Supporting Information

Evaluation of Fe^{3+} fixation into montmorillonite clay and its application in the polymerization of ethylenedioxythiophene

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1. General methods

1.1 Materials

The solutions were made with deionized water. The montmorillonite used in this study was from Tehuacán, Puebla, Mexico. The reagents were bought to Aldrich Co. and were used without further purification. $FeClO_4$ hydrated (98%), $NaClO_4$ monohydrate HPLC grade (≥99.0%), potassium thiocyanate, ≥99.0% and hydrochloric acid, 37%, 3,4-ethylenedioxythiophene (96.5%), chloroform HPLC grade, ≥99.9% and acetonitrile HPLC grade, ≥99.93% were used in this work.

1.2 Equipment

X-ray photoelectron spectroscopy (XPS) was made using a Thermo Scientific spectrometer model K-Alpha that uses Al Kα (1486 eV) monochromatic source and argon flow charge compensation system to analyze non-conductive samples. Infrared Spectroscopy Attenuated Total Reflection (IR-ATR) was made using Bruker spectrometer model Tensor 27. X-rays diffractometer Siemens D5000 was used for X-ray Diffraction Spectroscopy (XRD) experiments. Diffraction pattern obtained at 4° interval and 70° in goniometry 2θ. In order to obtain average crystal size or crystallite we use Scherrer equation.[1] The specific surface area was determinate by Brunauer, Emmett and Teller method (BET), the analysis was made on a Autosorb iQ instrument. The Scanning Electron Microscopy (SEM) was carried out in a JEOL electron microscope model 5900LV equipped with the Oxford probe for EDS model 7274 resolution 133 eV. Atomic Force Microscope (AFM) ASYLUM RESEARCH microscope model MFP-3D Origin; operation mode tapping.

2. Experimental procedures

2.1 Modification of montmorillonite with Fe^{3+} cations and evaluation of Fe^{3+} kinetics absorption onto montmorillonite clay

Modification of montmorillonite with Fe^{3+} cations was studied using the batch method in two different ways: (a) Changing iron concentration at fixed temperature and (b) keeping constant iron concentration with changes of temperature. The range of concentration and temperatures used are:

a) 200 mg montmorillonite (solute) with 10 ml $Fe(ClO_4)_3$ solution of 50, 530, 6320, and 75500 ppm ($mg.L^{-1}$) at pH 1.5 at 20 °C. Ionic force was fixed with $NaClO_4$ at 0.5 M (solvent).
b) 200 mg montmorillonite (solute) with 10 ml $Fe(ClO_4)_3$ 530 ppm ($mg.L^{-1}$), pH 1.5 at 20 °C, 40 °C and 60 °C. Ionic force was fixed with $NaClO_4$ at 0.5 M (solvent).

2.2 Iron (III) quantification

The quantification of fixation of Fe^{3+} cations was made determining the remaining Fe^{3+} concentration using the thiocyanate method,[2] where the red-orange colored Fe^{3+} - thiocyanate complex in acidic solutions gives a absorbance maxima at 480 nm. For this, it was mixed 0.5 mL of potassium thiocyanate (20 %), hydrochloric acid 3 M (0.5 mL), aliquot sample (2.5 mL) and deionized water (2.5 mL). The absorbance of the obtained mixture was read at 480 nm using a UV-Vis spectrometer Perkin Elmer model Lambda 10. Calibration curve was made with solution of $FeClO_4$, in the range of concentration from 20 $mg.L^{-1}$ at 45 $mg.L^{-1}$. The more concentrated samples were diluted to fit in the calibration curve.

2.3 Synthesis and characterization of PEDOT polymerized onto montmorillonite

Poly-(ethylenedioxythiophene) (PEDOT) was chemically synthesized using oxidative polymerization.[3] For the PEDOT deposited onto montmorillonite, Fe^{3+} enriched montmorillonite (1g containing 6 mg of $Fe(ClO_4)_3$, per g of clay) was reacted with EDOT (7 μl, 65529 nmol) in 20 ml chloroform during 24 h with constant stirring at 10 °C. The obtained product (blue solid on the montmorillonite clay) was washed several times with chloroform and acetone in a Buchner filter and finally it was fitted in a Soxhlet and washed with acetonitrile during 24 h. The PEDOT-montmorillonite composite was dried at 60 °C over night and keep in a closed vial for analysis. For comparison, pure PEDOT was prepared by chemical polymerization using $Fe(ClO_4)_3$ solution (3.520 g, 9.93×10^{-3} mol in 30 mL acetonitrile) were EDOT solution (0.6655 g, 4.68×10^{-3} mol in 30 mL chloroform) was added slowly (10 min). The mixture was magnetically stirred during 24 h at 10 °C in an ice-water bath. The purification protocol was the same described above.

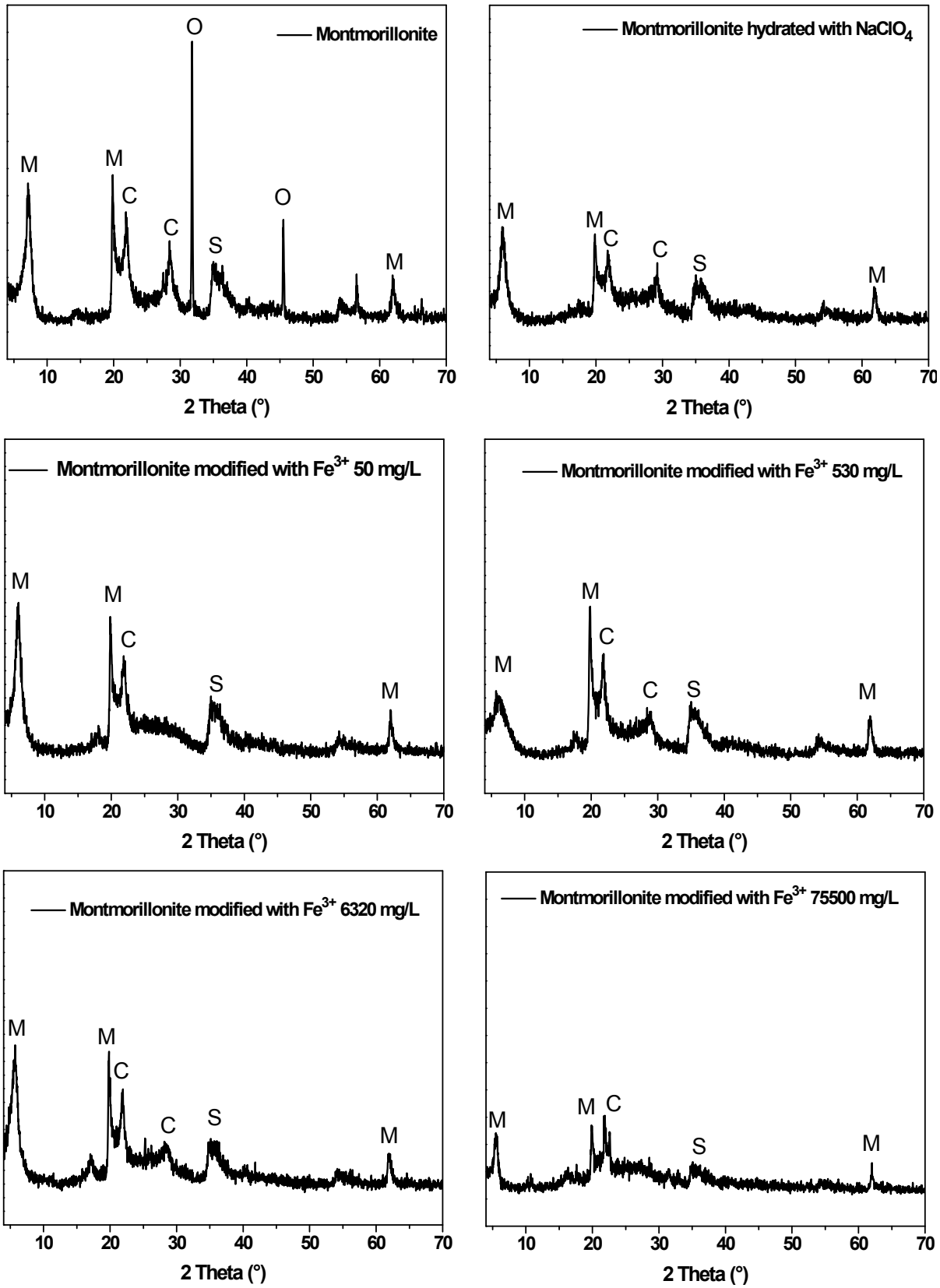

Fig S1. X-ray diffraction patterns of montmorillonite at different concentrations of iron

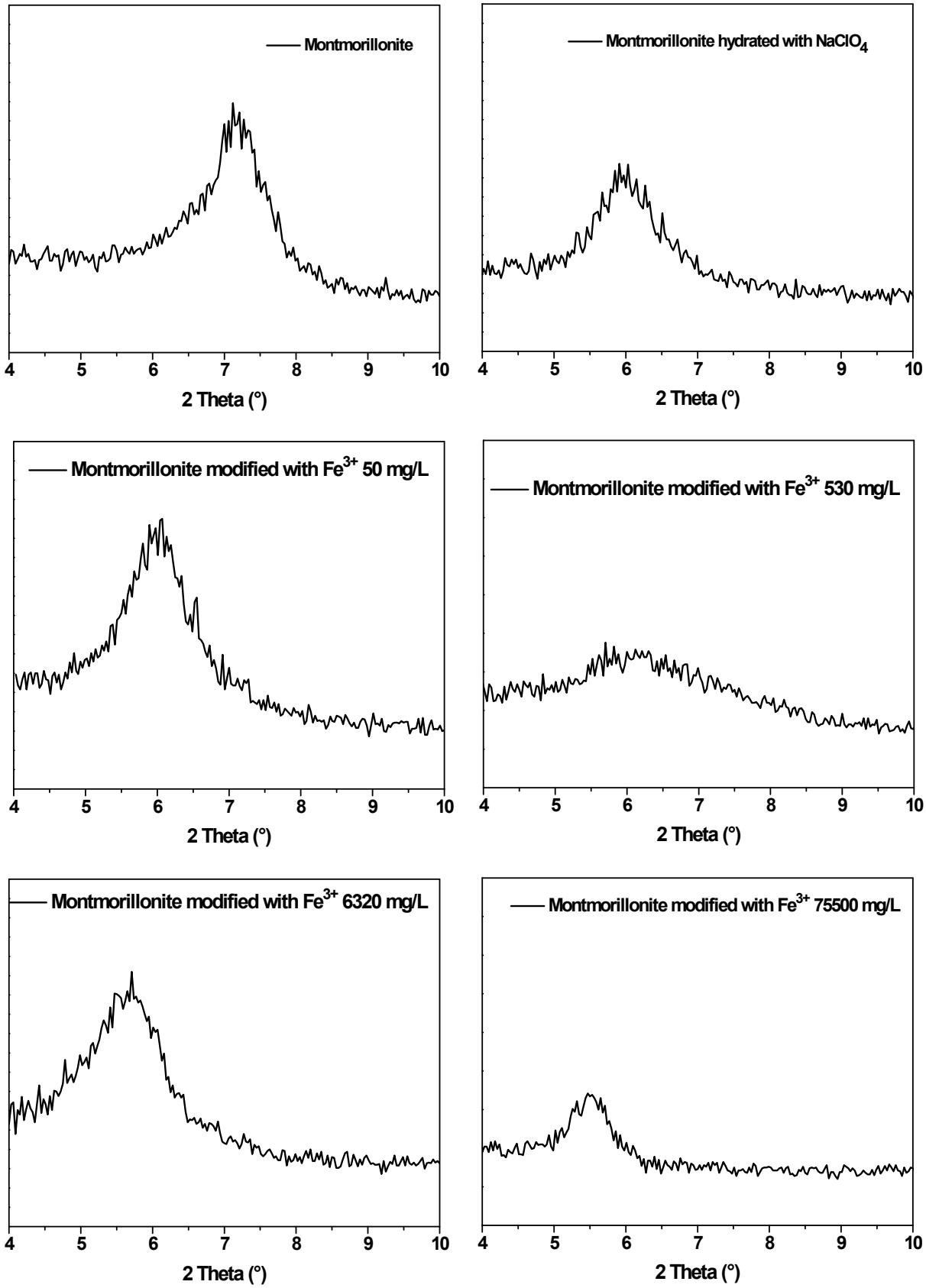

Fig S2. Evaluation of Miller index <0,0,1> for crystallite size

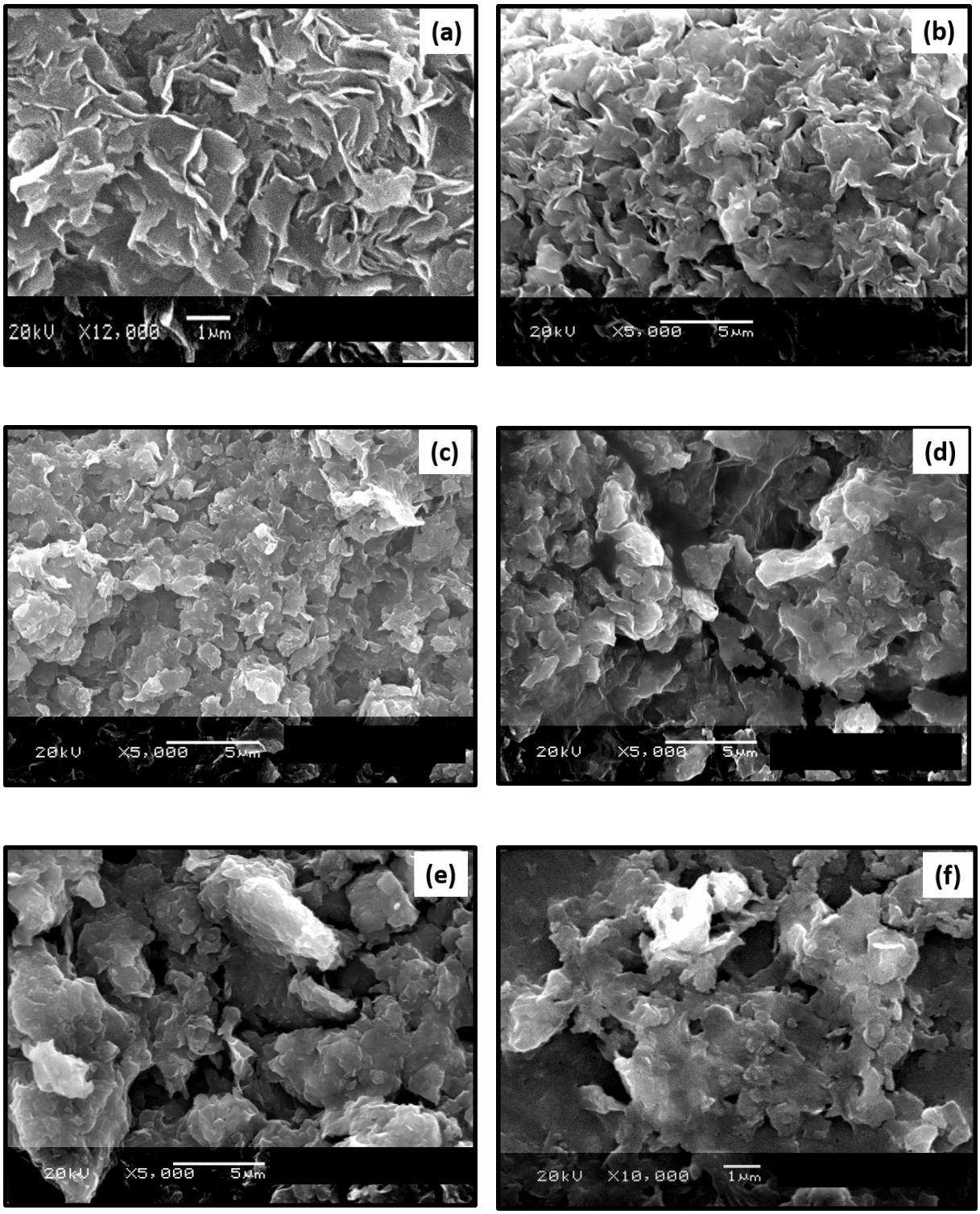

Fig S3. SEM images of motmorillonites: (a) natural, (b) hydrated with $NaClO_4$, (c) modified with Fe^{3+} 50 mg/L, (d) modified with Fe^{3+} 530 mg/L, (e) modified with Fe^{3+} 6320 mg/L (g) modified with Fe^{3+} 75500 mg/L

References

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