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Light-Induced Hydrolysis of Nitriles by Photoproduced α-MnO_2 Nanorods on Polystyrene Beads

Subhra Jana,[†] Snigdhamayee Praharaj,[†] Sudipa Panigrahi,[†] Soumen Basu,[†] Surojit Pande,[†] Chien-Hsiang Chang,[‡] and Tarasankar Pal*,[†]

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India, and NCKU, Taiwan

tpal@chem.iitkgp.ernet.in

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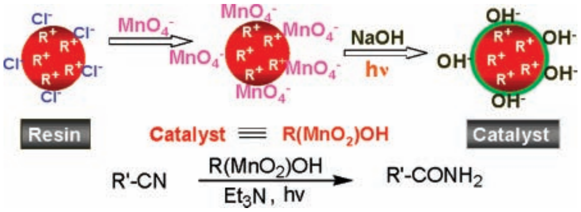
ABSTRACT



A green chemistry approach has been furnished for photochemical deposition of α-MnO_2 nanorods onto the surface of functionalized polystyrene beads through immobilization of MnO_4^- in alkaline condition under visible light. Then the composite material was exploited as a fruitful and novel solid-phase catalyst for the one-step and facile synthesis of amide compounds from nitriles under visible light in weakly basic medium.

One of the goals of modern catalysis is to synthesize well-defined monodispersed nanoparticles with controllable shape and structure at the nanolevel. This would represent a very exciting breakthrough in the field of catalysis.[1,2] The large surface-to-volume ratios and special binding sites of fine particles in homogeneous and heterogeneous catalysis creates the driving force in developing nanoparticle catalysts.[3,4] An important advantage of the solid-phase synthesis over the solution-phase synthesis[5,6] is simplified purification procedures and easy handling of multiple reaction vessels. Furthermore, the particles can be recycled after recovering them from the reaction mixture by simple filtration. As a result, synthesis involving solid-phase catalyst has now become an extremely valuable tool to scientists in combinatorial chemistry research.[7]

Of all the non-noble metals or transition metal oxides studied, manganese dioxide is one of the most attractive inorganic materials not only because of its physical and chemical properties and wide range of applications in catalysis, ion exchange, molecular adsorption, biosensor, and particularly energy storage[1,2] but also because of its low cost and environmentally benign nature. Especially in catalysis, MnO_2 becomes an obvious choice as an oxidant and most probably the oxidizing property of MnO_2 arises due to the presence of the “active oxygen” in the lattice as defects or adsorbed on the surface.[8] Beyond this advantageous property, MnO_2 is very promising in a neutral electrolyte system.[9−12] Different structural forms of MnO_2 exist in nature, such as,

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[†] Indian Institute of Technology.
[‡] NCKU.

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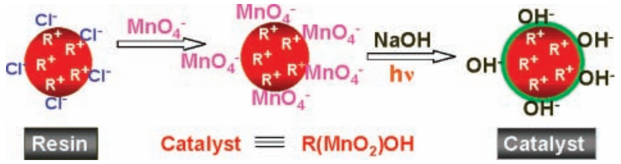
α-, β-, γ-, and δ-types, because the basic structural octahedral unit [MnO_6] can be linked in different ways, e.g., the α-type is constructed from a double chain of [MnO_6] octahedrons with 2 × 2 tunnels.[13] The crystallographic forms are generally believed to be responsible for their properties and the controlled synthesis of MnO_2 has always been the focus of material scientists.[14] Numerous methods, such as simple reduction,[9,10] oxidation,[15] coprecipitation,[12] sol−gel,[16] thermal decomposition,[11] etc., have been developed for the synthesis of MnO_2.

Herein, we have explored for the first time a green chemistry approach for in situ deposition of α-MnO_2 nanorods onto the surface of functionalized polystyrene beads through immobilization of metal precursor ions exploiting the electrostatic field force of the charged resin beads, followed by photochemical reduction in the presence of visible light under alkaline conditions. The chemical composition and the morphology of the as-synthesized particles were characterized by different physical methods. Finally, the particles have been exploited as a solid-phase catalyst for the one-step and facile synthesis of amide compounds from their corresponding nitriles in the presence of visible light in weakly basic medium.

The synthetic strategy involved for the deposition of MnO_2 nanorods on resin surface is as follows: Anion-exchange resin, SERALITE-SRA-400, a cross-linked polystyrene containing quaternary ammonium groups as the integral part, was purchased in the chloride form with ion-exchange capacity 3.5 mmol g^{-1}. First, 0.5 g of the anion-exchange resin, [R^+Cl^-], was treated with 25 mL of 1 M aqueous $KMnO_4$ solution and the solution was stirred to complete the exchange of Cl^- ions with MnO_4^- ions. Within 1 h, the purple solution became colorless indicating ready exchange of MnO_4^- with Cl^-. After that, the resin-bound permanganate moiety [$R^+MnO_4^-$] was washed several times with distilled water and completely reduced photochemically (24 h, 40 W tungsten lamp, fluence ~50 mJ/cm^2) while stirring in weakly alkaline conditions (0.1 M NaOH). Thus, the reduction of resin bound precursor ions led to the deposition of MnO_2 nanoparticles onto the resin surfaces (Scheme 1).

Scheme 1



The as-prepared shining black beads (see the Supporting Information) were washed thoroughly with plenty of water, dried at room temperature (25 °C) under vacuum, and employed as solid-phase catalysts for the hydrolysis of nitriles.

The phase purity of the composite materials was studied by X-ray diffraction (XRD), using a PW3040/60 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å) at a scanning rate 0.1 deg/s in the 2θ range from 10° to 70°, with the operation voltage and current maintained at 40 kV and 30 mA, respectively. The diffraction pattern of the free resin beads does not show any distinguishable peak, owing to the amorphous nature of the polystyrene beads (see the Supporting Information). Figure 1 shows the XRD patterns of α-MnO_2 nanoparticles. All the diffraction peaks can be readily indexed to a tetragonal phase of α-MnO_2 with a space group of $I4/m$ (no. 87) having lattice constants $a = 9.7847$ Å and $c = 2.8630$ Å (JCPDS card, No. 44-0141). The sharp diffraction peaks indicate the purity and crystallinity of the product.

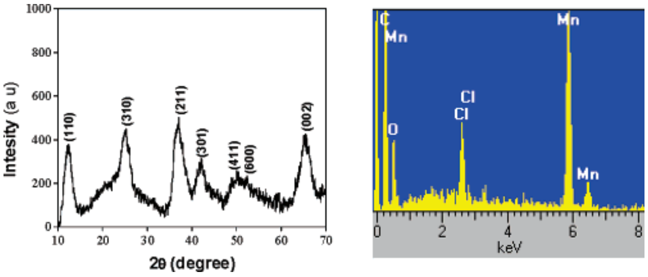


Figure 1. XRD pattern and EDX spectrum of the nanocomposite material.

The surface property and the composition of the catalyst were characterized from X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX). The EDX spectrum (shown in Figure 1) further authenticates the presence of Mn and oxygen in the nanocomposites. The Mn 2p core level spectrum (see the Supporting Information) illustrates that the observed binding energy 642.37 and 653.71 eV corresponds to $Mn2p_{3/2}$ and $Mn2p_{1/2}$ electrons, respectively, which is well in accordance with the literature values for MnO_2.[17] Thus, the result suggests the photochemical deposition of tetravalent Mn in the form of MnO_2 on the surface of resin beads.

The particle morphology and structural properties of α-MnO_2 nanoparticles were elucidated by transmission electron microscopy (TEM). Figure 2 represents the TEM image of the product, which consists of nanorods with diameter ~75 nm and length ~235 nm. The HRTEM image of α-MnO_2 nanorods (Figure 2) shows that the nanorod is structurally uniform with a fringe spacing of 0.311 nm, which corresponds to the lattice spacing of the (110) plane. These clear lattice fringes further confirm the single crystalline nature of the nanorods.

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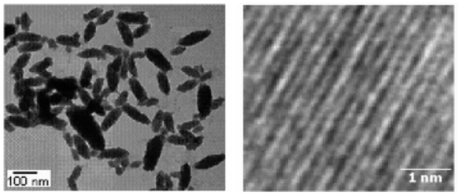

Figure 2. TEM and HRTEM images of α-MnO_2 nanorods.

The catalytic activity of the composite materials has been studied for the hydrolysis of nitriles to amides in the presence of visible light under weakly basic medium. The hydrolysis of nitriles to amides usually requires strongly acidic or alkaline condition and sometimes may be quite drastic.[18,19] In 1966, during oxidation of alcohols, Cook et al. observed that acetamide was produced under neutral condition at room temperature where commercial MnO_2 was used as a catalyst.[20] But the reaction time was quite long (80 h) with 40% yield. In our study, 50 mg of R(MnO_2)OH converts acetonitrile (CH_3CN) to acetamide (CH_3CONH_2) within 7 h under weakly basic condition and gives good yield (71% from 10 mL of neat acetonitrile) without any side product. A wide variety of bases like pyridine, Et_3N, $(EtOH)_3N$, Me_2NH, etc. were employed for the hydrolysis under ambient condition and they all serve the purpose well. Keeping the toxicity of pyridine in mind, we have selected Et_3N as the base for the above reaction. The same reaction strategy happens to be quite successful for the hydrolysis of propionitrile (EtCN), benzonitile (PhCN), acrylonitrile (H_2CCHCN), benzyl cyanide ($PhCH_2CN$), and 0.5 g of anthranilonitrile ($Ph(NH_2)$-CN); they all serve as good substrate. UV−visible absorption spectra of the products have been recorded before the separation of the amide compounds from the corresponding nitriles after the rection (see the Supporting Information). The products were characterized by GC-MS and NMR studies (see the Supporting Information). The yield of the reactions is presented in Table 1 and the quantum yield for the reactions lies in the range 0.29−0.97.

We checked the reusability (4 times) of the composite materials for the hydrolysis of acetonitrile. The recovered solid catalyst particles were further characterized by EDX analysis (see the Supporting Information) and were successfully employed for a series of consecutive runs. However, the reaction did not produce any result in the dark. Commercial MnO_2 as well as MnO_2 obtained from glass surfaces (particles in the μM dimension, see the Supporting Information) of the $KMnO_4$ storage bottle were also employed as catalyst under identical conditions for this reaction, but even after 24 h no product was obtained.

Table 1. Hydrolysis of Nitriles by R(MnO_2)OH Particles at Room Temperature and Pressure

substrates	reaction time (h)	yield (%) of corresponding amide
acetonitrile	7	71
propionitrile	6	65
acrylonitrile	6	82
benzonitrile	6	74
benzyl cyanide	10	50
anthranilonitrile	7	61

The catalytic activity of the α-MnO_2 nanorods results from their larger surface area and more active surface sites. MnO_2 nanoparticles in the composite material absorb photon in the ∼400 nm region.[21,22] The probable mechanism for this reaction is a solid-phase catalyzed hydrolysis involving water on the surface of the solid, as MnO_2 retains moisture tenaciously.[20] The reaction route for the synthesis of nanocomposites is devoid of any template or catalyst that might complicate the process, increasing the production cost and difficulty for scale-up production of 1D nanostructures. Apart from the aforementioned advantages, the ease of separation of the product and the mild conditions employed may be advantageous in the future.

In conclusion, the present work is related to a simple, reproducible, and straightforward technique for the photochemical synthesis of α-MnO_2 nanorods onto the surface of polystyrene beads and its catalytic application to produce amide compounds, through a green chemistry approach. The electrostatic field force helps in the immobilization of precursor ions through the ion exchange mechanism and in turn the deposition of MnO_2 nanorods onto the solid resin surfaces. At the end of the reaction, the catalyst particles remain active and can be easily separated from the reaction mixture. Moreover, the reaction route should be very attractive due to its simplicity, absence of any hazardous materials, reusability of the catalyst particles, and large-scale production under visible light.

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Supporting Information Available: XRD pattern of free resin beads, XPS spectrum of catalyst particles, SEM images of MnO_2 nanoshell coated resin bead and MnO_2 obtained from glass surfaces, UV−visible spectra of the products, and one representative GC-MS and NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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