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# Microstructure Effects on the Water Oxidation Activity of Co<sub>3</sub>O<sub>4</sub>-Porous Silica Nanocomposites

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**ABSTRACT:** We investigate the effect of micro structuring on the water oxidation (oxygen evolution) activity of two types of  $Co_3O_4$ -porous silica composites:  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles with varying shell thicknesses and surface areas, and  $Co_3O_4$ -mesoporous silica nanocomposites with various surface functionalities. Catalytic tests in the presence of  $Ru(bpy)_3^{2+}$  as a photosensitizer and  $S_2O_8^{2-}$  as a sacrificial electron acceptor show that porous silica shells of up to ca. 20 nm in thickness lead to increased water oxidation activity. We attribute this effect to either or a combination of an effective increase in catalyst active area and consequent higher local concentration of  $Ru(bpy)_3^{2+}$ , and/or to a decrease in the permittivity of the medium surrounding the catalyst surface and a consequent increase in the rate of charge transfer. Functionalized  $Co_3O_4$ -mesoporous silica nanocomposites show lower water oxidation activity compared to the parent non-functionalized catalyst, likely due to partial pore blocking of the silica support upon surface grafting. A more thorough understanding of the effects of microstructure and permittivity on water oxidation ability will enable the construction of next generation catalysts possessing optimal configuration and better efficiency for water splitting.

KEYWORDS. Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> core/shells, nanocomposites, nanocatalysts, water oxidation, microstructure effects.

#### Introduction

Electrochemical and photochemical water splitting are ways to produce molecular hydrogen gas,  $H_2$ , a potentially valuable and clean-burning fuel. Water oxidation is the most difficult half reaction in water splitting, involving the transfer of four electrons and the formation of oxygen-oxygen bonds.<sup>1</sup>

<sup>4</sup> After many studies devoted to developing more efficient and economic water oxidation catalysts,<sup>5</sup> cobalt-based materials have been identified as some of the most promising due to their relative abundance, high activity, and stability.<sup>2,6-8</sup>

The synthesis and size-dependent properties of cobaltbased catalysts for electrochemical oxygen evolution have been examined previously.<sup>9,10</sup> A pH-dependent study of cobalt-oxide electrocatalysts in fluoride-buffer has been reported.<sup>11</sup> Cobalt oxide decorated gold<sup>12</sup> or graphene<sup>13</sup> electrodes show some of the best catalytic performance in oxygen reduction and evolution reactions, while Co<sub>3</sub>O<sub>4</sub>-modified Ta<sub>3</sub>N<sub>5</sub> photoanodes show enhanced performance and stability.<sup>14,15</sup> Co(II)-modified, fluorine-doped tin oxide has high catalytic activity,<sup>16</sup> as do self-repairing cobalt-phosphate films<sup>17</sup> and diamond-supported Co<sub>2</sub>O<sub>3</sub> nanoparticles.<sup>18</sup> Co<sub>3</sub>O<sub>4</sub> mesopores prepared by hard-templating methods show increased stability and electrocatalytic ability.<sup>19-21</sup>

Several metal oxide-based photocatalytic systems have been developed in which the  $[Ru(bpy)_3]^{2+}$  complex cation and  $S_2O_8^{2-}$  serve as photosensitizer and sacrificial electron acceptor, respectively. These include: Mn<sub>3</sub>O<sub>4</sub> embedded in mesoporous silica,<sup>22,23</sup> colloidal IrO<sub>2</sub>,<sup>24</sup> MnO<sub>2</sub> nanotubes and wires,<sup>25</sup> amorphous manganese oxide,<sup>26</sup> MnO<sub>2</sub> on carbon nanotubes,<sup>27</sup> La-CoO<sub>3</sub>, CoWO<sub>4</sub>, NdCoO<sub>3</sub> and YCoO,<sup>28</sup> calcium manganese(III) oxide,<sup>29</sup> Mn-Ga-Co spinel,<sup>30</sup> cobalt/methylenediphosphonate,<sup>31</sup> Li<sub>2</sub>Co<sub>2</sub>O<sub>4</sub><sup>32</sup> and NiFe<sub>2</sub>O<sub>4</sub>.<sup>33</sup>

Other than heterogeneous catalysts, homogeneous cobaltbased water oxidation catalysts that also require  $[Ru(bpy)_3]^{2+}$ and  $S_2O_8^{2-}$  have been developed. Carbon-free cobalt polytungstate complexes show improved stability and catalytic ability over traditional homogeneous water oxidation catalysts.<sup>34-39</sup> Water soluble mononuclear cobalt complexes are converted into active Co(OH)<sub>x</sub> species during photocatalysis.<sup>40</sup> Co(OH)<sub>2</sub> derived from Co(II) adsorbed on silica shows high catalytic activity and stability.<sup>41</sup> Catalytic Co<sub>4</sub>O<sub>4</sub> cubanes are known to mimic photosystem II.<sup>42,43</sup>

Water oxidation over mesoporous silica-supported  $Co_3O_4$ clusters has drawn much recent interest.<sup>44</sup> The photo- and electrochemical activity of ligand-free  $Co_3O_4$  nanoparticles of different shapes on different supports have been studied.<sup>45</sup>  $Co_3O_4/SBA-15$  catalysts show higher activity than  $Co_3O_4/MCM41$  catalysts.<sup>46</sup> Smaller  $Co_3O_4$  clusters and 3-D connecting pore structures lead to better performance.<sup>47</sup> Mndoped mesoporous  $Co_3O_4$  performs better than pure  $Co_3O_4$ .<sup>48,49</sup> Cobalt complexes grafted on SBA-15, zeolite supported CoOx, and hollow  $Co_3O_4$  particles were also reported.<sup>50-54</sup> The mechanism of hole transport from  $[Ru(bpy)_3]^{2+}$  to the surface of  $Co_3O_4$  was studied using  $Co_3O_4/SiO_2$  core/shell catalysts impregnated with organic molecules as charge transfer media.<sup>55,56</sup>

Fundamental studies on the microscopic mechanism of water oxidation using both homogeneous (molecular) Co complexes<sup>57</sup> and heterogeneous  $Co_3O_4$  catalysts<sup>58</sup> provide useful leads for new catalyst design and optimization. Theoretical calculations have described the adsorption and oxidation of water molecules on the  $Co_3O_4(110)$  surface.<sup>59</sup> Here, we present our study on the effect of porous silica shell thickness and different surface grafted groups on the water oxidation activity of  $Co_3O_4/SiO_2$  core/shells and  $Co_3O_4$ -mesoporous silica composites, respectively.

#### Experimental

**Materials.** Cobalt acetate tetrahydrate  $(Co(OAc)_2 \cdot 4H_2O)$ , tetraethylorthosilicate (TEOS), Pluronic 123 (P-123, HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>20</sub>(CH<sub>2</sub>CH(CH<sub>3</sub>)O)<sub>70</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>OH), ammonium hydroxide (NH<sub>4</sub>OH 28 %wt. aqueous solution), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), cobalt(II) nitrate hexahydrate  $(Co(NO_3)_2 \cdot 6H_2O)$ , poly(ethylene glycol) tridecamer (HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>13</sub>H (EG<sub>13</sub> or PEG600), M<sub>n</sub> = 600 g/mol), aminopropyltriethoxysilane (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OEt)<sub>3</sub>), trimethylsilylchloride (Me<sub>3</sub>SiCl), tris(2,2'-bipyridyl)ruthenium(II) dichloride hexahydrate ([Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> · 6H<sub>2</sub>O), and deuterium oxide (D<sub>2</sub>O) were purchased from Sigma-Aldrich; ethanol (absolute, 200 proof), ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH), and hydrochloric acid (HCl, concentrated) from Fisher; cetyltrimethylammonium bromide (CTAB) from Alfa Aesar; phenyltrimethoxysilane (PhSi(OMe)<sub>3</sub>) from Gelest. All chemicals were used as received unless specified otherwise.

Synthesis.  $Co_3O_4$  nanocrystals were prepared by a slightly modified procedure involving the thermal decomposition of cobalt(II) oxalate.<sup>60</sup> A solution of 0.3 M cobalt acetate in ethanol (50 mL) was heated and kept at 50 °C for 30 min, followed by quick addition of oxalic acid (1.07 g, 11.9 mmol). After 2 h at 50 °C, the cobalt(II) oxalate product was collected by concentration under vacuum at 80 °C. Heating cobalt(II) oxalate powder to 400 °C in a crucible in air for 2 h yielded Co<sub>3</sub>O<sub>4</sub> nanocrystals. Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shells. Co<sub>3</sub>O<sub>4</sub> nanocrystals were coated with porous SiO<sub>2</sub> shells of varying thicknesses by modified literature procedures.<sup>61-63</sup> Co<sub>3</sub>O<sub>4</sub> (50 mg, 0.21 mmol) was added to a mixture of CTAB (0.22 g, 0.60 mmol), 28 %wt. aqueous NH<sub>4</sub>OH (4.2 mL, 62.3 mmol), and ethanol (50 mL). After 15 min sonication and 15 min vigorous stirring, TEOS (25 µL, 0.11 mmol for 3 nm shell; 150 µL, 0.67 mmol for 20 nm shell; 600 µL, 2.64 mmol for 44 nm shell) was introduced in multiple small additions (<50-100 µL/h). The solution was stirred for 19 h at room temperature (R.T.). Solids were collect by centrifugation (5,000 rpm, 10 min), and the surfactant was removed by calcination at 550 °C in air for 6 h. Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites. SBA-15<sup>64</sup> and Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites<sup>47,65</sup> were prepared by a modified literature procedures. P-123 (33 g, 5.69 mmol), concentrated HCl (16.6 g, 0.17 mol), and deionized water (517 g) were mixed by stirring vigorously at 35 °C for 30 min. TEOS (62.0 g, 0.30 mol) was added. After 1 day stirring, the mixture was moved to an oven pre-heated to 90 °C and kept at this temperature for 1 day. Solids were collected by filtration and dried at 90 °C. The template was removed by calcination at 550 °C in air for 6 h. SBA-15 (0.2 g) was added to a 0.022 M cobalt(II) nitrate solution in ethanol (5 mL, 0.11 mmol), and the resulting pink slurry stirred overnight until the solvent completely evaporated. This cobalt salt-impregnated SBA-15 was heated to 400 °C in air for 3 h. For surface grafting, Co<sub>3</sub>O<sub>4</sub>-SBA-15 composite (0.5 g) was degassed under vacuum at 110 °C for 2 h. Toluene (100)mL) and functional silane (44 mg of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OEt)<sub>3</sub>, 40 mg of PhSi(OMe)<sub>3</sub>, or 22 mg of Me<sub>3</sub>SiCl; 2 mmol) were added. The mixture was refluxed at 78 °C under a dry N<sub>2</sub> atmosphere for 6 h. Solids were collected by filtration, washed with toluene (200 mL), and dried at 90 °C.

**Structural Characterization.** Powder X-ray diffraction (XRD) data were recorded with a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation source (40 kV, 44 mA). *Nitrogen physisorption* was measured on a Micromeritics ASAP 2020 surface area and porosimetry system. Samples were degassed at 100 °C under vacuum overnight before analysis. Surface area was calculated with the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.005 to 0.25 of adsorption data. Pore size distribution was calculated with the Barret-Joyber-Halenda (BJH) method. *Transmission Electron Microscopy* (TEM) was measured on an FEI Tecnai G<sup>2</sup> F20 field emission scanning transmission electron microscope

(S/TEM) at 200 kV (point-to-point resolution <0.25 nm, lineto-line resolution <0.10 nm).

Spectroscopic Characterization UV-Vis absorption spectra were collected with a photodiode-array Agilent 8453 UV-Vis spectrophotometer. Pore accessibility study. Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell samples were examined by <sup>1</sup>H NMR spectroscopy using ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH or EG) and polyethylene glycol (HO( $CH_2CH_2O$ )<sub>13</sub>H or Poly600). Experiments were conducted on a Varian MR-400 spectrometer equipped with a OneNMR pulse-field-gradient probe operating at a <sup>1</sup>H frequency of 399.80 MHz. EG (233 mg, 3.75 mmol) and Poly600 (317 mg, 0.53 mmol) were mixed in D<sub>2</sub>O (5 g). A fraction of this EG-Poly600-D<sub>2</sub>O solution (50  $\mu$ L) and a solution of  $Co_3O_4$ /porous-SiO<sub>2</sub> in D<sub>2</sub>O (0.067 mM, 450 µL; 7.5 µg or 0.03 µmol of Co<sub>3</sub>O<sub>4</sub>) were mixed. NMR measurements of ethylene glycol and polyethylene glycol (Poly600) proton longitudinal  $(T_1)$  relaxation were conducted using the inverse recovery pulse sequence, and the transverse relaxation (T<sub>2</sub>) were measured using a two-pulse spin echo sequence. Solid state NMR spectra were measured with a Bruker Avance II 600 Spectrometer operating at 119.2 MHz for <sup>29</sup>Si equipped with a 4 mm Bruker MAS probe spinning at 10 KHz. <sup>29</sup>Si direct polarization magic angle spinning (DP-MAS) NMR spectra were recorded with a pulse width of 4 µs and a recycling delay of 1 min. <sup>29</sup>Si chemical shifts are referenced to TMS ( $\delta =$ 0 ppm).

Water Oxidation. A buffer solution of weakly coordinating ions was prepared from NaHCO<sub>3</sub> (0.353 g, 4.20 mmol) and Na<sub>2</sub>SiF<sub>6</sub> (0.619 g, 3.30 mmol) in deionized water (150 mL).<sup>31</sup> The pH was adjusted to 5.8 with added NaHCO<sub>3</sub>. Buffer (20 mL), Na<sub>2</sub>SO<sub>4</sub> (0.195 g, 1.37 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (65 mg, 0.27 mmol), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (22.5 mg, 0.03 mmol), and Co<sub>3</sub>O<sub>4</sub>-silica sample (1 mg or 4.2 µmol of Co<sub>3</sub>O<sub>4</sub> for Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shells, determined by optical density in solution; 2 mg or 8.4 µmol of Co<sub>3</sub>O<sub>4</sub> for Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites, determined by dry weight) were added to a 25 mL flask. The mixture was kept in the dark overnight, and degassed by bubbling with dry N<sub>2</sub>. O<sub>2</sub> evolution was unobserved by GC prior to illumination. Water oxidation experiments were conducted inside a Rayonet photoreactor under illumination with  $16 \times 575 \pm 100$  nm side-on lamps. 100 µL of headspace samples were directly analyzed each time using an Agilent 7890A GC system equipped with an HP-Molesieve column and a TCD detector.

#### **Results and Discussion.**

 $Co_3O_4$ /porous-SiO\_2 core/shells. Co<sub>3</sub>O\_4 nanocrystals were synthesized by thermal decomposition of cobalt(II) oxalate at 400 °C in air for 2 h (see Experimental). As shown in Figure 1, the powder XRD pattern of the as-synthesized Co<sub>3</sub>O<sub>4</sub> nanocrystals shows diffraction peaks that match those of the reference bulk spinel Co<sub>3</sub>O<sub>4</sub> phase. In contrast, none of the experimentally observed diffraction peaks match those of bulk CoO, suggesting that the nanocrystals are made of highly phase-pure Co<sub>3</sub>O<sub>4</sub>. The diffuse reflectance spectrum of Co<sub>3</sub>O<sub>4</sub> nanocrystals (Figure 2) shows two peaks at *ca*. 425 nm and 725 nm. This is consistent with the characteristic absorption of Co<sub>3</sub>O<sub>4</sub>, containing octahedral Co<sup>3+</sup> and tetrahedral Co<sup>2+</sup> ions.<sup>66</sup>

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**Figure 1.** Wide angle powder XRD data for  $17.2 \pm 3.8$  nm  $Co_3O_4$  nanocrystals (a),  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles with different shell thicknesses of  $3.1 \pm 0.6$  nm (b),  $19.8 \pm 1.4$  nm (c),  $44.1 \pm 8.3$  nm (d), and bulk  $Co_3O_4$  (e) and CoO (f).

As shown in Figure 3, transmission electron microscopy (TEM) shows that the Co<sub>3</sub>O<sub>4</sub> nanocrystals have truncated polvhedral shapes with an average size (diameter) of  $17.2 \pm 3.8$ nm. This is consistent with the grain size of 16 nm estimated from XRD peak widths using the Scherrer equation. Nitrogen physisorption analysis shows the specific surface area of  $Co_3O_4$  nanocrystals is 38 m<sup>2</sup>/g (Table 1, page 9), which is consistent with a surface area 49  $m^2/g$  estimated from a spherical particle model calculation. These Co<sub>3</sub>O<sub>4</sub> nanocrystals were coated with porous silica (SiO<sub>2</sub>) shells via CTAB-templated sol-gel condensation of tetraethylorthosilicate (TEOS) with NH4OH as catalyst in ethanol solvent. TEM shows different amounts of TEOS resulted in different Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles with various shell thicknesses  $(3.1 \pm$ 0.6 nm,  $19.8 \pm 1.4 \text{ nm}$  and  $44.1 \pm 8.3 \text{ nm}$ , Figures 1 and 3, and Table 1, page 9). The organic template, CTAB was removed via calcination at 550 °C under air for 6 h.



**Figure 2.** Diffuse reflectance spectra of bare (uncoated)  $Co_3O_4$  nanocrystals (a),  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles (19.8 ± 1.4 nm shell thickness) (b) and SBA-15-Co<sub>3</sub>O<sub>4</sub> nanocomposites (4.4 ± 0.8 nm Co<sub>3</sub>O<sub>4</sub> particle size) (c).

Representative powder XRD, diffuse reflectance and TEM data of  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles are summarized in Figures 1, 2 and 3. As the silica shell becomes thicker, no significant peak shifts or new peaks are observed. The XRD patterns also reveal that the phase and grain size of the  $Co_3O_4$  nanocrystals remain the same after silica coating,

suggesting that the basic environment employed for silica coating does not affect the nanoparticles'  $Co_3O_4$  cores. Similarly, no significant peaks appear in the low angle XRD region (data not shown) of the  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles. This implies that the porous silica shell may not be as ordered as other reported porous silica-coated materials that also use CTAB as a template or surfactant. In agreement with these XRD observations, diffuse reflectance and TEM confirm that the optical structure and size of the  $Co_3O_4$  nanocrystals did not change appreciably through the silica shell growth process (Figure 3).



**Figure 3.** TEM of  $17.2 \pm 3.8$  nm Co<sub>3</sub>O<sub>4</sub> nanocrystals (a), and Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles with different shell thicknesses of  $3.1 \pm 0.6$  nm (b),  $19.8 \pm 1.4$  nm (c),  $44.1 \pm 8.3$  nm (d).

The average core size and shell thicknesses for different  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles are summarized in Table 1 (page 9). Increasing amounts of TEOS clearly resulted in larger shell thickness. This suggests that consecutive addition of TEOS resulted in the growth of (more) silica on preexisting particles *via* heterogeneous nucleation, rather than forming new silica nuclei *via* homogeneous nucleation.

TEM reveals a foam-like surface structure is present atop the Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles (Figures 3b-d). Nitrogen physisorption experiments were also performed in order to characterize the pore structure and surface area of the Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> particles and their shells. The particles with  $19.8 \pm 1.4$  nm and  $44.1 \pm 8.3$  nm silica shells have a calculated pore size of 3.8 nm and 3.9 nm, respectively, as obtained by the BJH method (see Experimental, and Table 1, page 9). Core/shell particles with thinner silica layers did not show significant peaks by the BJH method. Across all samples studied, the specific surface area increased as the shell thickness increased. The pores in the silica shell are produced after the removal of CTAB molecules; the diameter of the pores is thus dictated by the size of the CTAB micelles formed during the sol gel process. Since the concentrations of CTAB, EtOH and H<sub>2</sub>O were the same in each run, the increase in surface area is consistent with increasing shell thickness while the pore size remains constant.

Probing pore accessibility by NMR. We then turned our attention to assessing the accessibility of the catalytically active Co<sub>3</sub>O<sub>4</sub> surface to small molecules. Infrared spectroscopy provides one way to assess the degree of surface coverage by a silica shell.<sup>67,68</sup> We specifically sought to probe pore accessibility using nuclear magnetic resonance (NMR). NMR measurements of two chemically related molecules with very different sizes, ethylene glycol (EG) and polyethylene glycol tridecamer (EG<sub>13</sub> or Poly600), were used in order to examine the pore accessibility of the Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles. For all measurements, the concentration of ethoxyl protons (-OCH2CH2O-) in both EG and Poly600 were kept the same (confirmed by chemical integration), as was the concentration of (bare or coated) Co<sub>3</sub>O<sub>4</sub> nanocrystals (confirmed by Co<sub>3</sub>O<sub>4</sub> optical density or absorbance). Thus, only the thickness of the porous silica shells varied in different specimens.



**Figure 4.** Longitudinal (T<sub>1</sub>) (a) and transverse (T<sub>2</sub>) (b, c, d) relaxation times for the ethoxyl protons ( $-OCH_2CH_2O$ -) in EG (HOCH<sub>2</sub>CH<sub>2</sub>OH) and Poly600 (HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>13</sub>H) in the absence or presence of Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles with different shell thicknesses in D<sub>2</sub>O (T<sub>2free</sub> = T<sub>2</sub> in the complete absence of Co<sub>3</sub>O<sub>4</sub>).

Figure 4 shows the longitudinal (T<sub>1</sub>) and transverse (T<sub>2</sub>) relaxation times for the ethoxyl protons ( $-OCH_2CH_2O_-$ ) in EG (HOCH<sub>2</sub>CH<sub>2</sub>OH) and Poly600 (HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>13</sub>H) in the absence and presence of Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shells. As expected, the T<sub>1</sub> values of EG and Poly600 do not change significantly with added Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub>, regardless of the thickness of the silica shell (Figure 4a). However, the T<sub>2</sub> values for both EG and Poly600 progressively increase with increasing shell thickness (Figure 4b). Magnetic particles have been shown to be T<sub>2</sub> relaxers.<sup>69</sup> Studies with Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> core/shells showed that the thinnest shells have the strongest T<sub>2</sub> shortening effect.<sup>70</sup> A polymer coated Fe<sub>2</sub>O<sub>3</sub> composite shows enhanced T<sub>2</sub> shortening near the particle surface.<sup>71</sup>

Naturally, this shortening of the  $T_2$  suggests that the magnetic  $Co_3O_4$  core has a much larger influence on helping relax those protons that can get closer to the magnetic surface. It follows that thicker silica shells should increasingly separate and minimize the magnetic screening of protons by the magnetic  $Co_3O_4$  core. Because the silica shells have a definite pore size (*ca.* 4 nm), we hypothesized that the smaller EG monomer

molecules should be able to penetrate the shell and continue to be impacted to a greater degree compared to the much larger Poly600 tridecamer molecules. To investigate this idea, the measured  $T_2$  values were parametrized by dividing them over the unaffected, natural  $T_2$  values ( $T_{2free}$ ) of EG and Poly600 (measured in the absence of Co<sub>3</sub>O<sub>4</sub>;  $T_2/T_{2free}$  and  $1 - T_2/T_{2free}$  in Figures 4c and 4d, respectively). After parametrization, it is clear that while the protons in both EG and Poly are relaxed by Co<sub>3</sub>O<sub>4</sub>, those in Poly600 are much more sensitive to the thickness of the silica shell.

We explain these observations as follows: With a hydrodynamic diameter of ~1 nm,<sup>72,73</sup> the larger Poly600 molecules have much greater difficulty diffusing through the longe, more tortuous pathway needed to reach the magnetic  $Co_3O_4$  core surface as the SiO<sub>2</sub> shell increases. In contrast, because the EG molecules are much smaller than the SiO<sub>2</sub> pores, thicker SiO<sub>2</sub> shells only slightly hinder the diffusion of EG molecules closer to the core. This results in a stronger T<sub>2</sub> shortening effect for EG.

Shorter diffusion pathways in  $Co_3O_4$ /porous-SiO<sub>2</sub> particles with thinner shells allow molecular probes to move closer to the magnetic core. For the thinnest shells and the bare (uncoated)  $Co_3O_4$  nanocrystals, small and large molecules are able to reach the magnetic surface and are affected equally. Together with the physisorption and TEM measurements presented above, these NMR experiments strongly suggest that that the surface of  $Co_3O_4$  nanocrystals is accessible by small molecular substrates and reagents through a vast network of well defined, *ca.* 4 nm pores. In contrast, the diffusion of large molecules such as Poly600 into the core region is hindered as their size becomes comparable with that of the pores. The porous silica shell thus serves as sieve or filter for larger molecules.

 $Co_3O_4$ -SBA-15 nanocomposites. Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites were prepared by the sol-gel reaction between TEOS and H<sub>2</sub>O, using HCl as catalyst, and the block copolymer P123 as a structure-directing agent. The organic template was removed by calcination at 550 °C under air. Wet impregnation of cobalt(II) nitrate and calcination at 400 °C in air yielded Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites with a nominal Co<sub>3</sub>O<sub>4</sub> loading of 4 wt.%. Further modification of the silica surface was conducted by post-grafting with various functional silanes (see Experimental).

Low-angle XRD measurements show three peaks at 1.03°, 1.77° and 2.01° corresponding to the (100), (110) and (200) planes in 2-D hexagonally packed SBA-15, respectively (Figure 5). The intensity of these three peaks remained unchanged after introduction of cobalt oxide, which suggests that the mesostructure of the SBA-15 support remained mostly intact. Wide-angle XRD measurements show that all modified (surface grafted) and unmodified Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites contain standard spinel Co<sub>3</sub>O<sub>4</sub> nanocrystals with a similar Scherrer particle size of  $4.4 \pm 0.8$  nm (figure 5). Nitrogen physisorption measurements show that, after the introduction of Co<sub>3</sub>O<sub>4</sub>, the surface area of Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites dropped from 734  $m^2/g$  to 570  $m^2/g$ , while the pore size remained nearly identical from 6.5 nm to 6.4 nm. Post-synthetic grafting with silanes slightly decreased the surface area, and also the pore size of the composites, by up to 140  $m^2/g$  and 0.6 nm, respectively (Table 2). It is noteworthy that the most dramatic decrease in surface area, pore size and pore volume occurred in the amino (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) modified specimen. However, no other significant changes in pore structure were observed in these surface modified Co<sub>3</sub>O<sub>4</sub>-SBA-15 composites. DP-MAS <sup>29</sup>Si NMR measurements were conducted to confirm the surface modification (Figure 6). New T bands (T<sup>3</sup> and T<sup>2</sup>) are observed for sites derived from NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OSi)<sub>3</sub>/NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OH)(OSi)<sub>2</sub> and PhSi(OSi)<sub>3</sub>/PhSi(OH)(OSi)<sub>2</sub> groups. A peak at *ca.* 15 ppm is observed for Me<sub>3</sub>Si(OSi)<sub>3</sub> groups.<sup>74-76</sup>



**Figure 5.** Low-angle (top) and wide-angle (bottom) powder XRD data for  $Co_3O_4$ -SBA-15 nanocomposites ( $4.4 \pm 0.8$  nm  $Co_3O_4$  particle size):  $Co_3O_4$ -SBA-15-SiPh (a),  $Co_3O_4$ -SBA-15-SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (b),  $Co_3O_4$ -SBA-15-SiMe<sub>3</sub> (c),  $Co_3O_4$ -SBA-15 (d), and SBA-15 (e). Bulk  $Co_3O_4$  (f) and CoO (g) are shown for reference.



Figure 6. DP-MAS <sup>29</sup>Si NMR spectra of  $Co_3O_4$ -SBA-15 nanocomposites before (a), and after surface functionalization (by grafting) with -(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> (b), -Ph (c) and -SiMe<sub>3</sub> (d) groups.

Effect of catalyst microstructure on water oxidation. The catalytic activity of  $Co_3O_4$ /porous-SiO<sub>2</sub> core/shell nanoparticles toward water oxidation reaction was measured using a photosensitizer (Ru[(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O), a sacrificial electron acceptor (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-Na<sub>2</sub>SO<sub>4</sub>), and an aqueous buffer (pH 5.8, NaSiF<sub>6</sub>-NaHCO<sub>3</sub>) medium. Reactions were conducted under continuous irradiation by 575 ± 100 nm lamps, and taking aliquots of the headspace and injecting them into a GC equipped with a TCD detector to measure the oxygen (O<sub>2</sub>) produced. Our setup (septum, etc.) was independently tested under similar conditions to ensure that there was no leakage or other non-catalytic sources of O<sub>2</sub>.

The overall cycle for water oxidation under these conditions is shown in Scheme 1.  $\text{Ru(bpy)}_3^{2+}$  is first excited by the incident radiation to form an excited state,  $\text{Ru(bpy)}_3^{2+*}$ . Subsequent electron transfer from  $\text{Ru(bpy)}_3^{2+*}$  to  $\text{S}_2\text{O}_8^{2-}$  yields  $\text{Ru(bpy)}_3^{3+}$  and  $\text{SO}_4$ .  $\text{SO}_4$ . further oxidizes another equivalent of  $\text{Ru(bpy)}_3^{2+}$  to  $\text{Ru(bpy)}_3^{3+}$ . This  $\text{Ru(bpy)}_3^{3+}$  reacts with water and oxidizes it on the surface of the  $\text{Co}_3\text{O}_4$  catalyst, producing molecular oxygen (O<sub>2</sub>). The free energy of the full process is calculated to be negative (exergonic or "downhill") and equal to -280 kJ/mol.

$$\begin{array}{lll} 2H_2O \rightarrow O_2 + 4H^+ + 4e^- & E_{red} = -1.23 \ V \\ S_2O_8^{2^-} + 4e^- \rightarrow 2SO_4^{2^-} & E_{ox} = 1.96 \ V \\ 2H_2O + 2S_2O_8^{2^-} \rightarrow O_2 + 4H^+ + 4SO_4^{2^-} & E_{rxn} = 0.73 \ V \\ \Delta G^\circ = \ -nFE = -4 \times 96485 \ C/mol \times 0.73 \ V = -280 \ kJ/mol \end{array}$$

**Scheme 1.** Water oxidation by  $S_2O_8^{2-}$  catalyzed by  $Co_3O_4/SiO_2$  and  $Ru(bpy)_3^{2+}$  (chloride salt) as photosensitizer.



Figure 7 and Table 3 show the experimentally observed oxygen evolution activities of different Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> nanocatalysts. In all cases, the amount of  $O_2$  in the reactor headspace increased until reaching a plateau after 40-90 min. We interpret this plateau as the point at which the maximum yield of O<sub>2</sub> production in each case was achieved. Among the Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> nanocatalysts studied, the bare, uncoated  $Co_3O_4$  had the lowest activity.  $O_2$  production then increased with increasing silica shell thickness, up to a point; activity reached a maximum for  $Co_3O_4$ /porous-SiO<sub>2</sub> with a 19.8 ± 1.4 nm shell, then decreased with a thicker shell (O<sub>2</sub> production activity was negligible in the absence of the nanocatalyst). We speculatively attribute this behavior to either one or both of two possible factors: (i) The positively charged  $Ru(bpy)_3^2$ photosensitizer may have a high affinity toward the negatively polarized SiO<sub>2</sub> surface. Thicker shells provide for a much larger SiO<sub>2</sub> surface (Table 1, page 9), increasing the effective concentration (and activity) of Ru(bpy)<sub>3</sub><sup>2+</sup> near or at the catalytically active Co<sub>3</sub>O<sub>4</sub> surface. (ii) The porous silica coating could increase the effectiveness (rate of) electron transfer steps necessary for catalysis due to the lower permittivity (dielectric constant) of silica (3.9) compared to pure water (80). The lower permittivity could decrease the reorganizational energy term as described by Marcus theory, increasing the overall rate of electron transfer. The carrier mobility in 1-D and 2-D semiconductor nanostructures is sensitive to permittivity,<sup>77</sup> as is that of single-layer graphene transistors in different dielectric environments.<sup>78</sup>

The catalytic activities of surface modified and unmodified Co<sub>3</sub>O<sub>4</sub>/SBA-15 nanocomposites were also measured for comparison (Figure 8 and Table 3). The concentration of  $O_2$  produced using Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites reached a maximum yield within 50-60 min, which is consistent with the afore-mentioned and with prior reports.22,44 Interestingly, among the composite catalysts it is the unmodified sample that possesses the best performance, while the other three modified samples possessed lower, similar activities. The composites containing the most hydrophobic surface groups (-SiPh and -SiMe<sub>3</sub>) and thus, a low permittivity, show relatively low activity, arguing against factor (ii) above. More generally however, we believe that the decrease in activity in the surface grafted composites is most likely attributable to a decrease in the SiO<sub>2</sub> surface available for binding by the Ru(bpy)<sub>3</sub><sup>2+</sup> photosensitizer (roughly opposite to factor (i) mentioned above), as indicated by physisorption measurements (Table 2, page 9). Albeit, this could be compensated somewhat by the introduction of surface -NH<sub>2</sub> groups in one of the nanocomposites.



**Figure 7.** Oxygen evolution (a) and maximum  $O_2$  yields (measured between 90-120 min, b) from the reaction of water with persulfate in the presence of  $[Ru(bpy)_3]Cl_2$  sensitizer and  $Co_3O_4/SiO_2$  core/shells under 575 ± 100 nm lamp illumination (the total  $Co_3O_4$  loading and concentration was maintained constant).

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Figure 8. Oxygen evolution (a) and maximum  $O_2$  yields (measured between 60-120 min, b) from the reaction of water with persulfate in the presence of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> sensitizer and  $Co_3O_4$ -SBA-15 nanocomposites under 575 ± 100 nm lamp illumination (the total Co<sub>3</sub>O<sub>4</sub> loading and concentration was maintained constant).

#### Conclusion

We have prepared several Co<sub>3</sub>O<sub>4</sub>-porous silica nanocomposites to investigate the effect of catalyst microstructure and its local environment on water oxidation activity. We have also utilized NMR relaxation time measurements of two different probe molecules (EG and Poly600) to study the pore accessibility of Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles with different shell thicknesses (but similar pore size and structure).

In our study of catalytic activity of Co<sub>3</sub>O<sub>4</sub>/porous-SiO<sub>2</sub> core/shell nanoparticles toward water oxidation (oxygen evolution reaction), the catalyst with a  $19.8 \pm 1.4$  nm shell had superior activity over the uncoated, thinner and thicker silica shell catalysts due to two possible factors: First, the higher surface area of the thicker porous silica shell helps to increase the local  $Ru(bpy)_3^{2+}$  concentration near the active  $Co_3O_4$  surface. Second, the reduced reorganization energy due to the lower dielectric constant of silica might also facilitate the charge transfer rate. Increasing shell thicknesses were detrimental to catalytic activity, possibly due to slower diffusion of reactant molecules in and out of the SiO2 pores.

In the case of Co<sub>3</sub>O<sub>4</sub>/SBA-15 nanocomposites, the unmodified sample possesses better activity than the modified samples. Surface modified composites (e.g., -SiPh and -SiMe<sub>3</sub>) have relative low local surface permittivity compared to the unmodified composites. However, the loss of possible  $Ru(bpy)_{3}^{2+}$  binding sites (hydroxyl group) and a measurable amount of pore blocking upon surface grafting results in the loss of reactivity. A more thorough understanding of the effects of microstructure and permittivity on water oxidation ability will enable the construction of next generation catalysts possessing optimal configuration and better efficiency for water oxidation and water splitting.

#### **Supporting Information**

Absorption and irradiance profiles of catalyst, sensitizer, and lamp. ICP-MS and colorimetric analyses of Co content in all materials studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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### ACS Catalysis

Table 1. Structural parameters of Co<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> core/shell nanoparticles with different shell thicknesses.

|   | Sample  | Core size $(nm)^a$ | Shell thickness (nm) <sup>a</sup> | $S_{\rm BET} \left({\rm m}^2/{\rm g}\right)^b$ | Pore size $(nm)^c$ | Pore volume $(cm^3/g)$ |
|---|---|--------------------|-----------------------------------|--|--------------------|------------------------|
|   | Co <sub>3</sub> O <sub>4</sub>                            | $17.2 \pm 3.8$     | 0                                 | 38   | N/A                | 0.15                   |
|   | Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> (3 nm)   | $19.1 \pm 3.1$     | $3.1 \pm 0.6$                     | 130  | N/A                | 0.15                   |
|   | Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> (20 nm)  | $19.9 \pm 3.0$     | $19.8 \pm 1.4$                    | 210  | 3.8                | 0.15                   |
| _ | Co <sub>3</sub> O <sub>4</sub> / SiO <sub>2</sub> (44 nm) | $24.1 \pm 3.5$     | $44.1 \pm 8.3$                    | 390  | 3.9                | 0.22                   |

<sup>a</sup>Determined by TEM. <sup>b</sup>Obtained by the BET method. <sup>c</sup>Obtained by the BJH method.

Table 2. Structural data of SBA-15 and Co<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposites.

| Sample   | $S_{\rm BET} ({\rm m^2/g})$ | Pore size $(nm)^a$ | Pore volume $(cm^3/g)$ |
|--|-----------------------------|--------------------|------------------------|
| SBA-15   | 730                         | 6.5                | 0.95                   |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15   | 570                         | 6.4                | 0.91                   |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiMe <sub>3</sub>   | 550                         | 6.3                | 0.79                   |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | 430                         | 5.8                | 0.70                   |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiPh  | 520                         | 6.4                | 0.74                   |

<sup>*a*</sup>Obtained by the BJH method.

Table 3. Maximum oxygen evolution performance of Co<sub>3</sub>O<sub>4</sub>-porous SiO<sub>2</sub> nanocatalysts.

| Sample   | Oxygen evolved (µmol) | Yield (%) |
|--|-----------------------|-----------|
| Co <sub>3</sub> O <sub>4</sub>   | 5.2                   | 3.8       |
| $Co_3O_4/SiO_2 (3 \text{ nm})^a$   | 8.7                   | 6.4       |
| $Co_3O_4/SiO_2 (20 \text{ nm})^a$  | 26.7                  | 19.6      |
| $Co_3O_4/SiO_2 (44 \text{ nm})^a$  | 19.8                  | 14.5      |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15   | 28.5                  | 20.8      |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiMe <sub>3</sub>   | 20.4                  | 15.0      |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | 15.4                  | 11.3      |
| Co <sub>3</sub> O <sub>4</sub> -SBA-15-SiPh  | 19.4                  | 14.2      |

<sup>*a*</sup>Approximate shell thickness (as in Table 1).

