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Short Communication

Is the Brus Equation Correct?

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Short Communication

Metal oxides were widely used in the domains of materials, physics, and chemistry and have been extensively used in catalysts, fuel cells, piezoelectric materials, sensor materials, and optical components. Among various metal oxides, CeO_2 is one of the extensively applied and discussed. It has a face-centered cubic structure with a high melting point (2400-2700 °C) and possesses remarkable properties such as the number of effective redox Ce^{3+}/Ce^{4+} sites and their ability to exchange oxygen [1]. Therefore, it has good optical properties, thermal stability and electrical conductivity, and oxygen storage function [2,3]. For instance, the optical property of UV-vis spectroscopy for the CeO_2 nanoparticles exhibits a blue shift with respect to the bulk material due to quantum confinement, which have two limiting case, depending on the ratio of the crystallite radius to the effective Bohr radius of the electron-hole pair [4].

Therefore, the crystal size and energy gap measurements were significant in applications. Thus, a discussion of crystal size with energy gap was required. The relationship between crystal size and energy gap can be described by the Brus Equation [5]. In addition, a modified Brus equation was proposed by Ferreira et al. [4], where the modified values were smaller than that obtained from the Brus equation. In order to conduct comparisons between the Brus equation, several reported data in the literature were collected.

In general, the crystal sizes are measured by XRD with the Scherer equation or the Williamson-Hall (W-H) method [1]. On the other hand, the energy gaps are determined using absorption coefficient (α) and frequency (ν) [1], as follows:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \qquad (1)$$

wherein A is constant, and E_g is the energy gap. Through a plot of α(hν) versus hν, the energy gap can be determined. The energy gaps of cerium oxide were found to be 3.26eV(380nm) and 3.22eV(385nm) [1], while the energy gaps for different solvents [3] were 3.44eV(361nm), 3.22eV(386nm), 3.45eV(361nm) and 3.2eV(388nm) for water, acetone, ethanol, and ethylene glycol, respectively.

The effect of size on the energy gap can be described by the Brus equation [5]:

$$E_g = E_{Bulk} + \frac{2h^2\pi^2}{d_p^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{3.6e^2}{\varepsilon_r\varepsilon_o d_p} \qquad (2)$$

Equation (2) describes that E_g is a function of the diameter of crystal, d_p. The second and third terms are represented by blue and red shifts, respectively. In addition, E_{Bulk} refers to the band gap (for CeO_2; E_{Bulk}=3.15eV); m_e and m_h are the effective masses of electron and electron

hole, respectively; ε_r and ε_0 are the relative dielectric constant of CeO_2, which is 24.5, and dielectric constant at empty, respectively.

We selected $m_e=m_h=0.4m$, where m is the mass of a free electron. In order to compare the reported data with the Brus equation, the equation can be calculated and expressed as a dotted line, as shown in Figure 1. In addition, the data with hydrothermal method obtained in here and from literatures with precipitation method [1,5-8] and sol-gel method [3] were also presented in this Figure 1. The particle sizes for the two runs in here were found to be 11.06nm and 8.05nm, for 100 °C and 150 °C, respectively. The corresponding energy gaps were 3.3eV and 3.59eV, respectively. The data presented were used in black triangle. All data were under the dotted line, indicating that the value of E_g evaluated by the Brus equation was overestimated when d_p is smaller than 20nm. According to the Brus equation, the bulk size (maximum size) can be determined by letting $dE_g/d(d_p)=0$. The final size was found to be 214nm, which is the bulk size of cerium oxide [9]. The corresponding E_{Bulk} is 3.15eV. Therefore, it needs to be modified further when we used Equation (2).

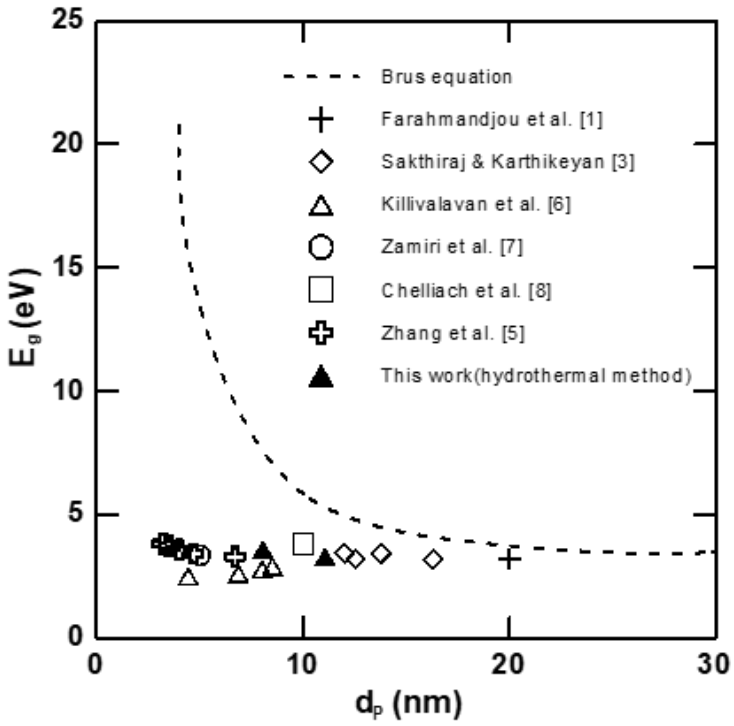

Figure 1: A plot of energy gap vs. crystal size for comparison.

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