Small metal nanoparticle recognition using digital image analysis and high resolution electron microscopy

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Abstract

In this paper, we present a system developed to identify metal nanoparticles at different orientations, using digital image processing and analysis. The correct identification is important in nanotechnology, where it is possible to build structures for different purposes at the nanometric level. The recognition system computes automatically different characteristics such as: nanoparticle area, polygons, symmetry and molecular arrays (twins) in order to recognize different nanostructures. All these characteristics are obtained through the use of morphological, texture (co-occurrence matrix) and region analysis. Complexity issues, advantages, and results are presented and discussed. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Pattern recognition; Nanotechnology; Image analysis and processing

1. Introduction

Nanotechnology is, without doubt, the technology of this new century, based (for example) on molecular systems with no more than thousands of atoms and a scale range of \(10^{-9}\) m (Ascencio et al., 1998). Nanotechnology has a big range of applications, from photonic to electronic, catalysis, and many others (José-Yacamán, 1996). The use of nanoparticles (Andres et al., 1996), nanorods, and nanotubes with different elements leads to a variety of properties that can be used in many new devices.

In this new technology, the parameters of elemental composition, size, shape, and internal structure determine the final property of the atomistic system. The characterization of nanostructures is very important and many techniques have been used in nanoparticle research, in order to characterize the atomic distribution in the nanometric scale (José-Yacamán, 1996).

Because of the size of these particles, high resolution electron microscopy (HREM) has been considered one of the best tools for getting information about their structure (Ascencio et al., 1998). This technique is based on the transmission of an electron beam through a sample and the analysis of the scattered signal, which is function of the sample structure and composition (José-Yacamán and Ascencio, 2000). HREM particularly refers to a resolution limit close to 2 Å that makes it possible to observe details of lattice spacing in crystalline materials (Williams and Carter, 1996). However, the images obtained by HREM show different problems such as poor contrast, noise, and image overlap that complicate correct pattern identification (Ascencio, 2000).

Until now, the common method for the recognition of nanoparticles is based on a visual inspection that requires a skilled technician with experience; therefore the process is time consuming and is prone to errors. These problems suggest the necessity of an automated system for identifying nanoparticles in a more efficient and faster way.

Because of its importance, several works in the literature, have reported analysis of nanoparticle structure using HREM and the Fourier transform (Ascencio et al., 1998; Ascencio, 2000; Schaf et al., 1997). However, these advances have opened up more possibilities of application; in this case, we applied pattern recognition tools for digital images in order to so further, towards the automatization of the recognition process.

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Our proposed solution is based on the design of a system that discriminates characteristics for every nanoparticle, such as regional properties (convexity, roundness, etc.), perimeter, parallel line arrangements, symmetry and polygonal contour. Based on these characteristics, it is possible to identify the nanoparticles from an HREM image.

2. The general problem

Nanoparticles are arrangements of atoms with controlled size and shape, involving sizes that allow researchers to develop new materials or structures with improved optical, electronic and magnetic properties (Andres et al., 1996). However, due to the size of nanostructures, the corresponding contrast is complicated to distinguish. For example in Fig. 1, a common image with many gold nanoparticles is shown; in the inset a structure of around 1.2 nm is observed. The particle corresponds to a cubic like structure, showing no more than 10 white dots in an hexagonal array, that correspond to columns of atoms. The inset nanoparticle has \( \sim 120 \) atoms and is clearly difficult to recognize with only this information.

In this case, the white dots contrast is produced by the columns of atoms and the possibility to have this contrast in the opposite way (black dots over a white matrix) is function of the defocus condition. There is a direct relation between the defocus and the corresponding contrast transfer depending also of the acceleration voltage, the optimum condition is known as Scherzer defocus that produce the maximum contrast in white dots from the column atoms corresponding to the (111) and (200) planes for the case of gold (by instance Scherzer defocus for a microscope with 400 keV and spherical aberration of \( C_s = 1 \) mm, is \( \Delta f = 40.5 \) nm), there is a second maximum of contrast black dots instead the white ones (at \( \Delta f = 70.2 \) nm for the mentioned microscope). Each microscope has different maximum depending on its parameters and operation conditions (Williams and Carter, 1996).

In fact, Fig. 1 shows a relatively simple orientation, but the probability of having it is low. The main reason is that the nanoparticles to be analyzed are deposited over an amorphous carbon substrate and the orientation can change greatly because the irregularity of the carbon substrate, as can be seen in Fig. 2. The orientations (relative to the electron beam incident direction) of the nanoparticles vary significantly and reorientation of the sample becomes almost impossible because, at the needed magnification, a small amount of tilt can result in losing the nanoparticle from the field of view. This implies the necessity of recognizing each structure at different orientations. In a previous paper (Ascencio et al., 1998), we reported a full catalog of simulated images that allows relating the observed contrast with a particular configuration and its specific orientation.

Clearly, HREM nanoparticle images can have higher-index orientations (Ascencio et al., 1998), where it is...
difficult to observe specific characteristics. These elements complicate further the recognition of the nanoparticles, since the images look very different from the different orientations, even if changes are minimal. Therefore, the specific characteristics of the changes for different orientations complicate the use of only one pattern-recognition technique, like Fourier transform (Ascencio et al., 1998) or correspondence analysis (Van Heel and Frank, 1980). Another problem is that, due to the complexity of the nanostructured construction, different characteristics will be present in every cluster of nanoparticles, as will be discussed in this paper.

3. Nanoparticle characteristics

The nanostructure models being studied are indicated in Fig. 3. FCC (face-centered-cubic) particles have three basic shapes: the cubo-octahedron (a), the truncated octahedron (b) and the special truncated octahedron with the entire edge lengths equal, which is commonly named tetrakaidecahedron (c). These shapes will be designated as CO, TO and TKD, respectively. In the case of the decahedron, there are also has three cases. First the decahedron or pentagonal bipyramid (d), with the second and third cases being variations of the original decahedron called Ino’s decahedron (e) and the truncated Marks decahedron (f), called Dh, I-Dh and t-Dh, respectively. Another cluster shape is shown in (g), which corresponds to the icosahedron named Ih. The final shapes considered in (h) are amorphous clusters of 55 atoms.

An important characteristic in decahedral and icosahedral particles is the presence of defects in system regularity that produce a change in the atomic orientation sequence, called twins. These twins are excellent discriminators, because they are not present in shapes like FCC or amorphous.

The main characteristics of the configurations considered are shown in Table 1. Our work involves 86 HREM images, 11 different orientations for every structure, with exception of amorphous clusters, which have just nine orientations. The characteristics in Table 1 are the basis for

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characteristics presented for every shape of nanoparticles</th>
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<tbody>
<tr>
<td><strong>FCC nanoparticles</strong></td>
<td></td>
</tr>
<tr>
<td>Cubo-octahedron</td>
<td>Truncated-octahedron</td>
</tr>
<tr>
<td>Characteristics: well-defined structures, like square or hexagon shape and the presence of arrays. In low index orientation, images present a structure showing only black dots representing the columns of atoms</td>
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<tr>
<td><strong>Twins nanoparticles</strong></td>
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<tr>
<td>Decahedron</td>
<td>Icosahedron</td>
</tr>
<tr>
<td>Pentagonal by-pyramid</td>
<td>Ino decahedron</td>
</tr>
<tr>
<td>Characteristics: twins presence, polygons with 4–8 sides, zig-zag arrays and symmetry in some cases. In low index orientation, images present a structure showing only black dots representing the columns of atoms</td>
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<tr>
<td>Amorphous nanoparticles</td>
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<td>Characteristics: amorphous structure, therefore the absence of well-defined structures</td>
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Fig. 3. Models of nanoparticles. (a) Cubo-octahedral particle; (b) truncated octahedral particle; (c) tetrakaidecahedron; (d) pentagonal bipyramid; (e) Ino decahedron; (f) Marks decahedron; (g) Icosahedron; and (h) amorphous clusters.
the development of the recognition system presented in this work.

4. Proposed system

The scheme for the proposed system is shown in Fig. 4. The system works as follows: First, the recognition system reads the HREM image to be identified and increases the image contrast 25%, in order to get a better definition of the atom column (black dots) against the background, due to the difference between the zones where the electrons are scattered versus the sites where the electrons are transmitted (Williams and Carter, 1996).

The second system block detects the region of the nanoparticle that corresponds to its area, eliminating the noise background produced by the carbon substrate, on which the nanoparticle was mounted. This action increases the efficiency because image analysis can then be concentrated just on the nanoparticle region instead of the full image.

After the nanoparticle area is selected, the system works with the reduced region of interest and a dynamic threshold is carried out over the original and inverted image; only the result with higher information will be selected. This processing is necessary because the HREM images are variable in all their parameters: illumination, contrast, background and focus are not always the same from one image to another.

Dynamic threshold, morphological operators and analysis region techniques (Del Bimbo, 1999) are applied in this stage. The threshold process uses a smoothed version of the original image (mean or gauss filter) as the local threshold, and a comparison between the original and the smoothed version gray values, produces those regions in which the pixels fulfill a threshold condition that corresponds dynamically to the smoothed image. In order to refine these regions the use of closing and opening morphological operators with a circle mask of 9 pixels is used. Finally,
the area and circularity of each region is used in order to eliminate those regions that do not correspond to the area of the nanoparticles.

At this point, the system has obtained two important pieces of information: regions representing the structure of the nanoparticle, and a contour that could be interpreted as a first approximation to the polygon that corresponds to its overall shape.

4.1. Region analysis

The next step is to analyze regions and find a polygon that represents the contour obtained in the above steps. Region analysis is done with the objective of finding information that will be of use in the identification process (this information search is based on the already mentioned data). Region analysis parameters like compactness, circularity, eccentricity, area, angles and Euclidean distance (Van Heel and Frank, 1980), it is possible to find the following:

- Number of atoms well defined (no overlapping).
- Low-index orientation.
- Number of parallel arrays.
- Angles and dimensions of every parallel array.
- Split result regions in circular and non-circular regions.

4.2. Polygon search

Another important characteristic is the polygon that forms the contour of the region of interest found in the previous action. The polygon search works as follows: first a new region enclosing only the pixels that could represent the vertex of a side is selected. The difference between the region of interest and the same region reduced by 40% produces this new region. Analyzing the position in columns and rows of candidates in the new region, it is possible to find only those regions that better adjust to the contour previously found. The process is further explained as follows.

- Analyze row of pixels and select only those pixels that are in the maximum or minimum intensity in the image. If there are points very close to \( R_m \) or \( R_l \) \((R_m \text{ and } R_l \text{ correspond to maximum and minimum row, respectively})\) then it means that there is a polygon side at an angle very close to \( 0^\circ \) \((90^\circ \text{ for columns})\); joining these points; analyze angles between lines and decide if there is only one side or more.
- The same analysis is done in the column axis. The ideal case is when there are four points \( R_m \text{ and } R_l \) \((R_m \text{ and } R_l \text{ correspond to maximum and minimum column, respectively})\), but it only happens infrequently.
- These points allow creation of a polygon with the selected pixels, as shown in Fig. 5.

4.3. Texture analysis

Texture analysis is carried out by using the polygon found in the previous process and parameters that can be obtained from a co-occurrence matrix (Haralick and Shapiro, 1992; Pratt, 1991; Jain et al., 1995; Anzai, 1989). Co-occurrence of gray values is specified in a \( k \times k \) matrix with relative frequencies \( P_{ij} \) \( (k \text{ corresponds to the number of gray values, } i \text{ and } j \text{ correspond to index pixels})\). Parameters like energy, correlation, local homogeneity, entropy, and contrast were obtained from a co-occurrence matrix with a direction of \( 0^\circ \) grades and a scale of 256 different gray values. Definitions of these parameters are:

\[
\sum_{i,j} P(i,j)^2 \text{ Energy}
\]

\[
\sum_{i,j} \frac{(i-\mu)(j-\mu) P_{ij}}{\sigma^2} \quad \mu = \sum_{i,j} i P_{ij} \text{ Correlation}
\]
Analyzing texture parameters will allow the system to find characteristics of symmetry and twins. The method is based on splitting the polygon or the area of interest in two equal parts. For every part a quantitative texture measurement is obtained. If both parts are similar in texture (co-occurrence matrix parameters), it means that the nanoparticle has symmetry or twins. Cuts are made using vertex and center sides as references points. In cases where the polygon method fails after reviewing all region cuts the system does not find any symmetry or twins) cuts are done every 150 from $\pi/2$ to $\pi$ using the contour obtained in the early stages of the process. Both methods are illustrated in Fig. 6.

After all the cuts have been analyzed, the system will find a nanoparticle with the symmetry characteristic from the data base, only if more than 95% of the cuts have the same parameters. In cases where twins are present in nanoparticles, the parameters will be the same only in one or two cases.

### 4.4. Image identification

The previously extracted characteristics produce a set of parameters that makes it possible to recognize a nanoparticle from its own structure and orientation. The recognition process is carried out in three different branches, one for FCC nanoparticles, another for nanoparticles with twins (icosahedron and decahedrons), and a final one dedicated only to amorphous particles. The search split is done because every group has a specific characteristic set and the system will just use the set of characteristics that produces a correct identification.

**Cubic nanoparticles.** Recognition is done by searching the following characteristics: parallel lines arrays, polygonal analysis, where it is only possible to have circular or linear regions. A more complete description of the characteristics belonging to each group is presented in Table 2.

**Nanoparticles with twins.** Recognize nanoparticles that belong to this group, the characteristics used are polygonal and texture analysis, symmetry, and presence of twins. A complete description is presented in Table 3.

**Amorphous.** In this case, using only characteristics provided by region analysis is enough for their recognition. Since amorphous nanoparticles do not present a well defined shape, it is not possible to find similar characteristics to another group.

### Table 2

<table>
<thead>
<tr>
<th>Characteristics identified and used by the proposed system in the recognition of a fcc nanoparticles</th>
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<tbody>
<tr>
<td><strong>Parallel arrays</strong></td>
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<td>---------------------</td>
</tr>
<tr>
<td>Cubo-octahedron</td>
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\(^a\) The number corresponds to the particles used in the analysis; however this can change depending on the nanoparticle size.
5. Results

The system was implemented using C and Halcon developer-software. The implementation and tests were carried out in a Pentium III 450 MHz PC-computer. To test the proposed system 86 images were used. These images present problems like bad contrast, noise, and bad focus in the peripheral and overlapping atoms that will complicate a correct identification.

In Fig. 7, the case of the cubic nanoparticle analysis is shown. For each image, the corresponding orientation is marked in fcc nomenclature. Fig. 7a shows the extracted characteristics at the different orientations of the cuboctahedron, while in Fig. 7b and c, the cases for the truncated octahedron and a particular tetrakaidecahedron are shown, respectively. In the figures, CO at [0,0,1] orientation shows a well defined 90° angle polygon, while both TO and TKD cases show 135° angle polygons. However, the proportion between the boundary length sides makes the identification possible because when the size length is similar, the image must correspond to TKD. Furthermore, in the case of the [0,1,1] orientation, it is possible to distinguish the configuration based on the proportion of side length, having the CO a similar proportion for each side, the TKD has a $2n - 1$ to $n$ proportion (where $n$ is the number of distinguished dots) and the TO shows a different relation. For the rest of the orientations, the way to distinguish between these structures is only by analyzing the roundness, because TKD tends to have rounded profiles and CO has flat sides. However, this recognition is not easy, since in this group it is not possible to find presence of twins since they show regular and symmetric images.

Results for the decahedral configurations are shown in Fig. 8 for three cases (the pentagonal bypyramid, the Ino’s decahedron and the truncated decahedron) in (a), (b) and (c), respectively. The coordinates used are based on the rhombohedral geometry. The pentagonal structures present mainly multiples of five sides in the polygon analysis and

![Fig. 7. Nanoparticle identification. The examples show the main orientations for: (a) cubo-octedra; (b) truncated octaedral and (c) tetrakaidecahedron.](image-url)
the symmetry axes. For Dh, all the analyzed images are
decagons or rhombs, with only alterations to the proportion
of the sides, that allow the identification of small
differences. This can be seen in the decagons from [0,0,1],
[1,1,2] and [0,2,1], where the side length and internal angles
change depending on the rotation axis, tending to rhombic
polygons; they can have two symmetry axes as in the [1,1,0]
orientation, while the [0,2,0] and [3,3,1] orientations show
just one symmetry axis. This symmetry pattern evidence is
also observed for the images of I-Dh and t-Dh. However, in
I-Dh, the characteristic polygon is a symmetric hexagon and
similarly to Dh, the length and angles of the sides change
depending on the orientation. The t-Dh case also shows
close-to-rhomb polygons for these mentioned orientations.
Furthermore the I-Dh profiles tend to a pentagon in the
[1,1,2] and [0,2,1]; however there is a clear evidence of
a error when the program cannot resolve the corners and it
looks like irregular hexagons by the edge effects. This error
is also present in the t-Dh images, where the profiles tend to
show 15 sides, but the program does not identify all the
corners. However, for bigger particles this mistake is not
observed and the polygons found have multiple sides
produced because of the negative curvature, which is
characteristic only of this kind of truncated particle
(Ascencio et al., 1998; Ascencio, 2000). The texture
analysis is similar in these configurations.

Icosahedron resolved images are shown in Fig. 9, where
the coordinates correspond to body centered orthorhombic,
which are the most suitable to this geometry. The case shows
interesting properties based on the symmetry that is
evidenced in all the profiles, which are regular hexagons
with proportioned sides with exception of the [1,1, −1],
which is known as the five-fold orientation. In the five-fold
orientation, the particle shows a decagon (dotted line), which
is unique. Besides the polygonal study, the texture is different
to any other structure, mainly because it does not present any
well defined compared to the previously analyzed structures.
A common error in the recognition was to find a triangle in the
interior of the image (shown with the arrow), which can be
identified as a product of poor contrast in the particle contour.
The program identifies the internal dots as significant because
the external image details are not discrete; it looks like a
continuous pattern. Finally, in the amorphous case the image
analysis corresponded directly to no symmetry and texture
defined, producing an easy way to identify that physically
imply it real sense, the no defined patterns.

Table 4 shows the time taken by the system in the
recognition of different nanoparticles. Only two samples per
group are shown. An average of all images showed that the time per sample was 11.16 s. The times are not the same due to the different searches that the system executed. Some cases are simple, as in Truncated Octahedral [1,2,3], while in others are more complex, as in Marks Decahedron [1,1,3]. This means that the Marks decahedron has a more complex structure than the truncated octahedral nanoparticle.

The experimental particles recognition is well improved with this recognition system, in the case of gold nanoparticles, the 89% of well cleaned particles in HREM images and when the noise over the image is bigger, the recognition capacity is reduced. An example of recognition of experimental images is shown in Fig. 10, an relatively easy identification is the truncated octahedron at [0,1,1] orientation as shown in Fig. 10a, the no twins and sides proportion allows the system to recognize it without problems. In the case of decahedrons, the system delayed more in the image of Fig. 10b, where couple of sides were lost, as can be seen in the figure, however the software recognized it as a Marks decahedron at the [0,0,1] orientation. In more complicated images, when the particles are bigger, the recognition was also successful as in the images shown in Fig. 10c and d as Ino’s decahedrons at [3,3,1] and [−1,3,1], and finally an icosahedron at [1, −1,1] orientation.

Table 4
Processing time for the case of representative nanoparticles. Two samples are shown for each group

<table>
<thead>
<tr>
<th>Nanoparticle (orientation)</th>
<th>Processing time (s)</th>
<th>Nanoparticle (orientation)</th>
<th>Processing time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubo-octahedron [0,1,1]</td>
<td>15</td>
<td>Ino Decahedron [1,1,3]</td>
<td>25</td>
</tr>
<tr>
<td>Cubo-octahedron [1,1,3]</td>
<td>15</td>
<td>Ino Decahedron [−1,2,0]</td>
<td>15</td>
</tr>
<tr>
<td>Truncated octahedron [0,1,1]</td>
<td>11</td>
<td>Marks Decahedron [1,1,0]</td>
<td>25</td>
</tr>
<tr>
<td>Truncated octahedron [1,2,3]</td>
<td>5</td>
<td>Marks Decahedron [1,1,3]</td>
<td>23</td>
</tr>
<tr>
<td>Tetraakidecahedron [0,1,1]</td>
<td>15</td>
<td>Icosahedron [1, −1,1]</td>
<td>15</td>
</tr>
<tr>
<td>Tetraakidecahedron [1,0,4]</td>
<td>5</td>
<td>Icosahedron [−1,3,1]</td>
<td>15</td>
</tr>
<tr>
<td>By-pyramide [0,2,1]</td>
<td>12</td>
<td>Amorphous [0,0,1]</td>
<td>10</td>
</tr>
<tr>
<td>By-pyramide [0,2,0]</td>
<td>13</td>
<td>Amorphous [1,0,0]</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 10. Examples of nanoparticle identification for experimental images. (a) Truncated octahedron at [0,1,1], (b) Marks decahedron at [001], Ino’s decahedron at [3,3,1] and [−1,3,1], and finally an icosahedron at [1, −1,1] orientation.
6. Conclusions

A system that allows the recognition and locating characteristics of HREM images of nanoparticles was presented. The structure of the system was found with the help of digital image analysis and processing. Techniques like co-occurrence matrix (texture analysis), morphological operators, dynamic threshold, and region analysis were used together with the polygon, symmetry and twins-detection algorithms in the characteristics search and identification process. The use of texture was well suited for the analysis and characterization of symmetry and twins, especially in images with difficult problems. The results presented show the efficiency and efficacy of the system.

A search for new characteristic is proposed for a further work using another source of information, where illuminations, contrast, defocus could be characterized for every nanoparticle studied. Another alternative is the inclusion in the system of 3D computer vision techniques to quantify the depth of the nanoparticle, obtaining information about its orientation and how it is mounted on the substrate.

After reading all the images, the present system could recognize 92% of the set and from experimental images of several different elements. Some images that were not identified by the system have an abundance of the problems mentioned above; therefore it was difficult therefore to find those discriminating characteristics that would produce identification. This system can be applied for nanoparticles from different elements and even for bimetallic clusters, where the contrast has an extra parameter fixed from the differences of scattering from each element, however after an contrast improving, the identification can be obtained and also the parameters from other crystalline systems can be included from the manipulation of the geometrical consideration of external shape and internal texture. This last condition allows this pattern recognition system to be parameterized and improved for other cluster types.

References


