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Electronic Supplementary Information

Silver-Phosphate based Melamine-Formaldehyde Polymer for Ambient Conditioned Reduction of Mono, Di, and Tri-Nitrophenols

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Experimental Section

Materials and Reagents

Melamine, formaldehyde, disodium hydrogen phosphate (Na₂HPO₄), silver nitrate (AgNO₃), p-nitrophenol (PNP), Di-nitrophenol (DNP), Tri-nitrophenol (TNP), sodium borohydride (NaBH₄), were of analytical grade and purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF) was of analytical grade and purchased from Finar. DI water was purchased from Vision.

Instrumentation

An FEI Tecnai G2 F30 (300Kv) instrument was used to perform Transmission electron microscopy (TEM). a Panalytical X Pert Pro A Instrument was used to record XRD pattern. The FTIR spectra were obtained on a PerkinElmer FTIR Spectrophotometer. The UV–Visible spectra were taken from Jasco V-730 spectrophotometer. High-resolution mass spectra (HRMS) were recorded on a Xevo G2-S Q TOF (Waters, USA) mass spectrometer.

Synthesis of Ag₃PO₄ decorated MFP (Ag₃PO₄-MFP)

The Melamine formaldehyde polymer was synthesized using a previously reported hydrothermal method. 800mg of melamine was mixed with 10ml formaldehyde and sonicated till dispersed. After that, the solution is transferred to a Teflon-lined autoclave reactor and placed in the oven at 180°C for 10h under autogenous pressure. The obtained brown solid product was centrifuged 4-5 times by using DI to remove the unreacted reagent and dried at 60°C. Finally, water-dispersible MFP powder was obtained. Then, using the co-precipitation method the Ag₃PO₄ decorated MFP nanocomposite was fabricated at room temperature. For co-precipitation, 300 mg of MFP was dispersed in 40 mL DMF solvent and sonicated for 30min. To this solution, 350 mg of silver nitrate was added and stirred continuously for 15min. To this, 30 mL (2M) disodium hydrogen phosphate (Na₂HPO₄) was added dropwise with continuous stirring, and the dark yellow product was obtained. The obtained solution was centrifuged with DI 6-7 times to remove the excess unreacted reagents. Finally, Ag₃PO₄ decorated MFP nanocomposite (Ag₃PO₄-MFP) was dried in the oven at 60°C.

Batch Experiments

To check the catalytic reduction properties of Ag₃PO₄-MFP nanocomposite, it was used for the reduction of different nitrophenols (NPs) such as PNP, DNP and TNP. For this, 20 mM stock solution of these nitrophenols was prepared in volumetric flasks. Then, a 10ml solution of each nitrophenol was taken in a conical flask prepared by diluting as required. First, NaBH4 was added to nitrophenol solution and kept for 5 min to attain the equilibrium, and then Ag₃PO₄-MFP was added at room temperature and the reaction was monitored for the next 60 min. 1 mL aliquot was taken out from the reaction mixture at fixed time intervals (10 min) and centrifuged to separate from the catalyst and the obtained solutions were used to determine the absorbance value of the reduced product using UV-vis spectroscopy. The UV-Visible absorption spectra of the PNP, DNP and TNP give characterstic absorption band for the corresponding phenolate ion. For PNP, the phenolate ion peak occurs at 400nm, this peak decreases gradually in 40 mins. A new peak appeared at 300nm corresponding to aminophenol. For DNP and TNP the absorption band of phenolate ion peak appears at 434nm and 390nm, respectively and this band gradually decreases in 60 min. The control study was performed with MFP, Ag₃PO₄, and Ag₃PO₄-MFP.

Further, various batch studies were performed to optimize the concentration of NPs, amount of reducing agents and catalyst loading by following the same methodology. The concentration variation study was done with 5 mM, 10 mM, 15 mM, and 20 mM NPs at fixed catalyst loading of 3 mg mL⁻¹ with 2 mg mL⁻¹ NaBH₄ in 10 ml DI water. The NaBH₄ variation was done with 10 mg, 15 mg 20 mg and 25mg of NaBH₄ at a fixed concentration of NPs (10 mM) and catalyst loading of 3 mg mL⁻¹. The catalyst variation study was done with 10 mg, 20 mg, 30 mg, 40 mg Ag₃PO₄-MFP at fixed concentration of 10 mM and with 2 mg mL⁻¹ NaBH₄. To find the rate of reaction kinetic study was performed by taking different concentrations of NPs 5 mM, 10 mM, 15 mM, and 20 mM with Ag₃PO₄-MFP (3 mg mL⁻¹) and 2 mg mL⁻¹ NaBH₄ in 10 mL DI water by following the same methodology. The recyclability of Ag₃PO₄-MFP was checked by decanting the solution and seperating the residue that is spent catalyst, ,washed it with DI water several time and dried in an oven at ~60°C and used for reduction experiment.

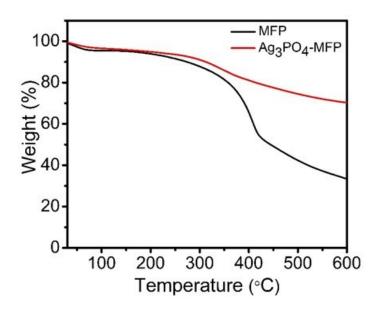


Figure S1: Comparative TGA analysis of MFP and Ag₃PO₄-MFP.

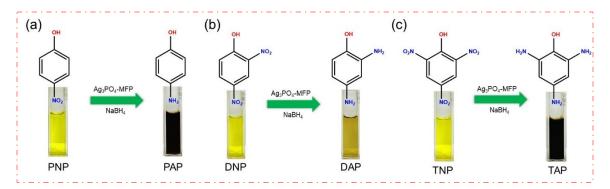


Figure S2: Digital photographic images of NPs and corresponding reduced product along with their chemical structure (a) PNP and PAP; (b) DNP and DAP and (c) TNP and TAP.

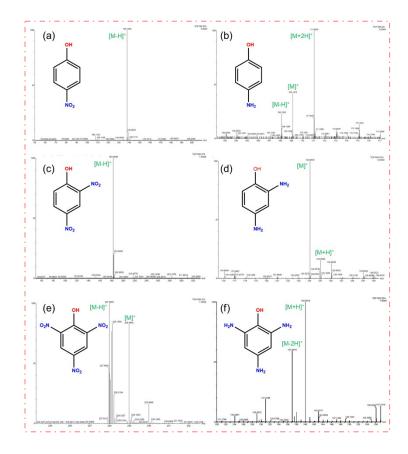


Figure S3: HRMS data of NPs and corresponding reduced product (a) & (b) PNP and PAP; (c) & (d) DNP and DAP and (e) & (f) TNP and TAP.

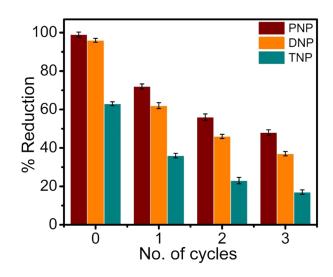


Figure S4: Recycle study of Ag₃PO₄-MFP.

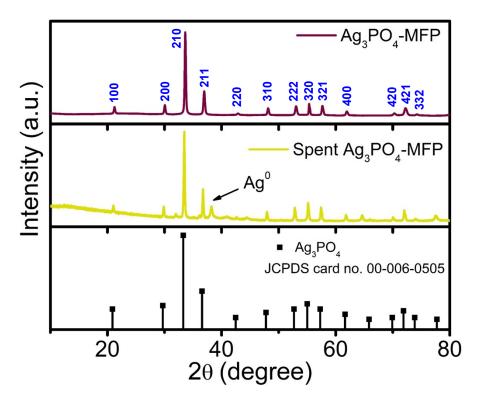


Figure S5: pXRD analysis of Ag₃PO₄-MFP before (wine color line) and after (mustard color line) the nitrophenol reduction reaction along with the corresponding JCPDS data.