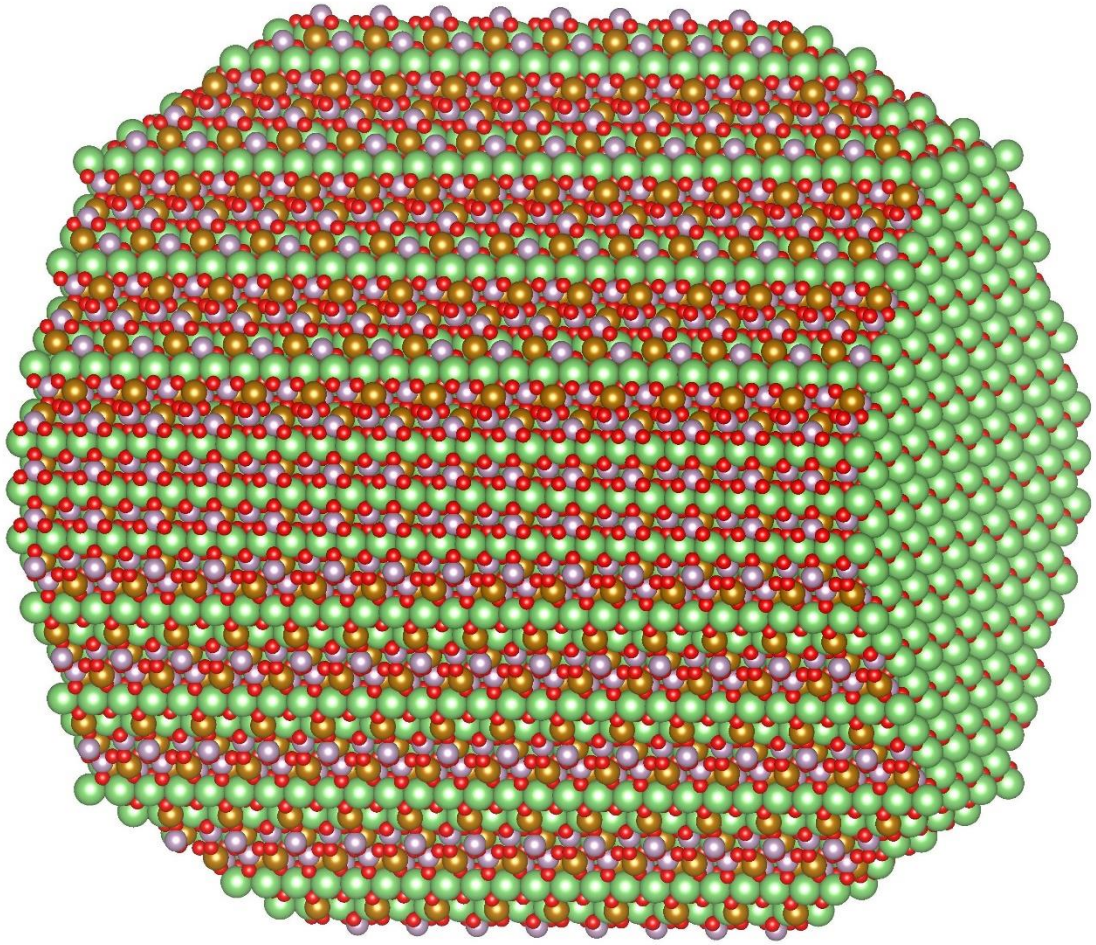
# NanoCrystal



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http://nanocrystal.vi-seem.eu/CrystalTool

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# 1. Introduction

Nanoparticles are nano-engineered structures with size between 1-100 nm, with various, mainly industrial, applications such as in drug delivery systems (1), quantum computers, textiles (technical, medical, electrocontucting, anti-stain), industrial catalysts, food packaging and many others and are formed by crystals of materials. Individual crystals grow based on their crystal habits, which give the characteristic external shape of a crystal, but crystallographic files contain only the crystal structure and not its crystal shape. However, creating an initial starting conformation for modeling and simulation is tedious, because every crystalline material grows with a different crystal habit that determines its symmetry in nature. That gave us the motivation to provide an easily accessible web based crystallographic tool which can produce nanoparticles for simulation from any material as they grow in nature of any type, any size and any shape.

## 2. Methodology

In order to create nanoparticle models from any crystal structure guided by their preferred equilibrium shape in standard conditions (crystal habit), our algorithm uses input from quantum mechanical calculations based on the Wulff construction. The Wulff construction employs energy minimization arguments to demonstrate that certain crystal planes are preferred over others, with their distance from the origin being proportional to their surface energy (2). The input parameters for determining this equilibrium nanoparticle structure are the preferred growing planes as Miller indices, the energy of each plane, and the desired size of the nanoparticle.

After inputting this data, the equilibrium shape is created with the following methodology. First, based on the crystallographic space group, the symmetric planes are produced based on the Miller indices, the fractional coordination system and the lattice parameters. In this procedure, we place the origin on the negative side of these planes and then we calculate the intersection points per three of the planes, discarding those that are on the positive side of at least one of the planes. Then, we obtain the faces of the equilibrium shape using the Quickhull algorithm on the remaining intersection points and the equilibrium shape is constructed by connecting these faces (3). The unit cell of the crystal structure is produced from the asymmetric one (figure 1a), using again the lattice parameters and the symmetry operations of the crystallographic space group on the coordinates of the atoms. Finally, the supercell is constructed by replication of the unit cell across all three spatial directions (figure 1b) until the equilibrium shape is filled (figure 1c), and the coordinates are output to the user. Additionally, the user has the option to create the crystal habit by truncating the shape exactly at the crystal habit boundary or to include all atoms that form coordination polyhedra with atoms inside the equilibrium shape.

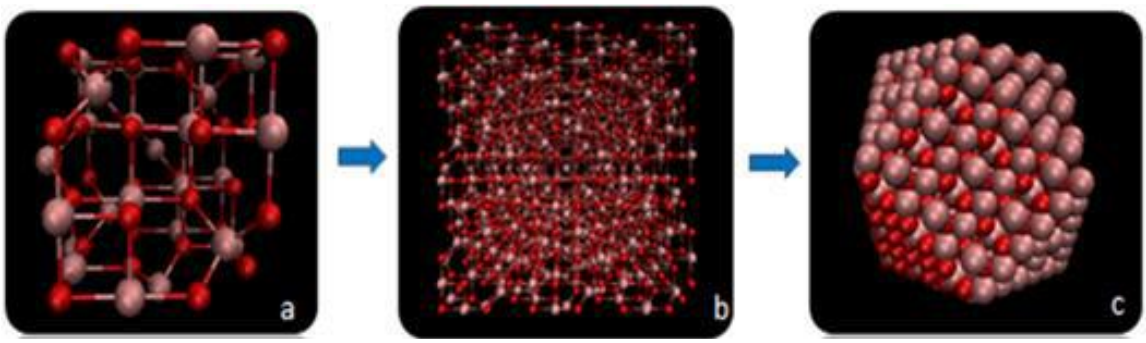



Figure 1 Given (a) an initial unit cell and (b) its replication in three dimensions, (c) the crystal habit of the nanoparticle can be reproduced in Cartesian coordinates using our algorithm given the Miller indices of the preferred growing planes, their energies and the desired nanoparticle size.

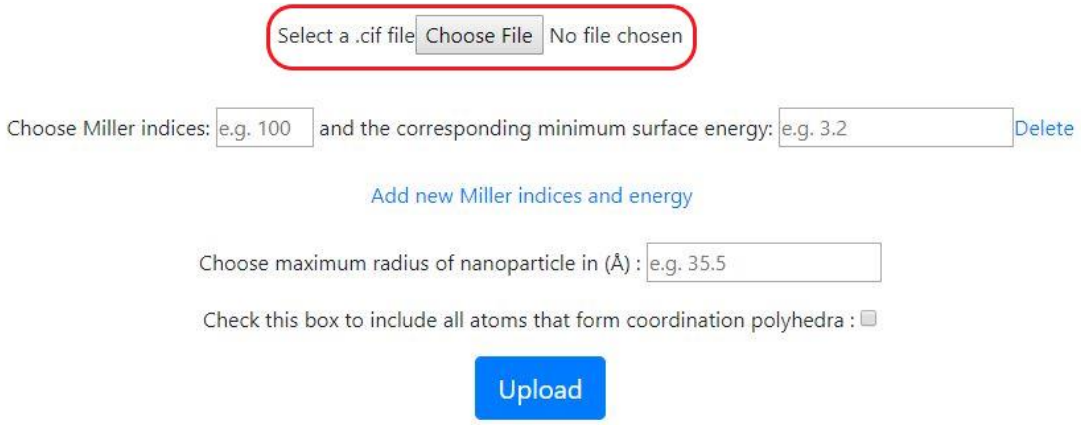
# 3. Description of the Program

This tool may be used to construct nanoparticles of any material given the crystal structure as input, the size of the nanoparticle, and the preferred growing planes and energies. It has been implemented as a web server using C++ and PHP, and can be accessed at: http://nanocrystal.vi-seem.eu/CrystalTool.

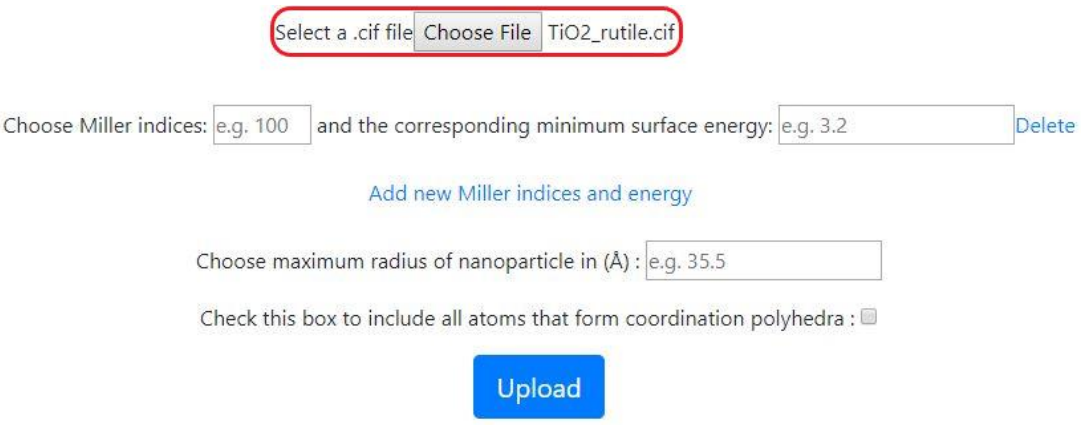
## 1. Input

### a) Crystal structure

The first input is the crystal structure given as a .cif file.

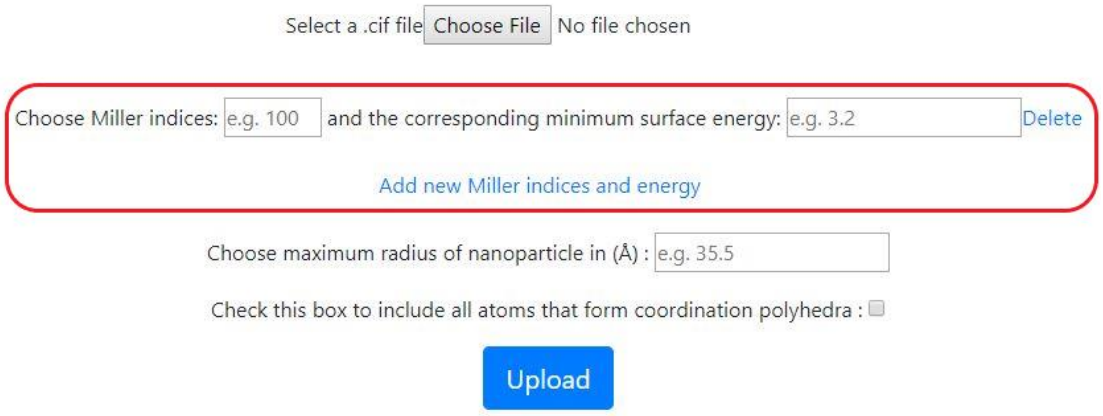



For example we select the TiO2 rutile .cif file which can be downloaded from http://www.crystallography.net/cod/9009083.html (4).

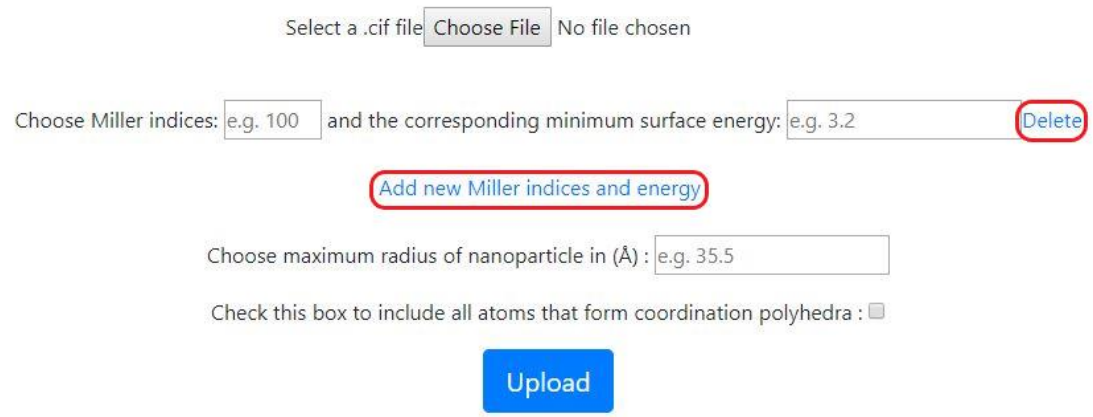


## b) Miller indices and energies

The next inputs are the Miller indices and their corresponding minimum surface energies which can be found either from bibliography or from your own quantum mechanical calculations based on the Wulff construction. These energies can be in any units (but the same between them) because the Wulff construction results in a polyhedron that depends only on ratios between surface tensions and not on their absolute values.



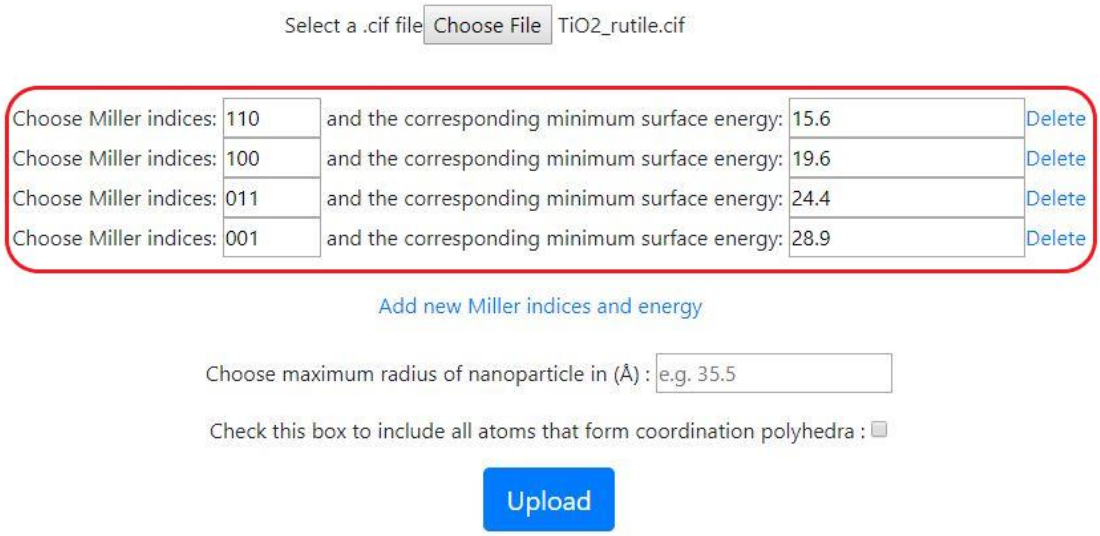

There is an option to add many hkl triplets along with their minimum surface energies and to delete one in case that more are added.




In the TiO2 example the given Miller indices and their corresponding surface energies found in bibliography (5) are:

| Miller indices | Energies |
|---|---|
| 110 | 15.6 |
| 100 | 19.6 |
| 011 | 24.4 |
| 001 | 28.9 |

and inserted the following way:



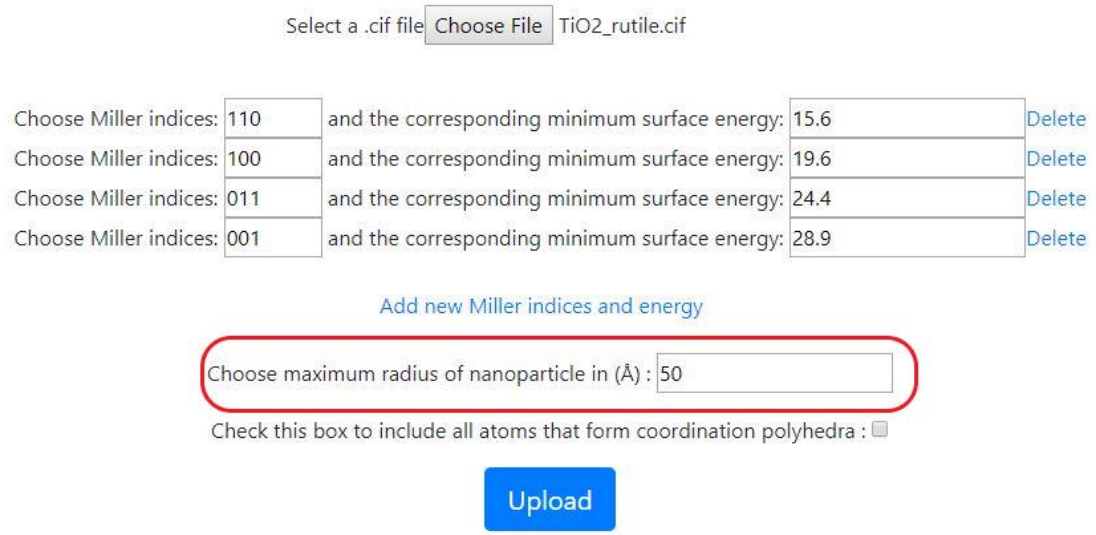

**Important note**: The program now accepts Bravais-Miller indices (4 parameter lattice coordinates).

**Important note**: The given Miller indices in combination with the crystal's space group symmetry operations should form a convex hull, otherwise the program will not run. If you are sure that the given hkl indices form a convex hull and you still get an error please contact us.

### c) Size of nanoparticle

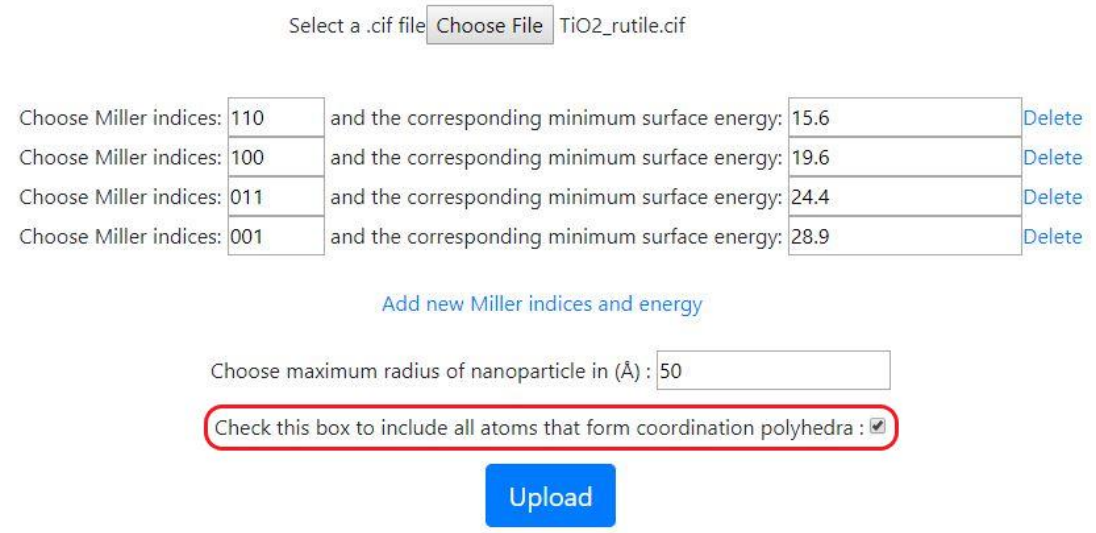
The next input is the maximum radius of the nanoparticle in Angstroms which determines the size of the nanoparticle the user wants. The maximum allowed radius in our web-server is 250 Angstroms. If you need to build a larger nanoparticle, please contact us.

In our example let's choose 50 Angstroms.




## d) Include coordination polyhedral

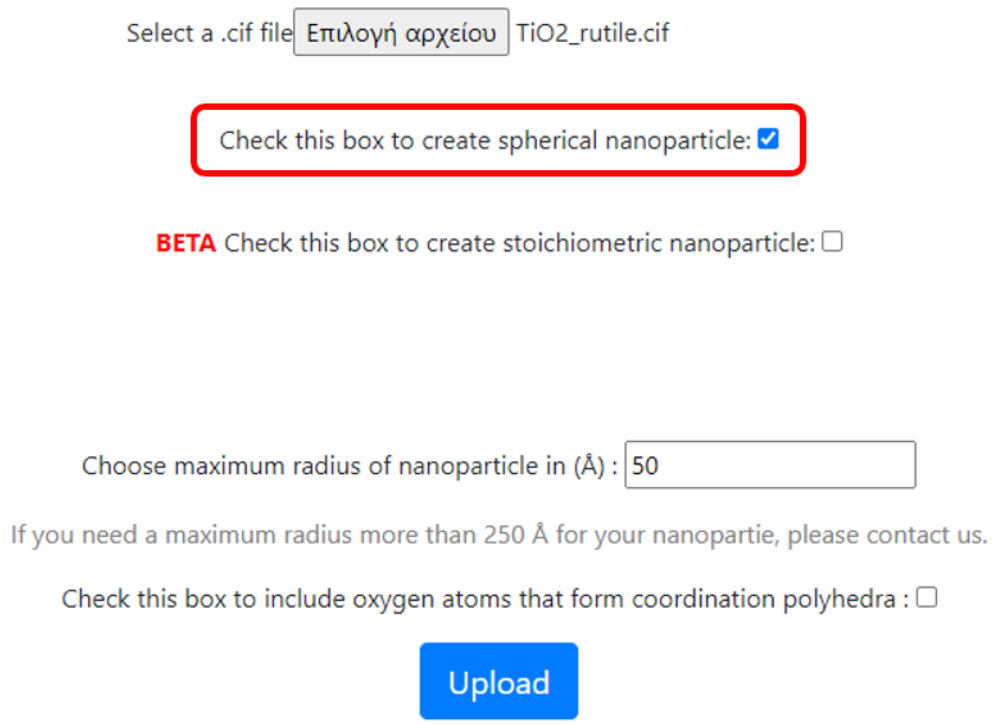
Additionally, the user has the option to create the crystal habit by truncating the shape exactly at the crystal habit boundary (Fig. 2A) or to include all oxygen atoms that form coordination polyhedra with atoms inside the equilibrium shape (Fig. 2B).




After all these required inputs are fulfilled then hit the Upload button.

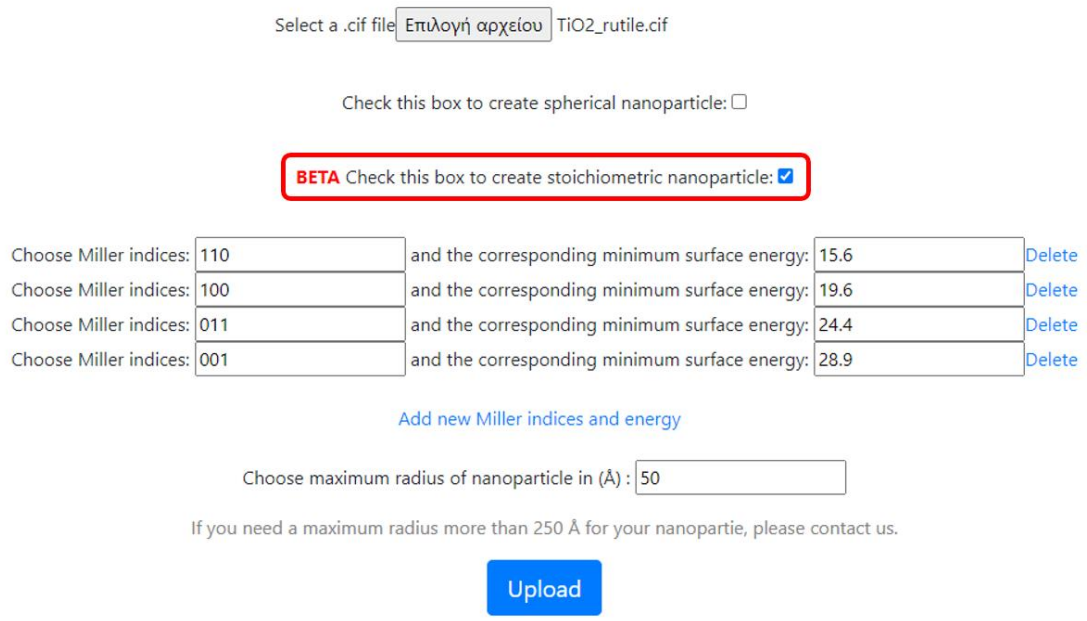
### e) Spherical nanoparticle

A new feature of NanoCrystal that allows the construction of spherical nanoparticles (Fig. 3A). This feature does not need Miller indices. Moreover, this feature can be combined with “Include coordination polyhedral” feature. It should be noted that spherical nanoparticles do not exist in nature.




### f) Stoichiometric nanoparticle

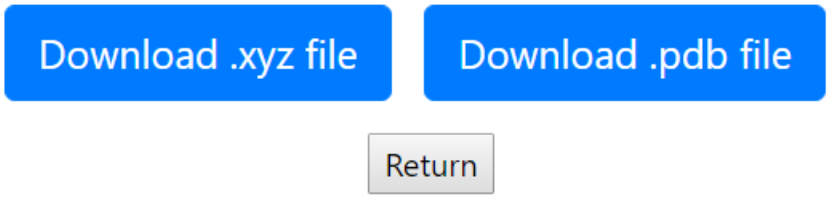
A new feature of NanoCrystal that allows the construction of stoichiometric nanoparticles. This feature needs to be combined with Miller indices that form a convex hull or with the “Spherical nanoparticles” feature, but it does not work with the “Include coordination polyhedral” feature. To keep the stoichiometry of the system, more atoms are added beyond the requested maximum radius (Fig. 3B). The final maximum radius is written in the second line of the .pdb and .xyz files in the results.




**Important note**: In order to keep the stoichiometry of the system, the "_chemical_formula_sum" property must be specified in the .cif file, i.e.,
_chemical_formula_sum 'O2 Ti'

## 2. Output

As a result you have the choice to download the coordinates of the atoms in a .xyz file and a .pdb file, and visualize the nanoparticle using JSmol (6, 7).



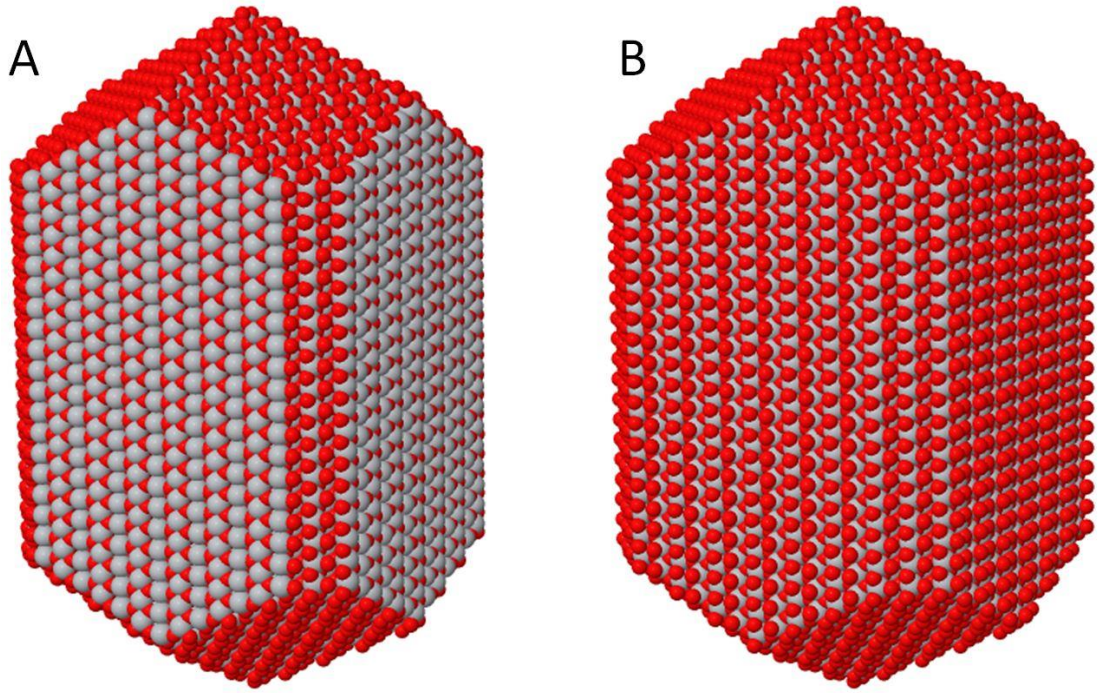




**Figure 2: (A) Creation of the crystal habit by truncating the shape exactly at the crystal habit boundary. (B) Creation of the crystal habit by including all atoms that form coordination polyhedra with atoms inside the equilibrium shape.**

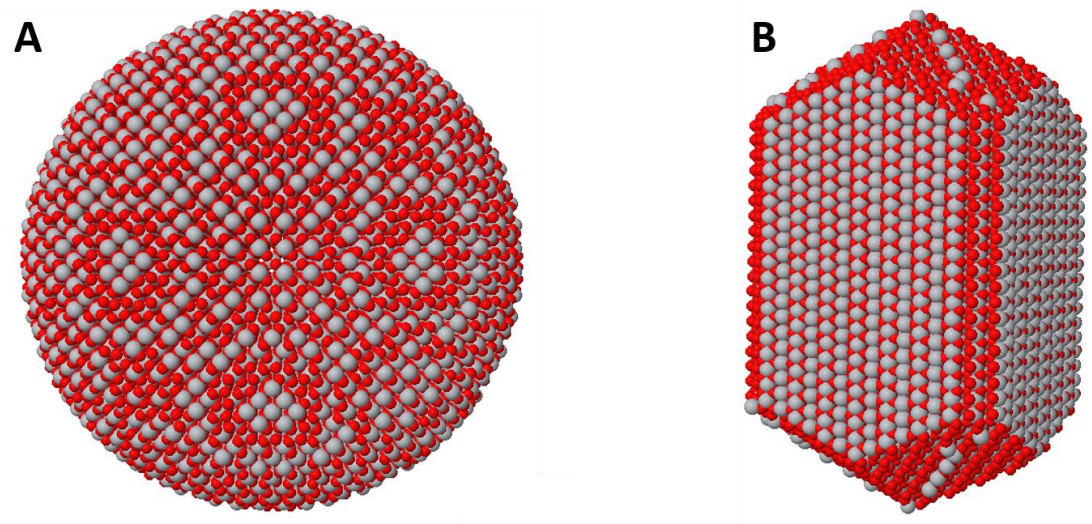



**Figure 3: (A) Creation of spherical nanoparticle. (B) Creation of the crystal habit by including necessary atoms in order to keep the system's stoichiometry intact.**

# 4. Error with the cif?

If you encounter any problem with the input please check that:

- The marked elements in the following figure in the red boxes exist, with their values in the same line and not in a new line below them.
- The _chemical_formula_sum or _atom_site_type_symbol exist.
- The symmetry operations are under the _symmetry_equiv_pos_as_xyz element (blue box).
- The marked elements in the yellow and green boxes exist.
- The atom names in the _atom_site_label matches those in the _chemical_formula_sum.

If you still encounter problems please feel free to contact us at: a.chatzigoulas@gmail.com .

```
_chemical_formula_structural       Rh3Se8
_chemical_formula_sum              'Rh3 Se8'
_space_group_IT_number             148
_symmetry_space_group_name_Hall    '-P 3*'
_symmetry_space_group_name_H-M     'R -3 :R'
_cell_angle_alpha                  90.73
_cell_angle_beta                   90.73
_cell_angle_gamma                  90.73
_cell_length_a                     5.9648
_cell_length_b                     5.9648
_cell_length_c                     5.9648
_cell_volume                       212.169
_exptl_crystal_density_diffrn      7.360
_cod_original_sg_symbol_H-M        'R -3'
_cod_database_code                 9008145
loop_
_symmetry_equiv_pos_as_xyz
x,y,z
-z,-x,-y
y,z,x
-x,-y,-z
z,x,y
-y,-z,-x
loop_
_atom_site_label
_atom_site_U_iso_or_equiv
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Rh  0.00380  0.00000  0.50000  0.50000
Se1  0.00380  0.38160  0.38160  0.38160
Se2  0.00380  0.88770  0.11660  0.62040
```

# 5. Bibliography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