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Photochemical Synthesis of a Water Oxidation Catalyst Based on Cobalt Nanostructures

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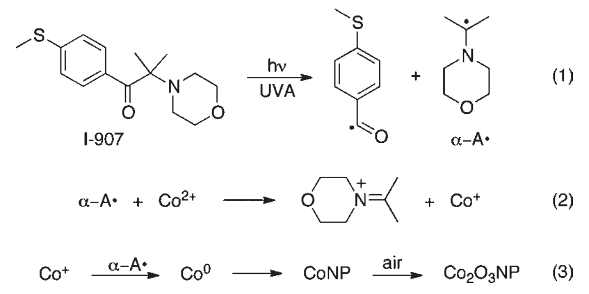
Supporting Information

ABSTRACT: New cobalt-based nanocomposites have been prepared by photoreduction of Co^{2+} salts to generate cobalt nanoparticles deposited on carbon-based materials such as nanocyrstalline diamond and carbon felt. Spontaneous air oxidation converts the metal to Co_2O_3 which has been tested as a water oxidation catalyst. This work demonstrates that the cobalt oxide nanostructures can be deposited on various carbon surfaces and can catalyze the four-electron oxidation of water to oxygen under anodic bias.

A challenge in the pursuit of a viable artificial photosynthetic system for the storage of solar energy in a useful fuel lies in the discovery of a cost and energy efficient water oxidation catalyst. Many commonly investigated catalysts rely on expensive and scarce elements such as iridium and ruthenium.[1] Recent work has drawn much attention to the use of cobalt, a much more abundant and affordable material, for water oxidation.[2] Herein, we present a photochemical procedure for the synthesis of nanometric Co_2O_3 and demonstrate its catalytic properties for the oxidation of water to O_2 when in the presence of phosphate ions. Photochemical nanostructure synthesis has the advantage of providing spatial and temporal control; in particular, the spectral properties, time dependence and intensity of the exciting light can be used to control the size and morphology of the metal nanostructures.[3]

Previously, we have demonstrated the photoinduced formation of gold, silver, and copper nanoparticles from the corresponding ions in solution by use of benzoin photoinitiators.[3−5] Ketones are good photosensitizers for nanoparticle synthesis, not because of the energy they can absorb or deliver, but rather because of the reducing free radicals they can generate. Thus, efficient nanoparticle generation requires careful selection of substrates and experimental conditions such that free radical generation occurs with high quantum efficiency and metal ion precursors do not inhibit radical formation. Since many transition metal ions are excellent excited state quenchers, a key consideration for achieving nanoparticle synthesis with short exposure times is minimization of excited state quenching by metal ions.[5] Benzoin-based methods take advantage of the short triplet lifetimes of the radical precursor,[6] and thus allow for fast, one-pot synthesis of metal or metal oxide nanostructures with only mild, noncovalent stabilizers. The resulting weak surface interactions allow easy exchange of surface groups for additional derivatization and/or catalytic applications.

Scheme 1. Mechanism for the Formation of CoNP and Their Spontaneous Air Oxidation To Form Co_2O_3NP



Given the recent interest in the use of cobalt as a water oxidation catalyst, we have explored the application of a similar aromatic-ketone-based photochemical method for the generation of cobalt oxide nanoparticles and then probed their catalytic viability. The photochemical synthesis of Co_2O_3 nanoparticles (Co_2O_3NP) employed the photoreduction of $CoCl_2$ in dry acetonitrile with Irgacure I-907 (Scheme 1). Upon photoexcitation with UVA light, Irgacure I-907 generates a strongly reducing[7] α-aminoalkyl radical capable of reducing Co^{2+} ions to the metal in solution. During irradiation, the clear light-blue solution of $CoCl_2$ turns dark green, and black, insoluble paramagnetic particles begin to precipitate. These are presumably clusters of cobalt nanoparticles (CoNP),[8] that later undergo spontaneous oxidation in air to form the desired catalyst, Co_2O_3NP, as black particles.

Characterization of the cobalt oxide material was performed by X-ray diffraction (XRD, Rigaku Ultima IV) and high-resolution transmission electron microscopy (HRTEM) for colloidal suspensions and for particles deposited on nanodiamonds, Co_2O_3NP-NCD (vide infra). The XRD analysis, as seen in the pattern for Co_2O_3NP-NCD in Figure 1, reveals primarily the presence of Co_2O_3, although less intense bands at $2\Theta = 36.3°$ and $42.45°$ indicate the existence of a small amount of CoO. The lattice

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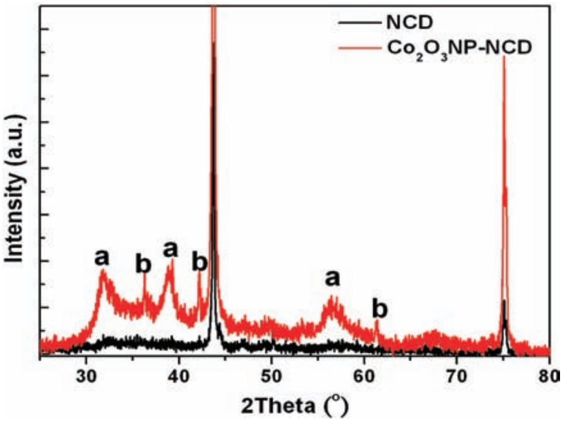

Figure 1. XRD pattern of (black) nanocrystalline diamond (NCD) particles and (red) Co_2O_3NP decorated NCD particles. For the Co_2O_3NP NCD spectra, peaks marked (a) show the presence of Co_2O_3 while peaks marked (b) indicate the presence of CoO.

spacing of 2.38 Å obtained by HRTEM (JEM-2100F, JEOL) also indicates that the resulting cobalt oxide is primarily Co_2O_3.

To ascertain the catalytic properties of the photochemically prepared Co_2O_3NP for electrochemical oxidation of water to oxygen, films of Co_2O_3NP were prepared on a glassy carbon electrode. To prepare the film, a solution containing Co_2O_3NP was sonicated to suspend the particles, a 50 μL aliquot of the solution was pipetted onto the face of the electrode, and the solution was allowed to dry to a film in air. After preparation, the electrode was placed in an aqueous solution containing supporting electrolyte and 0.1 M phosphate buffer at pH 7. Analysis by cyclic voltammetry of these films revealed the onset of large anodic currents upon reaching potentials near 1.1 V versus AgCl/Ag (Figure 2). The currents obtained from the films greatly exceed those from a glassy carbon electrode lacking any Co_2O_3NP and indicate catalytic water oxidation by the cobalt oxide. Confirmatory evidence for oxygen evolution was also obtained using a NeoFox-FOXY oxygen probe (base on luminescence quenching), see Figure S6.

Because our interest in forming cobalt nanoparticles centered on the production of a catalytic material for use in photochemical water oxidation, controlling the deposition of the material on a surface is an important aspect for its future utilization. To probe the possibility of depositing the material on a surface simultaneously with its synthesis, we included nanocrystalline diamonds (NCD) (MICRO MDA+, Element Six) in the reaction mixture prior to illumination in the hope that they would provide a suitable support for CoNP and Co_2O_3NP growth. Nanocrystalline diamond has drawn much attention in various areas of modern technology due to its unique physical properties such as thermal conductivity and chemical inertness, and its surface affinity for carboxyl and amino groups.[9−11] It has been reported that the surface of the diamond nanoparticles contains 10^4 mmol/g surface $-COO^-$ groups, which translates to a molecular density of 1.4×10^{14} molecules/cm^2, suggesting that approximately 7% of the total surface carbon atoms exist as carboxyl groups, indicating an exceptionally high affinity for metal nanoparticle nucleation.[9,11,12]

The supported cobalt oxide on nanocrystalline diamond was produced in a manner similar to that outlined for Co_2O_3NP.[8] For the preparation of Co_2O_3NP-NCD, a suspension of 350 nm diameter diamond particles was sonicated for 20 min and then added to the deaerated reaction mixture of 1 mM $CoCl_2$ and 2 mM I-907 prior to illumination. During UVA irradiation, it is likely the positive metal ions first randomly adsorb to defect sites on the diamond surface, then interact with the carboxylate groups, which serve as nucleation sites for the growth of CoNP and eventually Co_2O_3 clusters. The TEM images in Figure 3 illustrate the distribution of cobalt oxide nanocrystals on the diamond surface. The surface cobalt oxide particles average in size ∼20 nm. After formation, excess cobalt particles, salts, and I-907 were removed by performing centrifugation−redispersion with acetonitrile. The total cobalt content loading of the final diamond-supported cobalt-based catalyst was about 2.5 wt %. Electrochemical measurements of the Co_2O_3NP-NCD material showed the onset of catalytic current after reaching 1.1 V versus AgCl/Ag in phosphate-buffered solution.

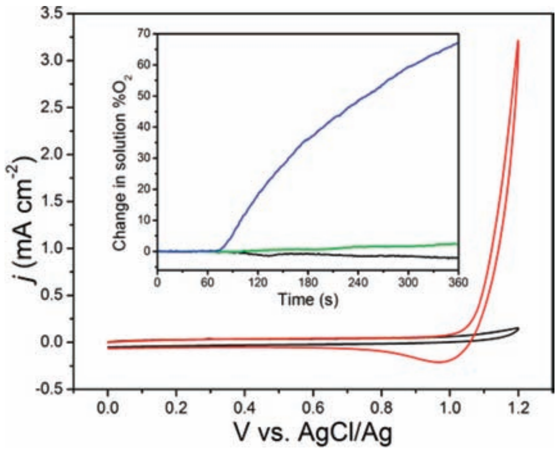

Figure 2. Cyclic voltammogram of (red) Co_2O_3NP particles deposited on a glassy-carbon working electrode and (black) a bare polished glassy carbon electrode. All scans taken at 100 mV/s in aqueous solution with 0.1 M KNO_3 and 0.1 M phosphate buffer pH 7. (Inset) Percent dissolved oxygen relative to air-saturated water as measured with a Clark electrode. A carbon felt electrode with photodeposited Co_2O_3NP was poised at (blue) 1.2 V, (green) 1.0 V, and (black) 0 V with all voltages referenced to AgCl/Ag. Potential was applied at t = 60 s.

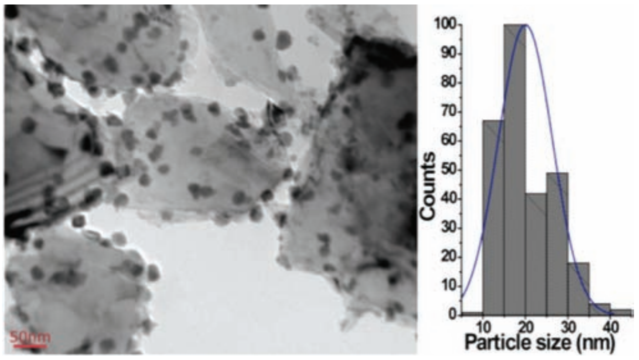

Figure 3. TEM image and particle size distribution of Co_2O_3NP on the NCD support. The smaller, darker clusters of the Co_2O_3NP can be seen on the diamond support. The average cluster size is ∼20 nm.

To explore the deposition of Co_2O_3 on other materials, we also tested its formation on the surface of conductive carbon felt. It has been reported that the oxidation of the carbon felt by thermal

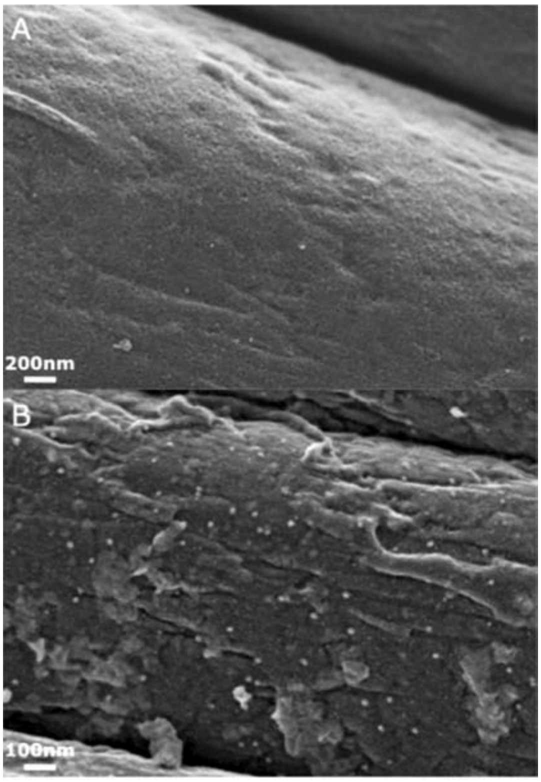

Figure 4. SEM images of cobalt oxide deposits on a carbon felt support: (A) carbon felt not heated prior to cobalt deposition and (B) carbon felt heated to 400 °C for 4 h and then cooled to room temperature prior to cobalt deposition. The small white dots are the cobalt oxide particles.

treatment allows for better surface interactions.[13] For this reason, samples of carbon felt were first heated at 400 °C for 4 h under air before undergoing the synthesis of the oxide as outlined earlier.

As with the functionalized nanocrystalline diamond particles, regions of cobalt oxide nanoparticles were observed on the surface of the carbon felt after the photochemical synthesis. The difference in the density of Co_2O_3NP deposits on the carbon felt with and without thermal treatment is illustrated by the SEM pictures in Figure 4. The increase in the number of micropores and attached cobalt oxide nanoparticles in the case of the heat-treated felt samples is in good accord with an increase in the surface area and the number of C−O and C=O functional groups formed after heating.[9,12] The attachment of cobalt oxide to the surface may occur via interaction with one or both (chelation) of the oxygen atoms of the carboxylate ion.[12,14]

Electrochemical analysis of the carbon felt samples in phosphate-containing electrolyte showed strong anodic currents as well as the generation of bubbles at the surface of the felt (Figure S3). A Clark electrode was used to monitor oxygen levels in solution during controlled potential experiments shown in Figure 2 (inset). High currents obtained at potentials positive of 1.1 V versus AgCl/Ag with the carbon felt electrodes correlated with substantial increases in solution oxygen levels. This demonstrates that Co_2O_3NPs are capable of water oxidation, a key property in terms of the future applications of these materials. Oxygen evolution activity persisted for over 2 h and the amount of O_2 formed exceeded 100-fold that could be hypothetically produced from the cobalt oxide alone (see analysis of turnover frequency in Supporting Information).

This work reports a new method for preparing Co_2O_3NP photochemically from solutions containing a readily available Co^{2+} precursor and demonstrates that the nanoparticles can be deposited on electrodes. Electrochemical studies establish that electrodes prepared with these nanoparticles behave qualitatively like other recently reported systems involving cobalt[2] and indicate that the Faradaic current and corresponding increase in solution oxygen levels results from the four-electron oxidation of water to oxygen upon the application of sufficient overpotential. Experiments to determine the exact mechanism are being pursued. The unique photochemical process for synthesizing these particles provides a well-controlled method for depositing the material on a surface, and we are currently pursuing the development of photoelectrodes using this approach of catalyst deposition. Developing new ways of preparing metal oxide catalysts is important because methods could be found that lead to materials having lower overpotential requirements, or even that perform reversibly—the ultimate "Holy Grail" of catalysis of the O_2/H_2O half reaction which remains elusive to all efforts.[15]

ASSOCIATED CONTENT

Ⓢ Supporting Information. An explanation of oxygen measurements, cyclic voltammograms of NCD and Co_2O_3NP-NCD on glassy carbon, cyclic voltammograms of Co_2O_3NP-NCD on carbon felt, bubble generation during a controlled potential experiment, a preliminary estimation of the turnover frequency, and cyclic voltammograms of Co_2O_3NP in the presence and absence of phosphate buffer. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Harriman, A.; Pickering, I. J.; Thomas, J. M.; Christensen, P. A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2795–2806. Kiwi, J.; Gratzel, M. *Nature* **1979**, *281*, 657–658.

(2) Jiao, F.; Frei, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1841–1844. Kanan, M. W.; Nocera, D. G. *Science* **2008**, *321*, 1072–1075. Shevchenko, D.; Anderlund, M. F.; Thapper, A.; Styring, S. *Energy Environ. Sci.* **2011**, *4*, 1284–1287.

(3) Stamplecoskie, K. G.; Scaiano, J. C. *J. Am .Chem. Soc.* **2010**, *132*, 1825–1827.

(4) Maretti, L.; Billone, P. S.; Liu, Y.; Scaiano, J. C. *J. Am. Chem. Soc.* **2009**, *131*, 13972–13980. McGilvray, K. L.; Decan, M. R.; Wang, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 15980–15981. Pacioni, N. L.; Pardoe, A.; McGilvray, K. L.; Chretien, M. N.; Scaiano, J. C. *Photochem. Photobiol. Sci.* **2010**, *9*, 766–774.

(5) Marin, M. L.; McGilvray, K. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **2008**, *130*, 16572–16584.

(6) Jockusch, S.; Landis, M. S.; Freiermuth, B.; Turro, N. J. *Macromolecules* **2001**, *34*, 1619–1626.

(7) Scaiano, J. C. *J. Phys. Chem.* **1981**, *85*, 2851–2855.

(8) Scaiano, J. C.; Netto-Ferreira, J. C.; Alarcon, E.; Billone, P.; Alejo, C. J. B.; Crites, C. O. L.; Decan, M.; Fasciani, C.; Gonzalez-Bejar, M.; Hallett-Tapley, G.; Grenier, M.; McGilvray, K. L.; Pacioni, N. L.; Pardoe, A.; Rene-Boisneuf, L.; Schwartz-Narbonne, R.; Silvero, M. J.; Stamplecoskie, K. G.; Wee, T. L. *Pure Appl. Chem.* **2011**, *83*, 913–930.

(9) Krueger, A. *Chem.—Eur. J.* **2008**, *14*, 1382–1390.

(10) Liu, K. K.; Zheng, W. W.; Wang, C. C.; Chiu, Y. C.; Cheng, C. L.; Lo, Y. S.; Chen, C. P.; Chao, J. I. *Nanotechnology* **2010**, *21*, 315106. Wee, T. L.; Mau, Y. W.; Fang, C. Y.; Hsu, H. L.; Han, C. C.; Chang, H. C. *Diamond Relat. Mater.* **2009**, *18*, 567–573.

(11) Liu, Y.; Gu, Z. N.; Margrave, J. L.; Khabashesku, V. N. *Chem. Mater.* **2004**, *16*, 3924–3930.

(12) Nguyen, T. T. B.; Chang, H. C.; Wu, V. W. K. *Diamond Relat. Mater.* **2007**, *16*, 872–876.

(13) Kim, K. J.; Park, M.-S.; Kim, J. Y.; Kim, Y.-J. *ECS Meet. Abstr.* **2010**, *1002*, 405.

(14) King, S.; Hyunh, K.; Tannenbaum, R. *J. Phys. Chem. B* **2003**, *107*, 12097–12104.

(15) Hambourger, M.; Moore, T. A. *Science* **2009**, *326*, 1355–1356.