Green Synthesis of Flower-Like BiVO₄ Nanoparticles by Solution Combustion Method Using Lemon (Citrus Limon) Juice as a Fuel: Photocatalytic and Electrochemical Study

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Experimental section

Materials and methods

In order to prepare the BiVO₄ nanoparticles by solution combustion method, Bismuth nitrate and Ammonium vanadate were used as oxidiser and lemon juice as a fuel. Solution A was prepared by dissolving 0.485 g (1mmol) of Bi(NO₃)₃•5H₂O in 0.5mL of concentrated nitric acid to which 2.5 mL of lemon juice was added. Solution B was prepared by dissolving 0.116 g (1mmol) of NH₄VO₃ in 5mL of distilled water and 2.5 mL of lemon juice was added. Solution B was mixed with solution A and stirred to get homogeneous solution. This mixture was introduced into preheated muffle furnace maintained at 400°C, smouldering type of combustion reaction takes place and within 5 min nanocrystalline BiVO₄ is formed. The product is calcined at 500°C for 1hr. Similarly, the experiment was repeated for 5 mL of lemon juice by keeping bismuth nitrate and ammonium nitrate as constant.

Material Characterization

Bi(NO₃)₃•5H₂O and NH₄VO₃ were purchased from SD fine chemicals and used without further purification. The prepared BiVO₄ sample was characterized using several spectroscopic techniques: Powder X-ray diffraction (PXRD) patterns were recorded in Rigaku smart lab X-ray diffractometer with Cu Kα radiation (λ=1.5418Å). Fourier transform infrared (FTIR) spectrum of the samples was collected from Bruker Alpha-P spectrophotometer. Optical properties were analysed using Agilent Cary 60 UV-Vis spectrophotometer. Photoluminescence studies were performed using Agilent Cary Eclipse Fluorescence Spectrophotometer equipped with Xenon lamp. Electrochemical measurements were performed using cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) techniques with a CHI 6194 B (CH Instruments, Texas, USA) electrochemical workstation. All measurements were carried out at room temperature in a glass cell comprising a platinum wire as counter electrode, an Ag/AgCl (sat. KCl) as reference electrode and modified or unmodified glassy carbon (GC) electrode (dia. = 3 mm) as working electrodes. The solutions were degassed using nitrogen gas for 10 min, prior to electrochemical measurements. All pH measurements were carried out using Control Dynamics pH meter (APX 175). TEM images were obtained from JEOL JEM-3010 with an accelerating voltage of 300kV. Field emission scanning electron microscopy (FESEM) images of the samples were acquired on Nova-Nano SEM-600 (FEI, Netherlands).

Photocatalytic activity

The photocatalytic experiments were carried out with the help of photo reactor, slurry was prepared by adding 60 mg of catalytic load in 2 × 10⁻⁵ M Indigo Carmine (IC) dye taken in 100mL of 4 quartz tubes. These reactor tubes were kept in a photo reactor with aeration to achieve and adsorption-desorption equilibrium between photocatalyst and dyes. The visible light irradiation (300 W) was passed through the reactors. The concentration of residual IC in the solution after irradiation was determined by monitoring the absorbance intensity of the solution samples by withdrawing a known volume of slurry at regular intervals. It was then subjected for centrifugation to get rid of any interference due to the presence of catalyst and the
absorbance was recorded at $\lambda = 610$ nm by using UV-Visible spectrophotometer to assess the rate of degradation. The photo degradation efficiency of IC was calculated using the following equation.

$$\text{percentage of degradation} = \frac{C_i - C_f}{C_i} \times 100$$

Here $C_i$ the initial IC dye concentration, $C_f$ is IC dye residual concentration in solution after the degradation. The experiment was carried out varying experimental parameters such as dye concentration, catalytic load etc.

**Electrode modification**

The electrode interface (glassy carbon electrode) surface was polished on a polishing pad with aqueous slurry of alumina powder till it gave a mirror like finished surface. Further, the electrode was washed with double distilled water and left to dry at room temperature. Then the as prepared BiVO$_4$ was dispersed in water (5 mg/mL) and was sonicated for 15 minutes. Subsequently, 5 μL of the suspension was coated on the glassy carbon electrode surface and was dried at ambient temperature for about 24 hrs.

**Analytical procedure**

An aliquot of stock solution of Hg (II) was taken into standard volumetric flask and further diluted to appropriate volume and this solution was then transferred to an electrochemical cell with a volume of 10 mL capacity containing an electrolytic solution to carry out electrochemical experiments. For electrochemical characterization, cyclic voltammetry (CV) technique was adapted and performed the experiment under the optimized parameters between the potential range of -0.3 to 0.3 V (frequency, 15 Hz; amplitude, 25 mV and increment potential, 4 mV). The solution was stirred using a magnetic stirrer at 300 rpm which promoted the accumulation of Hg (II) ions on the electrode surface. Then commanded a reduction potential of -0.4 V in order to reduce all the pre-concentrated metal ions into its atomic state and subsequently stripped off from the electrode interface to the bulk of the electrolytic solution after the quiescent time of 20 seconds.