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Determination of surface crystallography of faceted nanoparticles under TEM imaging and diffraction mode

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Synopsis: A general method to determine surface crystallography and therefore shape of faceted nanoparticles by TEM is proposed.

ABSTRACT In this paper, we propose a general calculation method to characterize the crystalline planes and directions of a faceted nanoparticle under TEM imaging and diffraction mode. With the determination of the edge vectors and then the plane normal vectors in the screen coordinate system of TEM, their Miller indices in the crystal coordinate system can be calculated through coordinate transformation. The method is helpful for the related studies on determination of the surface structure of nanoparticles.

1. Introduction

Recently, much attention has been focused on faceted nanoparticles with various shapes due to their unique properties and potential applications in catalysis (Narayanan & El-Sayed, 2005; Xiong *et al.*, 2007), surface-enhanced Raman scattering (SERS) (Orendorff *et al.*, 2005) and optoelectronics (Maillard *et al.*, 2003). It has been demonstrated that many shape-related properties of nanoparticles can be attributed to their surface crystallographic structure. For instance, tetrahexahedral Pt nanoparticles with high-index {730} plane exhibit enhanced catalytic activity for the electro-oxidation as compared with that of spherical particles (Tian *et al.*, 2007). Also the surface crystal structure plays a critical role in the anisotropic growth of nanocrystals. The selective binding of capping molecules on different crystal planes may alter their surface energies and thus change their growth capacities (Lee *et al.*, 2003; Stekolnikov & Bechstedt, 2005). Therefore, the characterization of surface crystallographic features of nanoparticles has become an important issue for the study of their surface related properties and the investigation of their shape evolution mechanism in growth process.

The application of TEM techniques to crystallographic analysis has been suggested for several years (Zaefferer, 2002). In the present case of a nanoparticle, the surface plane indices are conventionally indexed through comparing its diffraction pattern with its projection in image after bringing the plane to the edge on position in TEM. Sometimes, high-resolution TEM (HRTEM) images that record the atomic spacing of the on edge planes are used to verify the determination of the surface plane index (Xiang *et al*., 2006; Lee *et al*., 2002). The method is particularly suitable for nanoparticles with conventional shapes (Xiong *et al.*, 2007), *i.e.*, the particles are enclosed by symmetric low-index facets, as in most cases the low-indexed planes can easily satisfy the diffraction condition and generate diffraction spots. However, for particles with unconventional shapes (Xiong *et al.*, 2007), *i.e.* covered with high-index facets, the method shows limitation. In such cases, it is often difficult to obtain the corresponding diffraction spots for those high-index planes. To solve this problem, an attempt has been made by measuring the angles between the surface plane projections when the planes are simultaneously on edge-on position and comparing them with the theoretical interfacial angles to conclude the miller

indices of the facet (Tian *et al.*, 2007). Obviously, the method requires great effort in searching for the edge-on positions and sometimes it is even impossible to obtain such position for some planes when the shape of the particle is not favorable. Moreover, the study of unconventional shaped nanoparticles has recently become intensive due to their unique catalytic properties resulting from the high index surface facet. Naturally, the correct indexing of such surface planes constitutes one of the important bases for the further property and growth kinetics investigation. Therefore, a general and accurate determination method appears to be in great need. In response to such a requirement, we developed a general calculation method that can be applied to determine any faceted surface plane indices of nanoparticles without requiring the corresponding diffraction spots, provided that the edges of the facets are visible under TEM imaging mode. This technique will facilitate the surface related properties research in nanoscience.

2. Methodology

The basic principle of this method is to determine the edge vectors that define the surface facets of a nanoparticle in the TEM screen coordinate system and then obtain the surface plane normal by cross product and further calculate their Miller indices in the crystal coordinate system through coordinate transformation. The full method will be detailed as follows.

2.1 Setting of coordinate systems

Considering the characteristics of TEM for sample loading and imaging, it is convenient to introduce three Cartesian coordinate systems in addition to the lattice base of the crystalline and its reciprocal base. All the coordinate systems are of the same handedness and the Cartesian coordinate systems are orthonormal. In the present work, we choose the right-hand set. Of the three Cartesian coordinate systems, one is referenced to the screen of the TEM that records the image of the particle. Its Z-axis is set in the inverse direction of the incident electron beam, one coordinate system is set to the sample holder also with its Z axis in the inverse direction of the incident electron beam when the holder is in non-tilt position and the third one to the crystal under the convention described in the "*International Table of Crystallography*" (Hahn, 1996). The orientation

relationships between the Cartesian coordinate systems are defined as a set of rotations (Euler angles in Bunge notation (Bunge *et al.*, 1981)) transforming one system into the other.

2.2 Determination of the edge vectors in the screen coordinate system

To determine the coordinates of a edge vector in the screen coordinate system, two sample positions are required. Assume that the unit edge vector in the sample holder coordinate system is $\mathbf{v}(x,\ y,\ z)$ and let the equivalent vectors in the screen coordinate system with respect to the two sample holder positions be $\mathbf{v}^1(x^1,\ y^1,\ z^1)$ (position 1) and $\mathbf{v}^2(x^2,\ y^2,\ z^2)$ (position 2). Under TEM imaging mode, let the orientation relationship between the screen coordinate system and the first sample position described by rotation $R(\varphi_1,\Phi\ ,\varphi_2)$ and the rotation from the first sample position to the second sample position $\Delta R(\Delta\varphi_1,\Delta\Phi\ ,\Delta\varphi_2)$, as shown in Fig. 1. For simplicity, the first sample position could be taken without tilt operation. R is then characterized by a single rotation around the Z axis of the screen coordinate system caused by the magnetic rotation of the electron beam which is magnification dependent. Thus, the following relations between the unit vectors $\mathbf{v}$, $\mathbf{v}^1$ and $\mathbf{v}^2$ hold for

$$\mathbf{v}^1 = \mathrm{M}_1 \cdot \mathbf{v} \qquad (1a)$$

$$\mathbf{v}^2 = \mathrm{M}_1 \cdot \mathrm{M}_2 \cdot \mathbf{v} \qquad (1b)$$

where M_1 and M_2 are the corresponding rotation matrices of R and ΔR, and are known. Then the relation between the $\mathbf{v}^1(x^1,\ y^1, z^1)$ and $\mathbf{v}^2(x^2,\ y^2, z^2)$ can be deduced as:

$$\mathbf{v}^1 = \mathrm{M}_1 \cdot \mathrm{M}_2^{-1} \cdot \mathrm{M}_1^{-1} \cdot \mathbf{v}^2 \qquad (2)$$

where M_1^{-1} and M_2^{-1} are the inverse matrices of M_1 and M_2. According to the imaging principle of the TEM, an image of a nanoparticle is the rotated (around the Z axis of the screen coordinate system and dependent on the magnification) and amplified projection of the particle. As the Z axis of the screen coordinate system is set parallel to the incident beam, *i.e.*, the Z axis is parallel to the projection direction, the X and Y coordinates of

$\mathbf{v}^1$ and $\mathbf{v}^2$ in the screen coordinate system can be measured. Only z^1 and z^2 are unknown. With the three linear equations offered by Eq. (2), the two unknown z^1 and z^2 can be resolved. Thus the coordinates of the edge vector in the screen coordinate system are determined.

2.3 Coordinate transformation matrices

The coordinate transformation from the screen coordinate system to the crystal bases can be achieved through acquiring and indexing the electron diffraction pattern of the crystal. The diffraction pattern can either be in spot pattern or in Kikuchi line pattern. For simple operation, one of the two sample positions used to determine the edge vectors in the screen coordinate system could be dedicated to obtain a diffraction pattern of a low index zone axis. There is no automatic program available to directly determine the orientation of the crystallite with respect to either the sample holder or the screen of the microscope by indexing the spot pattern. Such software to determine the orientation by indexing the Kikuchi pattern is available. Thus we will treat the spot pattern and the Kikuchi pattern separately in this work.

According to the diffraction geometry, the TEM diffraction spot pattern of a crystallite is the amplified 2-dimentional reciprocal plane of the crystallite, which is perpendicular to the incident beam or the Z-axis of the screen coordinate system. Each spot in this reciprocal plane represents one set of diffracting planes expressed with Miller indices (*h k l*). The reciprocal vector with components (*h, k, l*) in the reciprocal base is perpendicular to the plane with Miller indices (*h k l*) in the direct lattice space. Thus with the correctly indexed diffraction pattern, it is easy to find two vectors $\boldsymbol{r}^1$ and $\boldsymbol{r}^2$ that are coincident with two reciprocal lattice vectors (h^1 k^1 l^1) and (h^2 k^2 l^2) in the XOY plane of the screen coordinate system. By vector cross product, one can easily obtain the 3rd vector $\boldsymbol{r}^3$ in the Z direction as shown in Fig. 2. The three vectors should be referred to the same basis, either to the reciprocal space or to the direct space. It should be noted that $\boldsymbol{r}^3$ is not necessarily a reciprocal lattice vector. The coordinate transformation of the vectors between the direct space and the reciprocal space can be easily realized with the direct metric tensor or the reciprocal metric tensor (Eqs. (A1) and (A2) in Appendix 1). Here

we referred the three vectors to the reciprocal space. Therefore, the coordinate transformation matrix from the screen coordinate system to the $\boldsymbol{r}^1$-$\boldsymbol{r}^2$-$\boldsymbol{r}^3$ reference base $\boldsymbol{M}_{\boldsymbol{I}\to\boldsymbol{g}}$ is:

$$\boldsymbol{M}_{\boldsymbol{I}\to\boldsymbol{g}} = \begin{bmatrix} \left\|\boldsymbol{r}^1\right\| \cdot \cos\eta & \left\|\boldsymbol{r}^2\right\| \cdot \cos(\eta+\theta) & 0 \\ \left\|\boldsymbol{r}^1\right\| \cdot \sin\eta & \left\|\boldsymbol{r}^2\right\| \cdot \cos(\eta+\theta) & 0 \\ 0 & 0 & \left\|\boldsymbol{r}^3\right\| \end{bmatrix} \tag{3}$$

where η is the angle between X-axis and $\boldsymbol{r}^1$, and θ is the angle between $\boldsymbol{r}^1$ and $\boldsymbol{r}^2$. The coordinate transformation matrix from the $\boldsymbol{r}^1$-$\boldsymbol{r}^2$-$\boldsymbol{r}^3$ reference base to the reciprocal space, $M_{g\to r}$ is:

$$\boldsymbol{M}_{\boldsymbol{I}\to\boldsymbol{r}} = \begin{bmatrix} h^1 & h^2 & r_{a^*}^3 \\ k^1 & k^2 & r_{b^*}^3 \\ l^1 & l^3 & r_{c^*}^3 \end{bmatrix}^{-1} \tag{4}$$

where $r_{a^*}^3$, $r_{b^*}^3$ and $r_{c^*}^3$ are the components of $\boldsymbol{r}^3$ referred to the reciprocal space. In this way, the coordinate transformation matrices from the screen coordinate system to the reciprocal space $M_{I\to R}$ and that to the direct space $M_{I\to l}$ are:

$$M_{I\to R} = M_{I\to r} \cdot M_{r\to R} \tag{5}$$

and

$$M_{I\to l} = M_{I\to R} \cdot G^* \tag{6}$$

in which G^* is the metric tensor of the reciprocal basis (Shmueli, 1996) (Eq. (A2) in Appendix 1).

The orientation of the crystallite with respect to the sample coordinate system can be directly determined by indexing the Kikuchi line pattern using the commercial software Euclid's Phantasies (EP) (Morawiec, 1999; Morawiec *et al.*, 2002). The orientation of the crystalline is expressed with three Euler angles ($\varphi_1, \Phi, \varphi_2$) (in Bunge notation) rotating

the sample holder coordinate system to the Cartesian crystal coordinate system. The orientation relationship between the Cartesian crystal coordinate system and the Bravais lattice basis is set under the convention given by the "*International Table of Crystallography*" (Hahn, 1996) described in Appendix B. Thus the screen- to- reciprocal lattice base transformation matrix $\boldsymbol{M}_{i\to R}$ and the screen-to-crystal coordinate system transformation matrix $\mathrm{M}_{i\to l}$ will be:

$$\boldsymbol{M}_{i\to R} = \boldsymbol{M}_{i} \cdot \boldsymbol{M}_{EP}\boldsymbol{M}_{C\to R} \tag{7}$$

and

$$\boldsymbol{M}_{i\to l} = \boldsymbol{M}_{i\to R} \cdot G^{*} \tag{8}$$

in which M_{i} is the rotation matrix from the screen to one of the sample holder positions where the Kikuchi pattern is acquired, M_{EP} is the transformation matrix from the sample holder coordinate system to the Cartesian crystal coordinate system and $\boldsymbol{M}_{C\to R}$ is the transformation matrix from the Cartesian crystal coordinate system to the reciprocal space.

Therefore, for any vector obtained in the screen coordinate system $\mathbf{v}^{i}(x_i, y_i, z_i)$ that corresponds to the sample position acquiring the diffraction pattern, its components in the lattice space can be calculated as:

$$\boldsymbol{M}_{i\to l}^{-1} \cdot \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} \tag{9}$$

and the intercepts of the plane that is normal to $\mathbf{v}^{i}(x_i, y_i, z_i)$ can be obtained as:

$$\boldsymbol{M}_{i\to R}^{-1} \cdot \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} \tag{10}$$

In this way, the Miller indices of the edges and surface planes of the crystalline can be determined.

3. Application

Hereafter, we present one example to illustrate the application of the above method. The nanoparticles used in this example are hematite (α-Fe_2O_3) synthesized via chemical route. They belong to the trigonal crystal system (space group $R\bar{3}c$) with lattice parameters a=b=c=0.5419nm, $\alpha=\beta=\gamma$=55.36°. Hereafter we express the miller indices in the trigonal base. The images and diffraction patterns of the hematite nanoparticle to be determined were recorded using PHILIPS CM 200 TEM at 200kV. Fig. 3 shows the TEM images of the hematite particle at the two sample positions and the corresponding diffraction patterns. The Kikuchi and spot diffraction images are inserted after correcting the additional rotation from the image of the particle. It can be seen that the particle has a polyhedron shape. The three distinct edges of the particle are denoted with the unit vector $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{v}_3$ and the three distinct surfaces are defined by the edge vectors are P_1, P_2, and P_3, as shown in Fig. 3. The rotation angles that characterize the orientation relationship between the screen coordinate system and the first sample position (position 1: no tilt) R and from the first sample position to the second position (position 2: tilted) ΔR are given in Table 1. The X and Y components of vector $\mathbf{v}_i$ corresponding to the two sample positions in the screen coordinate system were measured and their Z components were calculated. The results are displayed in Table 2. One Kikuchi pattern (the inset of Fig. 3(a)) was taken at sample position 1 and indexed using the Euclid's Phantasies (EP) (Moraviec *et al*., 2002). The set of Euler angles that denote the rotation from the sample coordinate system to the Cartesian crystal coordinate system is (182.63°, 80.11°, 33.99°). One diffraction spot pattern (the inset of Fig. 3(b)) was taken after the sample was tilted (position 2) where the [010] zone axis is on edge. The two reference vectors $\boldsymbol{r}^1$ and $\boldsymbol{r}^2$ coincident with the $(10\bar{1})$ and $(\bar{1}0\bar{1})$ spots, respectively. The third vector $\boldsymbol{r}^3$ that is in Z direction and calculated by vector product has the components (0.333, 0.584, 0.333) in

the reciprocal space. The angle between the X-axis of the screen coordinate system and $\boldsymbol{r}^1$ is 50.986° and that between $\boldsymbol{r}^1$ and $\boldsymbol{r}^2$ is 90°.

The Miller indices of the surface planes and the edges of the particle were calculated separately by indexing the diffraction spot pattern and the Kikuchi pattern, as given in Table 3. The results showed that hematite particles were enclosed by high-index facets.

4. Conclusions

In conclusion, a new method for determining the crystalline planes and directions of the surface facets and edges of nanoparticles has been proposed in this paper. By determining the edge vectors and then the plane normal vector of a surface facet in the TEM screen coordinate mode, their Miller indices can be calculated through coordinate transformation. The method offers a general and a systematical way to characterize the surface crystallographic features of a nanoparticle and will facilitate the related studies.

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References

Bunge, H. J., Esling, C. & Muller, J. (1981). *Acta. Crystallogr. A* **37**, 889-899.

Hahn, T. (1996). *International Tables for Crystallography. Vol. A Space-group Symmetry, 4th Ed.* London: Kluwer Academic Press.

Lee, S., Cho, S. & Cheon, J. (2003). *Adv. Mater.* **15**, 441-444.

Lee, S., Jun, Y., Cho, S. & Cheon, J. (2002). *J. Am. Chem. Soc.* **124**, 11244-11245.

Maillard, M., Giorgio, S. & Pileni, M. (2003). *J. Phys. Chem. B* **107**, 2466-2470.

Morawiec, A. (1999). *J. Appl. Cryst.* **32**, 788-798.

Morawiec, A., Fundenberger, J., Bouzy, E. & Lecomte, J. (2002). *J. Appl. Cryst.* **35**, 287.

Narayanan, R. & El-Sayed, M. A. (2005). *J. Phys. Chem. B* **109**, 12663-12676.

Orendorff, C. J., Gole, A., Sau, T. K. & Murphy, C. J. (2005). *Anal. Chem.* **77**, 3261-3266.

Schwarzer, R. A. (1997). *Ultramicroscopy* **67**, 19-24.

Shmueli, U. (1996). *International Tables for Crystallography. Vol. B Reciprocal space, 1th Ed.* London: Kluwer Academic Press.

Stekolnikov, A. A. & Bechstedt, F. (2005). *Phys. Rev. B* **72**, 125326.

Tian, N., Zhou, Z., Sun, S., Ding, Y. & Wang, Z. L. (2007). *Science* **316**, 732-735.

Xiang, Y., Wu, X., Liu, D., Jiang, X., Chu, W., Li, Z., Ma, Y., Zhou, W. & Xie, S. (2006). *Nano Lett.* **6**, 2290-2294.

Xiong, Y., Wiley, B. J. & Xia, Y. (2007). *Angew. Chem. Int. Ed.* **46**, 7157-7159.

Zaefferer, S. (2002). *Adv. Imag. Electron. Phys.* **125**, 355-415.

Table1
The rotation angles that characterize the coordinate transformation from the screen coordinate system to the first sample position R and that from the first sample position to the second position ΔR

$R\,(\varphi_1, \Phi, \varphi_2)$	$\Delta R\,(\Delta\varphi_1, \Delta\Phi, \Delta\varphi_2)$
(165.84°, 0, 0)	(0, 10.26°, -5.80°)

Table 2
Coordinates of the unit edge vectors $\mathbf{v}_i$ with respect to the two sample holder positions (Positions 1 and 2) in the screen coordinate system calculated with their measured trace coordinates in the screen coordinate system.

	x^1	y^1	z^1	x^2	y^2	z^2
$\boldsymbol{v}_1$	-0.364	-0.685	-0.631	-0.456	-0.743	-0.490
$\boldsymbol{v}_2$	-0.188	0.530	-0.827	-0.171	0.396	-0.902
$\boldsymbol{v}_3$	0.950	-0.163	0.267	0.940	-0.212	0.267

Table 3

Calculated Miller indices of the edge vectors $\mathbf{v}_i$ and the planes P_i from indexing the corresponding diffraction spot pattern and Kikuchi line pattern.

	$[uvw]$						(hkl)				
	Spot		Kikuchi		Refined indices		Spot		Kikuchi		Refined indices
Edge	Indices	Deviation from the refined indices	Indices	Deviation from the refined indices		Plane	Indices	Deviation from the refined indices	Indices	Deviation from the refined indices	
$\mathbf{v}_1$	[-1.562 -1.080 1.870]	1.56°	[-1.471 -1.200 1.837]	2.57°	$[\bar{4}\,\bar{3}\,5]$	P_1	(1.288 2.083 -2.613)	0.87	(1.254 2.285 -2.484)	2.3	$(35\bar{6})$
$\mathbf{v}_2$	[-0.123 -1.074 -0.917]	3.58°	[-0.025 -1.070 -1.000]	1.23°	$[0\bar{1}\,\bar{1}]$	P_2	(1.341 4.705 3.837)	0.75	(1.121 4.542 3.864)	2.6	(3 11 9)
$\mathbf{v}_3$	[2.022 -0.841 0.325]	0.87°	[2.005 -0.761 0.313]	1.18°	$[25\,\overline{10}\,4]$	P_3	(-3.091 1.712 -1.593)	1.63	(-3.256 1.556 -1.591)	0.89	$(\bar{2}\,1\bar{1})$

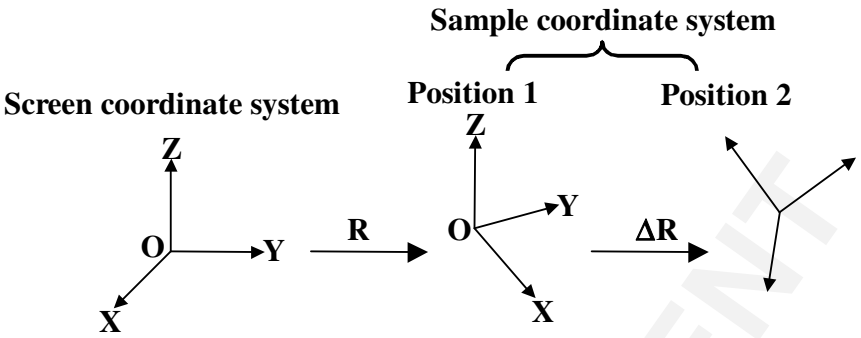

Figure 1
Relative positions of the Screen coordinate system and the Sample coordinate system.

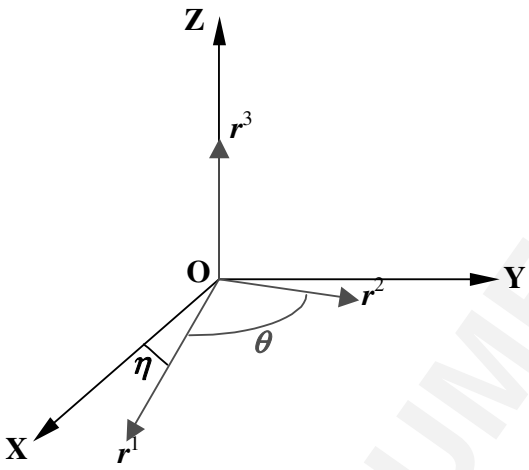

Figure 2
Illustration of the screen coordinate system and the reference base of $\boldsymbol{r}^1$-$\boldsymbol{r}^2$-$\boldsymbol{r}^3$. *The* $\boldsymbol{r}^1$ and r^2 are reciprocal lattice vectors determined by indexing the spot diffraction pattern. The $\boldsymbol{r}^3$ calculated by cross product is expressed in the reciprocal space. It should be noted that $\boldsymbol{r}^3$ is not necessarily a reciprocal lattice vector.

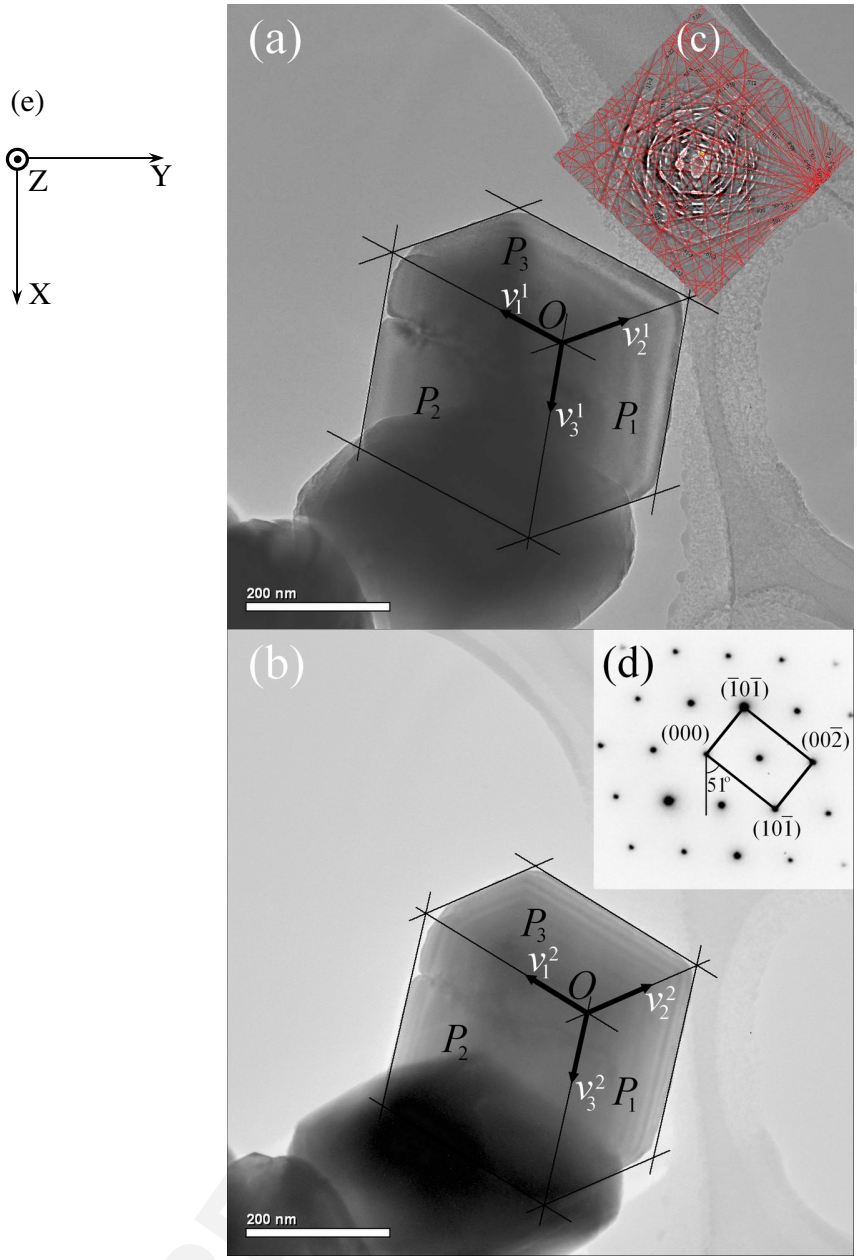

Figure 3
TEM images of hematite particle at (a) initial position and (b) tilted position. The inserts are their corresponding (c) Kikuchi pattern and (d) spot pattern. (e) is the screen coordinate system.

Appendix 1. Metric tensors of the direct and reciprocal bases

Let the crystal basis be defined by three base vectors **a**, **b** and **c** with the respective length of a, b and c. The angles between each pair of base vectors are α, β and γ. Its reciprocal space is defined by the three lattice vectors **a***, **b*** and **c*** with the respective length a^*, b^* and c^*. The computational and algebraic aspects of these mutually reciprocal bases can be conveniently expressed in terms of the metric tensors of these bases. The matrix of the metric tensor of the direct basis ***G*** or briefly the direct metric is:

$$G = \begin{vmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ba\cos\gamma & b^2 & bc\cos\alpha \\ ca\cos\beta & cb\cos\alpha & c^2 \end{vmatrix} \qquad \text{(A1)}$$

The corresponding reciprocal metric is:

$$G^* = \begin{vmatrix} \frac{b^2c^2\sin^2\alpha^2}{V^2} & \frac{abc^2(\cos\alpha\cos\beta-\cos\gamma)}{V^2} & \frac{ab^2c(\cos\alpha\cos\gamma-\cos\beta)}{V^2} \\ \frac{abc^2(\cos\alpha\cos\beta-\cos\gamma)}{V^2} & \frac{a^2c^2\sin^2\beta}{V^2} & \frac{a^2bc(\cos\beta\cos\gamma-\cos\alpha)}{V^2} \\ \frac{ab^2c(\cos\alpha\cos\gamma-\cos\beta)}{V^2} & \frac{a^2bc(\cos\beta\cos\gamma-\cos\alpha)}{V^2} & \frac{a^2b^2\sin^2\gamma}{V_2} \end{vmatrix} \qquad \text{(A2)}$$

in which $V^2 = a^2b^2c^2(1+2\cos\alpha\cos\beta\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma)$. With Eq. (A1) and (A2), the vector calculations and the coordinate transformation of the vectors between the two bases can be easily realized.

Appendix 2. Coordinate transformation matrices between the Cartesian crystal coordinate system and the direct lattice space and its reciprocal space

With the automatic Kikuchi pattern indexing software packages, such as HKL's Channel software package, TSL's OIM software package and the Euclid's Phantasies (EP), the crystallographic orientation of a crystal can be determined by indexing the Kikuchi patterns of the crystallite. The orientation of the crystallite is always expressed by a set of rotations (Euler angles) from the sample coordinate system to the Cartesian

coordinate system attached to the crystal. Therefore, the coordinate transformation matrices from the Cartesian coordinate system to the Bravais lattice base and its reciprocal base are always in need. The derivation of such matrices would be helpful for the related calculations. According to the "*International Table of Crystallography*" (Hahn, 1996), the Cartesian system is set at the same origin of the Bravais lattice base with its X axis parallel to the base vector ***a*** and the base vector ***c*** is in the XOZ plane of the Cartesian coordinate system, as shown in Fig. A1. Thus the components of ***a***, ***b*** and ***c*** in the Cartesian coordinate system are as follows:

$$
\begin{aligned}
a_x &= a \\
a_y &= 0 \\
a_z &= 0
\end{aligned}
$$

$$
\begin{aligned}
b_x &= b \cdot \cos\gamma \\
b_y &= \frac{b}{\sin\beta}\sqrt{1+2\cos\alpha\cdot\cos\beta\cdot\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma} \\
b_z &= \frac{b}{\sin\beta}(\cos\alpha-\cos\beta\cdot\cos\gamma)
\end{aligned}
\qquad \text{(A3)}
$$

$$
\begin{aligned}
c_x &= c \cdot \cos\beta \\
c_y &= 0 \\
c_z &= c \cdot \sin\beta
\end{aligned}
$$

Therefore, the transformation matrix from the Cartesian coordinate system to the lattice base is:

$$
\begin{bmatrix} a_x & b_x & c_x \\ 0 & b_y & 0 \\ 0 & b_z & c_z \end{bmatrix} \qquad \text{(A4)}
$$

and the transformation matrix from the lattice base to the Cartesian coordinate system is:

$$\begin{bmatrix} \frac{1}{a_x} & \frac{c_x \cdot b_z - b_x \cdot c_z}{a_x \cdot b_y \cdot c_z} & -\frac{c_x}{a_x c_z} \\ 0 & \frac{1}{b_y} & 0 \\ 0 & -\frac{b_z}{b_y \cdot c_z} & \frac{1}{c_z} \end{bmatrix} \tag{A5}$$

The transformation matrix from the Cartesian coordinate system to the reciprocal base is:

$$\begin{bmatrix} \frac{1}{a_x} & 0 & 0 \\ \frac{b_z \cdot c_x - b_x \cdot c_z}{a_x \cdot b_y \cdot c_z} & \frac{1}{b_y} & -\frac{b_z}{b_y \cdot c_z} \\ -\frac{c_x}{a_x \cdot c_z} & 0 & \frac{1}{c_z} \end{bmatrix} \tag{A6}$$

and the transformation matrix from the reciprocal base to the Cartesian coordinate system is:

$$\begin{bmatrix} a_x & 0 & 0 \\ b_x & b_y & b_z \\ c_x & 0 & c_z \end{bmatrix} \tag{A7}$$

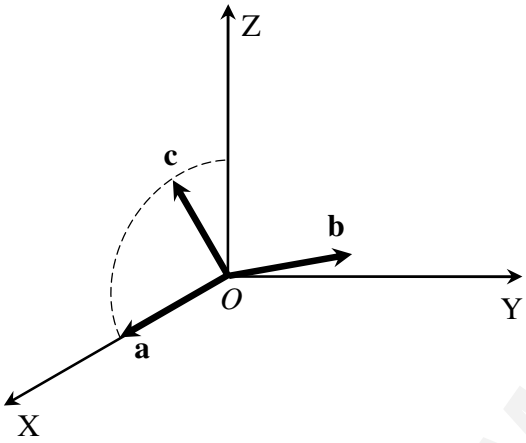

Figure A1
Relationship between the Cartesian coordinate system and the lattice base under the convention of "*International Table of Crystallography*" (Hahn, 1996).