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Preparation of ultra long α-MnO_2 and Ag@MnO_2 nanoparticles by seedless approach and their photocatalytic performance

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ABSTRACT

The reaction between aqueous MnO_4^-, cysteine, and Ag + ions constitutes a new seedless arrangement for the production of α-MnO_2 and Ag@MnO_2 bimetallic nanocomposites at room temperature. UV-visible absorption spectroscopy measurement reveals that presence of Ag^+ ions in an aqueous solution of MnO_4^- and cysteine changes the entire shape of the α-MnO_2 visible spectrum, and leads to a formation of broad band at ca. 425 nm. Thus-prepared nanomaterials were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersion X-ray spectroscopy (EDX), Raman spectroscopy, X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. For the degradation of methyl orange and congo red, nanomaterials were used as the photocatalyst. The results show almost complete degradation (ca. 99%) of congo red in ca. 25 min. The α-MnO_2 nanorods possess high photo degradation efficiency toward congo red in comparison to methyl orange.

1. Introduction

Metal oxides are important in the atmospheric chemistry of pollutants in general and Mn(IV) in particular [1,2]. The chemistry of manganese oxide, MnO_2 has significant important in other areas of environmental concern. Synthesis and characterization of colloidal and/or nanosize MnO_2 polymorphic forms (such as α-, β-, γ, and δ) have been the subject of interest from decades because of their wide range of potential applications such as catalysis, ion exchange, molecular adsorption, biosensors, and particularly, energy storage in batteries with and without templates [3–12]. It is well known that MnO_2 is a non-stoichiometric compound and is present in nature with different structural forms due to the special linkage of basic structural octahedral unit [MnO_6] in different ways (α-, and β- types are constructed from a double- chains of [MnO_6] octahedrons with 2 × 2 tunnels and single chains of the [MnO_6] octahedron, respectively) [13]. Due to the presence of the "active oxygen" in the lattice as defects or adsorbed on the surface, MnO_2 becomes an obvious choice as an oxidant in catalysis. Henglein et al. suggested that the small metal particles in solution have been found to be advantageous over the water-insoluble forms because a UV-visible spectrophotometer can be used to monitor the optical changes that accompany the surface reactions of metal and semiconductor nanoparticles with plasmon resonance lines in the visible range [14]. It is well know that water-soluble small metal particles are advantageous over the water insoluble forms because UV–visible spectrophotometric methods can be used to monitor the optical changes during the surface reactions [14]. Therefore, the development of the solution-based and morphologically controllable synthesis of MnO_2 nanoparticles is urgently important.

Perez-Benito and his coworkers reported a solution based chemical reduction method to the synthesis of prefect transparent brown color water soluble colloidal MnO_2 using MnO_4^--$S_2O_3^{2-}$ redox reaction in neutral aqueous medium [5]. They also suggested that as prepared MnO_2 sols are stable for at least several years in the absence of coagulating agents. Pal et al. developed various simple wet chemical reaction, low-temperature, low-cost, and chemical reduction methods to synthesize 1-D and 2-D nanostructures of α-MnO_2 nanowire [10], α-MnO_2 nanowires, and δ-MnO_2 nanosheets [11], α-MnO_2 nanorods [15], β- MnO_2 nanospheres and nanorods [16], spherical β- MnO_2 nanoparticles in an organic solvent [17]. These investigators also prepared metal–metal oxide nanocomposites of hierarchical hollow Au@MnOOH flowers [18], and

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Ag-doped MnO_2 flower-like nanostructures and suggested that these nanocomposites are thermally stable, good catalyst, and better surface enhanced Raman scattering platform than the individual components [19,20]. Wang and Li developed a low-temperature hydrothermal method to synthesize 1-D MnO_2 nanostructure using $Mn^{2+} - S_2O_8^{2-}$ redox reaction [21]. Xie et al. used a homogeneous catalytic route to the synthesis of urchin-like α-MnO_2 nano structures [22]. Chu et al. synthesized the cuneiform-like MnO_2 particles with dodecylbenzenesulfonic acid as a stabilizer in an aqueous solution [23]. Ma et al. used redox-precipitation method for the synthesis of α-MnO_2 nanoparticles in aqueous solution at pH 8 [24]. Li et al. reported a facile synthesis of γ-MnOOH nano-rods and their conversion to β-MnO_2, Mn_3O_4 at 180 °C for 24 h [25].

Kostowskyj and his coworkers synthesized Ag–Mn nanowires using a unique electroless deposition technique, and as prepared nano-composites were used as catalysts for alkaline fuel cells [26]. They pointed out that the equal performance of Ag and Ag–Mn nano-composites was attributed to the presence of inactive MnO and low concentrations of MnO_2 in the nanowires. It has been established that the observed activity of Ag-nanoparticle catalysts supported on activated carbon, metal oxides, MnO_2, and polymers (bimetallic nano catalyst), found that there was an overall increase in activity compared to the pure metal phases [19,20,27–30] ($Ag@MnO_2$ is an efficient bifunctional and/or bimetallic catalyst for electrical conductivity, surface enhanced Raman scattering, as probe molecules, metal-air batteries and alkaline fuel cells). Li et al. in their pioneering review suggested that solution-based chemical synthetic strategies provide simple and powerful routes to nanocrystals (zero-dimensional, 1-D nanowires and nanorods, hollow structures, and super lattice) [31].

Bakshi in his pioneering review suggested that the formation of Au nanorods depends on the nature of the stabilizing and/or capping agents [32]. They also used seed-growth method to the synthesis of flower-like Au@Pd bimetallic nanoparticles at room temperature in presence of a strongly hydrophobic surfactant and proposed a mechanism to the formation of Au@Pd nanomaterials [33]. Ge and Qe reported the degradation of azo dye acid red B on MnO_2 in the absence and presence of ultrasonic irradiation [34]. The photocatalytic degradation experiments were also performed with two anionic organic dyes, namely, methyl orange and congo red (azo dyes containing azo bonds (-N=N-) are known to be highly toxic, carcinogenic and harmful for living creatures and should be degraded before exposure to the environment [35,36]. Herein, we report for the first time a green chemistry approach for the synthesis of tunnels-like α-MnO_2 at room temperature using cysteine (sulphur containing amino acid has three donor atoms and/or coordination sites: at the N–, O–, and S-centers) as a reducing agent and $Ag@MnO_2$ nanocomposites by seedless chemical redox reaction between aqueous MnO_4^-, cysteine, and Ag^+ ions. In this paper, a new solution-based seedless method was developed to synthesize open porous hierarchically structured $Ag@MnO_2$, where cysteine solutions were added into a reaction mixture containing MnO_4^- and Ag^+ ions solutions in stoichiometric ratio at pH 5.5. These methods give rise to high quality tunnels-like α-MnO_2 nanomaterials in a single step reaction without the use of any stabilizer, or growth controlling agent, and an in-depth mechanistic information about the growth of $Ag@MnO_2$ leaves and/or nanorods. To the best of our knowledge, such tunnels-like α-MnO_2 nanoparticles have not been reported previously. The chemical composition and the morphology of the as-synthesized nanomaterials were characterized by conventional physical, chemical, and spectroscopic methods.

2. Experimental

2.1. Materials

Doubly distilled, CO_2-free, and deionized water (specific conductance $(1–2) \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) was used as solvent to the preparation of all reagents solutions. $KMnO_4$ (Fluak, Puriss, Germany, 99.9%), $AgNO_3$ (BDH, 99.9%), and cysteine ($HSCH_2CH(NH_2)COOH$, Koch-Light, Puriss, Germany, 99%) were used as received. All inorganic salts were also purchased from BDH. The $KMnO_4$ solution was prepared by the reported method of Jones and Noyes [37]. The solutions of $AgNO_3$ and $KMnO_4$ were stored in amber colored glass bottles to arrest the photochemical degradation. $KMnO_4$ solutions were standardized by titration with standard sodium oxalate solution.

2.2. Synthesis of MnO_2 and $Ag@MnO_2$ nanocomposites

Preliminary observations showed that the MnO_4^- pink color changes to brown upon addition of cysteine solution within the time of mixing at room temperature, indicating the formation of water soluble nano size colloidal MnO_2 [38]. Stability of as prepared perfect transparent dark brown solution strongly depends on the [cysteine] as well as [MnO_4^-] at room temperature. Therefore, the choice of the best conditions for the preparation of MnO_2 nanoparticle is a critical problem that we address first. In a typical experiment, cysteine ($3.0\ cm^{3,\ 0.01\ mol\ dm^{-3}}$) was added in a reaction mixture containing $KMnO_4$ ($3.0\ cm^3$; $0.01\ mol\ dm^{-3}$) and distilled water = $44\ cm^3$ (for dilution), perfect transparent brown color sols appeared during the mixing. On the other hand, black brown precipitate was appeared instead of transparent color at higher [cysteine]. In order to prepare $Ag@MnO_2$ nanocomposites, the required volume of $AgNO_3$-cysteine solution ($AgNO_3 = 10.0\ cm^3$ of $0.01\ mol\ dm^{-3}$ + cysteine = $3.0\ cm^3$ of $0.01\ mol\ dm^{-3}$) was added in a MnO_4^- solution and monitored the formation of yellow-brown color at different time intervals. The as prepared MnO_2 sols and $Ag@MnO_2$ sols were centrifuged at 10000 rpm for 20 min. The supernatant was discarded, and the residue was collected, washed several times with distilled water, and used for the surface morphology determination.

2.3. Determination of rates of $Ag@MnO_2$ formation

The required solutions of $KMnO_4$ and $AgNO_3$ were taken in a two-necked reaction vessel equipped with a double-surface condenser to prevent evaporation. The reaction was initiated with the addition of required volume of thermally equilibrated cysteine solution at same temperature. The progress of the reaction was followed spectrophotometrically at 525 nm, and 450 nm to the reduction of MnO_4^- and formation of $Ag@MnO_2$ composites, respectively, with a Multi Spec-1501, UV-visible spectrophotometer, Shimadzo, Japan, quartz cuvettes of path length 1 cm were used. Neither cysteine nor permanganate shows any absorption peak at 420 nm. Pseudo-first-order conditions ([cysteine] ≥ [MnO_4^-]) were used to determine the rate constants (k_{obs}, s^{-1}). The pH of the reaction mixture was also measured at the end of each kinetic experiment and observed that pH drift during the course of the reaction is very small (with in 0.05 unit).

2.4. Characterization of as prepared nano particles

All spectra of the samples (UV-visible, Raman, and FT-IR) were recorded by using a UV-visible a Multi Spec- 1501, UV-visible spectrophotometer, Shimadzo, Japan, MultiRAM stand Alone FT-Raman spectrometer, equipped with a broad band quartz beam