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Hydrothermal Synthesis of Polyaniline intercalated Vanadium Oxide Xerogel hybrid nanocomposites: An effective control of morphology and structural characterization

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Rietveld Analysis:

One of the great achievements of Rietveld's powder structure refinement method[1-4] using traditional XRD data is ability to characterize both structure and micro/nano-structure as well as quantitative phase estimation of individual phases in a multiphase material. We have adopted it in the present study to characterize the structural and micro/nano structural changes of PANI/vanadium oxide nanocomposites with different morphologies. This method involves XRD pattern simulation using available respective ICDD files and fitting the experimental XRD

pattern by refining structure and microstructure parameters of the simulated pattern employing the Marquardt least-square refinement procedure (in terms of an analytical function). Since Bragg reflections always contribute to the intensity (y_i) at any arbitrary point, the calculated intensities (y_{ci}) can be described according to:

$$Y_{ci} = S\sum_{k} L_k |F_k| 2\Phi(2\theta_i - 2\theta_k) P_k A + y_{bi} \quad (1)$$

where S is the scale factor, k represents the Miller indices (hkl) for a Bragg reflection, L_k represents the Lorentz polarization and multiplicity factors, Φ is the reflection profile function, P_k is the preferred orientation function, F_k is the structure factor for the kth Bragg reflection, A isthe absorption function, and y_{bi} is the background intensity of the i-th step. The Rietveld software MAUD 2.26 is specially designed to refine simultaneously both structural and microstructure parameters governing the equation (1). As the peaks are significantly broadened with asymmetry, the shape of the diffraction profiles is modelled with a pseudo-Voigt (pV) function with asymmetry as it takes care for both the particle size and strain broadening of the experimental profiles individually. To fit the experimental profiles of the samples taking into account all kinds of instrumental corrections, we have modelled the simulated patterns by refining some important structural and microstructure parameters such as particle (coherently diffracting domain) size, r.m.s lattice strain, preferred orientation, lattice parameters, atomic coordinates, etc. The background of each pattern is fitted by a polynomial of degree 5. The process of refinement was an iterative method and the probable value of different parameters depended on the goodness of fit (GoF). This can be expressed as the ratio of reliable index parameters R_{wp} to R_{exp} The weighted residual error (R_{wp}) and expected residual error (R_{exp}) are defined as:

$$R_{wp}=\left[\frac{\sum_i w_i(I_O-I_C)^2}{\sum_i w_i(I_O)^2}\right]^{1/2}$$

$$R_{exp}=\left[\frac{(N-P)}{\sum_i w_i(I_O)^2}\right]^{1/2}$$

where I_0 and I_C are the experimental and calculated intensities, w_i $(=1/I_O)$ and N are the weight and number of experimental observations and P the number of fitting parameters. In the present work the value of GoF is very close to 1.0 and this indicates the quality of refinement is quite good.

To account for the crystal orientation effect, we adopt the March-Dollase equation as the model to fit the texture distribution along the direction of growth of nanorods. The March equation was first introduced to determine the preferred orientation of anisotropic particles[5]. Dollase later modified the March equation to fit the preferred orientation in Rietveld analysis and the modified March-Dollase equation is:

$$T_{hkl}=\frac{1}{N}\sum_{i=1}^{i=N}\left(\tau^2 Cos^2\phi_{hkl}^{\ i}+\frac{1}{\tau}Sin^2\phi_{hkl}^{\ i}\right)^{-3/2}$$

where T_{hkl} is the preferred orientation factor, τ is the preferred orientation parameter which is refinable in Rietveld analysis, ϕ is the angle between the preferred orientation vector and the normal to the planes generating the diffracted peak, N is the symmetrically equivalent reciprocal lattice points. In the present study, we have determined the preferred orientation and texture parameters of rod shaped PV2 using this March-Dollase equation with the help of Rietveld software MAUD 2.26[6].

XPS Analysis:

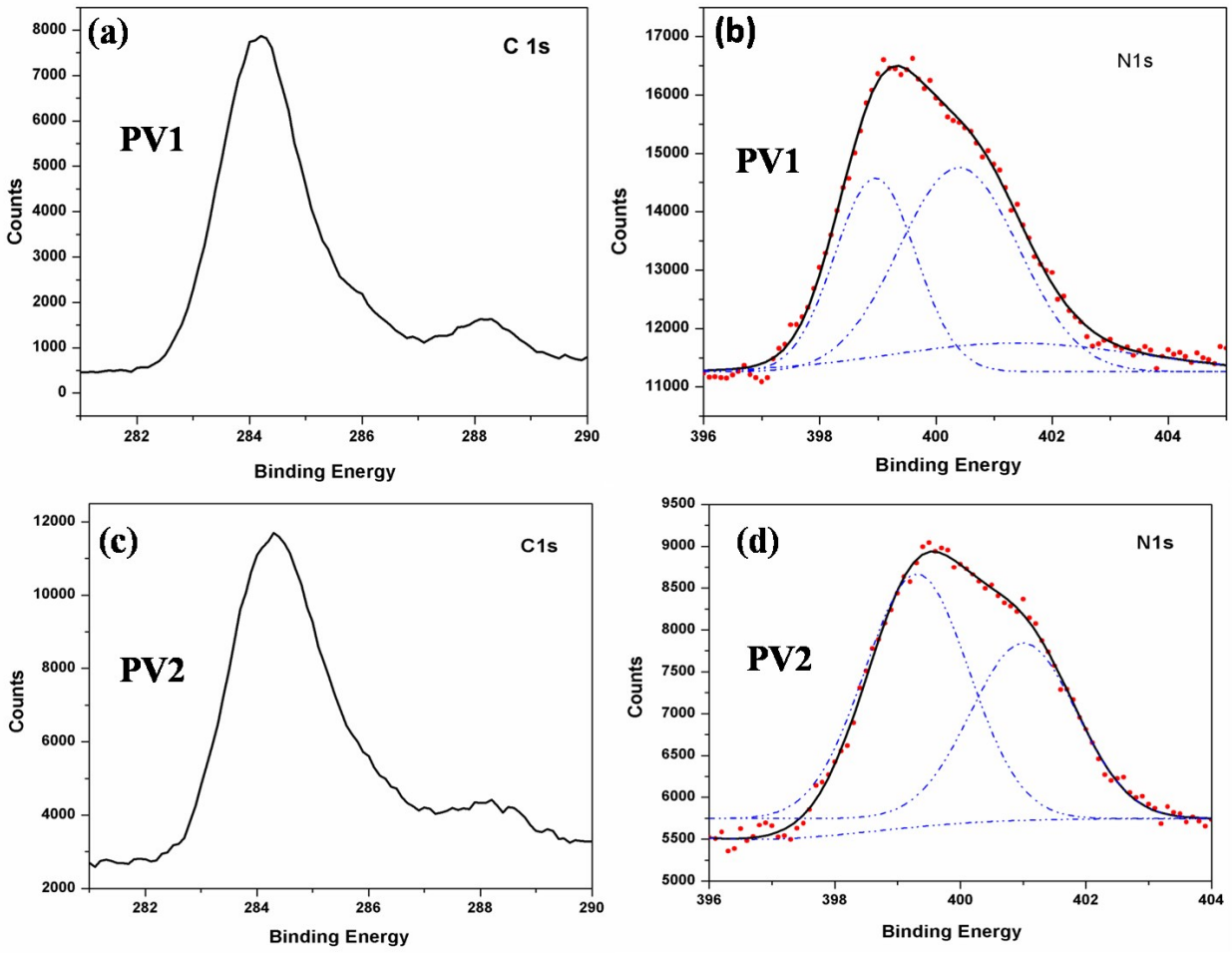

Figure S1: XPS spectra of the PANI/Vanadium oxide nanocomposite for (a, c) C1s and (b, d) N1s peaks for PV1 and PV2 respectively.

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