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Heterostructured Core@shell Nanoparticles: PVG/TiO_2@MoO_3 and PVG/MoO_3@TiO_2

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Abstract – Heterostructured core@shell nanoparticles of TiO_2 and MoO_3 have been synthesized by a metallo-organic decomposition process (MOD). The IDC methodology promoted a linear mass increase, resulting in a controlled core size and controlled shell thickness. The HRTEM images show that these nanoparticles are crystalline and have average size distributions of 5.22 nm for PVG/5TiO_2@7MoO_3 and 4.89 nm for PVG/5MoO_3@7TiO_2. The quantum confinement effects are observed in all structures using diffuse reflectance spectroscopy, band gaps dates, and Raman spectroscopy (blue shift of the E_g band of the TiO_2 anatase).

In recent years, semiconductors core@shell nanoparticles (CSN) structures represent a new type of constructional unit and have attracted much attention in the chemistry of advanced materials. These particles have incredible potential applications in various fields, such as modulation of optical properties, photonics, biological detection, magnetism, and catalysis, as a result of the synergic effect between its components.[1]

The CSN, TiO_2@MoO_3 and MoO_3@TiO_2, dispersed into porous Vycor glass (PVG, Corning Glass®), were prepared by metallo-organic decomposition process (MOD). The impregnation followed by the decomposition of the precursors titanium (IV) di-(propoxy)-di-(2-ethylhexanoate), $Ti(OnPr)_2(Hex)_2$, or molybdenum (VI) 2-ethylhexanoate, $Mo(Hex)_6$ were done in the PVG. For the decomposition process, the impregnated PVG were submitted to thermal treatments under air at 750 ºC/8 h and 550 ºC/8 h, respectively. This procedure is denominated as impregnation-decomposition cycle (IDC). The sample masses were determined by weighting after IDC.

The IDC methodology promoted a linear mass increase resulting in a controlled core size and controlled shell thickness of the sphere-like core@shell nanoparticles. Images obtained using high-resolution transmission electron microscopy (HRTEM) on PVG/5TiO_2@7MoO_3 and PVG/5MoO_3@7TiO_2 exhibited crystalline particles with well-defined lattice fringes and with average size distributions of 5.22 nm and 4.89 nm, respectively. The quantum size effects were observed by diffuse reflectance spectra (DRS) results (Table 1), which show that the edge absorption of the CSN PVG/TiO_2@MoO_3 and PVG/MoO_3@TiO_2 samples and of the isolated PVG/TiO_2 and PVG/MoO_3 nanoparticles occurred together and are dependent to the mass increases and the respective numbers of IDC. Besides, the CSN present different colors in comparison to the isolated nanoparticles, Figure 1. This phenomenon happens due to the alignment of the bands of energy when the oxides are combined to form heterostructured CSN and is influenced directly by the shell thickness. The Raman spectroscopy studies in all systems show a slight shift of the *Eg* band of the TiO_2 anatase to higher wavenumbers, which is due to the quantum confinement of the phonon states.[1,2] This *Eg* related band is not affected by the numbers of IDC when MoO_3 is located at the shell. However, the MoO_3 band at 996 cm^{-1} (related to surface Mo=O bonds) decreases its intensity when TiO_2 is located at the shell. This suggests that, in this case, an interaction among the two oxides occurs through this Mo=O surface bonds.

Table 1: Band gaps of the isolated and core@shell nanoparticles

IDC	*gap* (eV)	IDC	*gap* (eV)
PVG/3TiO_2	3.90	PVG/3MoO_3	3.66
PVG/5TiO_2	3.78	PVG/5MoO_3	3.51
PVG/7TiO_2	3.68	PVG/7MoO_3	3.44
PVG/5TiO_2@3MoO_3	3.74	PVG/5MoO_3@3TiO_2	3.74
PVG/5TiO_2@5MoO_3	3.69	PVG/5MoO_3@5TiO_2	3.70
PVG/5TiO_2@7MoO_3	3.64	PVG/5MoO_3@7TiO_2	3.65
PVG/3TiO_2@5MoO_3	3.80	PVG/3MoO_3@5TiO_2	3.69
PVG/5TiO_2@5MoO_3	3.66	PVG/5MoO_3@5TiO_2	3.66
PVG/7TiO_2@5MoO_3	3.61	PVG/7MoO_3@5TiO_2	3.55

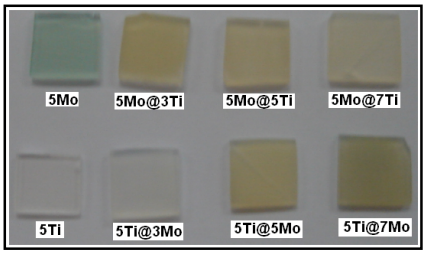

Figure 1: Image of the nanoparticles into PVG with IDC different.

References
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[2] I. O. Mazali; A. G. Souza Filho; B. C. Viana; J. Mendes Filho; O. L. Alves. J. Nanopart. Res. 8(2006) 141-148.