irresistible

The Catalytic Properties of Nanomaterials

Students manual

Responsible Research and Innovation www.irresistible-project.eu

Colophon

IRRESISTIBLE is a project on teacher training, combining formal and informal learning focused on Responsible Research and Innovation. It is a coordination and support action under FP7-SCIENCE-IN-SOCIETY-2013-1, ACTOVITY 5.2.2. Young people and science: Topic SiS.2013.2.2.1-1 Raising youth awareness to Responsible Research and Innovation through Inquiry Based Science Education. The project IRRESISTIBLE is funded by the EU as FP-7 project number 612367

www.irresistitle-project.eu
Coordinator: j.h.apotheker@rug.nl

The Catalytic Properties of Nanomaterials

Students manual

This material will help you to participate in meetings in a successful manner. Active participation in classes allow to improve your knowledge about responsible research and innovation (RRI), nature of science, scientist' work, catalytic properties of nanomaterials, nanotechnology and planning and designing exhibits.

Here you can find: background information, topics for discussions, exercises in different forms, worksheets, students instructions, self-assessment sheets, additional literature and other useful materials.

Take responsibility for your learning! Be active!

1. Lesson No.1 Nature of Science 9

2. Lesson No.2 Visit to a Research Institute 15

3. Lesson No.3 The Creation of Interactive Exhibits 24

4. Lesson No.4 Bread Made from the Air 30

5. Lesson No.5 Cars, Soot & Sorption 35

6. Lesson No.6 Size Makes a Difference 44

7. Lesson No.7 A Catalyst 49

8. Lesson No.8 A Diesel or a Gas/Petrol Car? 54

9. Lessons 9 & 10 Photocatalysis 62

10. Student Self-Assessment Sheet 70

1

Nature of Science

Lesson No.1

Nature of Science

Author: intararit / Fotolia

Exercise 1.1

Mark the matches: a scientist – a coincidence associated with him/her

table 1.1
[table title]

Coincidence	Scientist
1. Falling apple	A. A. Einstein
2. Dream of devils tied with tails or the Ouroboros serpent eating its own tail	B. M. Skłodowska-Curie and P. Curie
3. Mouldy scale pan with bacteria cultures	C. F. A. Kekule
4. Roll of film near a sample of uranium	D. I. Fleming
5. Dream of chasing (overtaking) a ray of sunshine	E. Archimedes of Syracuse
6. Bath filled to the brim	F. I. Newton
7. Nitro-glycerine spilled on the ground	G. A. Nobel
Your answer:	

Exercise 1.2

Connect the researchers and the views (achievements), presented by them using lines; state whether the opinions are relevant today

N. Bohr	S. Arrhenius	J. N. Brønsted	L. Pauling		J. Dalton
Planetary model of atomic structure	Theory of electrolytic dissociation	Theory of acids and bases	Covalent bond theory	Exceptional biological role of vitamin C	Theory of the structure of matter assuming the indivisibility of atoms
H. Lorentz	J. J. Thomson	G. E. Stahl	Irène Joliot-Curie	Maria Goeppert-Mayer	Dorothy Crowfoot
Ether theory	'Raisin bread' theory of atomic structure	Phlogiston theory	Discoverer of artificial radioactivity	Atomic nucleus coating structure	Structure of penicillin, cholesterol, vitamin B12

Exercise 1.3

Develop the scheme of conduct in scientific method – prepare a poster by putting the steps of the research process in the correct sequence. The choices are as follows:

problem identification	posing a research question	analysis of the previous knowledge on the issue
formulating a hypothesis	public presentation of the results and conclusions	conducting scientific research (experimental, observation)
analysis of the data obtained (searching for dependencies, making a chart, comparing quantities)	evaluation of measurement errors	drawing conclusions (synthesis)
verification of the hypothesis	planning the research - selecting methods, defining variables and number of trials	submitting the results and conclusions for critical analysis of other scientists

Additional literature

Difference between a theory and a law: http://www.sciencealert.com/this-infographic-breaks-down-the-top-five-misconceptions-about-evolution

2

Visit to a Research Institute

Lesson No.2

Visit to a Research Institute

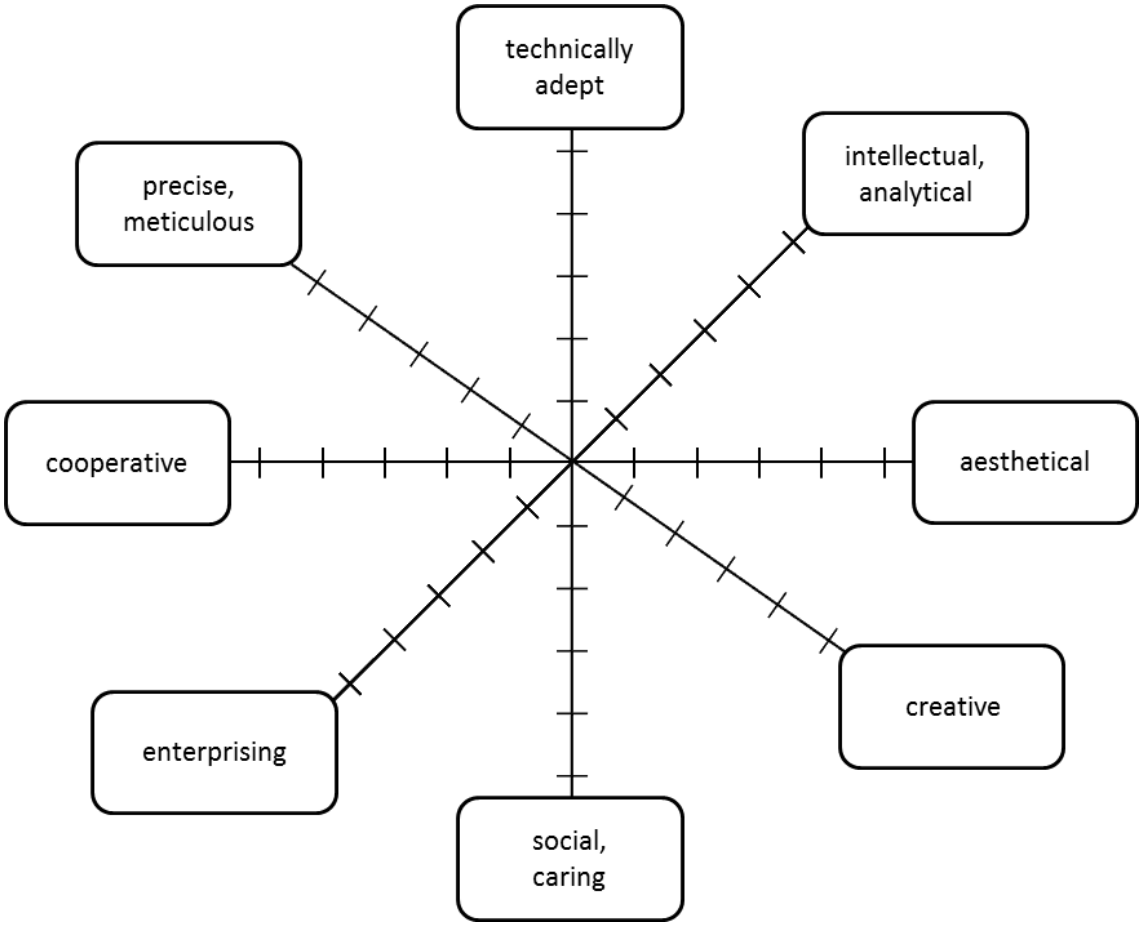
Photo: Beata Sobocińska

I. Features of a scientist

1. How important are the following features for a scientist?

Mark with a cross on the axis. If the feature is very important, mark near the outer end of the axis; if the feature is not very important, mark near the centre.

A scientist should be[1]:



2. Consider and answer the questions:
   - Who may be a scientist?
   - List the three most important features of a scientist.
   - What should be the composition of scientific/research teams?
   - What should determine whether a new person is or is not accepted to a research team, and what is unimportant?
   - Should a scientist be a good teacher? Why?

---

[1] Developed by Ilka Parchmann et al., IPN- Leibniz Institute for Science and Mathematics Education, Germany

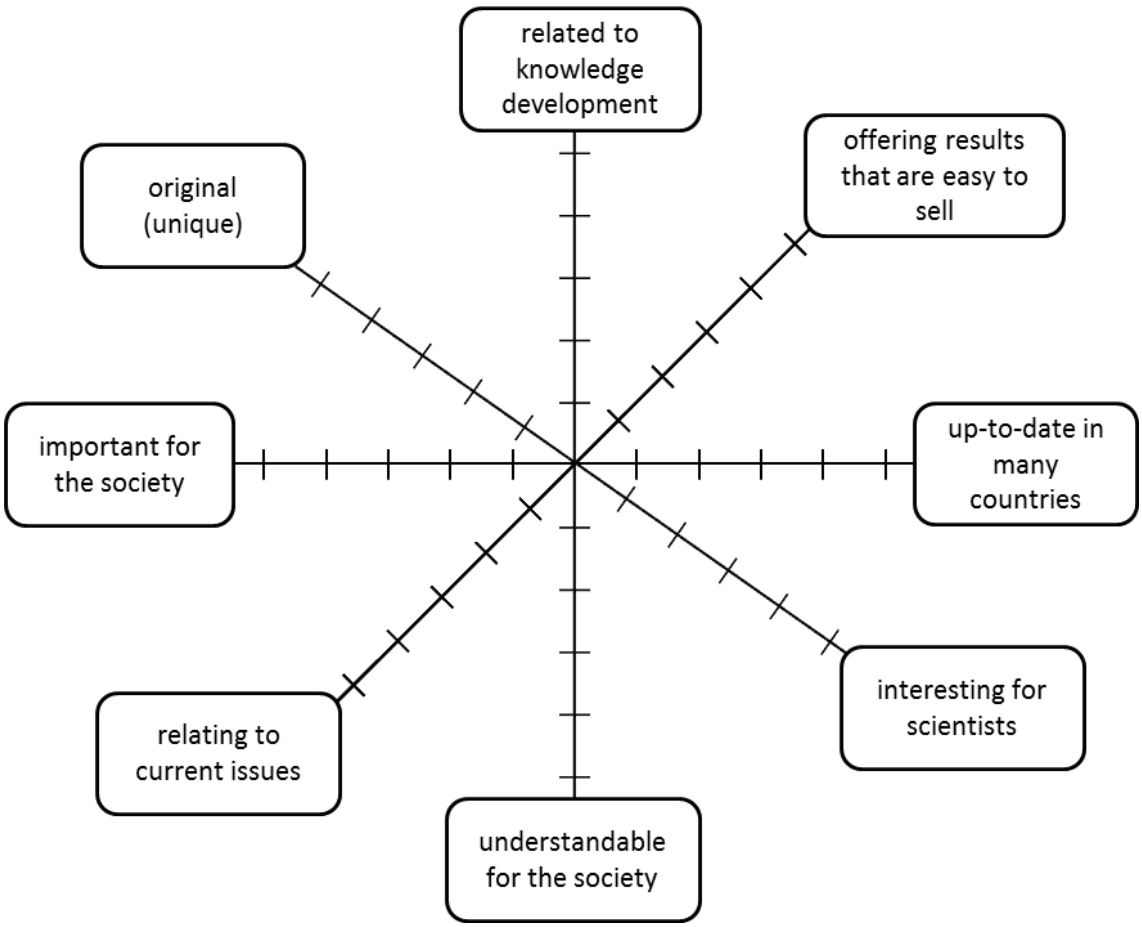
3. Discuss your answers in the group, agree on the conclusions, write them down on the enclosed card, and then present them to the other participants of the meeting

II. Research topics

1. What should be the features of a research topic?

Mark with a cross on the axis. If the feature is very important, mark near the outer end of the axis; if the feature is not very important, mark near the centre.

A research topic should be:



2. Mark one or several answers.

Who should decide on:	Scientists	Government	Society
a. the topic of the research			
b. science development directions			
c. industry development directions			
d. financing research			
The access to the research results should be granted to:			

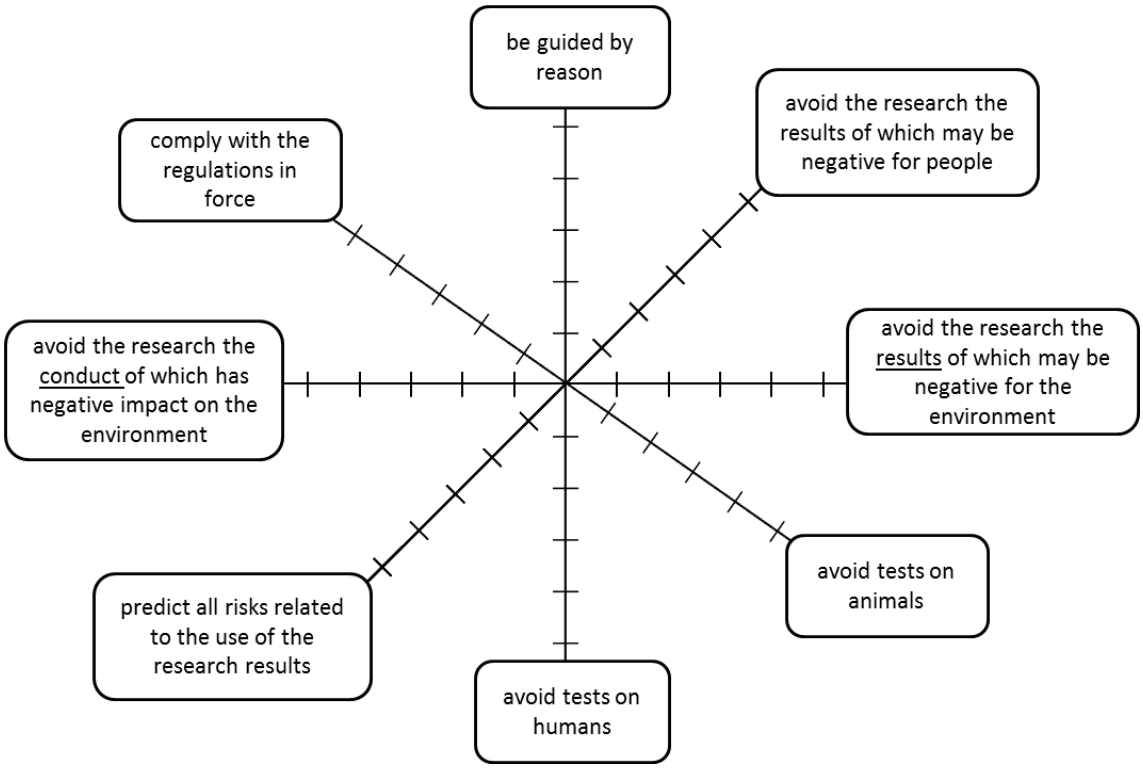
3. Discuss your answers in the group, agree on the conclusions, write them down on the enclosed card, and then present them to the other participants of the meeting.

III. Ethics in scientific research

1. To what extent should scientists, when planning and conducting their research, be guided by moral principles(by the concept of good and evil)?

Mark with a cross on the axis. If the feature is very important, mark near the outer end of the axis; if the feature is not very important, mark near the centre.

A scientist, when planning and conducting research, should:



2. What ethical issues (benefits and risks) do you associate with the topic being a part of the IRRESISTIBLE project related to the use of nanomaterials and catalysis in environmental protection?

3. Discuss your answers in the group, agree on the conclusions, write them down on the enclosed card, and then present them to the other participants of the meeting.

IV. Innovation and new technologies - implementation ethics

1. When implementing innovations and new technologies for widespread use, to what extent should the effects of their use be predicted?

In the diagram below, select to what extent you agree with the following statements.

Persons and institutions involved in the innovation implementation should:

I disagree		I agree
	Predict the possible negative results for people	
	Predict the possible negative results for the environment	
	Take into account safe disposal of wastes	
	Monitor the use, paying special attention to the results that were predicted beforehand	
	Monitor the use, paying special attention to inappropriate usage (for a wrong purpose)	

2. Who bears the greatest responsibility for the consequences of the implementation of innovations and new technologies for widespread use? *Arrange the items on the list in the order of importance:*
   a) Government or self-government
   b) Producers
   c) Sellers
   d) Inventors
   e) Non-governmental organisations
   f) Users

Enter the proposed order (from the most to the least responsible) in the following diagram:

3. Discuss your answers in the group, agree on the conclusions, write them down on the enclosed card, and then present them to the other participants of the meeting.

V. Research and innovation – information

1. In your opinion, where can one find information on the latest research results?
   a) Popular science magazines
   b) Patent Office
   c) Scientific journals
   d) Facebook
   e) National Ministry of Science and Higher Education
   f) Websites of universities and research centres
   g) Open lectures
   h) Textbooks
   i) Daily press

   Select 3 sources from the list above:

   The most reliable – …….
   The most easily accessible (for you) – ……

2. Apart from researchers, who should have free, unlimited access via the Internet to the results of the research financed from public funds? Complete

   …….

3. Should the persons involved in research and innovation also be dealing with the promotion of natural, exact and technical science in schools?

   YES/NO

4. If you answered 'yes' to question 3 – describe how,
   If you answered 'no' – justify your answer below

Discuss your answers in the group, agree on the conclusions, write them down on the enclosed card, and then present them to the other participants of the meeting.

3

The Creation of Interactive Exhibits

Lesson No.3

The Creation of Interactive Exhibits

Photo: Piotr Zwoliński

1. Exhibit Evaluation Card

Exhibit name	
Describe the actions taken to perform the experiment.	
Did you manage to perform the experiment? What could disturb your performance and what could help you in it?	
Was the experiment result satisfactory?	
What did you understand based on the experiment? In your opinion, what is its basic idea?	
Was the experiment's description clear to you? What can be improved in it?	
Do you like the look of the exhibit? What can be improved in it?	
What would you change in that exhibit?	
Other comments	

2. Interactive Exhibit Analysis Sheet

Exhibit:	Descriptive evaluation	What to do to make the exhibit better?
Compatibility with the current state of knowledge		
Interactivity level		
Which and how many dimensions of RRI have been taken into account?		
Possibility to use Web 2.0 tools		
Opportunity of registration of the viewers' opinion		
Other comments		

Interactive exhibits instructions

MEMORY GAME

Put the cards, face down, on the table in a random arrangement.
One by one, each person (or a group of persons) takes two cards and shows them.
If two cards with identical images are exposed, remove them from the playing area. Then, in the group, discuss the issue that has been described on the cards.
Note the conclusions from the discussion on a separate sheet of paper (the conclusions card).
Continue the game by exposing other cards.

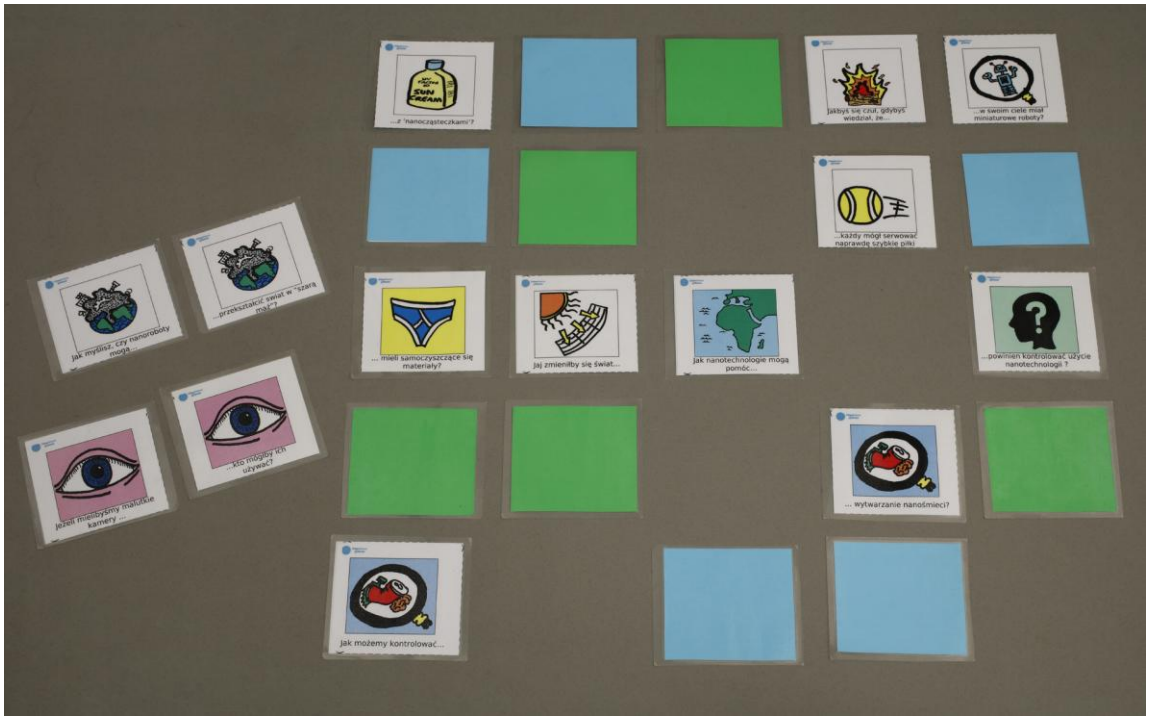


Figure: 3.1: Memory game “Nanotechnology” (Photo: Marcin Banaś)

NANOSILVER BOOK

In the book, the use of nanosilver in medicine has been presented briefly. In the first part of the book there is a description of the issue, while the second part consists of several open questions concerning the opinions and feelings of the reader. You may answer the questions individually or discuss selected questions in the group and note down your joint answers.

TWO DICE

It is best to play the game in a group of several people. First, throw two dice. On the first dice there are 6 nanotechnology methods described that can be used in environmental protection. On the second dice there are 6 dimensions of RRI listed. After throwing the two dice, during a group discussion you should find a possible way to combine these two elements. Write down your conclusions on small pieces of paper and stick them on the answers board.

Figure 3.2: Two Dices – Nanotechnology in environmental protection
(Photo: Elżbieta Serafin)

4

Bread Made from the Air

Lesson No.4

Bread Made from the Air

Author: nnerto / Fotolia

A catalyst – the substance which, when introduced into the reacting system, increases the rate of the reaction, is involved in a chemical reaction, but afterwards remains in an unchanged amount.

Worksheet – planning an experiment

Research question **Hypothesis** with the justification**:**
Determining the variables: *Which variable/quantity will you change? (independent variable)* *Which variable/quantity will you measure - observe? (dependent variable)* *What will you not change in your experiment? (control variables)*
Number of measurements:
Description of particular steps/ Experimental procedure
Way (method, means) of analysis of the results:
Way (method, means) of presentation of the conclusions:

Homogeneous catalysis – single-phase catalysis; all substrates, the catalyst and the products are in the same physical state i.e. they are, for example, gaseous substances and they form a single-phase system.
Heterogeneous catalysis – multi-phase catalysis; the catalyst is present in the state of matter (usually as a solid) that is different to that of the reactants and products (mostly they are gases).

I Fritz Haber (born in 1868 in Wrocław [Germany/Poland]; died on 29 January, 1934 in Basel, Switzerland)

A German chemist of Jewish origin, the laureate of the Nobel Prize in Chemistry in 1918 for the synthesis of ammonia from nitrogen and hydrogen. Since 1904 he began work on the balance by the formation of ammonia from nitrogen and hydrogen at high temperatures and high pressures. The study was associated with the famine in Europe that was projected for the 1930s (where for over two centuries the number of inhabitants had quadrupled). In the study he used the discovery of the 1940s indicating that nitrogen compounds stimulate plant growth. The press wrote at the time that Haber "made bread from the air". Today, world production of nitrogen fertilizers produced using the Haber-Bosch method reaches several hundred thousand tons per year. With the production of nitrogen fertilizers, Haber became a millionaire. In addition to the fortune, the discovery gave him fame and honours. He became the head of the Kaiser Wilhelm Institute of Physical Chemistry and Electrochemistry in Berlin (today renamed for Haber).

II

After the outbreak of World War I, ammonia replaced the saltpetre imported from Chile for the production of explosives and ammunition. Germany quickly and cheaply complemented their arsenals. Haber, commissioned by the German General Staff, began work on the use of chemical substances for the army. He was one of the main organisers of the manufacture and use of poison gas by the German army. In the 1920s his associates, under his personal supervision, developed the technology to produce Zyklon-B which, although originally meant as a disinfectant and pest control agent, later on was used by the Nazis in gas chambers during World War II.

III Clara Immerwahr (1870-1915)

Most famous as the wife of Fritz Haber, this remarkable woman was a brilliant chemist in her own right. She was the first woman to earn a Ph.D. in chemistry from a German university. Her career was cut short by her marriage and the commitments it entailed to running a household and raising a family. Undeterred, she became her husband's assistant and translator, a latter-day Madame Lavoisier. Her quiet efforts earned her a dedication in Fritz Haber's seminal textbook on thermodynamics. A

Driven by his patriotism, and perhaps a need to overcome the prejudice his faced for his Jewish ancestry, Haber pioneered the weaponisation of chemistry on behalf of Germany. Clara openly opposed his work, describing it as a 'perversion' of science. She was publicly denounced by him and the nation for her 'treasonous' attitude. Ultimately, following the first deployment of

chlorine gas at Ypres, she committed suicide with her husband's pistol. Her motives are unknown.

While she may not have been a synthetic organic chemist, her moral stand against her husband's wartime research is a lesson to us all.

Source: http://behindnmrlines.blogspot.com/2013/02/inspirational-women-chemistry-edition.html

5

Cars, Soot & Sorption

Lesson No.5

Cars, Soot & Sorption

Author: Jürgen Fälchle / Fotolia

Soot –is a complex carbonaceous material consisting of fine solid particles formed as a result of the incomplete combustion of fossil fuels. In addition to carbon, soot contains a few percent of hydrogen and oxygen compounds and, in lesser amounts, nitrogen and sulphur compounds.

The size of soot grains

- 50 - 90% of the number of all exhaust fumes' particles are 5– 50 nm in size and they constitute up to 20% of the exhaust fumes' weight
- 80 - 90% of the exhaust fumes' particles are 50 - 1000 nm in size, on average - 200 nm.

Source: http://www.ciop.pl/CIOPPortalWAR/file/71288/diesel_wytyczne.pdf

Carbon structure models

Source: http://www.fizyka.zsp2.edu.pl/projekty.html

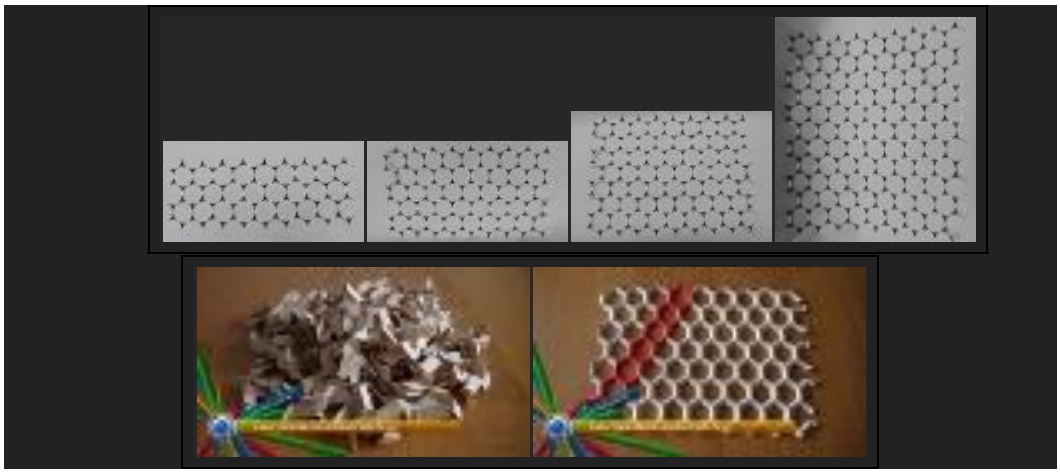
Nanotube models: C114, C150, C186, C220

Nanotubes – a supramolecular structure in the form of hollow cylinders. Carbon nanotubes' walls are constructed of rolled-up graphene (monatomic layers of graphite).

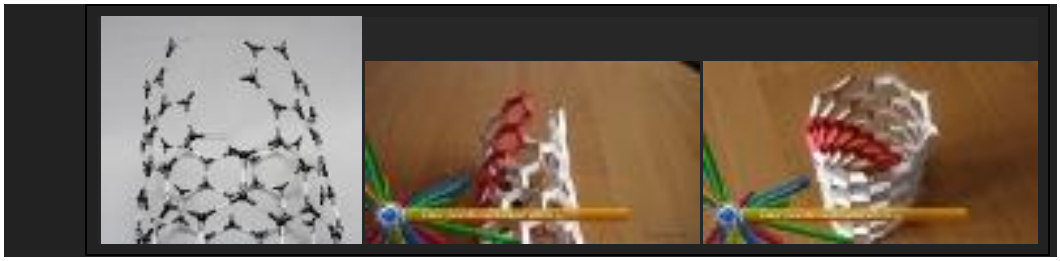
Step 1: Make a basic element in the amount depending on the type of nanotubes (i.e. for C114 nanotubes perform 114 items; for C150 - 150 elements etc.).

- use the video: www.youtube.com (https://www.youtube.com/watch?v=YIhdTzX4cis)
- print the template c60_squares in sufficient quantity.

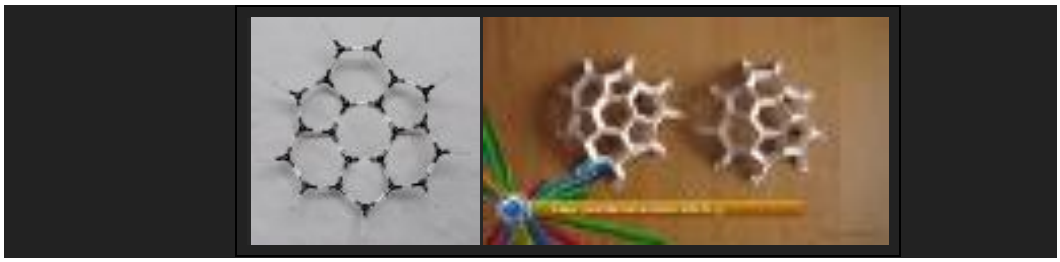
Step 1a: With the elements prepared, follow the graphene plane. The illustration shows the side wall nanotubes



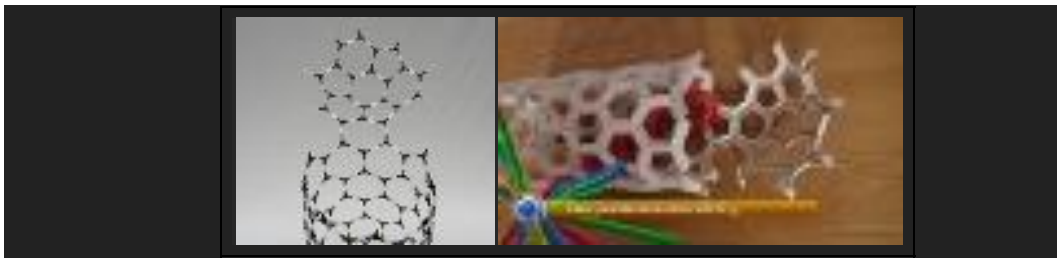
Step 2: 'Close' the graphene sheet, forming the side wall of the nanotube, as shown



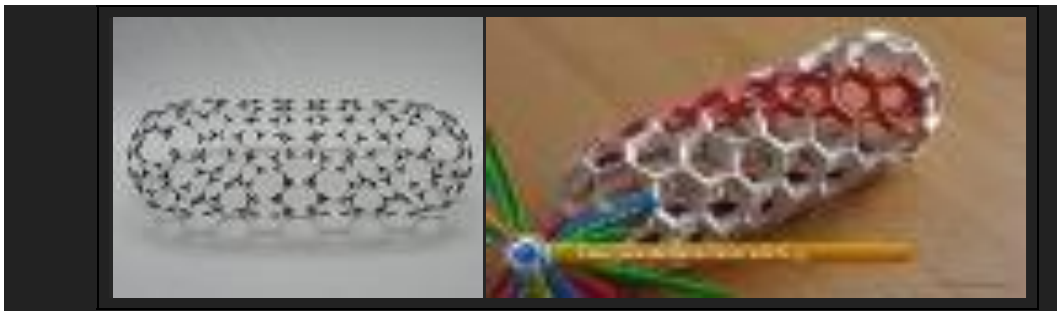
Step 3: Make the caps of the nanotubes for each of its ends (2 pieces)



Step 4: Align the nanotubes caps



The following example shows the nanotube C186. The length of the carbon nanotubes depends on the size of the base element.



The impact of soot on human health

a) long exposure to diesel engine exhaust fumes increases the risk of developing lung cancer
http://jnci.oxfordjournals.org/content/104/11/855
b) the risk of cancer increases by 40% in people working in air contaminated with diesel engine exhaust fumes
http://www.ifap.asn.au/documents/safetywaaugust_web2012.pdf
c) the composition of diesel engine exhaust fumes, harmfulness, laboratory tests and research on people and places where we are exposed to exhaust fumes
http://www.cancer.org/cancer/cancercauses/othercarcinogens/pollution/diesel-exhaust
d) Health Assessment Document For Diesel Engine Exhaust
http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=29060#Download

Properties of soot investigation – worksheet

Research question **Hypothesis** with the justification**:**
The variables: *independent variable* *dependent variable* *control variables*
Description of particular steps/ Experimental procedure
Observations/results:
Analysis of the results:
Conclusions:

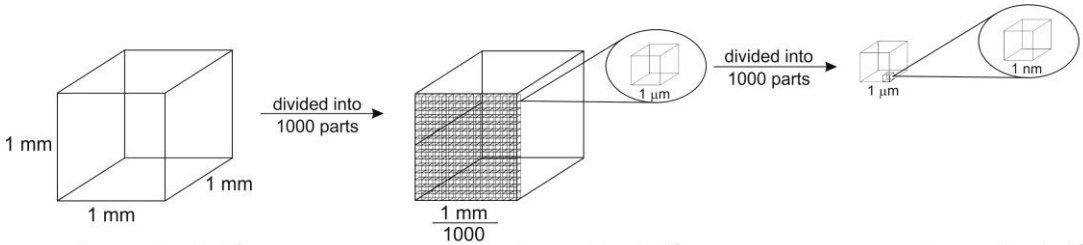
Absorption vs. adsorption

Such a process is scientifically referred to as sorption. When a given substance is concentrated on the surface – the molecules of substance 1 are retained on the surface of substance 2 – we talk about adsorption (substance 1 is adsorbed on the surface of another substance – called the adsorbent– only); and when the process takes place in the whole volume of the other substance (the absorbent), the process is called absorption.

Calculation exercises – Instructions

Assumptions: the length of the initial crystal's wall is 1 mm.

We divide it 1,000 times into the lumps with the side's length of 1 μm. We repeat the process for the 1 μm crystal, obtaining the lumps whose side's size is 1 nm.



$S_C = 6 \cdot (a)^2$
$1\ mm = 10^{-3}\ m$
$S_c = 6 \cdot (10^{-3} m)^2$
$S_c = 6 \cdot 10^{-6}\ m^2$

$S_C = 6 \cdot (a)^2$
$1\ \mu m = 10^{-6}\ m$
$S_T = 6 \cdot (10^{-6} m)^2$
$P_c = 6 \cdot 10^{-12} m \cdot 10^{9}$
$P_c = 6 \cdot 10^{-3}\ m^2$

$S_C = 6 \cdot (a)^2$
$1\ nm = 10^{-9}\ m$
$S_T = 6 \cdot (10^{-9} m)^2$
$S_c = 6 \cdot 10^{-18} m \cdot 10^{18}$
$S_c = 6\ m^2$

Comparison of porous and not porous plasters (houses elevations)

Photo 5.1, 5.2: Comparison of facades in Krakow (Photo: Paulina Maciejowska)
Yellow facade covered with smooth plaster, grey facade covered with porous plaster

Specific surface area is the total surface area of a solid *S* per the mass of the substance m (S/m)); it is inversely proportional to the particles' size.

European emission standards

The regulations regarding permissible limits of emission of harmful substances, such as nitrogen oxides (NOx), particulate matter (PM), hydrocarbon (HC) and carbon monoxides (CO), found in most motor vehicles sold in the EU are imposed by the European Union in the EURO standards. The restrictions apply to cars and trucks, buses, trains, tractors, agricultural machinery and river vessels. The EURO 6 Standard, established in 2008 by the European Parliament, has been in force since the beginning of 2014.

table 5.1

Permissible emission limits for diesel vehicles in individual EURO standards

g/km	EURO 1	EURO 2	EURO 3	EURO 4	EURO 5	EURO 6
CO	3.16	1	0.64	0.5	0.5	0.5
HC	-	0.15	0.06	0.05	0.05	0.05
NOx	-	0.55	0.5	0.25	0.18	0.08
PM	0.14	0.08	0.05	0.009	0.005	0.005

Additional literature

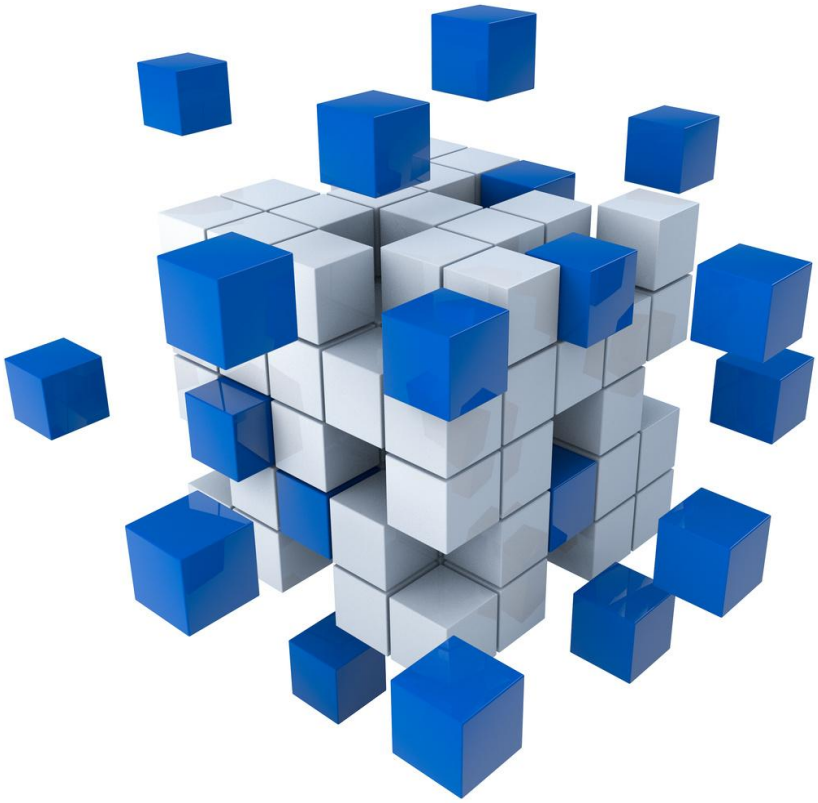
Small can be big – a French cheesy perspective
https://www.youtube.com/watch?v=2NySRur62gg

6

Size Makes a Difference

Lesson No.6

Size Makes a Difference



Author: trahko / Fotolia

Try to determine the relationship between the number of the catalyst's grains and their size

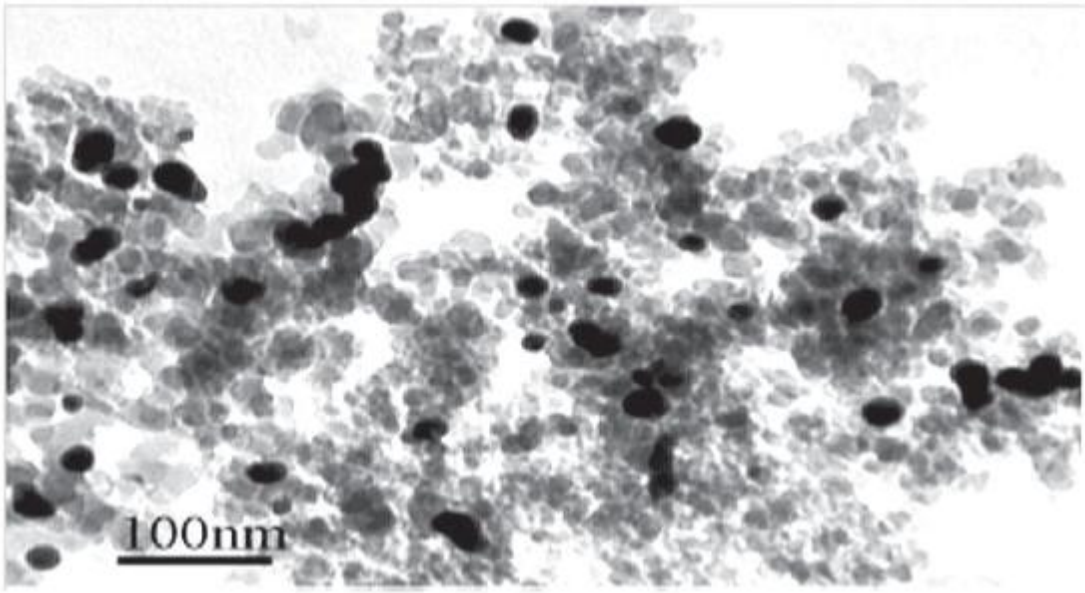


Figure 6.1: Photo of the Au/SiO_2 catalyst made using the TEM technique (X. Jiang, H. Deng, X. Wang, Colloids and Surfaces A:Physicochem.Eng.Aspects, 358(2010)pp.122–127)

Strategies for creating catalytic materials

There are many methods for creating nanostructures; they can be divided into two types, namely the 'top-down' and the 'bottom up' method. The former consists in crushing solid materials to nanoparticles by crushing and grinding them in ball mills, or various kinds of lithography*. The 'bottom-up' methods consist of the growth of nanocrystallites (nano-sized crystals) and controlled discontinuation of the growth. It is done through the self-assembly of individual atoms into larger units- the so-called clusters- and their further aggregation to nanoparticles. Thus nanomaterials are obtained through chemical synthesis as well as by the use of appropriate physical processes. Examples of commonly used 'bottom-up' methods can be: co-precipitation of nanoparticles in solutions; decomposition of organic precursors; hydrolysis of reactants and their subsequent condensation etc.

Evaluation – Name all the elements of the picture presented below which explains two strategies for obtaining nanoparticles:

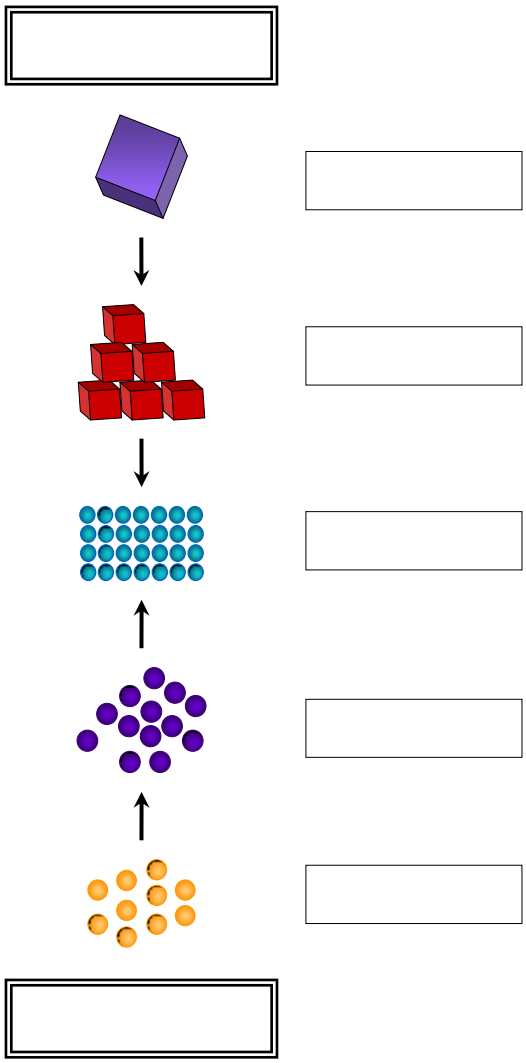


Figure 6.2: Approach to nanoparticles construction
(G. Madhumitha and Selvaraj Mohana Roopan, Devastated Crops: Multifunctional Efficacy for the Production of Nanoparticles, http://www.hindawi.com/journals/jnm/2013/951858/)

Self-assessment sheet

	After today's class I can		
	exactly	more or less	poorly
Specify the methods of obtaining nanomaterials			
Enumerate various optical tools which allow me to observe some details of the catalyst			
Explain the relationship between the catalyst's activity and the size of the grains			

Additional references

Shenhar R., Rotello V. M.: *Nanoparticles: Scaffolds and Building Blocks.* Acc. Chem. Res. 2003, **36**, pp. 549–561.

Lu W., Lieber C. M.: *Nanoelectronics from the Bottom Up.* Nat. Mater. 2007, **6**, pp. 841–850.

7

A Catalyst

Lesson No.7

A Catalyst

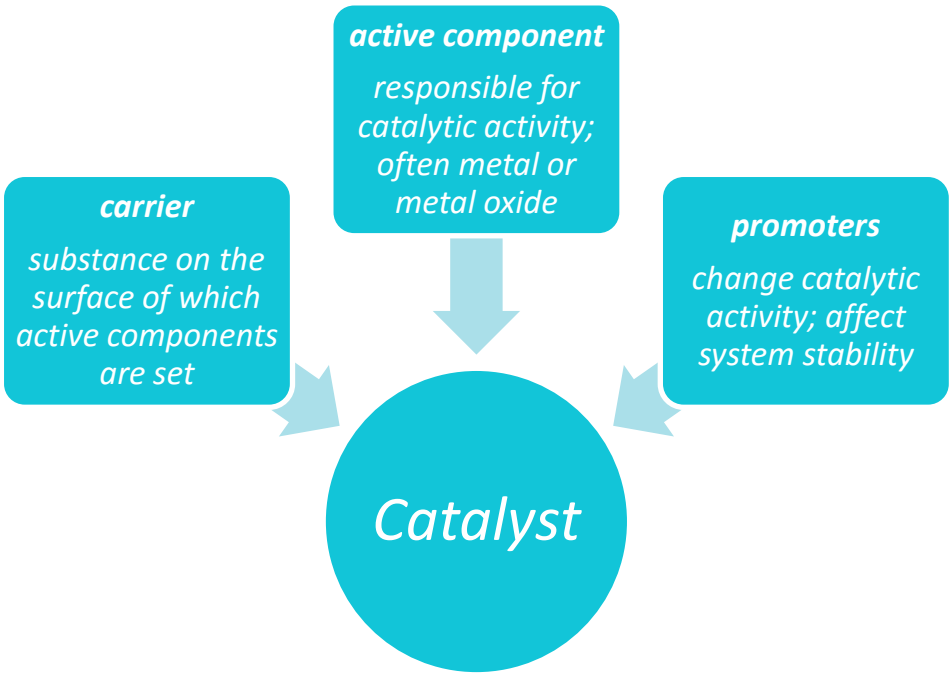
Author: mipan / Fotolia

Search on the internet – What more can be done with the obtained residues of substances to make them have different surface areas?

Heterogeneous catalysis mechanism

A heterogeneous catalyst has **active sites**, which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site in a metallic catalyst may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. (...) For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto active sites on the iron particles. Once physically adsorbed, the reagents undergo chemisorptions that results in dissociation into adsorbed atomic species, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is broken, which would be extremely uncommon in the gas phase due to its high activation energy for dissociation.

When we say 'a catalyst', we mean: a carrier/supporter, active components and promoters.



Heterogeneous catalysts are typically ‘supported’, which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimises their cost. Supports prevent or reduce agglomeration and sintering of the small catalyst particles, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly zeolites or various kinds of activated carbon.

Evaluation worksheet

Definition is:	Yes	Partially	Difficult to say	No
correct without any factual/chemical errors				
clear, understandable				
full, contains all relevant information				
linguistically and stylistically correct				

Additional literature

Arnim Lühken, H. J. (2001). Hochtemperaturchemie im Haushalts-Mikrowellenofen. CHEMKON, 8 (1), pp. 7-14. doi:10.1002/ckon.20010080103

8

A Diesel or a Gas/ Petrol Car?

Lesson No.8

A Diesel or a Gas/Petrol Car?

Author: wsf-f / Fotolia

The catalyst for the removal of soot in exhaust gases should be characterised by high activity, selectivity (the formation of CO_2 and the elimination of CO), good mechanical resistance to thermal shocks (continuous temperature changes associated with the cycles of engine operation), resistance to a high concentration of CO_2, H_2O, and low manufacture cost.

Text for reading:

1. Volkswagen – the 'dieselgate' scandal

http://www.telegraph.co.uk/business/2016/06/28/vw-to-pay-147bn-to-settle-dieselgate-claims-in-the-us/

a) Explaining Volkswagen's Emissions Scandal

"Volkswagen has admitted that 11 million of its vehicles were equipped with software that was used to cheat on emissions tests. The company is now contending with the fallout.

How Did the System Work?

The software sensed when the car was being tested and then activated equipment that reduced emissions, United States officials said. But the software turned the equipment down during regular driving, increasing emissions far above legal limits, most likely to save fuel or to improve the car's torque and acceleration. The software was modified to adjust components such as catalytic converters or valves used to recycle some of the exhaust gasses. The components are meant to reduce emissions of nitrogen oxide, a pollutant that can cause emphysema, bronchitis and other respiratory diseases.

Exhaust system of a Volkswagen Golf

Volkswagen has used two basic types of technology to reduce emissions of nitrogen oxides from diesel engines, by either trapping the pollutants or treating them with urea.

Nitrogen oxide trap

This system traps nitrogen oxides, reducing toxic emissions. But the engine must regularly use more fuel to allow the trap to work. The car's **computer** could save fuel by allowing more pollutants to pass through the exhaust system. Saving fuel is one potential reason that Volkswagen's software could have been altered to make cars pollute more, according to researchers at the International Council on Clean Transportation.

The Emissions Tests That Led to the Discovery of VW's Cheating

The on-road testing in May 2014 that led the California Air Resources Board to investigate Volkswagen was conducted by researchers at West Virginia University. They tested emissions

from two VW models equipped with the 2-liter turbocharged 4-cylinder diesel engine. The researchers found that when tested on the road, some cars emitted almost **40 times** the permitted levels of nitrogen oxides.

Which Cars Are Affected?

The Environmental Protection Agency said in September [2015] that it would order Volkswagen to recall seven of its American car models with affected engines, which amount to nearly 600,000 vehicles. Volkswagen has not released a list of international models which make up the majority of the 11 million affected vehicles, that have engines with the software in question. The E.P.A. said on Nov.2 that it had found the same test-cheating software on additional Volkswagen and Audi diesel models and on a Porsche model. The agency said it covered about 10,000 cars sold in the United States since the 2014 model year. But, in meetings with the E.P.A. on Nov. 19 and 20, the company admitted that all model years since 2009 with its 3-liter diesel engines contained the software as well. The latest disclosure covers an additional 75,000 vehicles.

Who Knew About the Deception, and When?

The 78-year-old company's unusual culture — confident, cutthroat and insular — has come under scrutiny as potentially enabling Volkswagen's lawbreaking behavior. Signs of irregularities in Volkswagen cars were first discovered in 2014 by a nonprofit group, the International Council on Clean Transportation. But the decision by employees to cheat on emissions tests was made more than a decade ago, after they realized they could not meet United States clean-air standards legally. In the subsequent years, several high-ranking company officials are believed to have been briefed about the so-called 'defeat devices, though the extent of who knew remains unclear. Mr. Winterkorn, the former chief executive, was given a memo about emissions irregularities in 2014, though the company continued to install defeat devices in its cars until last year. On June 20, German prosecutors said Mr. Winterkorn was under investigation for market manipulation because he had waited too long to disclose that the company faced an inquiry over the emissions scandal. For the first time, the investigation reached the top echelon of Volkswagen's management. In the meantime, the company has been conducting an internal investigation of people who may have had knowledge or involvement in the deception. "

http://www.nytimes.com/interactive/2015/business/international/vw-diesel-emissions-scandal-explained.html?_r=0

b) VW cars can also cheat European emissions tests

"A laboratory test carried out for BBC Panorama shows that Volkswagen diesel cars programmed with a "defeat device" can cheat official European pollution tests, as well as tests in the US.

The company told the BBC it believes this is the first time the cheating software has been filmed in action.

VW has admitted it used the device to rig tighter pollution tests in America.

But it's been more ambiguous about whether it used the same tactics to actively cheat official

European tests.
Panorama's results suggest that it did.
It could have huge implications for the company, which says it is still yet to determine whether the cheating software even breaks the law in Europe.
VW has confirmed that 8.5 million European cars have the software, 1.2 million of them in the UK.
The defeat device is a programme in the car's computer that can work out when it is being tested in a laboratory, and then cut poisonous nitrogen oxide (NOx) gas pollution from the exhaust pipe.
For years, this software allowed the company to pass strict US emissions laws yet still make a car that performed well on the road. Now it looks possible that VW was also cheating in Europe.
A side-effect of cutting NOx can often be lower miles-per-gallon.
Panorama took a VW Passat Blue Motion diesel to an accredited testing laboratory in the Czech Republic. No British lab we asked would let us in, but this lab is governed by the same rules and regulations as those in the UK and it regularly certifies new cars and engines for the European market.
We also took a retired former government vehicle inspector, Ted Foreman, along to make sure everything was done by the book (a 280-page book).

Clever software
And we confirmed the Passat was programmed with the defeat device.
After prepping the car to the letter of the regulations, the lab ran the standard Euro 5 emissions test. It's the same exam this model of car would have had to have passed before it went on sale.
And it passed. Emitting just 167 mg/km of poisonous NOx gases. The Euro 5 limit is 180 mg/km.
VW's clever software knows when it's being tested, because the routine is the same every single time. Starting with a cold engine, in a lab that's between 20 and 30 degrees centigrade, it's then driven for six miles on a rolling road, no turns, with exactly the same gear changes at exactly the same times, and all within a speed at two km/h either side of set limits.
The whole thing, including some idle time, always lasts 20 minutes and 20 seconds.
So, we then tried to trick the computer into thinking it was out of the lab, by simply accelerating hard a few times, taking it above motorway speeds. Straight afterwards, we ran the Euro 5 test again, but with one simple difference. We started with a hot engine this time.
The same car failed, spectacularly. Emitting 435 mg/km of NOx (remember the EU limit is 180 mg/km).
So, drive the same drive, but fool the car into thinking it's on a real road, and it chucks out two-and-a-half times the amount of pollution as before.
When we showed VW our results, they confirmed the car had been cheating.
"With this software, it was possible for the vehicle to recognise laboratory test conditions and the engine control could switch over to emitting compliant nitrogen dioxide levels during the test cycle.

"This would have been the likely condition in your test. As you ran the second test (described as a hot test) immediately afterwards, the vehicle did not recognise this as a test condition and changed its emission strategy."
The car industry has always said that pollution is worse out on the roads because of bad driving, bad weather and hills. Panorama's test suggests that cars are also to blame. This scandal has a long way to run. We still don't know what might happen to all the "fixed" cars. Will they have a worse MPG for example? And we still don't know how many billions of euros it'll eventually cost the company.
http://www.bbc.com/news/business-34857404

2. Particulate filter

a) Stoke-on-Trent garages 'illegally remove car emissions filters'

“Car filters designed to stop harmful emissions escaping from diesel cars are being illegally removed by garages in Stoke-on-Trent and Staffordshire.
Out of ten garages approached by undercover reporters from BBC's Inside Out, five were prepared to take off the diesel particulate filter.
Short journeys can cause the filter (DPF) to clog up and stop the car running properly.
Trading standards spokesman Brandon Cook said their removal "was terrible".
The filter can cost thousands to replace so some garages are offering to remove them instead, the investigation showed.
"It's just a flagrant breach, there's no way that's right," said Mr Cook.
Diesel soot emissions are harmful to the environment and since February, any car that has had its filter removed should fail its MOT test.
But one garage exposed by the programme was able to get around the problem by removing the filter but replacing the empty container so an MOT tester would not spot it.
Mr Cook said: "The fact you can get away with it doesn't make it right - what you've come up with here is some flagrant breaches that need investigating - there's clear evidence there that what they're doing is illegal."
He said both the consumer and the garage was at fault and added: "These garages need to know they can't get away with this… this isn't something they can just do because it's difficult to detect. Someone needs to make sure these things can't be tampered with."
A Department of Transport statement said all MOT garages would be notified on 26 October they risk losing the authorisation to perform MoT tests if they offer to remove the filters.
"We welcome any information gathered by Inside Out on garages offering DPF removal so these cases can be investigated," the statement said.”
http://www.bbc.com/news/uk-england-stoke-staffordshire-29662760

b) Diesels illegally pumping out pollutants after garages remove filters designed to cut emissions

"Tens of thousands of diesel cars are illegally pumping out dangerous pollutants because unscrupulous garages have removed exhaust filters designed to cut emissions of deadly particulates.

Air pollution from diesel particulates has been linked to 29,000 deaths a year. Despite a government crackdown last year, backstreet garages and tuning shops are still advertising services to remove factory-fitted diesel particulate filters (DPFs) and reprogramme on-board computers to allow cars to be serviced more cheaply, deliver more power and trick emissions-testing equipment.

Diesel particulates enter the lungs and bloodstream; they have been shown to stunt children's brains, and have been linked to autism, heart disease and cancer. Labour has joined air quality campaigners to accuse the Government of "negligence" over air quality regulation.

In the wake of the VW scandal – which centres on nitrogen oxides rather than particulates – testing authorities across Europe have been focusing on diesel engines. Last week, police in Spain raided eight garages in Madrid after a tip-off that they were removing DPFs and reprogramming software. However, in the UK, a legal loophole allows garages to remove the devices without fear of prosecution. An Independent on Sunday investigation has found that more than 1,000 garages, backstreet mechanics, and tuning firms are offering this service,

The filter has been mandatory on any new diesel vehicle since 2009, but can become blocked after 80,000 miles and can cost up to £1,500 to replace. Last year, the Government introduced new rules so that a car should not pass its MOT if the filter has been removed; however, many garages reportedly fail to inform customers of this, while others openly boast that their work won't be spotted during an MOT test.

"This will add to growing public concern about pollution from diesel cars, and the impact on air quality," said Kerry McCarthy the Shadow Environment Secretary. "Air quality regulations exist to protect public health, but we are being let down by a negligent Government that is failing to enforce them."

The revelation that thousands of drivers are still flouting the law by having their DPF removed and accompanying software altered has dismayed clean air campaigners. Simon Birkett, director of Clean Air in London, said the scale of DPF removal uncovered was "shocking".

"Frankly, at least VW had a chip, even if it cheated during testing. Removing factory-fitted DPFs involves tricking or disengaging the whole emissions chip, all the time, on gases and particles," he said.

Chris Roberts, managing director of Quantum Tuning, which provides DPF deletion-capable software to more than 280 garages and tuning firms, said garages were responding to "demand" from customers who "don't have the money to spend on a £1,500 new filter for a car that might be worth £2,000". He said: "Either they scrap the car or get something done about it. And if they are going to have it done, they may as well have it done properly by a garage that will explain what the MOT implications are, as our dealers do." Mr Roberts said many customers viewed driving without a DPF as comparable to a minor speeding offence.

Campaigners say the MOT fails to catch DPF removal because it only includes a “visual inspection” of the hardware – which is often welded back together – and an “optical smoke test” which cannot detect dangerous particulate matter. A Department for Transport spokesman said: “If a car is fitted with a DPF and it is removed, it is illegal to be driven on the road. We continue to monitor how many vehicles are failing the MOT for this reason, and explore steps to stamp out this practice.”
http://www.independent.co.uk/life-style/motoring/motoring-news/diesel-cars-illegally-pump-out-dangerous-pollutants-after-garages-remove-filters-designed-to-cut-a6689191.html

Discuss in your working group – and try to answer the questions:

- What did the inappropriate behaviour/actions of the persons in the texts consist in?
- In your opinion, what was the reason for such behaviour?

9

Photo-catalysis

Lessons 9 & 10

Photocatalysis

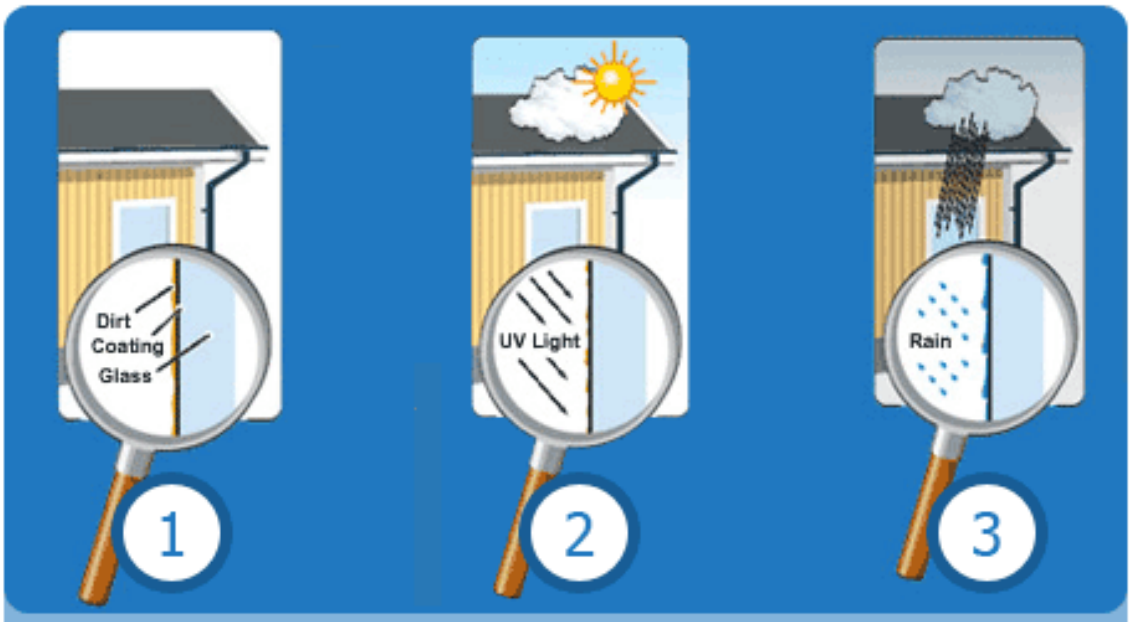


Figure 1: Coating is activated by UV light
After installation the special coating needs 5 to 7 days exposure to daylight to activate fully.

Figure 2: Organic dirt is broken down
The coating breaks down organic dirt and by doing so, reduces the adherance of inorganic dirt.

Figure 3: Rain washes away the dirt
Water droplets spread out to form a "sheet". Dirt particles on the surface are picked up by water and washed off the glass - a remarkable difference you can actually see.

https://www.pilkington.com/en-gb/uk/householders/types-of-glass/self-cleaning-glass

Photocatalysis – Worksheet

The K1 skyscraper, referred to as 'Błękitek', is 105 m high. It is built on a square plan, with the length of the sides of 50 m. The entire facade of the building is covered with glass. Calculate the cost of washing the facade of the building if 1 employee is able to wash 1 m^2 of the facade within 5 minutes and the cost of his work amounts to PLN 75 per hour.

Experiment 9.1

Solution A: 5 cm^3 of DCIP, 0.5 cm^3 of glycerol, a pinch of TiO_2
Solution B: 5 cm^3 of DCIP, 0.5 cm^3 of glycerol, a pinch of SiO_2 or Al_2O_3
Solution C: 5 cm^3 of DCIP, 0.5 cm^3 of glycerol

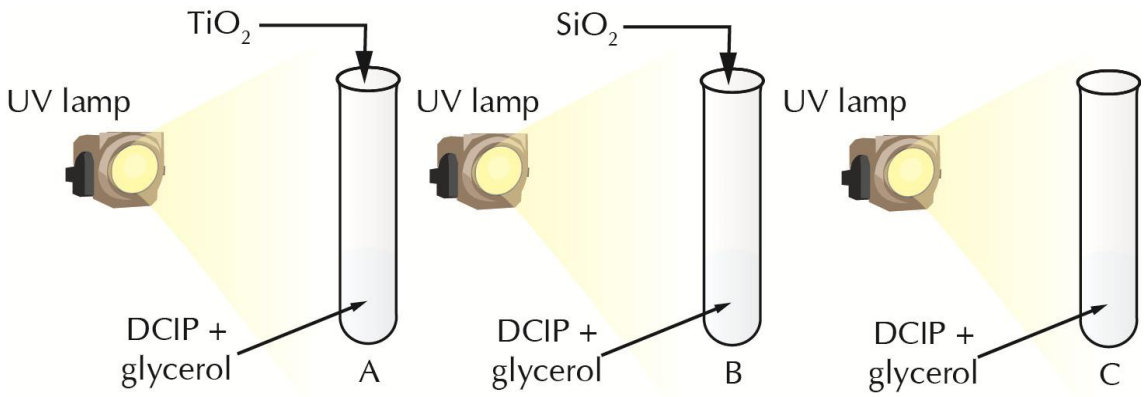


Figure 9.1: Photocatalytic decomposition of 2,6-dichlorophenolindophenol by TiO_2 in the presence of glycerol and UV light

Observations	Conclusions

Experiment 9.2

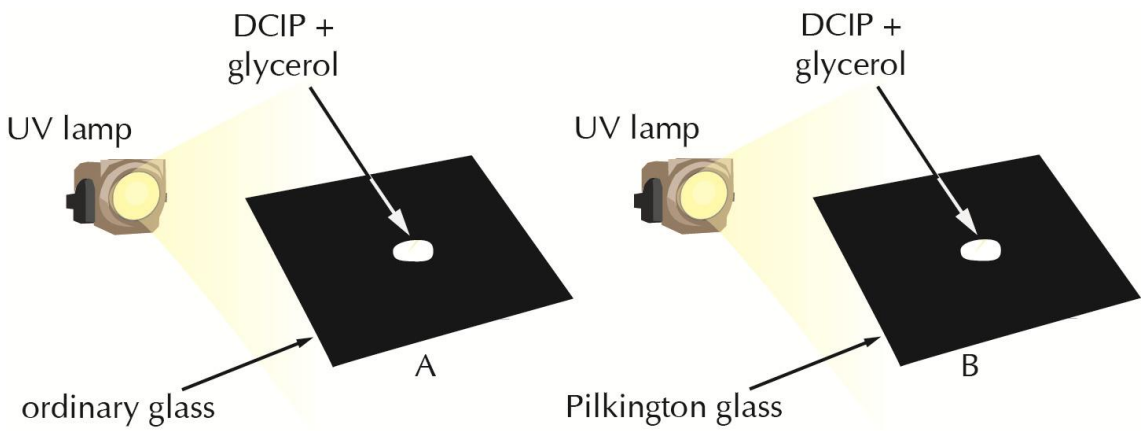


Figure 9.2: Photocatalytic decomposition of 2,6-dichlorophenolindophenolon a self-cleaning windowpane

Observations	Conclusions

Additional literature

Nanopinion http://www.nanopinion.eu

Self-cleaning glass windows https://www.youtube.com/watch?v=UgbT2fJTqFY

PPG introduces SUNCLEAN self-cleaning glass for commercial applications http://corporate.ppg.com/Media/Newsroom/2012/20121022B

Photocatalysis – Worksheet

You can use the reagents and equipment presented during the lesson and in addition:

- Titanium oxide crystallites larger than 70 nm, various polymorphs of titanium dioxide with the size of ~20 nm.
- Different sources of light (UV lamps, fluorescent lamps, incandescent lamps, daylight, LEDs of various colours).
- Common laboratory reagents.

The solutions used during the previous lesson:

- Photocatalytically active suspension: 5 cm^3 of DCIP + 0.5 cm^3 of glycerol, a pinch of TiO_2.
- Solution applied on the windowpane: 5 cm^3 of DCIP + 0.5 cm^3 of glycerol.

Plan an experiment in which you will investigate the impact of selected factors on the course of one of the processes presented during the lesson (reaction in a test tube or on a windowpane).

Research question:

……

……

Hypothesis together with the justification:

……

……

……

Variables:

a) independent – ……

b) dependent – ……

c) controlled – ……

Experimental procedure:

……

……

……

……

Results

Conclusions

Nanomaterials, nanotechnology and nanoscience[2]

Nanomaterials are substances comprising nano-objects (i.e. particles, layers, fibres, pores etc., having one or more dimensions on the nanometre scale, approximately from 1 to 100 nm) and showing the properties (electrical, optical, catalytic, surface etc.) different than those of the materials containing corresponding objects with macroscopic dimensions. The group of nano-objects does not include small molecules(inherently with the size of about 1 nm) of typical chemical compounds that do not exhibit outstanding properties typical for the nanoscale. Nanotechnologies are technologies involving the design, characterisation, production and application of nanomaterials in practice, but the research dealing with nanotechnologies is part of nanoscience.[3]

In some definitions of nanotechnology its important aspect is the formation of nano-objects by manipulating individual atoms or molecules.[4] Since the natural limitation of such a method of producing nanomaterials would be extremely low efficiency, the need to construct

[2] Edited by Wacław Makowski

[3] NANOTECHNOLOGIES: Principles, Applications, Implications and Hands-on Activities -a compendium for educators, Luisa Filipponi, Duncan Sutherland, 2013 EUR 24957, European Commission Directorate-General for Research and Innovation Industrial Technologies

[4] http://en.wikipedia.org/wiki/Nanotechnology

'nanorobots' capable of self-replication and forming other nano-objects has been postulated. For this purpose, it was suggested to create 'nano-machines'-nanometric counterparts of mechanical devices (engines, transmission gears, clutches etc.) as components of nanorobots. The proposals can be described as fantastical, since they are still very far from any implementation. Still, they function in the media, and they are also being propagated by some scientists.[5] Meanwhile, there is rapid progress in the research concerning nanomaterials and their practical applications.

Two basic reasons for the particular effect-associated properties of nano-objects can be determined, which may be summarised as 'geometric' and 'quantum' ones. The large external surface (as compared to the weight or volume) of nano-objects, as well as the large number of surface defects (e.g. atoms located at the nanoparticles' edges or corners) are due to the particular geometry of the nano-objects. Surface effects are responsible, among other things, for the specific chemical reactivity, catalyticand adsorption properties of nanomaterials. It is much more difficult to explain the unusual electrical, magnetic and optical properties of nanomaterials, which can be defined as quantum effects. From the perspective of physics and quantum chemistry, nano-objects are located between atoms and molecules in which orbitals, i.e. 'discrete' wave functions, are used to describe electron pairs, or even single electrons, and solids, for which the existence of 'continuous' (valence and conduction) bands is assumed that describe the states of a large number of electrons. None of the descriptions is fully adequate in relation to nanoparticles. More accurate descriptions are so advanced that they go far beyond the scope of the upper secondary school curriculum.

Nanomaterials and nanotechnologies are often presented as a result of the scientific discoveries of the late 20th century.[5] However, many industrial technologies using nanomaterials had been developed much earlier (e.g. catalysts containing nanoparticles of precious metals used, for example, for the purification of the exhaust gases from automobile engines, or zeolites-so-called molecular sieves i.e. porous aluminosilicates allowing separation of hydrocarbon molecules due to their size and shape). The traditional scientific disciplines involved in nanomaterials research and related industrial applications usually are not included in the field of nanotechnology.

Since nanomaterials and nanotechnologies are the objects of certain fashion, sometimes they are uncritically attributed extraordinary 'magical' properties, which may involve both especially advantageous applications as well as extraordinary threats.[5]

---

[5] *Welcome to the Nanoworld* - Planete TV documentary series, 2009

Additional useful links &literature

Projects:

- NanoEIS: Nanotechnology Education for Industry and Society http://www.nanoeis.eu/
- Time For Nano http://www.timefornano.eu/pl/
- Nanopinions http://www.nanopinion.eu/pl/about-nano
- NANOTECHNOLOGIES: Principles, Applications, Implications and Hands-on Activities –a compendium for educators, Luisa Filipponi, Duncan Sutherland, 2013 EUR 24957, European Commission Directorate-General for Research and Innovation Industrial Technologies

10

Student Self-Assessment Sheet

Student Self-Assessment Sheet

Author: sindler1 / Fotolia

Name and surname: .....Date: .....

For the last ..... months self-evaluation, we focused on the work done in the inquiry unit 'The Catalytic Properties of Nanomaterials'

Looking at <u>my learning</u>

I know .....
.....
.....
I learnt .....
.....
.....
I can .....
.....
.....
I plan .....
.....
.....

Looking at <u>my achievements</u>

I am proud of .....
.....
.....
I am good at ...
.....
.....
I do better at .....
.....
.....
I enjoyed .....
.....
.....
My goal is .....
.....
.....

Looking at <u>my thinking</u>

I wonder .....

.....

.....

My question is .....

.....

.....

I changed (opinion, attitude etc.) .....

.....

.....

Summary

We hope that through the participation in the activities of the "..." module, you have got acquainted with the threats and opportunities for the mankind offered by the development of modern technologies, and nanoscience in particular. You have also found out what the role of catalytic processes in ensuring the sustainable development of society is, and how nanomaterials can be used in catalysis, in particular that one used for the protection of the environment. It is obvious that chemicals can harm humans and environment (e.g. soot), and thus chemical knowledge enabling us to prevent the damage and eliminate it is even more important. However, taking appropriate decisions in everyday life and work based on such knowledge is as important as the knowledge itself, and it is equally vital as involving you – the members of modern society – in the process of RRI.

Author: nbnserge / Fotolia