methods. By using nanomaterials made by Layer-by-Layer (LBL) and ZnO nanostructures, capacitive desalination can cut the cost of water purification by half or better. What are the benefits? Clean water can be made safely for agriculture (lower standards @ 1500 ppm) and for drinking (higher standards).

7. Layer-by-Layer (LBL) Structures

Ionic self-assembly of colloidal nanoparticles is a useful method to construct the multilayer thin films that have possible applications as electronic devices. Self-organized fabrication of devices has been carried out starting with colloidal nanoparticles as building blocks. Multilayer thin films of gold nanoparticles stabilized by glutamates and zinc sulfide nanoparticles capped with chitosan were self-organized by a modified polyelectrolyte deposition process. The LBL process of making multilayered films is shown as a schematic in Figure 14. By alternative dipping in positively and

negatively charged species, a layered structure is obtained. The structure can possess unique optical or electrical properties— or even be used as a pressure sensor.

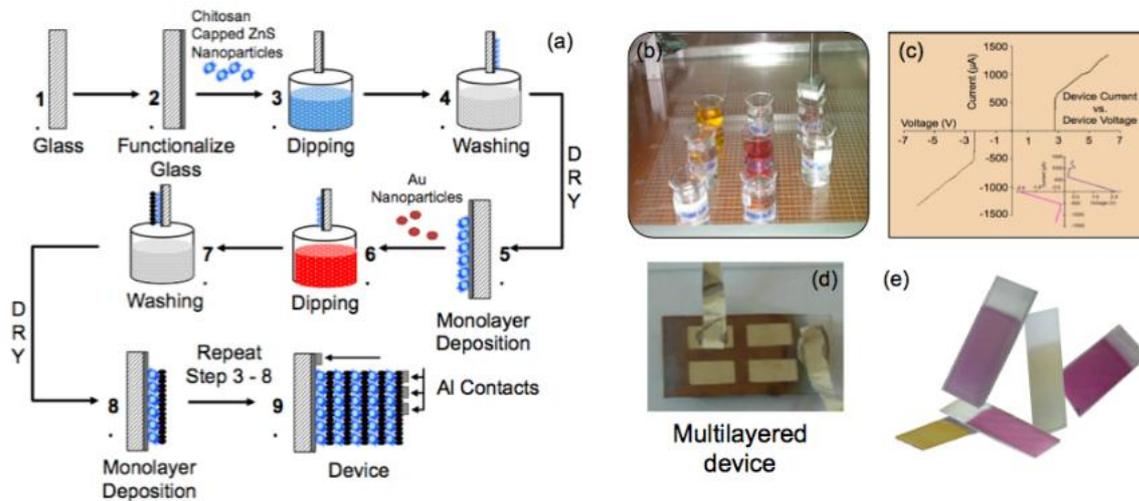


Figure 14: A Layer-by-Layer (LBL) scheme of structure

A homemade mechanized system for making LBL films has been developed at the CoEN@AIT for studying properties of LBL films. For Au-ZnS LBL films, a resistive current-voltage characteristic was observed in devices with less than 50 layers. Electrical and optical studies on multilayered films developed using different nanoparticles like Au, ZnS, ZnO, SiO₂, etc. are being carried out on multilayered films grown on silicon and glass. The process is conducted under ambient room conditions.

4.3 Noble metal nanoparticles

4.3.1 Gold colloid synthesis from the bottom-up

One remarkable property of nanometallic gold is its ability to change color as a function of size. Optical properties of metal nanoparticles widely vary with particle size and shape, particle-particle distance, and the dielectric properties of the surrounding solution due to a phenomenon called surface plasmon resonance (SPR). A plasmon is a wave phenomenon that can be considered as a collection of interacting electrons. Plasmons occur on the surface of a metal and are quantized. When light (an electromagnetic wave) is incident on metal nanoparticles, its electric field disturbs the electron cloud and excites electrons to oscillate. This creates surface charge separation due to the dipolar resonance absorption— resulting in specific and size-dependent colors shown in Figure 15.

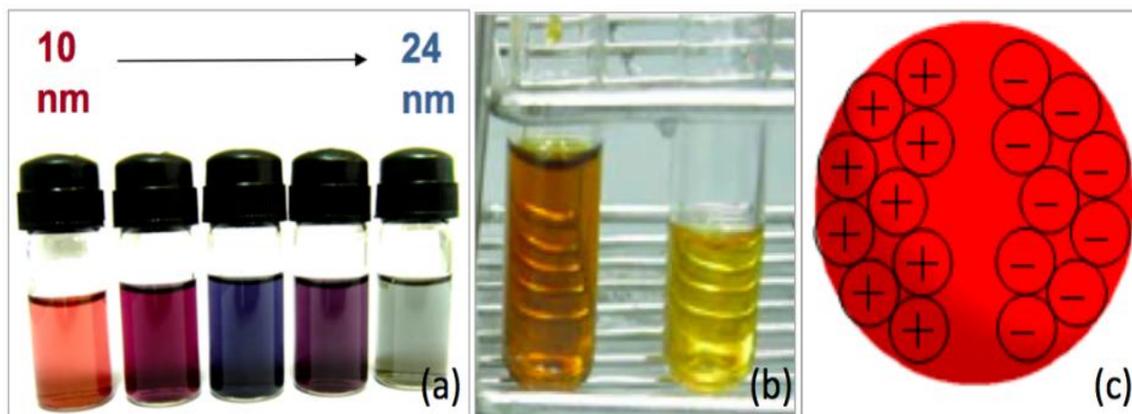
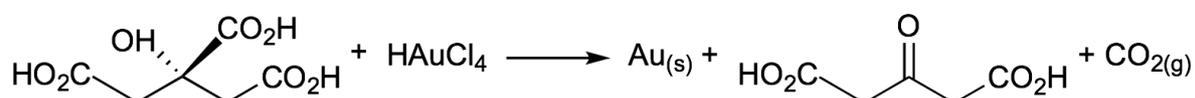


Figure 15: The various colors of gold nanoparticles are shown as a function of size. (Image courtesy: Center of Excellence in Nanotechnology, Asian Institute of Technology)

When the frequency of the electromagnetic field resonates with the coherent electron motion due to dipolar oscillations, there is a strong absorption in the optical spectrum, which is the origin of the colors observed in gold colloids with different particle sizes. We all are familiar with the color of gold in the bulk phase. In the nanophase, gold assumes alternative states with different colours.

4.3.2 Gold colloid applications

Gold nanoparticles can be synthesized from the bottom up by the well-known and well-defined Turkevich method according to the following generalized bottom-up scheme:



A source of gold (chloroauric acid) is mixed with a reducing agent (citrate). Trisodium citrate is used in most cases. Following reaction, gold colloids are produced. The reaction takes place in boiling water. Silver nanoparticles are produced by a similar procedure. Size of nanoparticles is controlled by manipulation of experimental parameters like concentration, pH and temperature. Metal colloids are formed from the bottom-up with simple chemicals under relatively mild experimental conditions. Applications gold colloids include fingerprint detection (Figure 16), heavy metal detection (Figure 17) and formation of gold nanotubes (Figure 15). Other applications include their use in optical filters, catalytic conversion of carbon monoxide, pressure sensors, and medical therapeutical treatments.

1. Fingerprint Detection

Fingerprints can be detected using gold nanoparticle by application of lipophilic organic ligands to gold nanoparticles. Optical contrast is enhanced when Au-ligand complexes are applied onto latent fingerprints. Agglomeration of gold nanoparticles onto the lipid residues pre-treated with lipophilic

chitosan was found to be the most optimum method. Ridges of the fingerprint are clearly distinguished by this method– features that would otherwise not be recovered after, for example, an application of rain. This method shows promise for forensic adaptation.

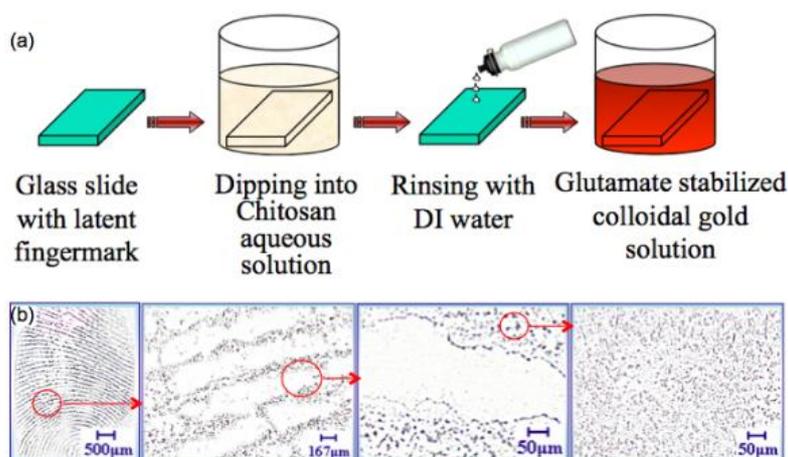


Figure 16: A new fingerprint detection method based on gold colloids (Image courtesy: Center of Excellence in Nanotechnology, Asian Institute of Technology)

Figure 16 shows a new fingerprint detection method based on gold colloids. Water is able to wash away fingerprints however, with Au-colloids capped with glutamate, fingerprints can still be recovered. Glutamate is able to bond to the fatty acid residues left by a fingerprint.

2. Trace Metal Detection

A novel strategy for detection of heavy metal ions like Zn^{2+} and Cu^{2+} in water has been developed using chitosan capped gold nanoparticle. The heavy metal chelating property of chitosan has been effectively used for the detection of low concentrations of heavy metal ions like Cu^{2+} and Zn^{2+} . Chitosan has free amines in some of its repeat units get protonated in dilute acidic condition forming the multiple bonding sites that are useful in chelating heavy metals ions. A comparison of the optical absorption spectra of the colloidal gold nanoparticle suspension before and after exposure to metal ions is indicative of the concentration of the heavy metal ions (Fig. 17).

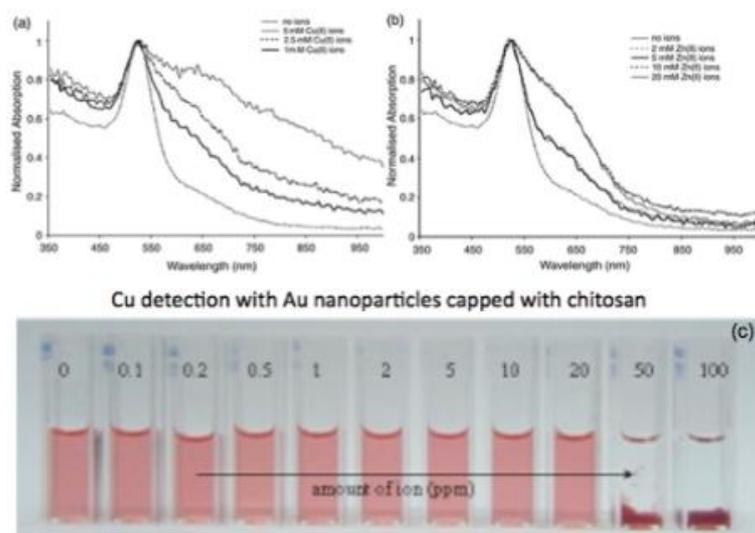


Figure 17: A comparison of the optical absorption spectra of the colloidal gold nanoparticle suspension before and after exposure to metal ions (Image courtesy: Center of Excellence in Nanotechnology, Asian Institute of Technology)

Heavy metal detection is easy to accomplish with specially treated gold nanoparticles. Depending on the metal, a special sensing chemical is placed on the gold colloid. If the concentration of the heavy metal in polluted water exceeds 50 ppm, the color of the solution changes to clear. This is useful to farmers in the field and environmental engineers.

3. Directed Self-Organization

Aspergillus niger can act as a template. Gold colloids stabilized with glutamates or other organic moieties can serve as a nutrient source for the mold. Once consumed, there is no other barrier to agglomeration for the inherently metastable gold nanoparticles and nanowires are formed upon removal of the biological component (Figure 18). The fungus is fed on the organic coating of the Au colloids placed in the solution. Once the coating was consumed, the colloids agglomerated to form wires. It is difficult to make tubes from top-down technology.

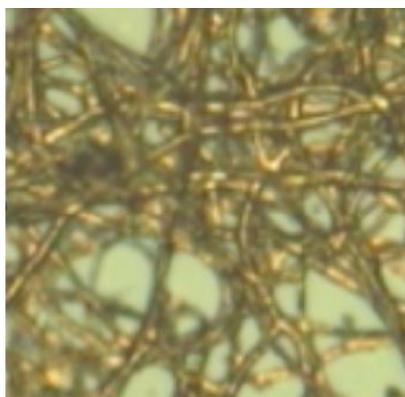


Figure 18: Gold nanotubes made from templating effect of hyphae of *Aspergillus niger*, the common mold

4.3.3 Silver colloid applications

Nanoscale silver (Ag) has antimicrobial properties and its use is widespread globally. The synthesis of Ag is similar to that of gold. It is solution based under mild conditions. A reducing agent is added to form silver from silver salt bearing chemicals dissolved in solution. Silver is the most often used substance in the generation of nanomaterials

4.4 Other materials

4.4.1 Templating materials

Nanomaterials can be fabricated inside template materials– e.g. materials that provide a structural geometry to the desired nanomaterial. Anodizing aluminum metal in polyprotic acids results in an oxide coating that is porous and honeycomb-like in structure (Figure 19). Anodic membranes are one of the most versatile of nanomaterials.

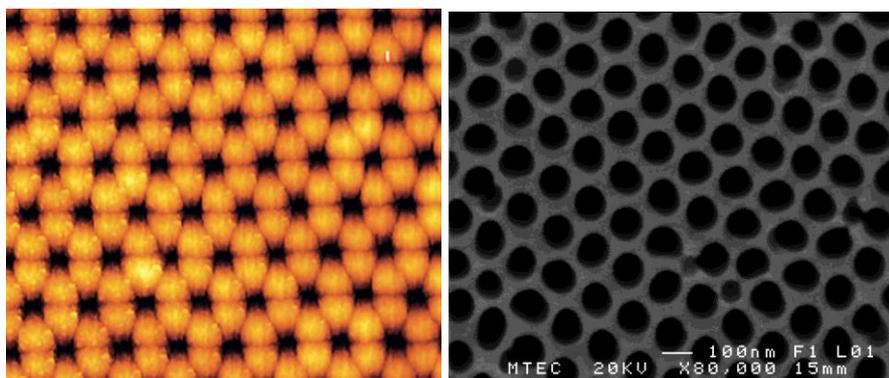


Figure 19: Porous and honeycomb-like structure of alumina membranes. On the left, an atomic force microscope (AFM) image of membrane with 80 nm pore diameter and on the right, a scanning electron microscope (SEM) image of a membrane with 100 nm diameter pores are depicted. (Image courtesy: Center of Excellence in Nanotechnology, Asian Institute of Technology)

Depending on the applied voltage (1 nm pore diameter per volt applied), pore diameter can be varied from a few nanometers to greater than 300 nm. Membranes with pore density ranging from 10^8 to 10^{14} pores per cm^2 can be fabricated. Metals, semiconductors and insulating materials can be synthesized within these pore channels. Anodizing is a technology that is over a hundred years old. All that is required is a power supply, a chiller, polyprotic acid electrolytes and some aluminum– one of the lowest tech of low-tech applications. The process is bottom-up and is easy to scale-up to industrial proportions.

4.4.2 Encapsulated agricultural products

There is great need for the development of more efficient fertilizers. Encapsulation of micron-scale and nanoscale nutrients such as potassium, nitrates and phosphorous in capping agents like chitosan allow for more efficient delivery.

4.4.3 Carbon nanotubes

Carbon nanotubes are made by bottom-up synthetic methods but are somewhat energy intensive. The chemical vapor deposition process is one of great simplicity but requires temperatures above 500 °C to operate. Research is conducted vigorously around the world to lower these barriers.

Applications of carbon nanotubes, and its cousin graphene, are multiplying. The manufacture of multi-walled carbon nanotubes is already in the phase of big business. Research is also conducted globally to make single-walled nanotubes monodisperse with regard to diameter (chirality), length and orientation.

Applications include ballistic conduction, energy-storing devices and batteries, structural materials and heat exchange materials. The Chinese have made incredible breakthroughs recently in carbon nanotube research and development.

5. Opinion

5.1 Remaining bottom-up perspectives

As promised, we shall touch upon and provide opinions about the remaining Bottom-Up species mentioned earlier in the report. The challenge of course is directed directly in the direction of Top-Down organizations– the governments, the regional organizations– for them to address.

5.1.1 Collaborations

Scientists in academia collaborate with each other seemingly regardless of any superior authority. For example, a scientist, depending on a complementary research need, simply exchanges business cards with another scientist, usually at a conference, and collaboration is born. From that collaboration, a scientific result of some value and a paper emerges. Scientists in business and industry have limitations with regard to collaboration due to guarding of proprietary information. However, businesses also collaborate but with higher levels of agreements in place. Regardless of what kind of collaboration, the result is usually in the form of research papers that have higher number of citations– this according to the 2011 WSF conference. What can Top-Down organizations do to enhance collaboration?

1. Provide funding first and foremost. Without funding, there is no collaboration. Release solicitations that attract Bottom-Up synthesis research after needs/ niches/ and opportunities have been defined
2. In alliance with academic institutions, associations and industry, the Top-Down organization needs to assist in supporting conferences, workshops and other venues of interaction.
3. Top-Down organizations (perhaps UNESCAP as per the suggestion of Dr. Ramanathan) need to assemble, support and operate a comprehensive science and engineering database from which scientists can accomplish Bottom-Up collaboration without too much oversight.
4. Top-Down agencies of emerging nanotechnology programs need to establish or sponsor centralized characterization and support laboratories that add value to collaborative efforts. Payment systems can be centralized and efficient. Thailand (with its Science Park) and the United States with the National Nanotechnology Infrastructure network (NNIN) are prime examples of programs that enhance collaboration (and research in general). Other countries of course (China, Pakistan etc.) also have impressive networks. The collaboration between the Center of Excellence in Nanotechnology at the Asian Institute of Technology (a PMNT but emerging laboratory) and NANOTEC in Science Park is a good representation of the need for a well-funded partner.
5. Top-Down organization(s) need to find a way to ensure that ALL scientists in its database have access to the latest journals– via internet means.
6. Top-Down organizations need to develop KEY PERFORMANCE INDICATORS (KPI) that allow for rapid evaluation of scenarios (per year with no hysteresis). One such indicator is needed to measure the degree and extent of collaboration. The placement of the database mentioned above would aid in evaluating such a metric.
7. Top-Down organizations need to make sure that funding and opportunity flow from the Bottom-Up and not primarily to big schools, big names, big companies or big organizations.

5.1.2 Small business development

Small business is at the heart of diversity. Unfortunately, small business is disappearing everywhere, especially in well-developed nations. What can Top-Down organizations do to enhance the prosperity of small business? And thereby enhance diversity? There are many obstacles in place– lack of funding, slow and expensive patent processes, cumbersome technology transfer and licensing, and perhaps lack of incentives that promote emerging business. If supported, PMNT, Bottom-Up synthesis and small business in particular have the capability to expand markets quickly. What issues should Top-Down organizations consider with regard to business development in emerging (and even well developed) nanotechnology programs?

1. Provide funding first and foremost. Small-scale funding for more business development is required. Innovative procedures are explained in a new book⁷. Initiate reform of patent, licensing and technology transfer procedures to assist in the form of indirect support. Provide incentives for small businesses to attend trade shows in the AP region.
2. Specific funding for the “Death Valley scenario” in which there is a good idea that is waiting to be commercialized but requires proof of concept and prototype development beforehand. Usually small amounts of funding are required. Although small business funding exists in many developed nations (e.g. Small Business Innovative Research or SBIR programs), it is still quite difficult to bridge the gap between basic-applied research and creation of an emerging business.
3. Top-Down support of PMNT businesses for the purpose of distributing LTNT products to those that need them the most.
4. Provide a centralized infrastructure that supports characterization and analysis similar to the landscape described in #4 described under ‘Collaborations’.
5. Provide incentives and aid that promote exports of small business products to other countries.
6. Initiate the development of nanotechnology economic clusters similar to those established in the Albany River Valley in New York and the Arizona Cluster in Phoenix, Arizona.
7. KPI are also required here, monitored from the Top-Down.

5.1.3 Local and national association support

Local associations form vital links between and among individuals residing in the sectors of academia, business and government. Local associations have the worm’s eye (Bottom-Up) view of the nanotechnology landscape. For example, they are vital components in bringing conferences and other events to a locality, coordinating job training and in providing educational materials. The recently formed Nanotechnology Association of Thailand is geared to support nanotechnology throughout the nation by influencing policy, sponsoring conferences and promoting education. What can Top-Down entities do to help associations gain memberships?

1. First and foremost, once again, funding is important in the forms of providing free space for meetings and funding of association programs
2. Providing a seat for associations in Top-Down organizational meetings so that input from the Bottom-Up is represented in future policy and strategy.

⁷ P. Ganguli and S. Jabade, Nanotechnology Intellectual Property Rights: Research, Design, and Commercialization, CRC Press, July 25, 2012.

3. Associations can bring together professionals in the field but also those who are involved in Top-Down organizations (e.g. governments in particular). The presence of such individuals is important to the viability of the association.

5.2 Questions for top-down entities

Obviously, the thrust of this report is centered on Bottom-Up elements of the nanotechnology landscape and how Top-Down organizations can make them thrive. Therefore, some questions are posted below for TD elements to address.

1. Which kind of fundamental nanotechnology must be pursued (TD or BU)?
2. What kinds of new products can be developed from BU methods?
3. Can this nanotechnology be scaled-up and eventually mass-produced?
4. How does that BU nanotechnology balance the needs of its population with the resources available to address those needs?
5. Where does a nation, especially one residing in or around the Pacific basin, find the perfect niche for its special brand of nanotechnology– one that it can soon lead the region and perhaps the world in terms of productivity?
6. Can this nanotechnology be made affordable, available to those that need it the most?
7. Will there be equity, productivity and sustainability?
8. How can BU collaboration be supported better? Should there be more conferences? Workshops? Faculty exchange programs? Other incentives?
9. Can a regional database be created that has as in its membership scientists, engineers, academic administrators and presidents, business managers and CEOs, and government representatives, policy makers and leaders?
10. Can a regional resource of internet information (e.g. electronic journals) be made available to all members?
11. How can we generate more small businesses? Can we provide funding to cover ‘Death Valley’ scenarios? With fewer strings attached?
12. Can we facilitate the patent process and make filing less expensive?
13. Can we facilitate the technology transfer process?
14. What role can basic research play in the AP theater– especially in South East Asia?
15. What conferences should AP Top-Down organizational representatives attend in the near future?

5.3 Equity, productivity and sustainability

5.3.1 Poor Man's Nanotechnology-Type I: Bottom-Up Synthesis

The discussion of “poor man's nanotechnology” (PMNT-I) is presented from the point of view of scientists and engineers. It is nanotechnology done with minimal resources. By default, it is nanotechnology accomplished from the Bottom-Up.

PMNT-I is nanotechnology conducted with minimal resources. This phrase applies to research and education programs in which funding is sparse. The phrase is additionally applied to emerging enterprises that do not have at hand significant capital resources or government aid in the form of grants. Therefore, PMNT-I is nanotechnology accomplished by the ‘seat of one's pants’. It is therefore strategic and wise to conduct Bottom-Up technology and partner with ‘those that have’. PMNT-I needs big friends.

5.3.2 Poor Man's Nanotechnology-Type II: The Consumers Without

In addition to forging ahead with nanotechnology enhanced products to make competitive marks in the AP region, PMNT-II is also interested in developing applications that make possible clean drinking water, cheap energy, safe food, cheap efficient fertilizers and the other products that add value to the living standards of people without– those without resources to afford such basic necessities that many of us have. Delivery of such technological promise is of course dependent on PMNT-III. Although we do not have direct contact with PMNT-II, we develop such technologies with the end consumer in mind– the consumer who cannot otherwise afford new technological products.

An additional aspect to consider is how do we ensure the equitable distribution of technology. Equity, as defined by Merriam-Webster, is ‘justice according to natural law and right’. It is the ‘state, quality or ideal of being just, impartial and fair’. Nice words for sure, but in the world of ‘everyone trying to make the big buck and the bottom line’ as objectives, how can resources be distributed to those that are most in need? One can easily find examples of non-equitable distributions of technology and technology-based services anywhere, especially, and ironically, in the greatest industrialized nations.

5.3.3 Poor Man's Nanotechnology-Type III: The Dot Connectors

This refers to connecting the dots between PMNT-I and PMNT-II accomplished by Top-Down organizations. Nanotechnology is known to have a high barrier of entry and therefore partnerships between and among business, government and academe are a necessity– especially for PMNT. How well this part performs to a great part determines how well nanotechnology is delivered from PMNT-I and PMNT-II. What are the key issues and impediments to providing and implementing nanotechnology in the southern and southeastern regions of Asia? Are there practical approaches to commercializing first the nanotechnology and then developing the requisite human resources?

It is PMNT-III's job to make equity the rule and not the exception. Nanotechnology's upside is immense and it is expected to solve many driving issues and dilemmas facing humankind in the 21st Century. The same question stated in the opposite sense is also compelling– will the technology be available only to those who have the means to afford it? PMNT-II needs some answers about such basic nanotechnologies and how they can be distributed.

6. Epilogue

This report finds its origins from the experience and perspective of scientists and not forecasters, economists, policy makers or funding agencies. The vision of this report is to help developing nations start nanotechnology industry programs without financial or technical aid from outside the region. Inter-regional efforts can run parallel with such Bottom-Up efforts without issues– perhaps symbiotically. The purpose of the report is to bring awareness in significant ways to the BU elements.

7. Appendix

World Science Forum Declarations

Text adopted by the 5th Budapest World Science Forum

on 19 November 2011

(definitive version)

Preamble

With the encouragement and support of our partner organisations, the United Nations Educational, Scientific and Cultural Organization (UNESCO), the International Council for Science (ICSU) and all invited organisations and fellow scientists, we, the participants of the Budapest World Science Forum held from 17 to 19 November in Budapest, recognizing the relevance of the outcomes of 1999 World Conference on Science (WCS) and taking into account the reports of the biannual World Science Forum (WSF), as well as the debates and the outcomes of this World Science Forum on the “Changing Landscape of Science: Challenges and Opportunities”, adopt the present declaration.

1. The treasure of scientific knowledge and its underlying research approaches are a common heritage of humankind. More than ever before, the world will be shaped by science.
2. The first decade of the third millennium has witnessed steady and fundamental changes in the global landscape of science. The scale and scope of these transformations are so robust that a new milestone in the history of science has been reached, and a new era of global science has commenced. This new era presents challenges and opportunities bringing political, social and policy implications on a previously unseen scale.
3. The growing complexity of grand challenges including population growth, climate change, food supply, energy shortages, natural and technological catastrophes, epidemics, and sustainability require that the world's scientific establishments assume new roles.
4. New scientific fields have appeared and continue to carve out their niches in the general field of science.
5. The unforeseen spread of information and communication technologies, the inexpensive and instant access to information resources and databanks, and the fall of communication barriers between countries and communities have accelerated the accumulation and dissemination of knowledge.

6. The former triadic dominance of North America, Europe and Japan in global knowledge production has been seriously challenged, and a new multipolar world of science has emerged accompanied by the rise of new scientific powerhouses, which are now not only prominent actors in world economy but have become key players in cutting edge research and development activities.
7. In this new context of global science, science diplomacy is now an acknowledged tool to promote partnership among nations by fostering scientific co-operation.
8. Educational systems have received strong support from their respective governments to the extent that emerging countries currently produce more university graduates and PhDs than the developed world thus rearranging the entire global “knowledge map”. In spite of these new developments the US, EU and Japan are still leaders in scientific performance and continue to invest heavily in research and innovation. The competition is more intense and more open than ever before in the world arena of science.
9. The expansion of scientific networks has also changed the circle of actors participating in research activities. A field once dominated by states and their research networks of national academies, learned societies, and universities is now complemented by a complex network of global companies, international organisations, and individual researchers who are attracted to the best available research infrastructure.
10. The accelerating “knowledge economies” have generated new migration patterns for scientists and increasing mobility. Both the winners and losers of brain drain are facing the need for more intensive co-operation between universities, public research organisations, and industry in both graduate and post-graduate education and the elite training of scientists.
11. The advancements in science have also shed light on new and previously unforeseen concerns. Climate change, the large-scale and irreversible impact of human civilization on the world’s fauna and flora, an overconsumption of natural resources, and their respective consequences require stronger involvement from both scientists and society. Developments in many research fields (e.g. genetics, biotechnology, neuroscience, nuclear physics, etc.) have considerable moral and ethical implications that require an urgent and global dialogue between scientists and the broader public.

In light of this declaration, we make the following recommendations:

1. Responsible and ethical conduct of research and innovation

In this era of global science, the scientific establishment needs to implement continuous self-reflection to appropriately evaluate its responsibilities, duties and rules of conduct in research and innovation. A universal code of conduct addressing the rights, freedoms and responsibilities of scientific researchers, and the universal rules of scientific research should be shared by the world’s scientific community. Furthermore, these rules and policies should be respected by the states and adopted by their national legislations. Scientists should strengthen their individual and institutional responsibilities to avoid possible harm to society due to ignorance or misjudgement of the consequences of new discoveries and applications of scientific knowledge. It is the responsibility of those who promote science and scientists to maintain the primacy of moral and social concerns over short-term economic interest in the selection and implementation of industrialised research projects.

2. Improved dialogue with society on scientific issues

In times of rapid and fundamental changes in the social environment, the sciences should be supported in their co-operative efforts to describe and evaluate with the best available methods the consequences of policy actions and explorations of both natural and social sciences.

Participation of societies should be promoted in order to make science more democratic and to build further trust in science. To this end societies must be prepared to knowledgeably discuss the moral and ethical consequences of science and technology by strengthening policies to enhance awareness and public understanding of science and improving and broadening the scope of education.

3. International collaboration in science should be promoted

Better international co-ordination is needed for science research projects focusing on global challenges. International co-operation is essential for decreasing the knowledge divide and regional disparities. The free co-operation and movement of scientists should be promoted by the elimination of harmful bureaucracy

and false regulation and by providing the funds to further international co-operation. To avoid repetition, redundancy, and excessive expense in scientific research, the international scientific community should be involved in the development of an improved method to monitor past and present research activities and their results.

4. Collaborative policies to overcome knowledge-divides in the World

The rapid development and increasing cost of science combined with the expansion of patent policies and regulations have further widened the knowledge and economic divide between the developed and developing world. In a world where the best science and the best researchers are attracted only by excellent research infrastructures, developing countries should be supported in their efforts to build their research capacities. However, co-funded actions for building capacities can only be successful if support is provided in a socially responsible way and if it creates a win-win situation for both the promoter and the recipient. Brain-drain and brain-gain policies should be co-ordinated for the joint benefit of all affected countries.

5. Capacity building for science needs to be strengthened

Scientific discoveries are foundations for innovation and social and economic development. Investment in science provides a capacity for future development at a national level and an opportunity to face global challenges internationally. It is primarily the responsibility of governments to increase support for science, and develop effective policies for technology and innovation. Comprehensive actions should be taken to strengthen the role of women in science and innovation and to expand the participation of women in science and science policy making. The socio-economic impacts of science and scientific capacity are well-documented. National parliaments and governments are urged to declare their commitment to seek scientific advice during the decision making process. An institutionalisation of such an advisory process is necessary; informed decisions result in great savings. There is an urgent need to elaborate new, effective science policies at national, regional and global levels to better co-ordinate and monitor scientific research worldwide, to harmonise university education systems, and to facilitate global and regional scientific co-operation based on equity and participation.

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